JOC The Journal of Organic Chemistry

Article

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b01272 • Publication Date (Web): 17 Jul 2019

Just Accepted

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

A General One-step Synthesis of Symmetrical or Unsymmetrical 1,4-Di(organo)fullerenes from Organo(hydro)fullerenes through A Direct Oxidative Arylation

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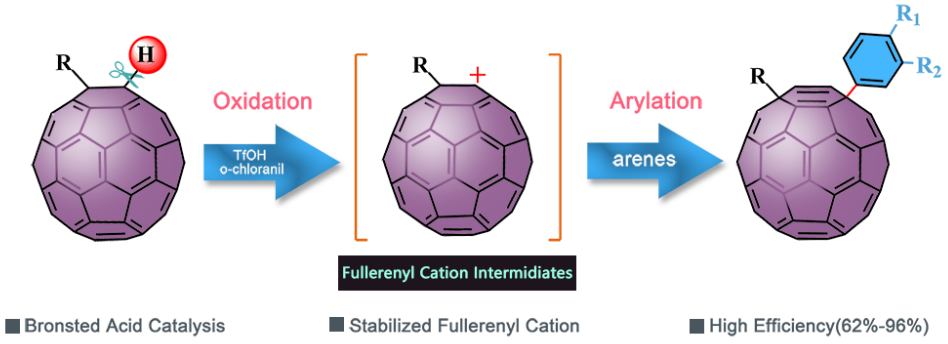


ABSTRACT: A general one-step synthesis of symmetrical or unsymmetrical 1,4-di(organo)fullerenes from organo(hydro)fullerenes ($RC_{60}H$) is realized by a direct oxidative arylation. The new combination of catalytic trifluoromethanesulfonic acid (TfOH) and stoichiometric *o*-chloranil is the first to be used to directly generate R-C_{60}^+ intermediate from common $RC_{60}H$, unexpectedly the in situ generated R-C_{60}^+ intermediate is shown to be quite stable in whole ^{13}C NMR spectroscopy characterization in the absence of cations quenching reagents. Because a direct oxidation of common $RC_{60}H$ to form the corresponding R-C_{60}^+ has never been realized, the present combination of TfOH and *o*-chloranil solves the challenges associated with the formation of stable RC_{60}^+ cations from common $RC_{60}H$ without any coordination of an R group.

INTRODUCTION

The chemical modification of fullerenes through the installation of suitable organic functional groups onto the fullerene core is a very successful approach for the preparation of fullerene-based nanocarbon materials.[1] Organo(hydro)fullerenes ($RC_{60}H$) bearing both organo and hydrogen functional groups can easily be synthesized by various organic reactions starting from pristine fullerene.[1b, 2] To achieve more stable fullerene materials for further applications, the C(sp^3)–H bonds of $RC_{60}H$ are usually functionalized into C–C bonds.[3] Owing to the acidity of the C(sp^3)–H bond,[4] organo(hydro)fullerenes have been functionalized with various alkyl groups[5] in the presence of base (Figure 1a).[6] Unlike alkyl groups, the introduction of aromatic groups bearing π electrons might give the aryl group-functionalized fullerene derivatives unique electronic properties. However, the direct and effective arylation of the C–H bond of $RC_{60}H$ remains challenging.[7] Itami and coworkers reported the first and only example of the C–H arylation of common $RC_{60}H$ species using Pd complexes as the catalysts via the key reaction intermediates of fullerenyl anions (Figure 1b).[8] The isolated yields for the arylation of their two different organo(hydro)fullerenes were reported to be 23% and 6%, and the low yield is due to the formation of large amounts of fullerene dimer or pristine fullerene byproducts under Pd catalysis in an alkaline environment.

