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Manganese(III) acetate-mediated free radical reactions of [60]fullerene with β-dicarbonyl compounds

Changzhi Li, Danwei Zhang, Xiaotong Zhang, Shihui Wu and Xiang Gao*
Department of Chemistry, Fudan University, Shanghai, 200433, PR China.
E-mail: gaoxiang@fudan.edu.cn

Received 3rd August 2004, Accepted 27th September 2004
First published as an Advance Article on the web 20th October 2004

[60]Fullerene reacted with various β-dicarbonyl compounds in the presence of $Mn(OAc)_3 \cdot 2H_2O$ to generate dihydrofuran-fused [60]fullerene derivatives or 1,4-bisadducts. Dihydrofuran-fused [60]fullerene derivatives **2** could be formed by treatment of α-unsubstituted β-diketones **1a–e** or β-ketoesters **1f** and **1g** with [60]fullerene in refluxing chlorobenzene in the presence of Mn(III). Solvent-participated unsymmetrical 1,4-bisadducts **3** were obtained through the reaction of [60]fullerene with dimethyl malonate **1h** or α-substituted β-dicarbonyl compounds **1i–1n** in toluene. A possible reaction mechanism for the formation of different fullerene derivatives is proposed.

Introduction

Since the discovery of the fullerenes[1] and a report of their production in preparative quantities,[2] a number of methods for modifying fullerenes have been developed.[3] Among them, those which utilize reactions involving free radical intermediates are particularly effective.[4–17]

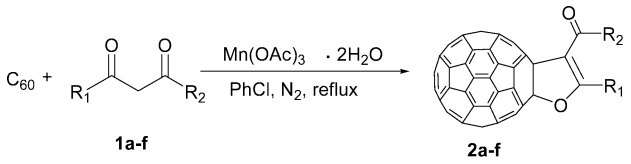
$Mn(OAc)_3$ is a highly efficient single-electron oxidant for the oxidation of β-dicarbonyl compounds to the corresponding radicals, which can directly react with alkenes and alkynes to produce discrete dicarbonyl derivatives.[18,19] Generally, the nature of Mn-mediated oxidation of β-dicarbonyl compounds to radicals depends on two variables: the rate of formation of the Mn(III) enolates, which is related to the pK_a of the α-hydrogens, and the oxidation of the enolates to free radicals. Recently, $Mn(OAc)_3$ has been shown to possess a good capability to mediate fullerene free radical reactions. For instance, Wang *et al.*[16,17] reported that reaction of [60]fullerene with several active methylene compounds led to novel 1,4-bisadducts. Previous results[20] from our group also showed that the reaction of [60]fullerene with tertiary amines in the presence of Mn(III) readily yielded pyrrolidinofullerene. In the present paper, we wish to detail our systematic investigation on the free radical reactions of some β-dicarbonyl compounds with [60]fullerene in the presence of manganese(III) acetate dihydrate.

Results and discussion

The Mn(III)-mediated reaction of various β-dicarbonyl compounds with [60]fullerene in chlorobenzene or toluene showed different tendencies to generate dihydrofuran-fused [60]fullerene derivatives or 1,4-bisadducts. The results are summarized in the Table 1.

In the presence of $Mn(OAc)_3 \cdot 2H_2O$, a novel free radical cyclization occurred through the reaction of α-unsubstituted β-diketones or β-ketoesters with the [60]fullerene in chlorobenzene, affording the dihydrofuran-fused [60]fullerene derivatives as illustrated by Scheme 1. Typically, a mixture of C_{60} (36.0 mg, 0.05 mmol), 1.5 equiv. of compound **1** and 3.0 equiv. of Mn(III) was refluxed under N_2 in 25 ml of chlorobenzene for 3 h to afford the cycloadducts **2**. The reaction of substrate **1g**, however, was completed within 10 min.

The structures of the dihydrofuran-fused [60]fullerene derivatives **2** were established on the basis of spectroscopic analysis. For example, the MALDI FT-MS of **2b** displayed a strong peak at *m/z* 907.1, corresponding to the M + 1 signal of a 1 : 1 cycloadduct of **2b**. The HRMS data revealed the expected elemental composition. In the ^1H NMR spectrum,



a: R_1,R_2=$CH_2C(CH_3)_2CH_2$
b: R_1,R_2=$CH_2CH(Ph)CH_2$
c: R_1,R_2=$CH_2CH_2CH_2$
d: R_1,R_2=CH_2CH_2
e: R_1=Me, R_2=Me
f: R_1=Me, R_2=OMe
g: R_1=Ph, R_2=OEt

