

Cu(II) acetate- and Mn(III) acetate-mediated radical reactions of [60]fullerene with ketonic compounds

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Received 3rd November 2004, Accepted 16th December 2004
First published as an Advance Article on the web 21st January 2005

The copper(II) acetate monohydrate- or manganese(III) acetate dihydrate-mediated reaction of [60]fullerene with β -keto esters **1a–1c** or with β -diketones **1d, 1e** in the presence of 4-dimethylaminopyridine afforded only dihydrofuran-fused C₆₀ derivatives **2a–2e**. However, aromatic methyl ketones **3a–3c** gave two kinds of products: methanofullerenes **4a–4c** and dihydrofuran-fused C₆₀ derivatives **5a, 5b**. Possible reaction mechanisms are proposed.

Introduction

The functionalization of [60]fullerene (C₆₀) with various organic functional groups is an important subject in fullerene chemistry for further material and medicinal applications.^{1,2} Radical reactions of fullerenes were amongst the first to be investigated and continue to be of interest for fullerene functionalization.^{3–15} Over the past 30 years, free radical reactions promoted by transition metal salts and their oxides such as those of titanium, vanadium, manganese, iron, cobalt, copper, chromium, niobium and ruthenium¹⁶ have found widespread applications in organic synthesis, and exhibit remarkable advantages over traditional peroxide- or light-initiated processes. Manganese(III)-mediated free radical reactions have been explored extensively.^{16–18} Carbonyl compounds such as acids, ketones, esters, and aldehydes, malonic acid and its derivatives, β -keto acids, β -keto esters, β -keto amides, β -keto sulfoxides and β -diketones with an α -C–H bond(s) can be oxidized by manganese(III) acetate (Mn(OAc)₃) to give α -oxo- and α,α -dioxoalkyl radicals, which can then add to unsaturated substrates to form a variety of products. Copper(II) salts are usually employed together with Mn(III) salts in a radical reaction^{16–18} and seldom used alone.^{19,20} Recently we have successfully realized the Mn(OAc)₃·2H₂O-promoted reactions of C₆₀ with malonate esters, 2-substituted malonate esters, ethyl cyanoacetate and malononitrile in chlorobenzene and toluene and obtained some novel fullerene derivatives, *i.e.*, 1,4-adducts, 1,16-adducts and singly-bonded fullerene dimers.^{21,22} To the best of our knowledge, the Cu(II)-based radical reaction of C₆₀ has not been reported. In this paper, the radical reaction of C₆₀ with β -keto esters, β -diketones and aromatic methyl ketones in the presence of copper(II) acetate monohydrate (Cu(OAc)₂·H₂O) alone is described. The Mn(OAc)₃·2H₂O-mediated radical reaction of C₆₀ with these active methylene compounds was also investigated for comparison.

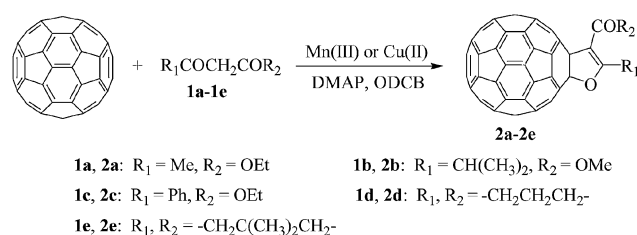
Results and discussion

The reaction of C₆₀ (28.8 mg) with ethyl acetoacetate (**1a**, 51 μ L, 10 eq.) and Cu(OAc)₂·H₂O (16.0 mg, 2 eq.) in the presence of 4-dimethylaminopyridine (DMAP, 24.4 mg, 5 eq.) for 1 h at 80 °C afforded dihydrofuran-fused C₆₀ derivative **2a**^{23–25} in 31% yield (83% based on consumed C₆₀). If the reaction was promoted by Mn(OAc)₃·2H₂O instead of Cu(OAc)₂·H₂O, product **2a** was obtained in 29% yield (81% based on consumed C₆₀).

