DMAP-Catalyzed [3 + 2] and [4 + 2] Cycloaddition Reactions between [60]Fullerene and Unmodified Morita–Baylis–Hillman Adducts in the Presence of Ac_2O

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Supporting Information

ABSTRACT: One-step DMAP-catalyzed [3 + 2] and [4 + 2] cycloaddition reactions between C_{60} and unmodified Morita– Baylis–Hillman adducts in the presence of Ac₂O have been developed for the easy preparation of cyclopentene- and cyclohexene-fused [60] fullerene derivatives. When the MBH adducts bear an alkyl group, two different reaction pathways could be controlled selectively depending on the conditions.



INTRODUCTION

The functionalization of [60]fullerene with various organic functional groups is an important subject in fullerene chemistry for further material and medicinal applications. A remarkable array of their chemical reactions has been explored over the last two decades.¹ Among which, 1,3-dipolar cycloaddition is one of the most used methodology to construct five-membered ringfused [60]fullerene derivatives containing one or two heteroatoms. Only a limited number of methods for the preparation of [60] fullerene fused cyclopentane and cyclopentene derivatives have been reported up to now, such as the [3 + 2] reaction of cyclopropanone or cyclopropenone ketal with C_{60} ² reaction of C₆₀ anion with 1,3-dihalogenated compounds or cyanosubstituted alkenes,³ cycloaddition reaction of C₆₀ with different zwitterionic species derived from dimethyl acetylenedicarboxylate,⁴ phosphine-catalyzed cycloaddition of C₆₀ with 2,3dienoates or electron-deficient alkynes,⁵ and photoreaction of C₆₀ with alkene linked with a cyclopropyl moiety through a biradical intermediate.⁶ Thermal reactions of [60]fullerene with tertiary amines and aldehydes to give cyclopentafullerene derivatives were reported by the Wang group.^{7a} Recently, they also reported the synthesis of C₆₀-Indane derivatives through the addition of AlCl₃ to the Mn (III)-mediated reaction of C₆₀ with α -aryl active methelene compounds or mesitylenesulfonic acid mediated rearrangement of C₆₀-fused tetrahydroisoquinolines.7b,c

The Morita–Baylis–Hillman (MBH) reaction is one of the most atom-economic reactions for the construction of densely functionalized products, which are useful intermediates in organic synthesis as C_3 synthons.⁸ In the past few years, Lu and co-workers pioneered the use of the modified MBH adducts (-X, -OAc, -OBoc) in [3 + 2] cyclizations and various cycloadditions.⁹ Afterward, this new kind of [3 + 2] annulation reaction was investigated on different C=C,¹⁰ C=N,¹¹ and

N=N¹² double bonds. The Lu, Barbas, Liu, and Shi groups have successfully applied this strategy to synthesize enantiopure spirocyclopenteneoxindole derivatives or functionalized bicyclic imides¹³ and the Tang group has investigated the intramolecular [3 + 2] reaction.¹⁴ To the best of our knowledge, the hydroxyl group on MBH adducts must be transformed to OAc, OBoc, or X (X = Cl, Br) and a phosphine must be used as the catalyst in this strategy and this kind of annulation has not been applied to the functionalization of C₆₀ yet. In the context of our general interest in fullerene chemistry,¹⁵ herein, we reported the DMAP-catalyzed [3 + 2] and [4 + 2] cyclization reactions between [60]fullerene and unmodified MBH adducts in the presence of Ac₂O to afford cyclopentene- and cyclohexene-fused [60]-fullerene derivatives, respectively.

RESULTS AND DISCUSSION

We initiated our studies by evaluating the reaction of C_{60} (36.0 mg, 0.05 mmol) with ethyl 2-(acetoxy(phenyl)methyl)acrylate 1a (2 equiv) using 20 mol % PPh₃ as the catalyst in toluene at 120 °C (Scheme 1). To our delight, the desired [3 + 2] cycloaddition product 2a was obtained as the single product in 29% yield after

Scheme 1. Phosphine-Catalyzed [3 + 2] Annulations of C₆₀ with Acetyl-Modified MBH Adduct 1



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		Ph CO ₂ Et Ac ₂ O, base toluene 4a	Ph CO ₂ E	t	
entry	$C_{60}/4a/Ac_2O/base/PPh_3$	base	T (°C)	time (h)	yield $(\%)^b$
1	1:5:5:5:1	DMAP	80	24	39 (82)
2	1:5:5:5:1	DMAP	120	1.5	37 (80)
3	1:5:5:5:0	DMAP	120	2	36 (86)
4	1:5:5:5:0	K ₂ CO ₃	120	10	0
5	1:5:5:5:0	Et ₃ N	120	10	0
6	1:5:5:5:0	N-methyl imidazole	120	10	trace
7	1:5:5:5:0	pyridine	120	10	trace
8	1:5:5:5:0	DBU	120	10	0
9	1:3:3:3:0	DMAP	120	4	36 (83)
10	1:2:2:2:0	DMAP	120	6	30 (89)
11	1:1:1:1:0	DMAP	120	10	19 (90)

^{*a*}To a mixture of C_{60} (36 mg, 0.05 mmol), 4a, base, and PPh₃ in 16 mL of dry toluene was added Ac₂O. The mixture was then stirred at the indicated temperature in a preheated oil bath. ^{*b*}Isolated yield. Values in parentheses were based on consumed C_{60} .

24 h. As commonly proposed in the literature, an allylic *P*-ylide formed through attacking of phosphine on the β -C of **1a**. We conjectured that, if ethyl 2-(acetoxymethyl)-3-phenylacrylate **1b** was used as the substrate, the isomer **3** would be generated. Nevertheless, the same product **2a** was isolated in 27% yield after 24 h under the similar conditions. The compound **3**, as the isomer of **2a**, was assumed to be more stable than **2a** for the existence of a conjugation effect between the phenyl group and double bonds. However, under different conditions, such as DBU, NaH, *t*-BuOK, MsOH, Et₃N/Pd(OAc)₂, or Et₃N/ Pd(PPh₃)₄, **2a** could not be converted to **3** either at room temperature or at 120 °C. We think that the big steric hindrance between the phenyl group and the fullerene skeleton increases the instability of **3**.

In an attempt to make this approach more efficient, a one-step [3 + 2] cycloaddition directly from unmodified MBH adduct **4a** and C₆₀ was tried. Ac₂O and a base were used as additive reagents to generate **1a** in situ. The influence of base, molar ratio of reagents, and temperature on the reaction was investigated in detail (Table 1).