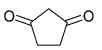
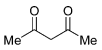
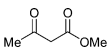
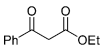
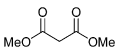
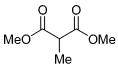
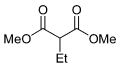
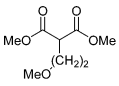
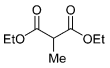
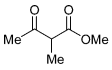
Scheme 1

the aromatic protons resonated at δ 7.33–7.44 and the two methylenes appeared as two multiplets centred at δ 2.97 and 3.36, respectively. The spectrum also contained a multiplet at δ 3.91 for the methine proton. In the ^{13}C NMR spectrum, the sp^2 carbons of the C_{60} cage resonated at δ 137.83–148.24, indicating an unsymmetrical structure. The characteristic sp^3-junction carbons of the C_{60} cage were observed at δ 69.67 and 105.52, respectively. It is noteworthy that other cycloadducts (**2a**, **2c**, **2e**, **2f** and **2g**) in these reactions all had C_s symmetrical structures as shown by the typical 30 lines (in the ^{13}C NMR spectra) for the sp^2 carbons of the fullerene skeleton. The UV-vis spectrum showed an absorption at 431 nm, diagnostic of the cycloadduct at the 6,6-junction. The presence of a carbonyl group was supported by a strong absorption at 1637 cm^{-1} in the IR spectrum. It is known that dihydrofuran-fused [60]fullerene derivatives could be prepared through nucleophilic addition reactions. For example, reaction of [60]fullerene with β-dicarbonyl compounds was mediated by piperidine[21] or under the HSVM condition.[22] The identities of **2c**, **2d** and **2f** were further established by comparison of their spectroscopic data with those reported in literature.[21,22]

As shown in Table 1, the reactions with α-unsubstituted β-diketones or β-ketoesters (**1a–g**, Table 1, Entries 1–11) in chlorobenzene afforded cycloadducts **2** in moderate yields. Compared with linear substrates **1e**, **1f** and **1g**, the reaction of cyclic substrates **1a–d** with C_{60} was significantly slower (with much lower C_{60} conversion rates). An extreme example was cyclopentane-1,3-dione **1d**, which reacted with C_{60} to afford only traces of cycloadduct, with about 10% of the C_{60} consumed (Entry 7), presumably because cyclic diketones are less easily converted to enols than their linear counterparts. Extending the reaction time in these cases (**1b–d**) could not improve the yields. The reaction of **1g** (a linear substrate) with C_{60} proceeded rather fast (10 min), giving **2g** in 44% yield based on the consumed C_{60} (Entry 11).

DOI: 10.1039/b411862f

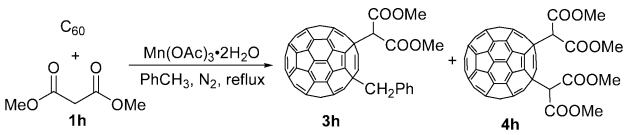
Table 1 Reaction of C_{60} with β-dicarbonyl compounds **1** mediated by Mn(III)

Entry	Substrate		Conditions	Conversion of C_{60} (%)	Yield (%)[a] **2**	**3**
1		**1a**	PhCl/3 h/reflux	34	52	—
2			$PhCH_3$/14 h/80 °C	43	17	—[b]
3		**1b**	PhCl/3 h/reflux	28	48	—
4			PhCl/16 h/reflux	52	28	—
5		**1c**	PhCl/3 h/reflux	17	79	—
6			PhCl/9 h/reflux	33	37	—
7		**1d**	PhCl/3 h/reflux	11	Trace	—
8			PhCl/24 h/reflux	14	Trace	—
9		**1e**	PhCl/3 h/reflux	42	34	—
10		**1f**	PhCl/3 h/reflux	49	48	—
11		**1g**	PhCl/10 min/reflux	45	44	—
12		**1h**	$PhCH_3$/20 h/reflux	63	—	15
13		**1i**	$PhCH_3$/20 h/reflux	44	—	59
14		**1j**	$PhCH_3$/16 h/reflux	43	—	70
15[c]		**1k**	$PhCH_3$/22 h/reflux	36	—	65
16		**1l**	$PhCH_3$/16 h/reflux	45	—	65
17		**1m**	$PhCH_3$/0.5 h/100 °C	49	—	47[d]

[a] Yield of isolated pure adducts based on the consumed C_{60}, with the molar ratio between **1**, C_{60} and Mn(III) being 1:1.5:3.0 in all runs except run 15. [b] A so far unidentified benzyl-containing adduct was also detected. [c] The molar ratio between **1k**, C_{60} and Mn(III) in this run was 1:2.0:3.0. [d] **3m** was a 1.5 : 1 mixture of two diastereomers as shown by ^{1}H NMR.

It is interesting to note that the reaction of **1a** in toluene resulted in a so far unidentified benzyl-containing adduct apart from the **2a** (Entry 2). Because under the given circumstances the only source of benzyl group was the solvent toluene, a solvent-participated reaction must have occurred. This deduction is also supported by some literature precedents. For instance, it is known that benzyl radicals could be generated from toluene through H-abstraction by *tert*-butoxy radical[5,6] or phthalimide-*N*-oxyl (PINO) radical.[23]