The presence of DMAP proved to be crucial for the success of this reaction, with either little or no yield being obtained in its absence. For example, there was no obvious reaction for the mixture of C₆₀, **1a** and Cu(OAc)₂·H₂O for 1 h at

80 °C in the absence of DMAP; the reaction of C₆₀ with **1a** and Mn(OAc)₃·2H₂O in the absence of DMAP at 80 °C for 20 min or longer afforded a mixture of C₆₀O and other fullerene derivatives (which have broad UV-vis absorptions around 440 nm, typical band for 1,4-adduct) based on HPLC analysis on a Buckyprep column with diode detector. No obvious reaction occurred if a mixture of C₆₀, **1a** and DMAP was heated for 1 h under air at 80 °C or room temperature. This result indicated that the oxidant was Cu(OAc)₂·H₂O or Mn(OAc)₃·2H₂O rather than oxygen existing in our reaction system. The effect of other bases such as triethylamine and pyridine were also examined; triethylamine resulted in <5% yield in both the Cu(OAc)₂·H₂O- and Mn(OAc)₃·2H₂O-mediated reactions, whilst for the Cu(OAc)₂·H₂O- or Mn(OAc)₃·2H₂O-promoted reaction of C₆₀ with **1a** the presence of pyridine had a negligible effect.

This reaction could be extended to other β -keto esters such as methyl *iso*-butyrylacetate (**1b**), ethyl benzoylacetate (**1c**) and β -diketones such as 1,3-cyclohexanedione (**1d**), 5,5-dimethyl-1,3-cyclohexanedione (**1e**), afforded dihydrofuran-fused C₆₀ derivatives **2b**, **2c**, **2d**,^{25,26} and **2e**^{24,26} respectively (Scheme 1).





Scheme 1

The yields and reaction times for the reaction of C₆₀ with **1a–1e** and Cu(OAc)₂·H₂O or Mn(OAc)₃·2H₂O in the presence of DMAP in a molar ratio of 1 : 10 : 2 : 5 at 80 °C are listed in Table 1. From the data in Table 1, it can be seen that the yields of **1a–1e** using either Cu(OAc)₂·H₂O or Mn(OAc)₃·2H₂O as the oxidant, are similar.

Products **2a**,^{23–25} **2d**,^{25,26} and **2e**^{24,26} are known compounds, and their identities were confirmed by comparison of their spectral data with those reported in the literature. The identification of compound **2b** was made by its MS, ¹H NMR, ¹³C NMR, FT-IR and UV-vis spectra. The MALDI-TOF mass spectrum of **2b** showed the molecular ion peak at *m/z* 862. The ¹H NMR spectrum of **2b** displayed a heptet at 4.20 ppm and a doublet at 1.60 ppm for the CH(CH₃)₂ group, and a singlet at 3.83 ppm for the methoxy group. In the ¹³C NMR spectrum of **2b** there are

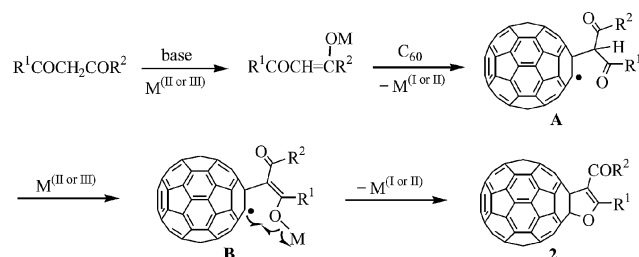
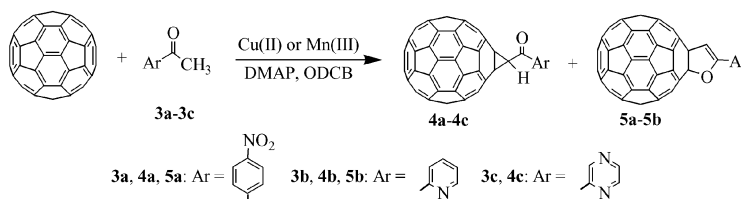
Table 1 The yields and reaction times for the reaction of C₆₀ with **1a–1e** and Cu(OAc)₂·H₂O or Mn(OAc)₃·2H₂O in the presence of DMAP at 80 °C

Substrate	Product	Cu(OAc) ₂ ·H ₂ O		Mn(OAc) ₃ ·2H ₂ O	
		Yield ^a	Time/min	Yield ^a	Time/min
CH ₃ COCH ₂ CO ₂ Et	2a	31% (83%)	60	29% (81%)	20
(CH ₃) ₂ CHCOCH ₂ CO ₂ Me	2b	31% (59%)	60	20% (49%)	20
PhCOCH ₂ CO ₂ Et	2c	27% (72%)	90	22% (67%)	20
	2d^b	16% (40%)	20	31% (92%)	20
	2e^b	30% (73%)	30	30% (83%)	20

^a Yield in parentheses based on consumed C₆₀. ^b Molar ratio of C₆₀ : **1d** (or **1e**) : Cu(OAc)₂·H₂O (or Mn(OAc)₃·2H₂O) : DMAP = 1 : 5 : 2 : 2.