To avoid the fullerenyl anion intermediates, we decide to develop an oxidative strategy through organofullerenyl cationic intermediates to realize the arylation of organo(hydro)fullerene (Figure 1c). According to previous literatures, organofullerenyl cationic intermediates were obtained from an oxidation of organofullerenyl anions that produced by deprotonation of organo(hydro)fullerene in an alkaline environment.[5,6] , or were produced from an oxidation of organofullerenyl dimers.[2g, 9] In addition, aziridinofullerene is also a useful precursor for the synthesis of 1,4-di(organo)fullerenes via a fullerenyl cationic intermediate.[10] Notably, Komatsu et al.[11] successfully made a direct oxidation of a special organofullerenyl dimer or a special organo(hydro)fullerene to the corresponding organofullernenyl cations, however, the subsequent arylation reaction was only suitable for the special organofullerenyl dimer, rather than the special organo(hydro)fullerene. Herein, a direct oxidative arylation of common $RC_{60}H$ has been realized by a novel combination of *o*-chloranil and TfOH with arenes as organofullerenyl cationic intermediate trap reagents (Figure 1c).

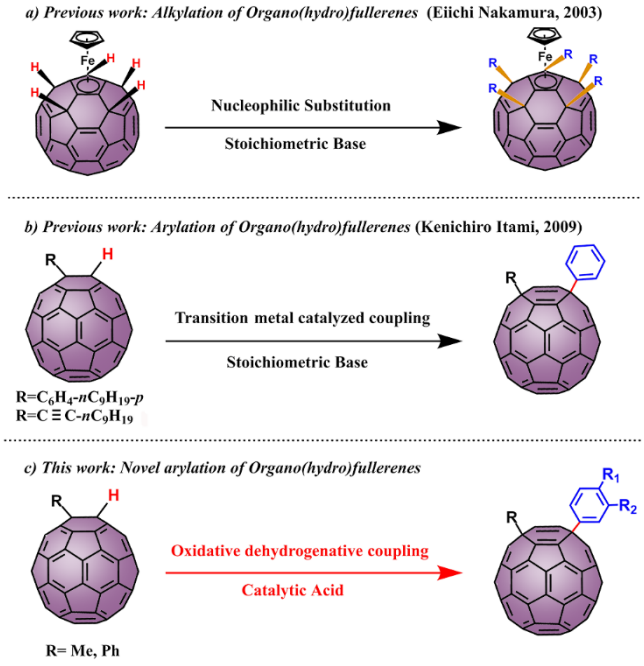


Figure 1. Previous representative works and this work for functionalization of the C(sp^3)–H bond in organo(hydro)fullerenes.

Fullerenyl cations are usually unstable because of their electronegativity.[12] To date, only three examples of the generation of fullerenyl cations as stable species have been reported. In 2000, the long-sought-after H–C_{60}^+ cation was first prepared by Reed and coworkers[13] through the direct protonation of C_{60} with an extraordinarily strong superacid involving an exceptionally inert carborane anion. Takeuchi et al.[15] reported the first example of organofullerenyl cation, R–C_{60}^+(R=$CHCl_2$ or CCl_2CH_2Cl), which was generated by ionization of the corresponding fullerenol (Figure 2a). The second example of R–C_{60}^+ was $(EtO)_2P(OH)CH_2$–C_{60}^+, which was prepared by Komatsu et al.[11] from $(EtO)_2P(O)CH_2$–$C_{60}H$ (Figure 2b). However, the both R–C_{60}^+ species are formed mainly due to the extra coordination stabilization of the cationic center by the chlorine atom or the phosphoryl group, therefore, the R group is actually not a common organo functional groups and which obviously limits the wide application of common organofullerenyl cations. To date, the production of a stable organofullerenyl cations (R–C_{60}^+) without any coordination from an R group has always been a challenge for chemists (Figure 2c). In this work, R–C_{60}^+ as stable species can be produced by a new combination of trifluoromethanesulfonic acid (TfOH) and *o*-chloranil directly from common organo(hydro)fullerene $RC_{60}H$ without any coordination of an R group (Figure 2c). More importantly, the stable organofullernenyl cations (R-C_{60}^+) were produced by the new combination are shown efficient in the general one-step synthesis of 1,4-di(organo)fullerenes from $RC_{60}H$.