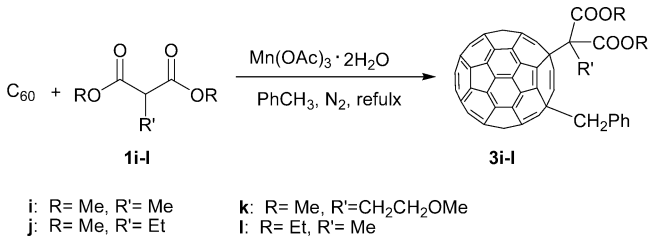
We also studied the reaction with dimethyl malonate **1h**. The results were in sharp contrast to those of the previous cycloaddition reactions. In refluxing chlorobenzene, the cycloadduct **2** was not detected at all. Instead, 1,4-bisadduct **4h** and singly bonded dimer were observed.[16] Interestingly, after refluxing in toluene under N_2 for 20 h, the reaction of C_{60} with **1h** in the presence of Mn(III) (with the molar ratio being 1 : 1.5 : 3.0) resulted in the solvent-participated unsymmetrical 1,4-bisadduct **3h** in 15% based on the consumed C_{60} and 1,4-bisadduct **4h** (Scheme 2, Table 1, Entry 12). Compared with that of **1a–g**, the ease with which the reaction of dimethyl malonate **1h** with C_{60} generated 1,4-bisadduct was different, probably because the enolization of **1h** was slow as a consequence of its lower acidity than that of the β-diketones or β-ketoester.[24] The slow enolization and the subsequent cyclization might not only lead to slow addition of malonyl group to C_{60} but also make it easier for the malonate radical to abstract a hydrogen atom from the bulk toluene to generate benzyl radical and resulted in the unsymmetrical 1,4-bisadduct **3h**.



Scheme 2

To optimize this solvent-participated free radical reaction, we then studied the reaction of a series of α-substituted β-dicarbonyl compounds **1i–m** with C_{60} in toluene (Scheme 3, Table 1, Entries 13–17). In all these runs 1,4-bisadducts **3i–m** were obtained as the major product. While the work along this line was in progress, a similar investigation was reported by Wang *et al*.[17]

The yields and conversions of C_{60} are listed in Table 1 (Entries 13–17). The β-diesters with different α-substituents **1i–l** could react with C_{60} to generate mainly the unsymmetrical 1,4-bisadduct



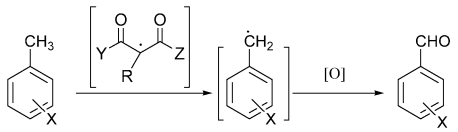
Scheme 3

3 in 59–70% in contrast to the run of unsubstituted β-diester **1g**. The presence of an α-substituent remarkably improved the yield of the unsymmetrical 1,4-bisadducts. Moreover, the reaction of C_{60} with methyl 2-methyl-3-oxobutanoate **1m** at 100 °C for only 0.5 h generated **3m** in 47% yield as a 1.5 : 1 mixture of the two diastereomers as shown by ^{1}H NMR. These results are consistent with our anticipation.

It is known that the presence of an α-alkyl substituent in β-dicarbonyl compound could facilitate the oxidation of Mn(III) enolate to radical.[18b] We deduced that the easier oxidation of the α-substituted β-dicarbonyl compound to the radical could facilitate generation of the benzyl radical. Introduction of the α-substituent could also create steric hindrance and thus hamper the formation of the **4h** type bisadducts. The yields of unsymmetrical 1,4-bisadduct were therefore improved.