Under the molar ratio of $C_{60}/4a/Ac_2O/DMAP/PPh_3$ as 1:5:5:5:1, 2a was obtained as expected in 39% yield after stirring at 80 °C for 24 h (Table 1, entry 1). When the reaction temperature was increased to 120 °C, a similar yield was obtained in a shorter reaction time (1.5 h) (Table 1, entry 2). Moreover, to our surprise, in the absence of PPh₃, 2a also could be formed in 36% yield (Table 1, entry 3). It was the first example that the amine, but not the phosphine, catalyzed this kind of intermolecular [3 + 2] reaction. The examination of different bases, such as K₂CO₃, Et₃N, N-methyl imidazole, pyridine, and DBU, revealed that only DMAP was the effective base in the absence of phosphine (Table 1, entries 4-8), and DBU gave an unidentified precipitate with the full conversion of C₆₀. Reducing the employed amount of 4a, Ac₂O, and DMAP to 3 equiv also gave 2a in 36% yield in a slightly longer time (Table 1, entry 9). Further reducing the amount of starting materials led to a longer reaction time and a lower yield of 2a (Table 1, entries 10 and 11). Eventually, the molar ratio of $C_{60}/4a/Ac_2O/DMAP$ as 1:3:3:3 and the reaction temperature as 120 °C were selected as the optimal conditions for the [3 + 2] cycloaddition reaction.

To determine the generality of this methodology, a variety of MBH adducts 4, derived from aromatic aldehydes, were used to

Table 2. Substrate Scope for the [3 + 2] Annulations^{*a*,*b*}



^{*a*}All the reactions were performed with 0.05 mmol of C₆₀ in the molar ratio of C₆₀/4/Ac₂O/DMAP = 1:3:3:3 in 16 mL of dry toluene at 120 °C for 3–10 h. ^{*b*}Isolated yield. Values in parentheses were based on consumed C₆₀.

react with C_{60} (Table 2). All of the reactions were completed in 3–10 h with a moderate to good yield of **2**. The electronic

properties of the substituent on the aromatic ring had little or no influence on the reactions. A substrate with a heteroaromatic group also reacted, affording the corresponding derivative 2d with 31% yield (Table 2, entry 4). All in all, different functional groups such as ester, nitrile, and ketone, could be introduced to the fullerene skeleton using this method.

Under the DMAP-catalyzed [3 + 2] reaction conditions, isomerization of the acetyl-modified MBH product **1a** into **1b** was observed. When **1a** was treated with 1 equiv of DMAP and 1 equiv of HOAc in toluene at 120 °C for 10 h, the ratio of **1a/1b** changed from 100/0 to 6.5/93.5, as determined by the ¹H NMR analysis (Scheme 2). To determine which one is the active





species, C_{60} was reacted with 3 equiv of 1a and 3 equiv of 1b, respectively, in the presence of 3 equiv of DMAP and 3 equiv of HOAc (the in situ generated 1a in a one-step reaction from unmodified MBH prouduct, Ac_2O , and DMAP would produce the same amount of HOAc). 1a gave the desired product 2a in 33% yield after 3 h. However, 1b only gave a trace of 2a after 24 h. When a catalytic amount of Ph₃P was added to the mixture and it was stirred for another 2 h, the reaction worked again. This proved that phosphine was more active than DMAP in this kind of [3 + 2] reaction and 1a is the actual active species in the absence of phosphine.

The [3 + 2] cycloaddition reaction tolerated different aromatic moieties in the MBH adducts 4 (R = Ar). When the MBH adduct **5a** bearing an alkyl group was employed in the reaction, no [3 + 2] product 7**a** was observed. Instead, the [4 + 2] cycloaddition product **6a** was isolated as the single product (Table 3, entry 1). Recently, there was a report on the amine-catalyzed [4 + 2]annulation of MBH allylic acetates with electron-deficient alkenes.¹⁶ Presumably, the high reaction temperature was beneficial to the elimination of HOAc and generation of the diene intermediate. Reducing the temperature to rt resulted in nearly no reaction (Table 3, entry 2). Various conditions were tried to get the [3 + 2] product 7a. With an additive of 0.1 equiv of PPh₃, no 7a was observed yet (Table 3, entry 3). We wanted to reduce the reaction temperature and used more active *n*-Bu₃P instead of PPh₃. When 0.1 equiv of *n*-Bu₃P was used, the reaction proceeded slowly and only a trace of 6a was observed on TLC analysis after 14 h (Table 3, entry 4). When the amount of n-Bu₃P was increased to 0.5 equiv, the desired [3 + 2] product 7a was obtained in 10% yield accompanying with 6% of [4 + 2] product **6a** (Table 3, entry 5). A further increase in the amount of n-Bu₃P to 1 equiv resulted in the improvement on the selectivity of the [3 + 2] product 7a in 24% yield accompanying with 6% of [4 + 2]product 6a (Table 3, entry 6). A trend toward an increased ratio of 7a/6a as the increased amount of *n*-Bu₃P was observed. When Na₂CO₃ was used as the base, higher selectivity and yield of 7a could be obtained (Table 3, entry 7). When 5b-5d was employed in the reaction, the [3 + 2] products 7b-7d and [4 +2] products 6b-6d also could be selectively formed under Na₂CO₃/*n*-Bu₃P and DMAP conditions, respectively (Scheme 3).

Scheme 3. [3 + 2] and [4 + 2] Cycloaddition between C₆₀ and Unmodified MBH Adducts Bearing an Alkyl Group



Table 3. Reaction between C_{60} and 5a Bearing an Alkyl Group in the Presence of Ac₂O and DMAP^a

	OH C ₆₀ + CO ₂ Et <u>Ac₂O, base</u> toluene 5a (3 equiv) conditions 6a	+ CO ₂ Et 7a	
entry	conditions	6a (%) ^b	7a (%) ^b
1	DMAP, 120 °C, 3 h	35 (87)	0
2	DMAP, rt, 14 h	trace	0
3	DMAP, PPh ₃ (0.1 equiv), 120 °C, 3 h	34 (90)	0
4	DMAP, <i>n</i> -Bu ₃ P (0.1 equiv), rt, 14 h	trace	0
5	DMAP, <i>n</i> -Bu ₃ P (0.5 equiv), rt, 14 h	6 (33)	10 (55)
6	DMAP, <i>n</i> -Bu ₃ P (1 equiv), rt, 9 h	6 (17)	24 (68)
7	Na ₂ CO ₃ , <i>n</i> -Bu ₃ P (1 equiv), rt, 9 h	5 (10)	36 (72)
8	Na ₂ CO ₃ , PPh ₃ (0.1 equiv), 120 °C, 9 h	trace	6 (92)

"All the reactions were performed with 0.05 mmol of C_{60} in the molar ratio of $C_{60}/5/Ac_2O/base = 1:3:3:3$ and the indicated amount of phosphine in 16 mL of dry toluene. "Isolated yield. Values in parentheses were based on consumed C_{60} .