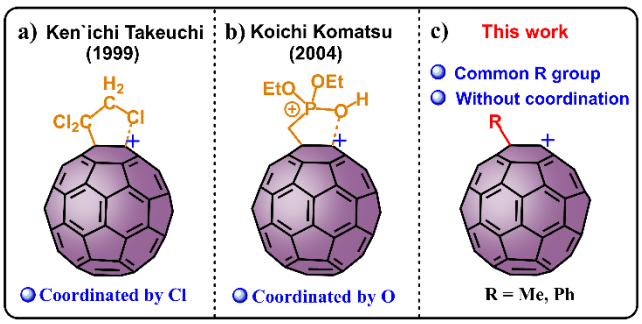
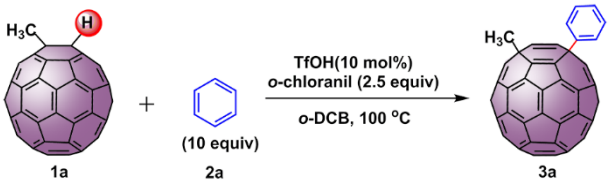


Figure 2. (a, b) Previous work: two stable fullerenyl cations owing to the extra coordination stabilization. (c) This work: stable fullerenyl cations R–C_{60}^+ without any coordination of an R group.

RESULTS AND DISCUSSION

C(sp^3)–H bonds of organo(hydro)fullerene are a type of allylic C(sp^3)–H bond. Inspired by the similar successful oxidation of a benzylic C(sp^3)–H to form the corresponding cation intermediate from Shi and coworkers,[15] we first chose 1,2-$C_{60}CH_3H$ (**1a**) as a model substrate; benzene (**2a**) as the simplest arene; 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), tetrachloro-para-benzoquinone (*p*-chloranil), or tetrachloro-ortho-benzoquinone (*o*-chloranil) as the oxidant; and transition-metal salts such as $FeCl_2$, $FeCl_3$, $Pd(OAc)_2$, $Sc(OTf)_3$, $Pd(OTf)_2$, or $Cu(OTf)_2$ as the catalyst. Under these conditions, the expected direct oxidative arylation reactions were inefficient and **1a** was barely consumed in the presence of quinone oxidants and transition-metal catalysts, as shown in entries 1-8 of Table S1. However, arylation product **3a** was obtained in 80% yield when the transition-metal catalyst was replaced by a Bronsted acid, TfOH, and *o*-chloranil was selected as the oxidant (Scheme 1 and Table S1, entry 10). The oxidative arylation reaction with another slightly weaker Bronsted acid, methanesulfonic acid, as the catalyst also provided an acceptable yield (Table S1, entry 9). Surprisingly, similar quinone oxidants DDQ and *p*-chloranil with catalytic TfOH did not generate the arylation products (Table S1, entries 11-12), indicating that the adjacent carbonyl of *o*-chloranil is crucial for the arylation reaction. The combination of *o*-chloranil (2.5 equiv) and TfOH (10 mol%) at 100 °C was found to be the optimal reaction conditions for the one-step synthesis of 1,4-di(organo)fullerenes with this new oxidative C(sp^3)–H strategy.

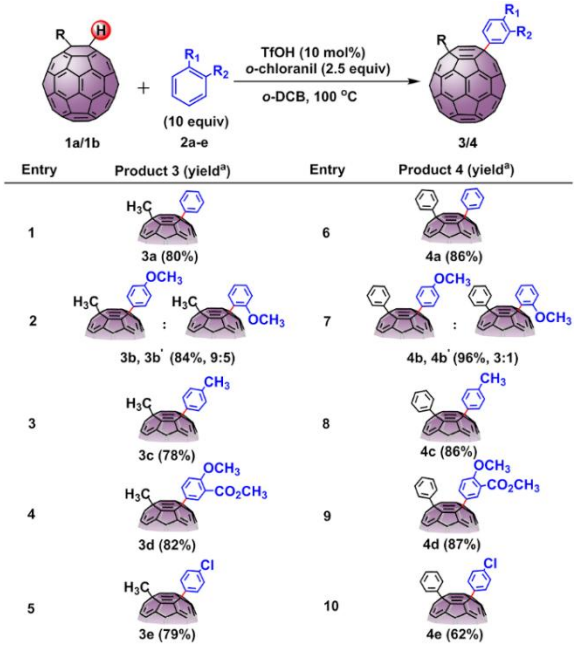


Scheme 1. TfOH-catalyzed oxidative arylation of organo(hydro)fullerene **1a**.