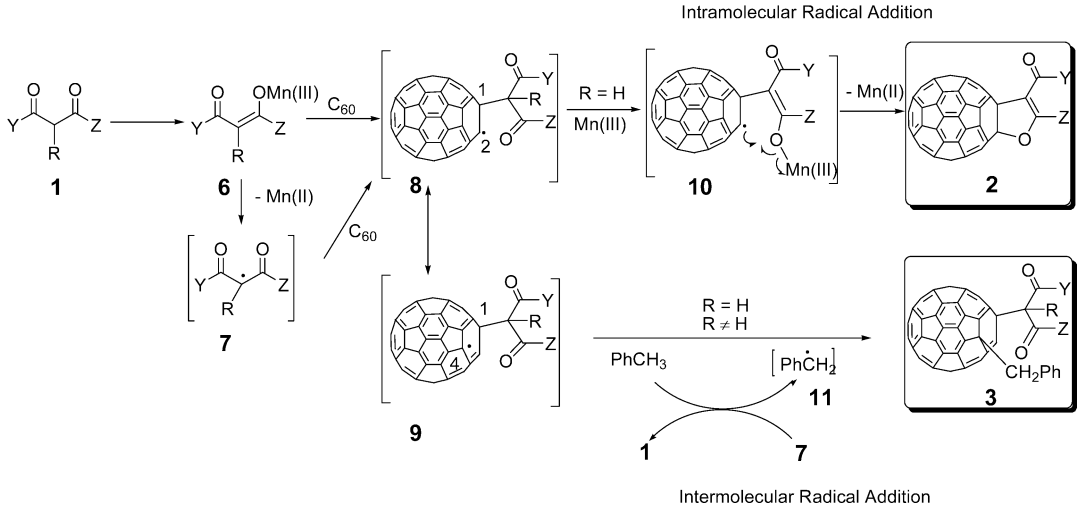
The structures of unsymmetrical 1,4-bisadducts **3h–m** were fully established on the basis of their MALDI FT-MS, NMR, IR and UV-vis spectra. The identity of the known **3l** was also confirmed by comparison of the spectroscopic data with those reported in the literature.[17] The structural elucidation of these compounds is exemplified here through assignment of **3i**: the MALDI FT-MS spectrum of **3i** displayed a peak at *m/z* 979.1 ($M + Na^+$) and a peak at *m/z* 811.1 for $[C_{60}CH_2Ph]^+$. In the ^{1}H NMR spectrum there were five aromatic protons of benzyl at δ 7.26–7.54, an AB system at δ 4.38 for methene ($J = 12.8$ Hz), a singlet of α-methyl group (δ 2.53) and two singlets of methoxyl groups (δ 3.89 and 3.97). The unsymmetrical structure was supported by the presence of more than 30 resonances of C_{60} sp^2-carbon signals (δ 137.01–156.91) and two sp^3-carbons of the fullerene cage at δ 60.08 (C_1) and 61.96 (C_4) in the ^{13}C NMR spectrum. The assigned structure was also confirmed by 2D NMR experiments (HSQC and HMBC). In the HMBC spectrum, 1,4-addition or 1,16-addition pattern was indicated by the $^2J_{(C,H)}$ and $^3J_{(C,H)}$ signals. Two methylene protons (δ 4.38, $J_{AB} = 12.8$ Hz) correlated with four fullerene carbons (sp^3-C_1, and three sp^2-carbons). No cross-peaks with sp^3-C_4 were observed. The sp^3-C_4 only had cross-peak with α-methyl protons (δ 2.53). Obviously, there was no direct bonding between the two sp^3-carbons of the fullerene cage, which correspond to the 1,4- and 1,16-pattern. A diagnostic absorption at around 448 nm was observed in the UV-vis spectrum of **3i**, which was consistent with that revealed by the 1,4-bisadducts reported.[12,15]

On the basis of the above results, we propose that the benzyl radical was generated by H-atom abstraction from the solvent (toluene) and served as a radical trapper in the reaction process. Several substituted toluenes (4-methylanisole, *p*-xylene, *m*-xylene and 1-chloro-4-methylbenzene) were then chosen as the solvent in efforts to obtain the substituted toluene-containing un-symmetrical 1,4-bisadducts. Unfortunately, such adducts were not been detected. Corresponding substituted benzaldehydes were generated rapidly in these reactions (Scheme 4) instead, which indicated that substituted benzyl radicals were indeed produced. However, the substituted benzyl radicals carrying an electron-withdrawing or electron-donating group, were all more reactive than the benzyl radical.[25] Therefore they readily underwent further oxidation to generate aldehydes.



Scheme 4

To rationalize these manganese(III) acetate-mediated free radical reactions, we postulated (based on the studies of the Mn(III)-mediated reaction of alkene with β-dicarbonyl compounds[18b]) a pathway as shown in Scheme 5. For those very acidic compounds (such as α-unsubstituted β-keto esters and β-diketones), enolization occurs readily and the oxidation is slow. For α-alkyl β-keto ester, enolization is slow whereas the oxidation is rapid. These also fit our fullerene reaction system. We propose that the enolization of **1** in the presence of $Mn(OAc)_3 \cdot 2H_2O$ results in enolate **6**. The radical **7** is generated *in situ via* oxidation of the Mn(III) enolates **6**. Then, the key intermediate fullerene radical **8** is formed through two paths. One is the addition of enolate **6** with [60]fullerene with loss of Mn(II), which might occur when enol **6** is slowly oxidized to radical **7**, as in the case of the enol of β-diketones **1a–c** and α-unsubstituted β-keto esters **1e**, **1f**. The other is the addition of radical **7** to [60]fullerene when the oxidation of **6** to **7** is rapid, as illustrated by the α-substituted β-dicarbonyl compounds **1i–m**. Similar processes have been proposed by comparing the Mn(III)-mediated reaction of α-unsubstituted β-keto esters and α-alkyl



Scheme 5

β-keto esters with alkene.[18b,26] In chlorobenzene, intermediate **8** is rapidly enolized again to generate **10**, which further undergoes a cyclization to afford dihydrofuran-fused [60]fullerene derivative **2** with loss of Mn(II). We assign this process as intramolecular radical addition. It is interesting to note that an intermolecular radical addition process occurred in toluene. Benzyl radical **11** was produced by H-atom abstraction from toluene in the presence of radical **7**. The solvent-containing unsymmetrical 1,4-bisadduct **3** was generated through the combination of **11** and **9**, which is the resonance structure of **8**.

In conclusion, we have studied Mn(III)-mediated reactions of [60]fullerene with β-dicarbonyl compounds in chlorobenzene or toluene. Different tendencies to generate dihydrofuran-fused [60]fullerene derivatives or 1,4-bisadducts were observed. A possible mechanism is also proposed.