It was clear that DMAP could catalyze both [3 + 2] and [4 + 2] reactions and phosphine is beneficial to the [3 + 2] reaction. With the MBH adducts derived from aliphatic aldehyde with an α -H, the [4 + 2] reaction proceeded much faster than the [3 + 2] reaction under DMAP conditions. To establish whether the phosophine could also catalyze the [4 + 2] reaction, the acetyl-modified BH adduct 8 was prepared and treated with PPh₃ and *n*-Bu₃P, respectively (Scheme 4). When PPh₃ was selected as the

Scheme 4. Reaction of C_{60} with Acetyl-Modified MBH Adduct 8



catalyst, the [3 + 2] product 7a was isolated as the main product under thermal conditions (7a/6a = 7:1). However, no reaction occurred at room temperature. When *n*-Bu₃P was used, an interesting phenomenon was observed. At 120 °C, the [4 + 2]reaction was predominant using a catalytic amount of *n*-Bu₃P. When the temperature was increased to rt, a trend of an increased ratio of 7a/6a from 19/21 to 38/6 was observed as the amount of *n*-Bu₃P was increased from 0.1 to 1 equiv. It revealed that the phosphine catalyzed not only the [3 + 2] reaction but also the [4 + 2] reaction because it also could act as an organic base like DMAP. We think that the basicity of *n*-Bu₃P was higher than that of PPh₃, which thus gave more [4 + 2] product when the same amount of phosphine was used. The origin of the trend of increased ratio of 7a/6a as the amount of *n*-Bu₃P was increased is not clear now.

The structures of C₆₀-fused cyclopentene and cyclohexene derivatives 2a-2h, 7a-7d, 6a, and 6d were fully established by their HRMS, ¹H NMR, ¹³C NMR, FT-IR, and UV-vis spectral data.¹⁷ Taking **2a** as an example, the MALDI-FTMS spectra of **2a** displayed the [M⁺] peak at 908.0816. The ¹H NMR spectrum of 2a showed two doublets at 8.08 and 6.21 ppm with a coupling constant of 1.8 Hz for the vinyl and methine hydrogen, two dq peaks at 4.29 and 4.36 ppm and a triplet at 1.28 ppm for the ethyl proton. It should be noted that all phenyl protons are magnetically inequivalent, probably due to the restricted rotation of the phenyl ring.^{3b} In the case of compound 2e, this phenomenon was not observed due to the long distance between the phenyl ring and the C_{60} skeleton. In the $^{13}\! \widetilde{\text{C}}$ NMR spectra of 2a, there are 59 partially overlapped peaks in the region of 127-157 ppm for all the sp^2 carbons, one peak at 164.2 ppm for the carbonyl group, two peaks at 14.29 and 61.34 ppm for the ethyl group, one peak at 63.35 ppm for the methine carbon, and two peaks at 74.86 and 77.26 ppm for the two sp³ carbons of the C_{60} , consistent with the cyclopentene structure. The UV-vis spectrum of 2a exhibited a characteristic absorption for the 1,2-adducts of C₆₀ at 431 nm.

The structures of **6** and 7 could be easily discriminated through their ¹H NMR spectra (Figure 1). For the example of **6a** versus **7a**, the H_a and H_b in **6a** directly attached with the fullerene had a noticeable downfield shift and the splitting pattern was different from that of the CH₂ group in **7a**. In the ¹H NMR



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Figure 1. Difference between 6 and 7 in their ¹H NMR spectra.

spectrum of **6b**, the two CH_2 groups showed a singlet at 4.36 ppm and a doublet at 4.19 ppm, respectively. However, no CH_2 group existed in the structure of **7b**. The methyl group showed a doublet at 2.07 ppm, and the methine group showed a qd peak at 5.02 ppm. Furthermore, there were about 30 peaks for the fullerene skeleton in **6b** due to the C_s symmetry. The molecular structure of **7b** had no symmetry and showed about 60 peaks for the fullerene skeleton.

A plausible mechanism is proposed in Scheme 5. The acetylmodified MBH product is generated in situ from the MBH product, Ac₂O, and base. When R is an aromatic group, a pyridinium salt 9 is formed through an S_N process under DMAP conditions. N-ylide intermediate 10 or the isomer 11 could be, respectively, formed through S_N reaction or deprotonation in the presence of AcO⁻. 10 serves as a surrogate of the 1,3-dipole to undergo a [3 + 2] cycloaddition with C₆₀ to generate 2. 11 is difficult to regenerate 9 under the action of DMAP. However, in the presence of phosphine, it can generate the P-ylide, which reacts with C_{60} to generate 2. When R is an aliphatic group, pyridinium salt 14 and phosphonium salt 16 were generated, respectively, under DMAP or n-Bu₃P/Na₂CO₃ conditions. A competing deprotonation of the γ -H and then elimination of DMAP from 14 provide the highly reactive 1,3-diene intermediate 15, and subsequent Diels-Alder reaction with C_{60} affords the [4 + 2] products 6. As for the phosphonium salt 16, two competing reactions exist depending on the reaction temperature. At room temperature, a P-ylide 17 is preferentially formed through an S_N-deprotonation process, which undergoes a [3 + 2] reaction with C₆₀ to give the product 7. More 1,3-diene intermediate 15 yields along with the increase of temperature, which leads to the generation of competing product 6.

CONCLUSION

In conclusion, one-step DMAP-catalyzed [3 + 2] and [4 + 2] cycloaddition reactions of C_{60} with unmodified MBH products in the presence of Ac₂O were realized and led to the easy preparation of cyclopentene- and cyclohexene-fused [60]-fullerene derivatives, respectively. The MBH adducts bearing aromatic groups only undertake the [3 + 2] process. It was the first example that DMAP catalyzed this kind of [3 + 2] reaction through the *N*-ylide, but not the *P*-ylide. The MBH adducts bearing alkyl groups could give the [3 + 2] and [4 + 2] products selectively depending on the reaction conditions. Moreover, the

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Scheme 5. Plausible Mechanism



difference between PPh₃ and *n*-Bu₃P on the [3 + 2] reaction was also investigated. A possible reaction mechanism was proposed to explain the formation of C₆₀-fused cyclopentene/cyclohexene derivatives.