30 peaks with two half-intensity ones at 147.65 and 146.92 ppm in the range 134–149 ppm due to the fifty-eight *sp*² carbons of the C₆₀ skeleton and two peaks at about 72 and 102 ppm due to the two *sp*³ carbons of the C₆₀ cage, fully consistent with the C_s symmetry of its molecular structure. The IR spectrum of **2b** showed absorptions at 1705 and 1622 cm⁻¹ due to the unsaturated ester moiety, and absorptions at 1429, 1187, 575 and 526 cm⁻¹ for the C₆₀ skeleton. The UV-vis spectrum of **2b** exhibited a peak at 427 nm, which is a diagnostic absorption for the 1 : 1 cycloadduct of C₆₀ at the 6:6-junction. Dihydrofuran-fused C₆₀ derivative **2c** was characterized by ¹H NMR, ¹³C NMR, MS, IR and UV-vis spectra in the same way.

A possible reaction mechanism for the oxidative addition of a β-keto ester and β-diketones to conjugated olefins in the presence of CuCl₂-pyridine leading to the formation of dihydrofurans was assumed to proceed *via* radical formation by homolytic addition of the enolate ligand of the 1,3-dicarbonyl compound, followed by cyclization.²⁷ The Mn(OAc)₃-promoted oxidative reactions of β-keto esters and β-diketones with unsaturated compounds to form dihydrofurans have been extensively investigated, and follow a similar reaction pathway to that with Cu(II) salts.^{16–18} Therefore, we propose a possible reaction mechanism for the formation of dihydrofuran-fused C₆₀ derivatives **2a–2e** from the Cu(OAc)₂·H₂O- or Mn(OAc)₃·2H₂O-promoted reaction of C₆₀ with β-keto esters **1a–1c** and β-diketones **1d–1e**, as shown in Scheme 2. A β-keto ester or β-diketone reacts with Cu(OAc)₂·H₂O (or Mn(OAc)₃·2H₂O) to produce its enolate salt of Cu²⁺ (or Mn³⁺), which adds homolytically to C₆₀ to form fullerene radical **A**, followed by the formation of the

**Scheme 2****Scheme 3**




corresponding enolate salt **B**, and then cyclization to afford the dihydrofuran-fused fullerene derivative **2**.

Oxidation of ketones by Mn(OAc)₃ produces oxoalkyl radicals, which react with alkenes to give various products.^{16,17} Reactions of aromatic methyl ketones with alkenes in the presence of Mn(OAc)₃ usually lead to the formation of cyclic ketones such as α-tetralone and noncyclic products.²⁸ In order to see if the reaction of C₆₀ with aromatic methyl ketones will give the tetralone derivatives of C₆₀ or noncyclic products with the general form C₆₀H(R), we investigated the Cu(OAc)₂·H₂O- or Mn(OAc)₃·2H₂O-promoted reaction of C₆₀ with 4-nitroacetophenone (**3a**), 2-acetylpyridine (**3b**) and 2-acetylpyridine (**3c**) in the presence of DMAP. The reaction was found, unexpectedly, to give methanofullerenes **4a**, **4b**²⁴ and **4c**²⁴ and dihydrofuran-fused C₆₀ derivatives **5a** and **5b** (Scheme 3).

The yields of **4a–4c** and **5a,5b** and reaction times for the reaction of C₆₀ with **3a** (**3b** or **3c**), Cu(OAc)₂·H₂O (or Mn(OAc)₃·2H₂O) and DMAP in a molar ratio of 1 : 10 : 5 : 2 at 100 °C are listed in Table 2.

