



Cite this: *RSC Adv.*, 2020, 10, 24549

Base-iodine-promoted metal-catalyst-free reactions of [60]fullerene with β -keto esters for the selective formation of [60]fullerene derivatives†

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Received 13th May 2020
Accepted 9th June 2020

DOI: 10.1039/d0ra04996d

rsc.li/rsc-advances

In this study, methanofullerenes and 2',3'-dihydrofuran C₆₀ derivatives were selectively synthesized in high yields via the reactions of C₆₀ with β -keto esters under mild conditions by controlling the addition sequence and molar ratio of iodine and base. The structures of the products were determined by spectroscopic characterization. Moreover, a possible reaction mechanism for the selective formation of fullerene derivatives was proposed.

Introduction

Fullerenes have attracted significant attention from chemists due to their unique geometric and electronic structures.^{1–3} To date, the functionalization of fullerenes is of great importance for fullerene chemistry since fullerenes can be synthesized and isolated in macroscopic quantities.^{4–7} Various fullerene derivatives are promising for the development of diverse fullerene-based materials possessing unique properties for application in materials and biological sciences.^{8–11} Accordingly, methanofullerenes and 2',3'-dihydrofuran C₆₀ derivatives (dihydrofuran-fused C₆₀ derivatives), as shown in Fig. 1, are classical fullerene derivatives containing a fused three- or five-membered ring, which have been synthesized in moderate yields via the Bingel–Hirsch reaction^{12,13} and transition-metal catalyst-mediated^{14,15} or high-speed vibration milling (HSVM).¹⁶ However, these methods frequently suffer from drawbacks such as the requirements of high temperatures, long reaction time, the use of transition-metal catalysts, and a heterogeneous reaction. Thus, the development of more simple and efficient methods for the synthesis of methanofullerenes and 2',3'-dihydrofuran C₆₀ derivatives is highly desirable.

Recently, we have selectively synthesized methanofullerenes and 2',3'-dihydrofuran C₆₀ derivatives as a single product in each reaction, respectively, in an iodine-base system by controlling the addition sequence and molar ratio of iodine and base, as shown in Scheme 1.

Results and discussion

Table 1 presents the screening of the reaction conditions. Ethyl acetoacetate was used for reaction screening. The experiment was designed to control the selective formation of a single product in a relatively high yield. It was divided into two types of

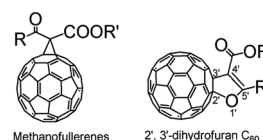
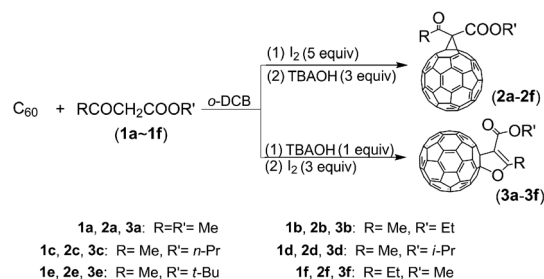


Fig. 1 Structures of methanofullerenes and 2',3'-dihydrofuran C₆₀ derivatives.



Scheme 1 Synthesis of the compounds 2a–2f and 3a–3f.

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† Electronic supplementary information (ESI) available: Spectra of all the synthesised compounds. See DOI: 10.1039/d0ra04996d



Table 1 Screening of the reaction conditions using ethyl acetoacetate^a

Entry	OH [−] (equiv.)	I ₂ (equiv.)	Temp (°C)	Time ^b (min)	Time ^c (min)	Product (% yield) ^d	
						2b	3b
1	3	5	0	30	30	6 (16)	27 (71)
2	3	5	0	60	60	9 (22)	28 (69)
3	3	5	rt	30	30	32 (36)	18 (20)
4	3	5	rt	30	60	29 (36)	18 (22)
5	3	5	rt	30	5	33 (39)	23 (27)
6	3	5	50	30	30	28 (32)	16 (18)
7	3	5	50	30	60	26 (34)	19 (25)
8	1	3	0	30	30	Trace	28 (70)
9	1	3	rt	30	30	7 (19)	27 (73)
10	1.2	3	rt	30	30	9 (23)	27 (69)
11	5	8	rt	30	30	—	—
12 ^e	3	5	rt	—	60	52 (65)	—
13 ^e	4	5	rt	—	60	46 (48)	—
14 ^e	5	5	rt	—	60	—	—
15 ^e	5	8	rt	—	60	—	—