EXPERIMENTAL SECTION

Preparation of 1a and 1b. To a mixture of 4a (228 mg, 1.1 mmol) and pyridine (119 mg, 1.5 mmol) in 8 mL of dry dichloromethane was added dropwise a solution of acetyl chloride (117 mg, 1.5 mmol) in 5 mL of dichloromethane at 0 °C. The temperature was kept for 5–10 min, and then warmed to room temperature, and the mixture continued to stir for 4–5 h. After completion of the reaction, detected by TLC, 20 mL of water was added to the mixture and then extracted with dichloromethane. The organic phase was dried over anhydrous Na₂SO₄. Evaporation of the solvent, followed by column chromatography on silica gel using petroleum ether/EtOAc (10:1) as the eluent, gave the corresponding product **1a** (219 mg, 80%) as a colorless oil. **1a**:^{18 1}H NMR (300 MHz, CDCl₃) δ 7.30–7.40 (m, SH), 6.68 (s, 1H), 6.40 (t, *J* = 0.9 Hz, 1H), 5.84 (dd, *J* = 1.3, 1.0 Hz, 1H), 4.17 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.13 (dq, *J* = 10.8, 7.2 Hz, 1H), 2.11 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H).

To a 25 mL one-neck flask was added **4a** (103 mg, 0.5 mmol), followed by 5 mL of dry toluene, then DMAP (92 mg, 0.75 mmol) and Ac₂O (77 mg, 0.75 mmol). The mixture was stirred at 80 °C for 24 h. After the same workup process as the preparation of **1a** and column chromatographic purification, pure **1b** (97 mg, 78%) was obtained as a colorless oil. **1b**:¹⁹ ¹H NMR (300 MHz, CDCl₃) δ 7.98 (s, 1H), 7.35–7.45 (m, 5H), 4.96 (s, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 2.11 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H).

Preparation of 8. An acetyl chloride (188 mg, 2.4 mmol) solution in 5 mL of dichloromethane was added dropwise to a mixture of **5a** (344 mg, 2 mmol) and pyridine (206 mg, 2.6 mmol) in 8 mL of dry dichloromethane at 0 °C. The temperature was kept for 5–10 min, and then the mixture was warmed to room temperature and continued to stir overnight. After the same workup process as the preparation of **1a** and column chromatographic purification, the product **8** (312 mg, 73%) was obtained as a colorless oil. **8**:²⁰ ¹H NMR (300 MHz, CDCl₃) δ 6.28 (s, 1H), 5.75 (t, *J* = 1.0 Hz, 1H), 5.64 (dd, *J* = 7.8, 4.6 Hz, 1H), 4.26 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.26 (dq, *J* = 10.8, 7.1 Hz, 1H), 2.08 (s, 3H), 1.58–1.80 (m, 2H), 1.26–1.46 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.3 Hz, 3H).

General Procedure for the DMAP-Catalyzed [3 + 2] Reaction between C₆₀ and MBH Adducts (4a–4h) in the Presence of Ac₂O. To a 25 mL one-neck flask was sequentially added C₆₀ (36.0 mg, 0.05 mmol), DMAP (18.3 mg, 0.15 mmol), BH adducts 4a–4h (0.15 mmol), and 16 mL of dry toluene. After ultrasonic dissolving, Ac₂O (15.3 mg, 0.15 mmol) was added and the mixture was stirred at 120 °C for 3–10 h. The solvent was evaporated in vacuo, and the residue was purified on a silica gel column using CS₂ as the eluent to give unreacted C₆₀. Subsequent elution with CS₂/toluene in the appropriate ratio afforded the [3 + 2] products 2a–2h.

2a: Brown solid, 16.5 mg, 36%, mp > 300 °C. ¹H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, J = 1.8 Hz, 1H), 7.76 (br, 1H), 7.64 (br, 1H), 7.49 (br, 1H), 7.39 (br, 1H), 7.31 (t, J = 7.4 Hz, 1H), 6.21 (d, J = 1.8 Hz, 1H), 4.36 (dq, J = 10.8, 7.2 Hz, 1H), 4.29 (dq, J = 10.8, 7.2 Hz, 1H), 1.28 (t, J = 7.1 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 164.22 (C=O), 156.63, 154.14, 151.32, 151.14, 147.67, 147.56, 146.61, 146.53, 146.34 (2C), 146.27 (2C), 146.24, 146.21, 146.12, 145.99, 145.95, 145.88, 145.82, 145.74, 145.68, 145.65, 145.61, 145.53, 145.32 (2C), 145.22, 145.19, 144.83 (2C), 144.67, 144.65, 144.60, 144.43, 143.32, 143.29, 142.89, 142.83, 142.76, 142.74, 142.62, 142.41 (2C), 142.36, 142.28, 142.18, 142.17, 142.00, 141.99, 141.97, 141.93, 141.83, 141.25, 140.74, 140.53, 140.31, 139.56, 139.11, 137.02, 136.33, 135.72, 134.37, 129.20 (br, 2C, aryl C), 127.96 (2C, aryl C), 77.26 (sp³-C of C₆₀), 74.86 (sp³-C of C₆₀), 63.35, 61.34, 14.29; UV–vis (CHCl₃) λ_{max}/nm 257, 310, 431; FT-IR $(\text{KBr}) \nu/\text{cm}^{-1}$ 2920, 2850, 1717, 1645, 1259, 1095, 1020, 802, 752, 698, 526; HRMS (MALDI-FTMS) m/z [M⁺] Calcd for C₇₂H₁₂O₂, 908.0837; found, 908.0816.

2b: Brown solid, 13.9 mg, 29%, mp > 300 °C. ¹H NMR (500 MHz, CS_2 -CDCl₂) δ 8.32 (br, 1H), 8.22 (br, 1H), 8.11 (s, 1H), 7.91 (br, 1H), 7.79 (br, 1H), 6.26 (d, J = 1.5 Hz, 1H), 4.24–4.36 (m, 2H), 1.31 (t, J =7.1 Hz, 3H); ¹³C NMR (125 MHz, CS_2 -CDCl₃) δ 162.93 (C=O), 155.47, 152.43, 150.29, 150.12, 148.10, 147.48, 147.40, 147.34, 146.41, 146.37, 146.19 (2C), 146.14, 146.11, 146.09, 146.05, 145.80 (2C), 145.59 (4C), 145.51, 145.44 (2C), 145.43, 145.38, 145.27, 145.19, 144.95, 144.43, 144.37 (3C), 144.22, 143.19, 143.16, 142.72, 142.71, 142.67, 142.61, 142.29, 142.14, 142.13, 142.08, 141.99, 141.96, 141.81 (2C), 141.75, 141.69, 141.67, 140.68, 140.56, 140.22, 139.60, 137.89, 136.43, 135.97, 135.70, 134.30, 128.36 (br, 2C), 124.18 (br, 2C), 77.06 (sp³-C of C₆₀), 76.91 (sp³-C of C₆₀), 62.79, 61.38, 14.34; UV-vis (CHCl₃) λ_{max} /nm 257, 309.5, 430.5; FT-IR (KBr) ν /cm⁻¹ 2920, 2850, 1714, 1652, 1514, 1342, 1263, 1226, 1096, 1022, 843, 702, 526; HRMS (MALDI-FTMS) m/z [M⁺] Calcd for C₇₂H₁₁NO₄, 953.0688; found, 953.0669.