Experimental

General methods

^{1}H and ^{13}C NMR spectra were obtained on Brucker AMX 500 spectrometers (^{1}H: 500 MHz; ^{13}C: 125 MHz) or JEOL 400M spectrometers (^{1}H: 400 MHz; ^{13}C: 100 MHz) with tetramethylsilane as the internal standard. UV-vis spectra were obtained on an Agilent 8453. FT-IR spectra were obtained on a Nicolet AVATAR 360 IR spectrometer. Mass spectra were obtained on an IonSpec (4.7 Tesla) MALDI FTMS.

Diketones (**1a–b**) were prepared following the procedure in the literature.[27] α-Substituted β-dicarbonyl compounds (**1i–m**) were prepared from the reaction of malonic ester with the corresponding halides mediated by sodium methanolate or sodium ethanolate.

General procedure for the reaction of [60]fullerene with β-dicarbonyl compound 1 and $Mn(OAc)_3 \cdot 2H_2O$

A mixture of [60]fullerene (0.05 mmol), β-dicarbonyl compounds **1** (0.075–0.10 mmol) and $Mn(OAc)_3 \cdot 2H_2O$ (0.15 mmol) in hot chlorobenzene or toluene (25 ml) was stirred under N_2. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel (eluting with toluene–hexane) to afford **2** or **3**.

Compound 2a. 5,5-Dimethylcyclohexane-1,3-dione, **1a** (10.5 mg, 0.075 mmol) was subjected to the general procedure in refluxing chlorobenzene for 3 h to afford **2a** (7.6 mg, 52% yield based on 34% consumed C_{60}). The spectroscopic data of **2a** were consistent with those reported in the literature.[22]

Compound 2b. 5-Phenylcyclohexane-1,3-dione, **1b** (14.1 mg, 0.075 mmol) was subjected to the general procedure in refluxing chlorobenzene for 3 hours to afford **2b** (6.2 mg, 48% yield based on 28% consumed C_{60}). Spectral data of **2b**: ^{1}H NMR (400 MHz, CS_2–$CDCl_3$) δ 2.97 (m, 2H, CH_2), 3.36 (m, 2H, CH_2), 3.91 (m, 1H, C*H*), 7.33–7.44 (m, 5H, arom *H*); ^{13}C NMR (100 MHz, CS_2–$CDCl_3$) δ 32.42 (*C*H), 40.47(*C*H_2), 44.91 (*C*H_2),69.67 (sp^3-C of C_{60}), 105.52 (sp^3-C of C_{60}), 113.61 (*C*=CCO), 126.80 (arom C), 127.53 (arom C), 129.10 (arom C), 135.01 (arom C), 140.11, 140.23, 141.28, 141.29, 141.72, 141.86, 142.14, 142.24, 142.40, 142.46, 142.50, 142.62, 142.71, 142.77, 143.39, 143.50, 144.02, 144.54, 144.55, 144.70, 145.01, 145.15, 145.46, 145.97, 146.02, 146.29, 146.42, 146.69, 146.92, 147.12, 147.90, 148.01, 148.24, 175.46 (*C*C=O), 192.74 (*C*O*C*H_2); MS (MALDI FTMS) *m*/*z* 907.1 (M + 1), 720.0 (C_{60}^+); HRMS (MALDI FTMS) calcd for $C_{72}H_{11}O_2^{+1}$ (M + 1), 907.0726, found 907.0754; IR ν/cm^{-1} (KBr) 2908, 2850, 1655, 1637, 1379, 1215, 910, 754, 696, 630, 526; UV-vis ($CHCl_3$) λ_{max}/nm 255, 317, 431.

Compound 2c. Cyclohexane-1,3-dione, **1c** (8.4 mg, 0.075 mmol) was subjected to the general procedure in refluxing chlorobenzene for 3 h to afford **2c** (5.6 mg, 79% yield based on 17% consumed C_{60}). The spectroscopic data of **1c** were consistent with those reported in the literature.[21]

Compound 2e. Pentane-2,4-dione, **1e** (7.7 μL, 0.075 mmol) was subjected to the general procedure to in refluxing chlorobenzene 3 h afford **2e** (5.8 mg, 34% yield based on 42% consumed C_{60}). The spectroscopic data of **1e** were consistent with those reported in the literature.[21,22]

Compound 2f. Methyl 3-oxobutanoate, **1f** (9.0 μL, 0.075 mmol) was subjected to the general procedure in refluxing chlorobenzene for 3 h to afford **2f** (9.8 mg, 48% yield based on 49% consumed C_{60}). Spectral data of **2f**: ^{1}H NMR (400 MHz, CS_2–$CDCl_3$) δ2.86 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3); ^{13}C NMR (125 MHz, CS_2–$CDCl_3$) δ15.36 (CH_3), 50.96 (OCH_3), 71.98 (sp^3-C of C_{60}), 102.67 (sp^3-C of C_{60}), 105.03 (*C*=CCO), 135.11, 137.31, 139.38, 139.72, 141.28, 141.43, 142.10, 142.15, 142.27, 142.36, 142.52, 142.60, 142.63, 144.04, 144.18, 144.35, 144.56, 144.85,145.01, 145.22, 145.47, 145.78, 145.85, 145.98, 146.04, 146.27, 146.99, 147.14, 147.87, 148.34, 164.38 (*C*C=O), 169.08 (*C*=O); MS (MALDI FTMS) *m*/*z* 834.1; IR ν/cm^{-1} (KBr) 2930, 2847, 1701, 1639, 1432, 1335, 1126, 1101, 976, 941, 783, 573, 526; UV-vis ($CHCl_3$) λ_{max}/nm 256, 316, 431.