^a Reaction conditions: (1) for the entries from 1 to 11, C₆₀ (36 mg, 50 μmol) and ethyl acetoacetate (500 μL, 79 equiv.) were put in *o*-DCB (*o*-dichlorobenzene) (15 mL). The mixture was stirred for 15 min under argon or nitrogen at a preset temperature. Then, OH[−] (TBAOH, tetra-*n*-butylammonium hydroxide, 1.0 M in CH₃OH) was added to the solution, and the reaction was allowed to proceed for a definite time^b. The reaction was then quenched with I₂ for a definite time^c. (2) For the entries from 12 to 15, C₆₀ (36 mg, 50 μmol), ethyl acetoacetate (500 μL, 79 equiv.), and I₂ were put into *o*-DCB (15 mL). The mixture was stirred for 15 min under argon or nitrogen at a preset temperature. Then, OH[−] (TBAOH, 1.0 M in CH₃OH) was added to the solution, and the reaction was allowed to proceed for a definite time^c. ^b Reaction time after base addition and before the addition of iodine. ^c Reaction time after iodine addition. ^d Yield in parentheses based on the consumed C₆₀. ^e Addition sequence is different from the entries 1 to 11, that is, iodine is added first followed by the addition of the base.

reactions according to the addition sequence of base and iodine as follows: (1) reaction involving the addition of base first and iodine later (entries from 1 to 11) and (2) reaction involving the addition of iodine first and base later (entries from 12 to 15). Both the compounds **2b** and **3b** were obtained when 3 equiv. of OH[−] with respect to C₆₀ was first added to the reaction mixture followed by the addition of 5 equiv. of iodine with respect to C₆₀ (entries from 1 to 7). Interestingly, only **3b** was obtained when the reaction was conducted at 0 °C by first adding 1 equiv. of OH[−] followed by the addition of 3 equiv. of iodine (entry 8).

Upon further increasing the amount of base to 5 equiv. and that of iodine to 8 equiv., a crude product was obtained, which was quite complex and difficult to separate, as indicated by the HPLC measurement performed using a Buckyprep column (entry 11). However, a reduction in the amount of iodine would result in bis-2',3'-dihydrofuran C₆₀ derivatives.¹⁷ In contrast, only **2b** was obtained when the reaction was carried out at room temperature by first adding 5 equiv. of iodine followed by the addition of 3 or 4 equiv. of OH[−] (entries 12 and 13). To achieve **2b** in a higher yield, it was better to use 3 equiv. of OH[−] (52%

Table 2 Conditions for the preparation of the compounds 2a–2f and 3a–3f

Entry	RCOCH ₂ COOR'	OH [−] (equiv.)	I ₂ (equiv.)	Temp (°C)	Product (% yield) ^a	
					2a–2f	3a–3f
1	1a: R = R' = CH ₃	1	3	0	—	3a: 29 (73)
2 ^b	1a: R = R' = CH ₃	3	5	rt	2a: 66 (74)	—
3	1b: R = CH ₃ , R' = CH ₂ CH ₃	1	3	0	—	3b: 28 (70)
4 ^b	1b: R = CH ₃ , R' = CH ₂ CH ₃	3	5	rt	2b: 52 (65)	—
5	1c: R = CH ₃ , R' = (CH ₂) ₂ CH ₃	1	3	0	—	3c: 27 (66)
6 ^b	1c: R = CH ₃ , R' = (CH ₂) ₂ CH ₃	3	5	rt	2c: 50 (63)	—
7	1d: R = CH ₃ , R' = CH(CH ₃) ₂	1	3	0	—	3d: 26 (60)
8 ^b	1d: R = CH ₃ , R' = CH(CH ₃) ₂	3	5	rt	2d: 51 (62)	—
9	1e: R = CH ₃ , R' = C(CH ₃) ₃	1	3	0	—	3e: 32 (66)
10 ^b	1e: R = CH ₃ , R' = C(CH ₃) ₃	3	5	50	2e: 38 (57)	—
11	1f: R = CH ₂ CH ₃ , R' = CH ₃	1	3	0	—	3f: 27 (61)
12 ^b	1f: R = CH ₂ CH ₃ , R' = CH ₃	3	5	50	2f: 45 (56)	—

^a Yield in parentheses based on the consumed C₆₀. ^b Addition sequence is different from that for the other entries (the addition sequence of the entries 1, 3, 5, 7, 9, and 11 involves the addition of base first and iodine later), that is, the addition of iodine first and base later.



isolated yield, 65% yield based on the consumed C_{60}) (entry 12). Similarly, upon further increasing the amount of base to 5 equiv. and that of iodine to 5 or 8 equiv., a crude product was obtained, which was quite complex and difficult to purify, as shown by the HPLC measurement conducted using the Buckyprep column (entries 14 and 15).