From Table 2 it can be seen that the reaction of C₆₀ with **3a** and **3b** could give both **4a**, **5a** and **4b**, **5b**, while the reaction of C₆₀ with

Table 2 The yields of **4a–4c** and **5a,5b** and reaction times for the Cu(OAc)₂·H₂O- or Mn(OAc)₃·2H₂O-promoted reaction of C₆₀ with **3a–3c** in the presence of DMAP at 100 °C

Substrate	Product	Cu(OAc) ₂ ·H ₂ O		Mn(OAc) ₃ ·2H ₂ O	
		Yield ^a	Time/h	Yield ^a	Time/h
	4a	11% (29%)	1	3% (10%)	3
	5a	12% (32%)		24% (85%)	
	4b^b	22% (49%)	0.5	10% (35%)	3
	5b^b	0%		18% (63%)	
	4c^b	20% (48%)	2	29% (93%)	3

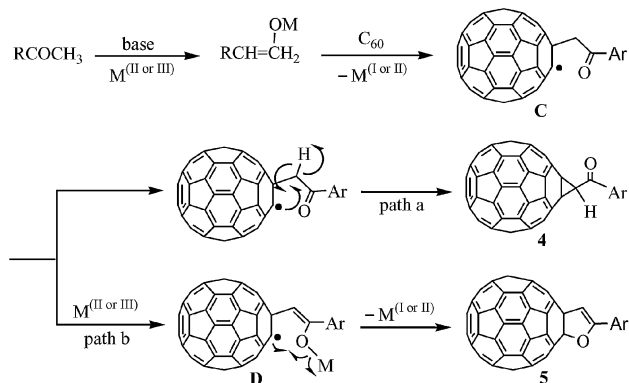
^a Yield in parentheses based on consumed C₆₀. ^b The reaction of C₆₀ with **3b** or **3c** in the presence of Cu(OAc)₂·H₂O was conducted at room temperature.

3c afforded only **4c**, and the percentage of methanofullerene **4** in the products increased from substrate **3a** to substrate **3c** for both $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ and $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$. These product distributions are probably related to the electronic properties of the substrates. Furthermore, $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ favors the formation of methanofullerenes **4**. For example, only **4b** was obtained when $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ was used as the oxidant in the reaction of C_{60} with **3b**.

Triethylamine and pyridine were also examined for the $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ - or $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ -promoted reaction of C_{60} with aromatic methyl ketones and found to be inferior to DMAP. For example, there was no reaction for the mixture of C_{60} , **3a** and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ in the presence of either triethylamine or pyridine for 1 h at 100 °C, just the same as the mixture of C_{60} , **3a** and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$. For the reaction of C_{60} with **3a** and $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ in the presence of triethylamine, only product **5a** could be obtained, but the yield was less than 5%, while the same reaction in the presence of pyridine afforded **5a** in low yield (<5%) along with other minor unidentified products, similar to that without the presence of any base.

Adducts **4b** and **4c** are known compounds, and their identities were confirmed by comparison of their spectral data with those reported by us previously.²⁴ The structure of **4a** was determined by its MS, ^1H NMR, ^{13}C NMR, FT-IR and UV-vis spectra. The FAB MS spectrum of **4a** exhibited the $(M + 1)$ ion peak at m/z 884. The ^1H NMR spectrum of **4a** showed a singlet at 5.60 ppm for the methine proton and two doublets at 8.50 and 8.61 ppm for the four aromatic protons. In the ^{13}C NMR spectrum of **4a**, besides the two peaks at 43.39 and 187.48 ppm for the CHCO group there was one peak at 71.32 ppm for two sp^3 carbons of the C_{60} moiety and twenty-nine peaks in the range 124–151 ppm for the fifty-eight sp^2 carbons of the C_{60} skeleton and phenyl carbons, indicating its C_s symmetry. The FT-IR and UV-vis spectra of **4a** showed similar absorption patterns as other methanofullerenes.²⁴ Compounds **5a** and **5b** had been fully characterized and exhibited similar spectral patterns as **2b**, **2c** and other dihydrofuran-fused C_{60} derivatives.^{23–26}

The proposed mechanism for the formation of methanofullerenes **4** and dihydrofuran-fused C_{60} derivatives **5** is shown in Scheme 4. In the presence of a base, aromatic methyl ketone **3** transforms to the enolate salt of Cu^{2+} (or Mn^{3+}) that adds homolytically to C_{60} to form fullerene radical **C**, which can either cyclize with the loss of a hydrogen radical from the methylene group to give methanofullerene **4** (path a) or form enolate salt **D** (path b), followed by cyclization to afford the dihydrofuran-fused C_{60} derivative **5**. The latter pathway is the same as that shown in Scheme 2.