Compound 2g. Ethyl 3-oxo-3-phenylpropanoate, **1g** (14.8 μL 0.075 mmol) in refluxing chlorobenzene for 10 min was subjected to the general procedure to afford **2g** (9.0 mg, 44% yield based on 45% consumed C_{60}). Spectral data of **2g**: ^{1}H NMR (400 MHz, CS_2–$CDCl_3$) δ 1.17 (t, J = 6.84 Hz, 3H, CH_3), 2.25 (q, J = 6.84 Hz 2H, CH_2), 7.58 (m, 3H, arom H), 8.09 (m, 2H, arom H); ^{13}C NMR (125 MHz, CS_2–$CDCl_3$) δ 14.00 (*C*H_3), 60.56 (*C*H_2), 73.16 (sp^3-C of C_{60}), 102.08 (sp^3-C of C_{60}), 104.72 (*C*=CCO), 127.84 (arom C), 129.48 (arom C), 129.97 (arom C), 131.01 (arom C), 135.45, 137.48, 139.36, 139.88, 141.46, 141.55, 142.24, 142.28, 142.42, 142.48, 142.64, 142.74 (4C), 144.19, 144.38, 144.47, 144.76, 144.98, 145.12, 145.39, 145.61, 145.91, 145.97, 146.13, 146.18, 146.40, 147.28, 147.36, 147.98, 148.31, 163.49 (*C*C=O), 166.36 (*C*=O); MS (MALDI FTMS) *m*/*z* 911.1 (M + 1); HRMS (MALDI FTMS) calcd for $C_{71}H_{11}O_3$ + 1 (M + 1), 911.0667, found 911.0703. IR ν/cm^{-1} (KBr) 2955, 2924, 2854, 1736, 1686, 1460, 1429, 1261, 1209, 1097, 1020, 810, 750, 687, 526; UV-vis ($CHCl_3$) λ_{max}/nm 257, 317, 431.

Compounds 3h and 4h. Dimethyl malonate, **1h** (10 μL, 0.075 mmol) was subjected to the general procedure in refluxing toluene for 20 hours to afford **3h** (4.4 mg, 15% yield based on 63% consumed C_{60}) and **4h** (6.5 mg, 21% yield based on 63% consumed C_{60}). Spectral data of **3h**: ^{1}H NMR (500 MHz, CS_2–$CDCl_3$) δ 3.43 (s, 1H, C*H*), 3.79 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 4.35 (AB, J_{AB} = 12.8 Hz, 2H, CH_2Ph), 7.41–7.44 (m, 1H, arom H), 7.50 (t, J = 7.5 Hz, 2H, arom H), 7.65 (d, J = 7.4 Hz, 2H, arom H); ^{13}C NMR (125 MHz, CS_2–$CDCl_3$) δ 48.85 (*C*H_2Ph), 52.48 (O*C*H_3), 52.63 (O*C*H_3), 55.87 (sp^3-C of C_{60}), 60.48 (sp^3-C of C_{60}), 60.66 (*C*H), 127.79 (*C*H, arom C), 128.73 (*C*H, arom C), 130.88 (*C*H, arom C), 135.89 (C, arom C), 137.36, 138.73, 139.10, 139.82, 140.62, 140.84, 142.06, 142.46, 142.57, 143.14, 143.20, 143.27, 143.31, 143.88, 144.02, 144.10, 144.18, 144.23, 144.46, 144.54, 144.94, 145.14, 145.49, 146.75, 146.87, 146.92, 147.06, 147.10, 148.47, 148.50, 148.62, 149.50, 150.49, 152.82, 157.33, 166.21 (C=O), 166.75 (C=O). MS (Ionspec MALDI FT-MS) *m*/*z* 997.1 (M + Na$^+$), 720.0 (C_{60}^+). IR ν/cm^{-1} (KBr) 2920, 1736, 1731, 1207, 1151, 1020, 752, 698, 526, 469. UV-vis λ_{max}/nm ($CHCl_3$) 258, 325, 448, 660. The spectroscopic data of **4h** were consistent with those reported in the literature.[16]

Compound 3i. Dimethyl 2-methylmalonate, **1i** (11.2 μL, 0.075 mmol) was subjected to the general procedure in refluxing toluene for 20 hours to afford **3i** (12.4 mg, 59% yield based on 44% consumed C_{60}). Spectral data of **3i**:^{1}H NMR (500 MHz, CS_2–$CDCl_3$) δ 2.53 (s, 3H, CH_3), 3.89 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 4.38 (AB, J = 12.8 Hz, 2H, CH_2Ph), 7.26–7.27 (m, 1H, arom H), 7.31 (t, J = 7.1 Hz, 2H, arom H), 7.54 (d, J =