The reactions were further examined using other β -keto ester substrates (**1a**, **1c–1f**) listed in Table 2. It was found that the methods were effective for the selective preparation of methanofullerenes (**2a–2f**) and 2',3'-dihydrofuran C_{60} derivatives (**3a–3f**) in relatively high yields. Methanofullerenes (**2a–2f**) could be obtained with the isolated yield of 38–66% (56–74% based on the consumed C_{60}) by adding iodine first and base later. However, the formation of 2',3'-dihydrofuran C_{60} derivatives (**3a–3f**) with the isolated yield of 26–32% (60–73% based on the consumed C_{60}) could be controlled by adding base first and iodine later. Generally, 0 °C was good for the synthesis of 2',3'-dihydrofuran C_{60} derivatives, and room temperature was good for the synthesis of methanofullerenes, except for **2e** and **2f**. Consequently, we found that 50 °C was better for the preparation of **2e** and **2f**.

The structures of the compounds **2a–2f** and **3a–3f** were characterized by MALDI-TOF MS and 1H NMR, ^{13}C NMR, and UV-vis spectroscopies. The MALDI-TOF MS spectrum of each compound exhibits a molecular ion peak that well matches with the theoretical value (see figures in ESI†). The resonances of the alkyl protons are shown in the 1H NMR spectra. The UV-vis spectra of all the compounds exhibit peaks at around 428 nm, which is attributed to the diagnostic absorption of the 1 : 1 cycloadduct of C_{60} at the 6,6-junction.¹⁶ For example, the MALDI-TOF MS spectrum of the compound **2f** (Fig. S42†) shows a molecular ion peak at m/z 848.0437. The ^{13}C NMR spectrum of **2f** (Fig. S44†) exhibits 22 peaks for the sp^2 carbon atoms of C_{60} , in agreement with the C_s symmetry of the molecule, two peaks at 195.93 ppm and 164.22 ppm due to the two carbonyl carbons in β -keto ester, respectively, and one peak at 72.31 ppm due to the two sp^3 carbons of the C_{60} cage. The MALDI-TOF MS spectrum of the compound **3f** (Fig. S46†) similarly shows a molecular ion peak at m/z 848.0425. However, the ^{13}C NMR spectrum of **3f** (Fig. S48†) displays 30 peaks for the sp^2 carbon atoms of C_{60} , consistent with the C_s symmetry of the molecule, one peak at 173.88 ppm due to the 5'-carbon atom of the heterocycle, one signal at 164.52 ppm due to the carbonyl carbon atom, one peak

at 104.26 ppm due to the 4'-carbon atom of the heterocycle, and two peaks at 102.87 ppm and 72.31 ppm assigned to the two sp^3 carbons of the C_{60} cage.

The proposed reaction mechanism for the formation of the compounds **2a–2f** and **3a–3f** is shown in Scheme 2. The reaction is initiated by the abstraction of an α -proton from β -keto esters (**1a–1f**) to generate the enolate anion **A**, which can either react with I_2 to afford the intermediate **B** when I_2 is present in the mixture at the beginning of the reaction, or attack C_{60} to form the intermediate **E** (RC_{60}^-) when I_2 is absent. The subsequent abstraction of an α' -proton from the β -keto ester moiety in **B** would take place to generate the intermediate **C** when extra OH^- is present. Then, the intermediate **C** would attack C_{60} and afford the intermediate **D**, followed by intramolecular nucleophilic substitution to provide methanofullerenes (**2a–2f**). In contrast, the intermediate **E** is completely oxidized by I_2 or partially oxidized by another molecule of neutral C_{60} to obtain the radical **F** in the presence of less OH^- . Intramolecular cyclization of the radical **F** with the release of a hydrogen radical affords the 2',3'-dihydrofuran C_{60} derivatives (**3a–3f**).

Conclusions

The chemistry presented herein provides rapid access to methanofullerenes and 2',3'-dihydrofuran C_{60} derivatives in high yields. The addition sequence of iodine and base is crucial for the control over the formation of these two types of products. Methanofullerenes can be selectively afforded by adding iodine first and base later. However, the 2',3'-dihydrofuran C_{60} derivatives were obtained by adding base first and iodine later. These simple and benign methods are highly selective, have short reaction times, and do not require transition metal catalysts.

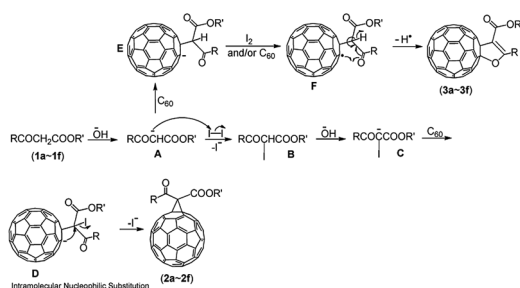
Experimental

General methods

All reactions were carried out under an argon or nitrogen atmosphere. All reagents were commercially obtained and used without further purification.