Scheme 4

In summary, $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ has been successfully utilized in the free radical reaction in fullerene chemistry for the first time. Only dihydrofuran-fused C_{60} derivatives were obtained for highly enolizable ketones such as β -diketones and β -keto esters with both $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ and $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ as the oxidants.²⁹ In contrast, either dihydrofuran-fused C_{60} derivatives

or methanofullerenes could be obtained as the main products selectively and methanofullerenes were even produced exclusively by selecting $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ and $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ as the oxidant when aromatic methyl ketones were used as the substrates. Further work on fullerene functionalization by free radical reactions promoted by inorganic compounds is in hand.

Experimental

General methods

^1H NMR and ^{13}C NMR spectra were recorded in CS_2 - CDCl_3 , CS_2 - $\text{DMSO}-d_6$ or CS_2 - $\text{C}_6\text{D}_4\text{Cl}_2$ at 300 MHz and 75 MHz, respectively, on a Bruker Avance 300 spectrometer. MALDI-TOF and FAB mass spectra were taken on a Bruker BiFlexIII mass spectrometer with 4-hydroxy- α -cyanocinnamic acid as the matrix and on a VG ZAB-HS mass spectrometer with 3-nitrobenzyl alcohol as the matrix, respectively. FT-IR spectra were recorded on a Shimadzu 8600 FT IR spectrometer. UV-vis spectra were obtained on a Shimadzu UV-2501PC spectrometer.

C_{60} (>99.9%) was purchased from 3D Carbon Cluster Material Co. of Wuhan University in China. All other commercial available reagents were of analytical grade.

Reaction of C_{60} with $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ or $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ and compounds **1a–1e** in the presence of DMAP

A mixture of C_{60} (28.8 mg, 0.04 mmol), a chosen β -dicarbonyl compounds **1a** (**1b**, **1c**, **1d** or **1e**), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (16.0 mg, 0.08 mmol) or $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ (21.4 mg, 0.08 mmol) and DMAP (24.4 mg, 0.2 mmol) in a ratio of 1 : 10 : 2 : 5 was dissolved in dichlorobenzene (7 mL) and stirred at 80 °C. The reaction was monitored by TLC, and stopped at the designated time. The reaction mixture was passed through a silica gel plug in order to remove the copper salt and any other insoluble material. After the solvent was evaporated under vacuum, the residue was separated on a silica gel column with toluene-carbon disulfide as the eluent to afford recovered C_{60} and dihydrofuran-fused C_{60} derivatives **2a**^{22–24} (**2b**, **2c**, **2d**²⁴ or **2e**²²).

Spectra data of **2b**: ^1H NMR (300 MHz, CS_2 - CDCl_3) δ 1.60 (d, $J = 6.9$ Hz, 6H), 3.83 (s, 3H), 4.20 (hepta, $J = 6.9$ Hz, 1H); ^{13}C NMR [75 MHz, CS_2 - CDCl_3 with $\text{Cr}(\text{acac})_3$ as relaxation reagent] (all 2C unless indicated) δ 19.74, 27.83 (1C), 50.77 (1C), 71.84 (1C), 102.32 (1C), 102.93 (1C), 134.87, 137.08, 139.09, 139.49, 141.09, 141.19, 141.90, 141.94, 142.06, 142.16, 142.30, 142.38, 142.40, 143.84, 144.06, 144.14, 144.45, 144.63, 144.79, 144.98, 145.28, 145.57, 145.63, 145.76, 145.84, 146.06, 146.83, 146.92 (1C), 147.65 (1C), 148.29, 164.10 (1C), 176.35 (1C); FT-IR ν/cm^{-1} (KBr) 2925 (m), 2851 (w), 1705 (s), 1622 (s), 1511 (m), 1461 (w), 1429 (m), 1331 (m), 1299 (w), 1278 (w), 1187 (m), 1122 (s), 1089 (s), 1070 (s), 977 (m), 938 (w), 929 (w), 779 (m), 575 (w), 526 (s); UV-vis (CHCl_3) $\lambda_{\text{max}}/\text{nm}$ (log ϵ) 254 (5.18), 315 (4.65), 427 (3.37), 688 (2.31); MS (MALDI-TOF) m/z 862 (M^-).