2c: Brown solid, 15.5 mg, 33%, mp > 300 °C. ¹H NMR (500 MHz, CDCl₃–CS₂) δ 7.99 (s, 1H), 7.15–7.04 (m, 2H), 6.88–6.75 (m, 1H), 6.10–5.94 (m, 3H), 3.88 (s, 3H); ¹³C NMR (125 MHz, CS₂-CDCl₃) δ 163.91 (C=O), 156.24, 153.72, 150.95, 150.70, 147.41, 147.32, 147.21, 146.38, 146.32, 146.10 (2C), 146.04 (2C), 146.02, 145.99, 145.79, 145.66, 145.64, 145.58, 145.54, 145.51, 145.43, 145.37, 145.28, 145.14, 145.09, 145.06 144.88, 144.51, 144.41, 144.36, 144.19, 143.12, 143.08, 142.70, 142.62, 142.57, 142.53, 142.44, 142.21, 142.18, 142.15, 142.06, 141.95, 141.93, 141.84, 141.79, 141.76 (2C), 141.61, 140.34, 140.16, 139.48, 138.58, 136.84, 136.04, 135.54, 134.71 (br), 134.05, 123.71 (br), 120.74 (br), 108.52 (br), 107.41 (br), 101.24, 76.78 (sp³-C of C₆₀), 74.62 (sp³-C of C₆₀), 62.85, 52.01; UV–vis (CHCl₃) λ_{max} /nm 257, 309, 430.5; FT-IR (KBr) ν /cm⁻¹ 2943, 2893, 1725, 1644, 1512, 1502, 1482, 1431, 1337, 1247, 1227, 1131, 1095, 1034, 928, 526; HRMS (MALDI-FTMS) *m*/*z* [M⁺] Calcd for C₇₂H₁₀O₄, 938.0597; found, 938.0586.

2d: Brown solid, 13.9 mg, 31%, mp > 300 °C. ¹H NMR (500 MHz, CDCl₃-CS₂) δ 7.97 (d, J = 2.0 Hz, 1H), 7.41 (d, J = 1.2 Hz, 1H), 6.51 (d, J = 3.2 Hz, 1H), 6.36 (dd, J = 3.2, 1.9 Hz, 1H), 6.21 (d, J = 1.9 Hz, 1H), 4.38 (dq, J = 10.7, 7.1 Hz, 1H), 4.32 (dq, J = 10.7, 7.1 Hz, 1H), 1.37 (t, J =

7.1 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃-CS₂) δ 163.11 (C=O), 155.50, 153.24, 152.80, 150.80, 150.58, 147.39, 147.28, 146.33, 146.29, 146.13, 146.07, 146.05, 146.03, 145.99, 145.97 (2C), 145.72, 145.66, 145.61, 145.59, 145.49 (2C), 145.39, 145.33, 145.23 (2C), 145.12, 145.07 (2C), 144.85 (2C), 144.52, 144.37, 144.33, 144.19, 143.06, 143.03, 142.69, 142.57, 142.55, 142.52, 142.41 (2C), 142.29, 142.20 (2C), 142.15, 142.04, 141.94, 141.90, 141.78 (2C), 141.76, 141.75, 141.55, 140.56, 140.31, 140.04, 139.34, 136.93, 136.27, 135.95, 135.52, 134.32, 110.94, 108.74, 76.61 (sp³-C of C₆₀), 73.93 (sp³-C of C₆₀), 61.12, 56.55, 14.42; UV-vis (CHCl₃) λ_{max}/mm 256.5, 310, 431; FT-IR (KBr) ν/cm^{-1} 2920, 2850, 1716, 1645, 1368, 1255, 1226, 1095, 1073, 1010, 738, 526; HRMS (MALDI-FTMS) m/z [M⁺] Calcd for C₇₀H₁₀O₃, 898.0630; found, 898.0647.

2e: Brown solid, 8.8 mg, 19%, mp > 300 °C. ¹H NMR (500 MHz, CS_2 -CDCl₃) δ 7.90 (d, J = 1.7 Hz, 1H), 7.41 (d, J = 7.3 Hz, 2H), 7.30 (t, J= 7.4 Hz, 2H), 7.22 (t, J = 7.3 Hz, 1H), 6.90 (d, J = 15.5 Hz, 1H), 6.74 (dd, J = 15.5, 9.8 Hz, 1H), 5.68 (dd, J = 9.7, 1.7 Hz, 1H), 4.44 (dq, J = 10.8, 7.2 Hz, 1H), 4.38 (dq, J = 10.8, 7.2 Hz, 1H), 1.43 (t, J = 7.2 Hz, 3H); ¹³C NMR (125 MHz, CS₂-CDCl₃) δ 163.83 (C=O), 156.12, 153.20, 151.05, 150.81, 147.50, 147.41, 146.43, 146.40, 146.29, 146.22 (2C), 146.19, 146.16, 146.13, 146.10, 145.90, 145.86, 145.81, 145.75, 145.61 (2C), 145.50 (2C), 145.41, 145.34, 145.25, 145.22 (2C), 144.61, 144.54, 144.41, 144.30, 143.88 (3C), 143.24, 143.17, 142.75 (2C), 142.69, 142.62, 142.44, 142.32, 142.30, 142.27, 142.13, 142.11, 142.07 (2C), 141.94 (2C), 141.78, 141.73, 140.60, 140.49, 140.22, 139.93, 138.83, 136.67, 136.65, 136.11, 135.60, 134.25, 134.18, 129.25, 128.68 (2C), 128.02, 126.84 (2C), 76.98 (sp³-C of C_{60}), 73.86 (sp³-C of C_{60}), 61.24, 60.86, 14.51; UV–vis (CHCl₃) λ_{max} /nm 257.5, 310, 431; FT-IR (KBr) $\nu/{\rm cm}^{-1}$ 2922, 2850, 1717, 1642, 1258, 1244, 1225, 1093, 959, 902, 745, 729, 690, 526; HRMS (MALDI-FTMS) m/z [M⁺] Calcd for C₇₄H₁₄O₂, 934.0994; found, 934.1005.