Preparation and spectral characterization of **2a**

Typically, 36 mg of C_{60} (0.05 mmol), 89 equiv. of **1a** (4.47 mmol, 500 μ L), and 5 equiv. of I_2 (0.25 mmol, 63 mg) were added to *o*-DCB (15 mL) followed by stirring under an argon or nitrogen atmosphere for 15 min at room temperature. Then, 3.0 equiv. of TBAOH (1.0 M in methanol, 150 μ L, 0.15 mmol) was added to the abovementioned solution, and the reaction was allowed to proceed for 60 min. The solvent of the reaction mixture was removed using a rotary evaporator under vacuum, and the residue was separated using a silica gel column with CS_2 /toluene (4 : 1 v/v) as the eluent to obtain methanofullerene **2a** (27.5 mg, 74% based on the consumed C_{60}) as an amorphous brown solid along with the recovered C_{60} (4.0 mg, 11%). MALDI-TOF MS m/z calcd for $C_{65}H_6O_3^+ [M]^+$ 834.0311, found 834.0305. 1H NMR (600 MHz, DMSO) δ 3.84 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (151 MHz, DMSO) δ 190.60 (1C, $COCH_3$), 163.23 (1C,



Scheme 2 Proposed mechanism for the formation of the compounds **2a–2f** and **3a–3f**.



CO₂CH₂CH₃), 145.24 (2C), 144.99 (6C), 144.92 (5C), 144.83 (2C), 144.71 (2C), 144.55 (2C), 144.52 (1C), 144.47 (4C), 144.37 (4C), 143.62 (2C), 143.60 (2C), 142.92 (1C), 142.87 (1C), 142.80 (8C), 142.02 (4C), 141.62 (2C), 141.59 (2C), 140.83 (2C), 140.79 (2C), 139.10 (2C), 137.98 (2C), 72.25 (2C, sp³-C of C₆₀), 59.06 (1C, CCOCH₃), 53.21 (1C, OCH₃), 27.86 (1C, COCH₃). UV-vis (in toluene) λ_{max}: 328, 428 nm.

Preparation and spectral characterization of 3a

Typically, 36 mg of C₆₀ (0.05 mmol) and 89 equiv. of **1a** (4.47 mmol, 500 μL) were added to *o*-DCB (15 mL) followed by stirring under an argon or nitrogen atmosphere for 15 min at 0 °C. Then, 1.0 equiv. of TBAOH (1.0 M in methanol, 50 μL, 0.05 mmol) was added to the abovementioned solution, and the reaction was allowed to proceed for 30 min. The reaction mixture was then quenched with 3 equiv. of I₂ (0.15 mmol, 38 mg) for 30 min. The solvent of the reaction mixture was removed using a rotary evaporator under vacuum, and the residue was separated using a silica gel column with CS₂/toluene (4 : 1 v/v) as the eluent to afford 2',3'-dihydrofuran fullerene **3a** (12.1 mg, 73% based on the consumed C₆₀) as an amorphous brown solid along with the recovered C₆₀ (21.6 mg, 60%). MALDI-TOF MS *m/z* calcd for C₆₅H₆O₃⁺ [M]⁺ 834.0311, found 834.0285. ¹H NMR (600 MHz, DMSO) δ 3.58 (s, 3H), 2.62 (s, 3H). ¹³C NMR (151 MHz, DMSO) δ 168.71 (1C, OCCH₃), 163.39 (1C, C=O), 148.39 (2C), 147.82 (1C), 147.16 (2C), 147.11 (1C), 146.24 (2C), 146.03 (2C), 145.97 (2C), 145.83 (2C), 145.76 (2C), 145.45 (2C), 145.20 (2C), 144.98 (2C), 144.83 (2C), 144.59 (2C), 144.35 (2C), 144.24 (2C), 144.03 (2C), 142.63 (2C), 142.60 (2C), 142.51 (2C), 142.38 (2C), 142.28 (2C), 142.15 (2C), 142.10 (2C), 141.42 (2C), 141.29 (2C), 139.71 (2C), 139.32 (2C), 137.25 (2C), 135.06 (2C), 105.03 (1C, CC=O), 50.84 (1C, OCH₃), 15.40 (1C, CH₃), (sp³-C of C₆₀ not found). UV-vis (in toluene) λ_{max}: 319, 428 nm.