7.1 Hz, 2H, arom H); ^{13}C NMR (125 MHz, CS_2–$CDCl_3$) δ 21.77 (CH_3), 48.20 (CH_2Ph), 52.57 (OCH_3), 52.70 (OCH_3), 60.09 (sp^3-C of C_{60}), 61.45 (CCH_3), 61.96 (sp^3-C of C_{60}), 127.26 (CH, arom C), 128.17 (CH, arom C), 130.82 (CH, arom C), 135.32 (C, arom C), 137.00, 138.54, 138.95, 139.22, 140.19, 140.31, 141.68, 141.96, 142.18, 142.37, 142.53, 142.58, 142.67, 142.70, 142.82, 143.07, 143.19, 143.60, 143.67, 143.77, 143.87, 143.98, 144.04, 144.12, 144.25, 144.33, 144.36, 144.51, 144.70, 144.92, 145.43, 146.18, 146.53, 146.63, 146.74, 146.79, 146.94, 147.06, 147.44, 148.14, 148.29, 148.61, 148.97, 149.04, 149.17, 151.95, 153.64, 156.92, 169.47 (C=O), 169.81 (C=O). MS (Ionspec MALDI FTMS) *m/z* 979.1 ($M + Na^+$), 811.1 $[C_{60}CH_2Ph]^+$, 720.0 (C_{60}). IR ν/cm^{-1} (KBr) 2920, 2850, 1736, 1452, 1429, 1259, 1117, 1016, 978, 698, 526, 467. UV-vis λ_{max}/nm ($CHCl_3$) 258, 325, 448, 623.

Compound 3j. Dimethyl 2-ethylmalonate, **1j** (11.3 μL, 0.075 mmol) was subjected to the general procedure in refluxing toluene for 16 hours to afford **3j** (14.6 mg, 70% yield based on 43% consumed C_{60}). Spectral data of **3j**:^{1}H NMR (500 MHz, CS_2–$CDCl_3$) δ 1.38 (t, J = 7.25 Hz 3H, CH_3), 3.15 (m, 2H, CH_2CH_3), 3.88 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 4.43 (AB, J_{AB} = 12.9 Hz, 2H, CH_2Ph), 7.28–7.29 (m, 1H, arom H), 7.34 (t, J = 7.4 Hz, 2H, arom H), 7.56 (d, J = 7.4 Hz, 2H, arom H); ^{13}C NMR (125 MHz, CS_2–$CDCl_3$) δ 10.85 (CH_3), 29.49 (CH_2CH_3), 48.28 (CH_2Ph), 52.26 (OCH_3), 52.42 (OCH_3), 60.19 (sp^3-C of C_{60}), 62.08 (CCH_2), 67.18 (sp^3-C of C_{60}), 127.32 (CH, arom C), 128.26 (CH, arom C), 130.87 (CH, arom C), 135.48 (C, arom C), 137.16, 138.17, 138.75, 139.03, 140.29, 140.37, 141.79, 142.07, 142.28, 142.46, 142.61, 142.66, 142.77, 142.80, 142.92, 143.10, 143.14, 143.26, 143.60, 143.72, 143.79, 143.85, 143.94, 144.05, 144.10, 144.20, 144.23, 144.36, 144.42, 144.77, 144.80, 145.00, 145.54, 145.92, 146.65, 146.73, 146.84, 146.92, 147.02, 147.14, 147.36, 148.22, 148.39, 148.69, 148.89, 149.16, 151.94, 153.63, 156.91, 169.46 (C=O), 169.76 (C=O). MS (Ionspec MALDI FT-MS) *m/z* 1009.1 ($M + K^+$), 993.1 ($M + Na^+$), 811.1 $[C_{60}CH_2Ph]^+$, 720.0 (C_{60}^+). IR ν/cm^{-1} (KBr) 2922, 2852, 1736, 1452, 1429, 1232, 1128, 1016, 802, 698, 669, 526, 467, 451. UV-vis λ_{max}/nm ($CHCl_3$) 257, 325, 448, 623.