Spectra data of **2c**: ^1H NMR (300 MHz, CS_2 - CDCl_3) δ 1.17 (t, $J = 7.1$ Hz, 3H), 4.24 (q, $J = 7.1$ Hz, 2H), 7.53–7.60 (m, 3H), 8.07–8.10 (m, 2H); ^{13}C NMR [75 MHz, CS_2 - CDCl_3 with $\text{Cr}(\text{acac})_3$ as relaxation reagent] (all 2C unless indicated) δ 13.60 (1C), 60.19 (1C), 72.70 (1C), 101.65 (1C), 104.27 (1C), 127.49, 129.03 (1C), 129.55, 130.68 (1C), 135.01, 137.05 (1C), 138.92, 139.43, 141.02, 141.10, 141.80, 141.84, 141.97, 142.04, 142.20, 142.28, 142.30, 143.75, 143.93, 144.02, 144.31, 144.53, 144.68, 144.95, 145.17, 145.47, 145.53, 145.69, 145.74, 145.96, 146.84 (1C), 146.90, 147.54 (1C), 147.86, 163.11 (1C), 165.96 (1C); FT-IR ν/cm^{-1} (KBr) 2922 (m), 2853 (w), 1705 (s), 1693 (s), 1509 (m), 1461 (w), 1440 (w), 1423 (w), 1367 (m), 1325 (s), 1256 (w), 1173 (w), 1155 (w), 1106 (s), 1086 (s), 998 (m), 951 (m), 923 (m), 792 (m), 688 (s), 591 (m), 574 (w), 562 (m), 526 (s); UV-vis (CHCl_3) $\lambda_{\text{max}}/\text{nm}$ (log ϵ) 255 (5.16), 314 (4.67), 426 (3.33), 685 (2.32); MS (MALDI-TOF) m/z 910 (M^-).

Reaction of C₆₀ with Cu(OAc)₂·H₂O or Mn(OAc)₃·2H₂O and compounds 3a, 3b, and 3c in the presence of DMAP

A mixture of C₆₀ (28.8 mg, 0.04 mmol, 1 eq.), aromatic methyl ketone 3a (3b or 3c, 10 eq.), Cu(OAc)₂·H₂O (16 mg, 0.08 mmol, 2 eq.) or Mn(OAc)₃·2H₂O (21.4 mg, 0.08 mmol, 2 eq.) and DMAP (24.4 mg, 0.20 mmol, 5 eq.) was dissolved in dichlorobenzene (7 mL) and stirred at 100 °C. The reaction was monitored by TLC, and stopped at the designated time. The reaction mixture was passed through a silica gel plug in order to remove the copper salt and any other insoluble material. After the solvent was evaporated under vacuum, the residue was separated on a silica gel column with toluene–carbon disulfide as the eluent to afford recovered C₆₀, cyclopropane-fused C₆₀ derivatives 4a (4b²⁴, or 4c²⁴) and dihydrofuran-fused C₆₀ derivatives 5a (5b).

Spectra data of 4a: ¹H NMR (300 MHz, CS₂-CDCl₃) δ 5.60 (s, 1H), 8.50 (d, *J* = 8.8 Hz, 2H), 8.61 (d, *J* = 8.8 Hz, 2H); ¹³C NMR [75 MHz, CS₂-CDCl₃ with Cr(acac)₃ as relaxation reagent] (all 2C unless indicated) δ 43.39 (CH, 1C), 71.32 (*sp*³-C of C₆₀), 124.13 (aryl C), 129.54 (aryl C), 136.32, 139.35, 139.85 (aryl C, 1C), 140.64, 140.89, 141.59, 141.67, 141.81, 141.97, 142.40, 142.61 (3C), 142.67, 142.76 (1C), 142.91, 143.27, 143.50, 144.08 (3C), 144.27, 144.29 (3C), 144.31 (4C), 144.69 (4C), 144.82 (4C), 144.86, 144.90, 145.27, 146.93, 150.58 (aryl C, 1C), 187.48 (CHCO, 1C); FT-IR *v*/cm⁻¹ (KBr) 2923 (s), 2853 (m), 1687 (m), 1599 (w), 1522 (s), 1463 (w), 1426 (w), 1408 (w), 1338 (s), 1317 (m), 1210 (m), 1184 (w), 1007 (m), 848 (s), 713 (w), 697 (w), 575 (w), 525 (s); UV-vis (CHCl₃) λ_{max}/nm (log ε) 259 (5.08), 313 (4.56), 426 (3.48), 690 (2.31); MS (FAB) *m/z* 884 (M + 1)⁺.