Preparation and spectral characterization of 2b

The procedure was similar to that used for the preparation of **2a**, except that **1b** (79 equiv., 3.95 mmol, 500 μL) was used instead of **1a**. The reaction afforded **2b** (22.0 mg, 65% based on the consumed C₆₀) as an amorphous brown solid along with the recovered C₆₀ (7.2 mg, 20%). MALDI-TOF MS *m/z* calcd for C₆₆H₈O₃⁺ [M]⁺ 848.0468, found 848.0438. ¹H NMR (600 MHz, DMSO) δ 4.31 (q, *J* = 7.2 Hz, 2H), 2.61 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (151 MHz, DMSO) δ 190.62 (1C, COCH₃), 162.71 (1C, CO₂CH₂CH₃), 145.35 (2C), 145.03 (2C), 145.00 (3C), 144.92 (5C), 144.86 (2C), 144.78 (2C), 144.54 (4C), 144.50 (1C), 144.47 (3C), 144.35 (4C), 143.63 (2C), 143.61 (2C), 142.93 (1C), 142.88 (1C), 142.81 (6C), 142.78 (2C), 142.03 (4C), 141.60 (4C), 140.83 (2C), 140.78 (2C), 139.13 (2C), 137.95 (2C), 72.26 (2C, sp³-C of C₆₀), 63.06 (1C, OCH₂CH₃), 59.23 (1C, CCOCH₃), 27.83 (1C, COCH₃), 14.46 (1C, CH₂CH₃). UV-vis (in toluene) λ_{max}: 326, 429 nm.

Preparation and spectral characterization of 3b

The procedure was similar to that used for the preparation of **3a**, except that **1b** (79 equiv., 3.95 mmol, 500 μL) was used instead of **1a**. The reaction afforded **3b** (11.8 mg, 70% based on the consumed C₆₀) as an amorphous brown solid along with the

recovered C₆₀ (21.6 mg, 60%). MALDI-TOF MS *m/z* calcd for C₆₆H₈O₃⁺ [M]⁺ 848.0468, found 848.0495. ¹H NMR (600 MHz, DMSO) δ 4.05 (q, *J* = 7.2 Hz, 2H), 2.61 (s, 3H), 1.07 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (151 MHz, DMSO) δ 168.57 (1C, OCCH₃), 162.99 (1C, C=O), 148.43 (2C), 147.82 (1C), 147.32 (2C), 147.11 (1C), 146.25 (2C), 146.02 (2C), 145.97 (2C), 145.82 (2C), 145.76 (2C), 145.47 (2C), 145.20 (2C), 144.98 (2C), 144.82 (2C), 144.62 (2C), 144.36 (2C), 144.32 (2C), 144.05 (2C), 142.64 (2C), 142.60 (2C), 142.52 (2C), 142.40 (2C), 142.29 (2C), 142.15 (2C), 142.11 (2C), 141.39 (2C), 141.30 (2C), 139.72 (2C), 139.15 (2C), 137.24 (2C), 135.06 (2C), 104.80 (1C, CC=O), 102.50 (1C, sp³-C of C₆₀, C₆₀-O), 72.07 (1C, sp³-C of C₆₀, C₆₀-C), 60.28 (1C, OCH₂CH₃), 15.36 (1C, CH₃), 14.52 (1C, CH₂CH₃). UV-vis (in toluene) λ_{max}: 320, 429 nm.

Preparation and spectral characterization of 2c

The procedure was similar to that used for the preparation of **2a**, except that **1c** (70 equiv., 3.50 mmol, 500 μL) was used instead of **1a**. The reaction afforded **2c** (21.6 mg, 63% based on the consumed C₆₀) as an amorphous brown solid along with the recovered C₆₀ (7.6 mg, 21%). MALDI-TOF MS *m/z* calcd for C₆₇H₁₀O₃⁺ [M]⁺ 862.0624, found 862.0601. ¹H NMR (500 MHz, CDCl₃) δ 4.48 (t, *J* = 7.0 Hz, 2H), 2.87 (s, 3H), 1.92 (m, 2H), 1.13 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 191.83 (1C, COCH₃), 163.10 (1C, CO₂CH₂CH₂CH₃), 145.20 (2C), 144.92 (3C), 144.91 (2C), 144.85 (5C), 144.76 (2C), 144.54 (2C), 144.48 (3C), 144.41 (3C), 144.38 (4C), 144.28 (2C), 144.27 (2C), 143.54 (1C), 143.51 (2C), 142.84 (1C), 142.80 (1C), 142.72 (6C), 142.67 (2C), 141.93 (4C), 141.53 (2C), 141.50 (2C), 140.75 (2C), 140.69 (1C), 139.12 (2C), 137.73 (2C), 72.11 (2C, sp³-C of C₆₀), 68.59 (1C, CO₂CH₂CH₂CH₃), 59.07 (1C, CCOCH₃), 28.03 (1C, COCH₃), 22.24 (1C, CH₂CH₂CH₃), 10.54 (1C, CH₂CH₂CH₃). UV-vis (in toluene) λ_{max}: 329, 429 nm.