2f: Brown solid, 15.1 mg, 35%, mp > 300 °C. ¹H NMR (500 MHz, CS₂-CDCl₃) δ 7.90 (d, J = 2.1 Hz, 1H), 7.65 (br, 2H), 7.48 (br, 2H), 7.37 (t, J = 7.4 Hz, 1H), 6.07 (d, J = 2.0 Hz, 1H); ¹³C NMR (125 MHz, CS₂-CDCl₃) δ 155.09, 152.03, 149.62, 148.96, 148.93 (2C), 148.87, 147.35, 147.25, 146.34, 146.28, 146.04 (3C), 146.00, 145.98, 145.92, 145.62, 145.53 (2C), 145.46, 145.38, 145.35, 145.31, 145.22 (2C), 145.17, 145.09, 145.06, 145.03, 144.45, 144.32, 144.28, 144.14, 144.10, 143.04, 143.02, 142.63, 142.57, 142.56, 142.51, 142.16, 142.08, 142.06, 141.94, 141.91, 141.84, 141.80,141.72, 141.67, 141.65 (2C), 141.56, 140.54, 140.32, 140.10, 139.44, 137.56, 136.47, 136.21, 135.32, 134.00, 129.44 (2C), 128.82 (2C), 119.22, 114.15, 73.58 (sp³-C of C₆₀), 64.69; UV-vis (CHCl₃) $\lambda_{max}/nm 256$, 310.5, 430; FT-IR (KBr) $\nu/cm^{-1} 2920$, 2850, 2223, 1511, 1453, 1428, 901, 883, 729, 705, 526; HRMS (MALDI-FTMS) m/z [M⁺] Calcd for C₇₀H₇N, 861.0578; found, 861.0590.

2g: Brown solid, 14.9 mg, 33%, mp > 300 °C. ¹H NMR (500 MHz, CS₂-CDCl₃) δ 7.86 (d, J = 2.2 Hz, 1H), 7.10 (br, 2H), 6.86 (br, 1H), 6.01 (s, 2H), 5.98 (d, J = 1.7 Hz, 1H); ¹³C NMR (125 MHz, CS₂-CDCl₃) δ 155.12, 152.07, 149.71, 148.98, 148.63 (3C), 148.04, 147.38, 147.28, 146.37, 146.31, 146.08, 146.06 (2C), 146.03, 146.01, 145.95, 145.64, 145.55 (2C), 145.46, 145.43, 145.39, 145.34, 145.35, 145.24, 145.20, 145.15, 145.09, 145.07, 144.47, 144.35, 144.33, 144.18, 144.14, 143.08, 143.04, 142.67, 142.59 (2C), 142.54, 142.20, 142.13, 142.09, 141.98, 141.94, 141.85 (2C), 141.77, 141.75, 141.70 (2C), 141.58, 140.56, 140.34, 140.14, 139.57, 136.53, 136.20, 135.39, 133.96, 131.30, 119.46, 114.12, 108.95 (br), 101.48, 76.84 (sp³-C of C₆₀), 64.54; UV-vis (CHCl₃) λ_{max}/mm 256.5, 310.5, 430; FT-IR (KBr) ν/cm^{-1} 2920, 2851, 2223, 1501, 1482, 1443, 1236, 1099, 1038, 928, 706, 526; HRMS (MALDI-FTMS) m/z [M⁺] Calcd for C₇₁H₇NO₂, 905.0477; found, 905.0471.

2*h*: Brown solid, 12.7 mg, 29%, mp > 300 °C. ¹H NMR (500 MHz, CS₂-CDCl₃) δ 7.96 (d, J = 1.7 Hz, 1H), 7.61 (br, 2H), 7.42 (br, 1H), 7.36 (br, 1H), 7.27 (t, J = 7.4 Hz, 1H), 6.20 (d, J = 1.6 Hz, 1H), 2.65 (s, 3H); ¹³C NMR (125 MHz, CS₂-CDCl₃) δ 194.12 (C=O), 156.26, 153.81, 150.82, 150.71, 147.35, 147.29, 146.41, 146.37, 146.30, 146.07, 146.05, 146.01 (2C), 145.98, 145.96, 145.66, 145.60 (2C), 145.59, 145.53, 145.49 (2C), 145.40, 145.35, 145.26, 145.11, 145.05, 144.98, 144.86, 144.49, 144.40, 144.31, 144.11, 143.70 (2C), 143.10, 143.07, 142.68, 142.59, 142.55, 142.50, 142.43, 142.16 (2C), 142.09, 141.99, 141.90 (2C), 141.74 (2C), 141.73 (2C), 141.60, 140.87, 140.55, 140.33,

140.16, 139.40, 136.90, 136.14, 135.44, 134.00, 129.13 (br, 2C), 127.82 (2C), 74.33 (sp³-C of C₆₀), 63.16, 27.96; UV–vis (CHCl₃) λ_{max}/nm 257, 310, 431; FT-IR (KBr) ν/cm^{-1} 2919, 2850, 1679, 1622, 1423, 1359, 1261, 1221, 1093, 1021, 799, 702, 526; HRMS (MALDI-FTMS) m/z [M⁺] Calcd for C₇₁H₁₀O, 878.0732; found, 878.0719.

General Procedure for [4 + 2] Reaction between C_{60} and MBH Adducts (5a–5d) in the Presence of Ac₂O and DMAP. To a 25 mL one-neck flask was sequentially added C_{60} (36.0 mg, 0.05 mmol), DMAP (18.3 mg, 0.15 mmol), MBH adducts **5a–5d** (0.15 mmol), and 16 mL of dry toluene. After ultrasonic dissolving, Ac₂O (15.3 mg, 0.15 mmol) was added and the mixture was stirred at 120 °C for 2–5 h. The solvent was evaporated in vacuo, and the residue was purified on a silica gel column using CS₂ as the eluent to give unreacted C_{60} . Subsequent elution with CS₂/toluene in the appropriate ratio afforded the [4 + 2] products **6a–6d**.

6a: Brown solid, 15.3 mg, 35%, mp > 300 °C. ¹H NMR (500 MHz, $CDCl_3-CS_2$) δ 7.81 (br, 1H), 4.65 (d, J = 14.2 Hz, 1H), 4.33-4.43 (m, 2H), 4.12 (d, J = 13.9 Hz, 1H), 3.85 (d, J = 11.5 Hz, 1H), 2.81-2.89 (m, 1H), 2.26–2.29 (m, 1H), 1.46 (t, J = 7.3 Hz, 3H), 1.44 (t, J = 7.1 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃-CS₂) δ 164.67 (C=O), 157.09, 156.91, 153.88, 147.69, 147.56, 146.86, 146.62 (2C), 146.52 (2C), 146.40, 146.26 (3C), 146.23, 145.87, 145.84, 145.79 (2C), 145.59, 145.56, 145.49, 145.45 (4C), 145.40, 145.37, 145.23, 144.80, 144.75, 144.61 (2C), 143.14 (2C), 142.73, 142.71, 142.67 (2C), 142.24 (3C), 142.16, 142.15, 142.11, 142.10, 141.92, 141.79, 141.66, 141.49, 141.41, 140.39 (2C), 139.06, 138.94, 136.32, 135.81, 135.74, 135.05, 134.93, 70.06 (sp³-C of C₆₀), 67.49 (sp³-C of C₆₀), 61.18, 49.75, 39.42, 26.09, 14.57, 13.71; UV–vis (CHCl₃) λ_{max} /nm 257, 309, 432.5; FT-IR (KBr) ν/cm^{-1} 2923, 2867, 1702, 1541, 1429, 1371, 1267, 1231, 1206, 1132, 1078, 730, 527; HRMS (MALDI-FTMS) m/z [M⁺] Calcd for C₆₉H₁₄O₂, 874.0994; found, 874.0962.