Spectra data of 5a: ¹H NMR (300 MHz, CS₂-C₆D₄Cl₂) δ 6.54 (s, 1H), 7.98 (d, *J* = 8.8 Hz, 2H), 8.17 (d, *J* = 8.8 Hz, 2H); ¹³C NMR [75 MHz, CS₂-C₆D₄Cl₂ with Cr(acac)₃ as relaxation reagent] (all 2C unless indicated) δ 73.92 (1C), 102.30 (1C), 103.98 (1C), 124.06, 135.47 (1C), 136.03, 137.37, 139.82, 140.64, 141.70, 141.79, 142.11, 142.19, 142.28, 142.68, 142.71, 142.79, 142.89, 142.99, 144.14, 144.25, 144.37, 144.91, 144.94, 145.07, 145.16, 145.32, 145.55, 145.94, 146.02, 146.11, 146.20, 146.30, 147.36 (1C), 148.08 (1C), 148.39 (1C), 148.92, 155.11 (1C); FT-IR *v*/cm⁻¹ (KBr) 2921 (m), 2851 (w), 1637 (w), 1593 (w), 1510 (s), 1425 (w), 1337 (s), 1179 (w), 1106 (m), 1065 (w), 1038 (s), 982 (s), 926 (m), 847 (m), 770 (w), 727 (m), 575 (w), 562 (w), 525 (s); UV-vis (CHCl₃) λ_{max}/nm (log ε) 255 (4.85), 321 (4.45), 424 (3.20), 691 (2.38); MS (FAB) *m/z* 884 (M + 1)⁺.

Spectra data of 5b: ¹H NMR (300 MHz, CS₂-DMSO-*d*₆) δ 7.00 (s, 1H), 7.38 (ddd, *J* = 7.4, 4.7, 1.4 Hz, 1H), 7.89 (td, *J* = 7.7, 1.8 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 8.73 (d, *J* = 4.7 Hz, 1H); ¹³C NMR [75 MHz, CS₂-DMSO-*d*₆ with Cr(acac)₃ as relaxation reagent] (all 2C unless indicated) δ 72.41 (1C), 100.94 (1C), 102.00 (1C), 119.42 (1C), 122.93 (1C), 134.49, 135.41 (1C), 136.00, 138.33, 139.21, 140.30, 140.47, 140.75, 140.77, 140.88, 141.23, 141.27, 141.47, 141.50, 142.85, 143.04, 143.18, 143.62 (4C), 143.72, 143.80, 143.84, 144.25, 144.49, 144.56, 144.63, 144.72, 144.86, 145.88 (1C), 146.64 (1C), 147.30 (1C), 148.26, 148.81 (1C), 155.05 (1C); FT-IR *v*/cm⁻¹ (KBr) 2921 (m), 2851 (w), 1575 (w), 1503 (s), 1465 (w), 1426 (m), 1325 (m), 1261 (m), 1069 (w), 1034 (m), 981 (s), 929 (m), 784 (m), 746 (s), 575 (w), 562 (w), 525 (s); UV-vis (CHCl₃) λ_{max}/nm (log ε) 255 (5.14), 313 (4.73), 426 (3.43), 690 (2.45); MS (FAB) *m/z* 840 (M + 1)⁺.

Acknowledgements

We are grateful for financial support from the National Science Fund for Distinguished Young Scholars (20125205), Fund for Innovative Research Groups of National Science Foundation of China (20321101), Anhui Provincial Bureau of Human Resources (2001Z019) and Anhui Provincial Natural Science Foundation (00045306). We thank Professor Roger Taylor of Sussex University for helpful discussion and manuscript reading.

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