Preparation and spectral characterization of 3c

The procedure was similar to that used for the preparation of **3a**, except that **1c** (70 equiv., 3.50 mmol, 500 μL) was used instead of **1a**. The reaction afforded **3c** (11.6 mg, 66% based on the consumed C₆₀) as an amorphous brown solid along with the recovered C₆₀ (21.2 mg, 59%). MALDI-TOF MS *m/z* calcd for C₆₇H₁₀O₃⁺ [M]⁺ 862.0624, found 862.0609. ¹H NMR (600 MHz, CDCl₃) δ 4.25 (t, *J* = 7.2 Hz, 2H), 2.89 (s, 3H), 1.73 (m, 2H), 1.00 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 169.01 (1C, OCCH₃), 164.00 (1C, C=O), 148.44 (2C), 147.93 (1C), 147.23 (3C), 146.35 (2C), 146.13 (2C), 146.07 (2C), 145.93 (2C), 145.87 (2C), 145.56 (2C), 145.29 (2C), 145.09 (2C), 144.93 (2C), 144.67 (2C), 144.44 (2C), 144.33 (2C), 144.14 (2C), 142.72 (2C), 142.69 (2C), 142.61 (2C), 142.47 (2C), 142.36 (2C), 142.24 (2C), 142.20 (2C), 141.48 (2C), 141.37 (2C), 139.81 (2C), 139.31 (2C), 137.38 (2C), 135.20 (2C), 105.01 (1C, CC=O), 66.12 (1C, CO₂CH₂CH₂-CH₃), 22.42 (1C, CH₂CH₂CH₃), 15.52 (1C, CH₃), 10.93 (1C, CH₂CH₂CH₃), (sp³-C of C₆₀ not found). UV-vis (in toluene) λ_{max}: 320, 429 nm.

Preparation and spectral characterization of 2d

The procedure was similar to that used for the preparation of **2a**, except that **1d** (69 equiv., 3.44 mmol, 500 μL) was used



instead of **1a**. The reaction afforded **2d** (22.0 mg, 62% based on the consumed C_{60}) as an amorphous brown solid along with the recovered C_{60} (6.5 mg, 18%). MALDI-TOF MS m/z calcd for $C_{67}H_{10}O_3^+ [M]^+$ 862.0624, found 862.0645. 1H NMR (600 MHz, $CDCl_3$) δ 5.42 (m, 1H), 2.85 (s, 3H), 1.52 (d, $J = 6.6$ Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.60 (1C, $COCH_3$, overlapped with the peak of CS_2), 163.01 (1C, $CO_2CH(CH_3)_2$), 145.59 (2C), 145.33 (2C), 145.29 (2C), 145.28 (2C), 145.22 (4C), 145.16 (2C), 144.96 (2C), 144.84 (2C), 144.79 (2C), 144.75 (4C), 144.64 (4C), 143.91 (2C), 143.89 (2C), 143.22 (1C), 143.18 (1C), 143.09 (6C), 143.04 (2C), 142.30 (4C), 141.91 (2C), 141.86 (2C), 141.11 (2C), 141.05 (2C), 139.44 (2C), 138.14 (2C), 72.52 (2C, sp^3 -C of C_{60}), 71.79 (1C, $OCH(CH_3)_2$), 59.54 (1C, $CCOCH_3$), 28.43 (1C, $COCH_3$), 21.93 (2C, $CH(CH_3)_2$). UV-vis (in toluene) λ_{max} : 330, 429 nm.

Preparation and spectral characterization of 3d

The procedure was similar to that used for the preparation of **3a**, except that **1d** (69 equiv., 3.44 mmol, 500 μ L) was used instead of **1a**. The reaction afforded **3d** (11.2 mg, 60% based on the consumed C_{60}) as an amorphous brown solid along with the recovered C_{60} (20.5 mg, 57%). MALDI-TOF MS m/z calcd for $C_{67}H_{10}O_3^+ [M]^+$ 862.0624, found 862.0660. 1H NMR (600 MHz, $CDCl_3$) δ 5.24 (m, 1H), 2.88 (s, 3H), 1.33 (d, $J = 6.0$ Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.04 (1C, $OCCH_3$), 163.81 (1C, $C=O$), 148.68 (2C), 148.13 (1C), 147.55 (2C), 147.41 (1C), 146.55 (2C), 146.32 (2C), 146.26 (2C), 146.12 (2C), 146.06 (2C), 145.77 (2C), 145.49 (2C), 145.29 (2C), 145.12 (2C), 144.88 (2C), 144.65 (2C), 144.58 (2C), 144.34 (2C), 142.92 (2C), 142.88 (2C), 142.80 (2C), 142.67 (2C), 142.56 (2C), 142.44 (2C), 142.40 (2C), 141.68 (2C), 141.57 (2C), 140.00 (2C), 139.42 (2C), 137.58 (2C), 135.38 (2C), 105.24 (1C, $CC=O$), 102.80 (1C, sp^3 -C of C_{60} , $C_{60}-O$), 72.34 (1C, sp^3 -C of C_{60} , $C_{60}-C$), 68.28 (1C, $OCH(CH_3)_2$), 22.31 (1C, $OCCH_3$), 15.67 (2C, $CH(CH_3)_2$). UV-vis (in toluene) λ_{max} : 320, 429 nm.