6b: Brown solid, 16.1 mg, 38%, mp > 300 °C. ¹H NMR (500 MHz, CDCl₃-CS₂) δ 8.01 (t, *J* = 5.8 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.36 (s, 2H), 4.19 (d, *J* = 5.8 Hz, 2H), 1.45 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃-CS₂) (all 2C unless indicated) δ 164.72 (1C, C=O), 156.40, 156.30, 147.71 (1C), 147.66 (1C), 146.58, 146.53, 146.29, 146.26, 145.81, 145.57 (4C), 145.48 (4C), 145.34, 145.13, 144.76, 144.65, 143.15, 142.65, 142.62, 142.24, 142.20, 142.14, 142.05, 141.70, 141.66, 141.18 (1C), 140.28, 140.18, 136.16 (1C), 135.76, 135.58, 65.66 (1C, sp³-C of C₆₀), 65.13 (1C, sp³-C of C₆₀), 61.20 (1C), 41.21 (1C), 38.89 (1C), 145.66 (1C);

6c: Brown solid, 10.4 mg, 25%, mp > 300 °C. ¹H NMR (500 MHz, CS₂-DMSO- d_6) δ 7.74 (s, 1H), 4.47 (d, *J* = 14.3 Hz, 1H), 4.29 (d, *J* = 14.3 Hz, 1H), 4.03–4.09 (m, 1H), 2.82–2.92 (m, 1H), 2.27–2.38 (m, 1H), 1.52 (t, *J* = 7.1 Hz, 3H); UV–vis (CHCl₃) λ_{max}/nm 256, 310, 431; FT-IR (KBr) ν/cm^{-1} 2955, 2925, 2869, 2219, 1513, 1454, 1428, 1184, 765, 572, 527; HRMS (MALDI-FTMS) m/z [M⁺] Calcd for C₆₇H₉N, 827.0735; found, 827.0767.

6d: Brown solid, 14.8 mg, 35%, mp > 300 °C. ¹H NMR (500 MHz, CDCl₃-CS₂) δ 7.69 (s, 1H), 4.78 (d, J = 12.4 Hz, 1H), 3.88–4.00 (m, 2H), 2.85–2.94 (m, 1H), 2.67 (s, 3H), 2.25–2.36 (m, 1H), 1.48 (t, J = 7.1 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃-CS₂) δ 194.78 (C==O), 157.12, 156.92, 153.78, 147.73, 147.55, 146.80, 146.65, 146.64, 146.52, 146.49, 146.37, 146.29, 146.27 (3C), 145.86, 145.78, 145.67 (2C), 145.60, 145.56, 145.51, 145.46 (3C), 145.43 (2C), 145.39, 145.29, 144.84, 144.80, 144.58, 144.55, 143.49, 143.16, 143.15, 142.74, 142.72, 142.67 (2C), 142.26, 142.22 (2C), 142.17, 142.12, 142.10, 142.06, 141.91, 141.80, 141.70, 141.45, 141.43, 140.46, 140.44, 139.06, 138.95, 136.19, 135.90, 135.32, 134.95, 70.01 (sp³-C of C₆₀), 67.32 (sp³-C of C₆₀), 49.77, 37.57, 26.10, 24.95, 13.79; UV-vis (CHCl₃) λ_{max}/nm 255, 310, 431; FT-IR (KBr) ν/cm⁻¹ 2956, 2922, 2851, 1668, 1511, 1427, 1376, 1264, 1182, 1084, 764, 527; HRMS (MALDI-FTMS) m/z [M⁺] Calcd for C₆₈H₁₂O, 844.0888; found, 844.0859.

General Procedure for the *n*-Bu₃P-Catalyzed [3 + 2] Reaction between C₆₀ and MBH Adducts 5a–5d in the Presence of Ac₂O and Na₂CO₃. To a 25 mL one-neck flask was sequentially added C₆₀ (36.0 mg, 0.05 mmol), Na₂CO₃ (15.9 mg, 0.15 mmol), BH adducts 5a– 5d (0.15 mmol), and 16 mL of dry toluene. After ultrasonic dissolving, Ac₂O (15.3 mg, 0.15 mmol) and *n*-Bu₃P (10.1 mg, 0.05 mmol) were added and the mixture was stirred at room temperature for the

designated time. After completion of the reaction, a solution of I₂ (32 mg) in methanol (0.5 mL) was added and the mixture was stirred for another 5 min (*Caution! Transform the n-Bu*₃*P to n-Bu*₃*P=O; avoid the further reaction at a higher temperature in the process of removing solvent*). The solvent was then evaporated in vacuo, and the residue was purified on a silica gel column using CS₂ as the eluent to give unreacted C₆₀. Subsequent elution elution with CS₂/toluene in the appropriate ratio afforded the major or exclusive [3 + 2] products 7a-7d.

7a: Brown solid, 15.7 mg, 36%, mp > 300 °C. ¹H NMR (500 MHz, CDCl₃-CS₂) δ 7.77 (d, *J* = 1.4 Hz, 1H), 5.02 (d, *J* = 7.4 Hz, 1H), 4.45–4.55 (m, 2H), 2.55–2.62 (m, 1H), 2.38–2.45 (m, 1H), 1.94–2.02 (m, 1H), 1.79–1.87 (m, 1H), 1.51 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃-CS₂) δ 164.91 (C=O), 157.23, 153.20, 151.73, 151.67, 147.66, 147.54, 146.77, 146.59, 146.54, 146.52, 146.35, 146.33, 146.30 (2C), 146.28, 146.25, 146.04, 145.94, 145.87, 145.69, 145.67, 145.63, 145.61 (2C), 145.47, 145.34, 145.30, 145.09, 144.77, 144.66 (2C), 144.52, 143.42, 143.34, 143.03 (2C), 142.97, 142.85 (2C), 142.77, 142.69, 142.49, 142.47, 142.43, 142.31, 142.24, 142.21, 142.11, 142.05, 141.93 (2C), 141.90, 140.69, 140.64, 140.25, 139.44, 136.92, 136.66, 136.03, 134.23, 77.77 (sp³-C of C₆₀), 73.77 (sp³-C of C₆₀), 61.40, 56.66, 36.79, 21.21, 14.65, 14.57; UV–vis (CHCl₃) λ_{max}/nm 257, 309, 431; FT-IR (KBr) ν/cm⁻¹ 2922, 2864, 1714, 1643, 1241, 1224, 1130, 1087, 902, 729, 526; HRMS (MALDI-FTMS) *m*/*z* [M⁺] Calcd for C₆₉H₁₄O₂, 874.0994; found, 874.1005.