Compound 3k. Dimethyl 2-(2-methoxyethyl) malonate, **1k** (19.5 μL, 0.10 mmol) was subjected to the general procedure in refluxing toluene for 22 hours to afford **3k** (11.7 mg, 65% yield based on 36% consumed C_{60}). Spectral data of **3k**: ^{1}H NMR (500 MHz, CS_2–$CDCl_3$) δ 3.28–3.38 (m, 2H, $CH_2CH_2OCH_3$), 3.39 (s, 3H, CH_2OCH_3), 3.81–3.83 (m, 2H, CH_2OCH_3), 3.82 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 4.45 (AB, J_{AB} = 13.0 Hz, 2H, CH_2Ph), 7.24–7.26 (m, 1H, arom H), 7.30 (t, J = 7.1 Hz, 2H, arom H), 7.53 (t, J = 7.2 Hz, 2H, arom H); ^{13}C NMR (125 MHz, CS_2–$CDCl_3$) δ 36.05 (CH_2CH_2O), 47.84 (CH_2Ph), 52.01 (OCH_3), 52.20 (OCH_3), 58.38 (OCH_3), 60.04 (sp^3-C of C_{60}), 61.70 (CCH_2), 63.94 (sp^3-C of C_{60}), 69.27 (CH_2O), 127.10 (CH, arom C), 128.05 (CH, arom C), 130.70 (CH, arom C), 135.20 (C, arom C), 138.66, 138.85, 140.03, 140.07, 141.57, 141.82, 142.05, 142.24, 142.38, 142.51, 142.55, 142.68, 142.91, 142.95, 143.05, 143.55, 143.58, 143.70, 143.82, 143.87, 144.00, 144.15, 144.20, 144.54, 144.57, 144.80, 145.31, 145.72, 146.39, 146.49, 146.59, 146.67, 146.79, 146.92, 147.22, 148.01, 148.14, 148.46, 148.66, 148.78, 149.19, 151.93, 153.26, 156.90, 168.34 (C=O), 169.69 (C=O). MS (Ionspec MALDI FT-MS) *m/z* 1023.1 ($M + Na^+$), 811.1 $[C_{60}CH_2Ph]^+$, 720.0 (C_{60}^+). IR ν/cm^{-1} (KBr) 2922, 2852, 1732, 1458, 1429, 1261, 1188, 1005, 1020, 804, 700, 526, 467. UV-vis λ_{max}/nm ($CHCl_3$) 258, 325, 448, 623.

Compound 3l. Diethyl 2-methylmalonate, **1l** (13.4 μL, 0.075 mmol) was subjected to general procedure in refluxing toluene for 16 hours to afford **3l** (14.4 mg, 65% yield based on 45% consumed C_{60}). The spectroscopic data of **3l** were consistent with those reported in the literature.[17]

Compound 3m. Methyl 2-methyl-3-oxobutanoate, **1m** (10 μL, 0.075 mmol) was subjected to general procedure in hot toluene (100 °C) for 0.5 hours to afford **3m** (10.8 mg, 47% yield based on 49% consumed C_{60}). Spectral data of **3m**: ^{1}H NMR (500 MHz, CS_2–$CDCl_3$) δ 2.42 (s, 0.6 × 3H, isomer 1), 2.52 (s, 0.4 × 3H, isomer 2), 2.60 (s, 0.4 × 3H, isomer 2), 2.68 (s, 0.6 × 3H, isomer 1), 3.95 (s, 0.6 × 3H, isomer 1), 3.99 (s, 0.4 × 3H, isomer 2), 4.36 (AB, J_{AB} = 12.8 Hz, 0.6 × 2H, CH_2Ph, isomer 1), 4.37 (AB, J = 12.8 Hz, 0.4 × 2H, CH_2Ph, isomer 1), 7.23–7.36 (m, 3H, arom H), 7.58 (d, J = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, CS_2–$CDCl_3$) δ 20.62 (CH_3, isomer 1), 20.86 (CH_3, isomer 2), 29.28 (OCH_3, isomer 1), 29.48 (OCH_3, isomer 2), 48.35 (CH_2Ph, isomer 1), 48.46 (CH_2Ph, isomer 2), 52.75 (CH_3CO, isomer 1), 52.84 (CH_3CO, isomer 2), 60.21 (sp^3-C of C_{60}, isomer 1 & isomer 2), 61.89 (CCH_3, isomer 1 & isomer 2), 67.09 (sp^3-C of C_{60}, isomer 2), 67.68 (sp^3-C of C_{60}, isomer 1), 127.31 (CH, arom C, isomer 1 & isomer 2), 128.22 (CH, arom C, isomer 1 & isomer 2), 130.94 (CH, arom C, isomer 1), 130.98 (CH, arom C, isomer 2), 135.50, 140.54, 141.77, 142.24, 142.35, 142.51, 142.64, 142.78, 142.87, 142.94, 143.07, 143.16, 143.20, 143.32, 143.72, 143.82, 143.97, 144.05, 144.11, 144.22, 144.33, 144.41, 144.49, 144.79, 144.86, 145.04, 145.56, 146.70, 146.78, 146.88, 146.95, 147.06, 147.20, 148.42, 148.72, 148.78, 149.16, 149.21, 149.38, 152.04, 152.11, 153.43, 153.70, 157.12, 171.06 (C=O). MS (Ionspec MALDI FT-MS) *m/z* 979.1 ($M + K^+$), 963.1 ($M + Na^+$), 811.1 $[C_{60}CH_2Ph]^+$, 720.0 (C_{60}^+). IR ν/cm^{-1} (KBr) 2922, 2852, 1710, 1500, 1452, 1429, 1351, 1248, 1188, 1097, 1020, 698, 669, 526, 462. UV-vis λ_{max}/nm ($CHCl_3$) 257, 325, 446, 623.

Acknowledgements

We thank the National Natural Science Foundation of China through Grant 29972007 for financial support.

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