Preparation and spectral characterization of 2e

The procedure was similar to that used for the preparation of **2a**, except that **1e** (62 equiv., 3.10 mmol, 500 μ L) was used instead of **1a**, and a temperature of 50 $^\circ$ C was used. The reaction afforded **2e** (16.6 mg, 57% based on the consumed C_{60}) as an amorphous brown solid along with the recovered C_{60} (11.9 mg, 33%). MALDI-TOF MS m/z calcd for $C_{68}H_{12}O_3^+ [M]^+$ 876.0781, found 876.0743. 1H NMR (600 MHz, $CDCl_3$) δ 2.85 (s, 3H), 1.73 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.82 (1C, $COCH_3$), 162.17 (1C, $CO_2C(CH_3)_3$), 145.55 (2C), 145.18 (2C), 145.08 (4C), 145.01 (6C), 144.97 (3C), 144.62 (4C), 144.56 (4C), 144.41 (4C), 143.71 (3C), 143.03 (1C), 142.99 (1C), 142.89 (6C), 142.86 (3C), 142.12 (3C), 141.74 (2C), 141.69 (2C), 140.90 (2C), 140.85 (2C), 139.17 (2C), 137.90 (2C), 84.87 (1C, $CO_2C(CH_3)_3$), 72.59 (2C, sp^3 -C of C_{60}), 60.32 (1C, $CCOCH_3$), 28.14 (1C, $COCH_3$), 27.92 (3C, $C(CH_3)_3$). UV-vis (in toluene) λ_{max} : 330, 429 nm.

Preparation and spectral characterization of 3e

The procedure was similar to that used for the preparation of **3a**, except that **1e** (62 equiv., 3.10 mmol, 500 μ L) was used instead of **1a**. The reaction afforded **3e** (14.0 mg, 66% based on

the consumed C_{60}) as an amorphous brown solid along with the recovered C_{60} (18.7 mg, 52%). MALDI-TOF MS m/z calcd for $C_{68}H_{12}O_3^+ [M]^+$ 876.0781, found 876.0753. 1H NMR (600 MHz, $CDCl_3$) δ 2.81 (s, 3H), 1.52 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.33 (1C, $OCCH_3$), 163.25 (1C, $C=O$), 148.53 (2C), 147.92 (1C), 147.48 (2C), 147.20 (1C), 146.35 (2C), 146.10 (2C), 146.06 (2C), 145.90 (2C), 145.85 (2C), 145.60 (2C), 145.28 (2C), 145.07 (2C), 144.90 (2C), 144.71 (2C), 144.52 (2C), 144.44 (2C), 144.16 (2C), 142.73 (2C), 142.68 (2C), 142.60 (2C), 142.50 (2C), 142.35 (2C), 142.21 (4C), 141.45 (2C), 141.38 (2C), 139.79 (2C), 139.17 (2C), 137.32 (2C), 135.19 (2C), 105.67 (1C, $CC=O$), 81.18 (1C, $CO_2C(CH_3)_3$), 28.35 (3C, $C(CH_3)_3$), 15.55 (1C, CH_3), (sp^3 -C of C_{60} not found). UV-vis (in toluene) λ_{max} : 320, 430 nm.

Preparation and spectral characterization of 2f

The procedure was similar to that used for the preparation of **2a**, except that **1f** (78 equiv., 3.90 mmol, 500 μ L) was used instead of **1a**, and a temperature of 50 $^\circ$ C was used. The reaction afforded **2f** (19.1 mg, 56% based on the consumed C_{60}) as an amorphous brown solid along with the recovered C_{60} (7.2 mg, 20%). MALDI-TOF MS m/z calcd for $C_{66}H_8O_3^+ [M]^+$ 848.0468, found 848.0437. 1H NMR (600 MHz, $CDCl_3$) δ 4.11 (s, 3H), 3.26 (q, $J = 7.2$ Hz, 2H), 1.39 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.93 (1C, $COCH_2CH_3$), 164.22 (1C, CO_2CH_3), 145.62 (2C), 145.31 (4C), 145.29 (4C), 145.24 (4C), 145.11 (2C), 144.99 (2C), 144.88 (2C), 144.76 (4C), 144.65 (4C), 143.92 (2C), 143.90 (2C), 143.22 (1C), 143.17 (1C), 143.09 (6C), 143.04 (2C), 142.29 (4C), 141.95 (2C), 141.91 (2C), 141.11 (2C), 141.07 (2C), 139.34 (2C), 138.16 (2C), 72.31 (2C, sp^3 -C of C_{60}), 58.96 (1C, $CCOCH_2CH_3$), 53.79 (1C, OCH_3), 34.77 (1C, CH_2CH_3), 8.54 (1C, CH_2CH_3). UV-vis (in toluene) λ_{max} : 330, 429 nm.