7b: Brown solid, 16.9 mg, 40%, mp > 300 °C. ¹H NMR (500 MHz, CDCl₃-CS₂) δ 7.77 (d, *J* = 1.7 Hz, 1H), 5.02 (qd, *J* = 7.2, 1.6 Hz, 1H), 4.42–4.52 (m, 2H), 2.07 (d, *J* = 7.3 Hz, 3H), 1.51 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃-CS₂) δ 164.11 (C=O), 156.63, 153.32, 151.44, 151.24, 147.50, 147.40, 146.43, 146.39, 146.36, 146.31, 146.22, 146.17 (2C), 146.13 (2C), 145.99, 145.88, 145.84, 145.77, 145.57 (2C), 145.51 (2C), 145.41, 145.35, 145.21 (3C), 144.63, 144.54, 144.45, 144.36, 143.28, 143.20, 142.20, 142.75 (4C), 142.69, 142.63, 142.52, 142.30, 142.29 (2C), 142.22, 142.13, 142.08 (2C), 141.99, 141.82, 141.76 (2C), 141.25, 140.59, 140.53, 140.20, 139.82, 136.60, 136.18, 136.04, 134.10, 73.38 (sp³-C of C₆₀), 61.20, 51.95, 21.32, 14.59; UV–vis (CHCl₃) λ_{max}/nm 257, 309, 430.5; FT-IR (KBr) *ν*/cm⁻¹ 2922, 2864, 1714, 1509, 1258, 1241, 1224, 1131, 765, 729, 526; HRMS (MALDI-FTMS) *m*/*z* [M⁺] Calcd for C₆₇H₁₀O₂, 846.0681; found, 846.0699.

7c: Brown solid, 12.4 mg, 30%, mp > 300 °C. ¹H NMR (500 MHz, CS₂-DMSO-d₆) δ 7.59 (br, 1H), 4.78-4.86 (m, 1H), 2.44-2.56 (m, 1H), 2.33-2.43 (m, 1H), 2.05-2.17 (m, 1H), 1.92-2.02 (m, 1H), 1.15 (t, J = 7.1 Hz, 3H); ¹³C NMR (125 MHz, CS₂-DMSO- d_6) δ 154.92, 150.52, 149.58, 149.12, 146.74 (2C), 146.54, 146.40, 145.52, 145.47, 145.45, 145.34, 145.26 (2C), 145.22, 145.20, 145.18, 144.87, 144.80 (2C), 144.78, 144.72, 144.68, 144.55 (2C), 144.53, 144.49, 144.36, 144.26, 143.76, 143.54 (2C), 143.45 (2C), 142.33, 142.26, 142.18, 141.89, 141.85, 141.80, 141.74, 141.43, 141.38, 141.34, 141.20 (2C), 141.15, 141.13, 141.07. 140.97, 140.88, 140.86, 140.82, 139.61 (2C), 139.20, 138.57, 135.43, 135.34, 135.23, 133.25, 120.15, 114.10 (CN), 76.84 (sp³-C of C₆₀), 71.45 (sp³-C of C₆₀), 57.35, 36.94, 20.92, 13.94; UV–vis (CHCl₃) λ_{max} /nm 256, 310, 431; FT-IR (KBr) ν /cm⁻¹ 2953, 2921, 2853, 2216, 1511, 1461, 1428, 1183, 1096, 883, 767, 574, 526; HRMS (MALDI-FTMS) m/z [M⁺] Calcd for C₆₇H₉N, 827.0735; found, 827.0728

7d: Brown solid, 15.6 mg, 37%, mp > 300 °C. ¹H NMR (500 MHz, CDCl₃-CS₂) δ 7.68 (s, 1H), 5.02–5.06 (m, 1H), 2.75 (s, 3H), 2.49–2.57 (m, 1H), 2.28–2.37 (m, 1H), 1.89–2.00 (m, 1H), 1.65–1.75 (m, 1H), 1.01 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃-CS₂) δ 195.39 (C=O), 156.89, 152.98, 151.23, 151.13, 148.20, 147.34, 147.27, 146.48, 146.36, 146.30, 146.24, 146.08 (2C), 146.01 (2C), 145.98, 145.89, 145.70, 145.61, 145.47, 145.42, 145.39 (3C), 145.34, 145.23, 145.06, 144.78, 144.56, 144.42, 144.35, 144.19, 143.18, 143.10, 142.75, 142.69 (2C), 142.62 (2C), 142.52, 142.49, 142.24 (2C), 142.14, 142.01, 141.95, 141.92, 141.84 (2C), 141.68, 141.66 (2C), 140.47 (2C), 140.11, 139.27, 136.82, 136.30, 135.89, 133.81, 77.80 (sp³-C of C₆₀), 73.20 (sp³-C of C₆₀), 56.57, 36.24, 27.69, 21.27, 14.54; UV–vis (CHCl₃) λ_{max}/nm 256, 310, 431; FT-IR (KBr) ν/cm⁻¹ 2950, 2920, 2852, 1673, 1629, 1507, 1426, 1360, 1220, 1183, 1083, 870, 766, 729, 526; HRMS (MALDI-FTMS) *m*/*z* [M⁺] Calcd for C₆₈H₁₂O, 844.0888; found, 844.0871.

General Procedure for Phosphine-Catalyzed Reaction between C_{60} and Acetyl-Modified MBH Adduct 8. To a 25 mL oneneck flask were sequentially added C_{60} (36.0 mg, 0.05 mmol), 8 (0.15 mmol), and 16 mL of dry toluene. After ultrasonic dissolving, phosphine catalyst (PPh₃, 0.005 mmol; or *n*-Bu₃P, 0.005–0.05 mmol) was added and the mixture was stirred at 120 °C or room temperature for the designated time. The solvent was evaporated in vacuo, and the residue was purified on a silica gel column using CS₂ as the eluent to give unreacted C_{60} . Subsequent elution with CS₂/toluene in the appropriate ratio afforded the [3 + 2] products 7a and [4 + 2] products 6a. (When *n*-Bu₃P was used, the same workup process was applied as that of the onestep reaction mentioned above.)

ASSOCIATED CONTENT

Supporting Information

NMR spectra of 1a, 1b, 2a-2h, 6a-6d, 7a-7d, and 8. This material is available free of charge via the Internet at http://pubs. acs.org.

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