Preparation and spectral characterization of 3f

The procedure was similar to that used for the preparation of **3a**, except that **1f** (78 equiv., 3.90 mmol, 500 μ L) was used instead of **1a**. The reaction afforded **3f** (11.4 mg, 61% based on the consumed C_{60}) as an amorphous brown solid along with the recovered C_{60} (20.2 mg, 56%). MALDI-TOF MS m/z calcd for $C_{66}H_8O_3^+ [M]^+$ 848.0468, found 848.0425. 1H NMR (600 MHz, $CDCl_3$) δ 3.87 (s, 3H), 3.34 (q, $J = 7.8$ Hz, 2H), 1.64 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.88 (1C, $OCCH_2CH_3$), 164.52 (1C, $C=O$), 148.68 (2C), 148.15 (1C), 147.42 (1C), 147.31 (2C), 146.56 (2C), 146.34 (2C), 146.26 (2C), 146.14 (2C), 146.07 (2C), 145.77 (2C), 145.50 (2C), 145.29 (2C), 145.14 (2C), 144.90 (2C), 144.64 (2C), 144.50 (2C), 144.34 (2C), 142.92 (2C), 142.89 (2C), 142.81 (2C), 142.66 (2C), 142.57 (2C), 142.45 (2C), 142.40 (2C), 141.71 (2C), 141.58 (2C), 140.01 (2C), 139.64 (2C), 137.59 (2C), 135.39 (2C), 104.26 (1C, $CC=O$), 102.87 (1C, sp^3 -C of C_{60} , $C_{60}-O$), 72.31 (1C, sp^3 -C of C_{60} , $C_{60}-C$), 51.26 (1C, OCH_3), 30.17 (1C, CH_2CH_3), 11.83 (1C, CH_2CH_3). UV-vis (in toluene) λ_{max} : 320, 429 nm.

Conflicts of interest

There are no conflicts of interest to declare.



Acknowledgements

This work was supported by the National Natural Science Foundation of China (21602192) and Shandong Provincial Government-Sponsored Study Abroad Program “Provincial School Joint Training Plan” (2019).

Notes and references

- 1 H. W. Kroto, J. R. Heath, S. O. Obrien, R. F. Curl and R. E. Smalley, *Nature*, 1985, **318**, 162.
- 2 H. W. Kroto, *Pure Appl. Chem.*, 1990, **62**, 407.
- 3 H. W. Kroto, A. W. Allaf and S. P. Balm, *Chem. Rev.*, 1991, **91**, 1213.
- 4 W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, *Nature*, 1990, **347**, 354.
- 5 R. Taylor and D. R. Walton, *Nature*, 1993, **363**, 685.
- 6 Y. Matsuo and E. Nakamura, *Chem. Rev.*, 2008, **108**, 3016.
- 7 H.-S. Lin and Y. Matsuo, *Chem. Commun.*, 2018, **54**, 11244.
- 8 E. Nakamura and H. Isobe, *Acc. Chem. Res.*, 2003, **36**, 807.
- 9 M. D. Tzirakis and M. Orfanopoulos, *Chem. Rev.*, 2013, **113**, 5262.
- 10 C. Tian, M. Chen, H. Tian, Z. Nan, Y. Liang and Z. Wei, *J. Mater. Chem. C*, 2019, **7**, 12688.
- 11 D. Iohara, F. Hirayama, M. Anraku and K. Uekama, *ACS Appl. Nano Mater.*, 2019, **2**, 716.
- 12 C. Bingel, *Chem. Ber.*, 1993, **126**, 1957.
- 13 X. Camps and A. Hirsch, *J. Chem. Soc., Perkin Trans. 1*, 1997, (11), 1595.
- 14 C. Li, D. Zhang, X. Zhang, S. Wu and X. Gao, *Org. Biomol. Chem.*, 2004, **2**, 3464.
- 15 G.-W. Wang and F.-B. Li, *Org. Biomol. Chem.*, 2005, **3**, 794.
- 16 T.-H. Zhang, G.-W. Wang, P. Lu, Y.-J. Li, R.-F. Peng, Y.-C. Liu, Y. Murata and K. Komatsu, *Org. Biomol. Chem.*, 2004, **2**, 1698.
- 17 S. Chen, Z.-J. Li and X. Gao, *J. Org. Chem.*, 2016, **81**, 121.