With the optimal conditions in hand, we first examined the effect of substituents on the arene (Table 1, entries 1-5). A variety of arenes with electron-donating or weak electron-withdrawing groups could provide the desired oxidative arylation products, and the general trend was that increased electron density on the aromatic ring improved the yield. However, with strong electron-withdrawing substituents, such as carboxylic acid, methyl ester or trifluoromethyl groups, on the aromatic ring, no arylation products were formed. Interestingly, the reaction of simple anisole with a strong donating group gave a mixture of para- and ortho-substituted (**3b**+**3b'**) regioisomers, while ortho-ester substituted anisole **2c** and other arenes provided **3c**-**3e** with high regioselectivity. Notably, substrates with electron-donating groups are much more reactive than those with electron-withdrawing groups. Therefore, the experimental results with various arenes show that the oxidative arylation reaction follows a Friedel-Crafts-type reaction mechanism.[15]

Next, we investigated another organo(hydro)fullerene substrate, 1,2-C_{60}PhH (**1b**). The arylation efficiency for 1,2-C_{60}PhH (**1b**) is slightly higher than that for 1,2-$C_{60}CH_3H$ (**1a**), (Table1 entry 6-10) probably because the more electron-donating phenyl group can further stabilize the in situ generated fullerenyl cation intermediate. With 1,2-C_{60}PhH (**1b**) as the starting material, the yields of the arylation products (**4a-4e**) were also consistent with a Friedel-Crafts-type reaction mechanism.

Table 1. TfOH-catalyzed oxidative arylation of organo(hydro)fullerenes **1a** and **1b** with various arenes.



[a]Isolated yields

Although the $RC_{60}H$ starting materials are 1,2-ortho-disubstituted (Figures S9, S15), the oxidative arylation products (**3a**-**3e** and **4a**-**4e**) are assumed to be regioselectively formed as the 1,4-para-di(organo)fullerene derivatives according to the UV-Vis data (Figures S10-14, S16-21).[14,16] Additionally, single crystals of **3d** and **4d** were obtained by diffusion methods, and the corresponding crystal structures unambiguously show that both **3d** and **4d** were regioselectively formed as the 1,4-para-substituted isomers (Figure 3, Figures S27-28 and Table S3).

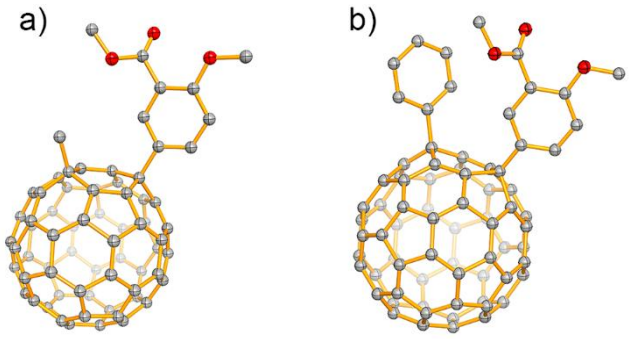


Figure 3. X-ray crystallographic structures of **3d** and **4d**. Hydrogen atoms and solvent molecules have been omitted for clarity.

According to our hypothesis, the direct oxidative arylation of organo(hydro)fullerenes is proceeded by the in situ generation of a fullerene cation and is followed by a Friedel-Crafts-type reaction. To confirm the in situ generation of fullerenyl cations, water was introduced as a trap reagent.[14] As expected, the hydroxyl adducts were obtained as shown in Figure S25 indicating that this arylation proceeds via a carbocation intermediate. Furthermore, in the absence of cation trap reagents, such as an arene, the in situ generated fullerenyl cation was observed as a long-lived and stable species by ^{13}C NMR spectroscopy of a mixed sample (**1b**, *o*-chloranil and TfOH).[11,13-14] The ^{13}C NMR spectrum of the cation species generated from **1b** shows fewer than 32 aromatic signals between 125 and 150 ppm and only one C(sp^3) signal at δ 53.25 ppm (Figure 4 and Figure S26), indicating a change in the symmetry from C_1 to C_s by a heterolytic cleavage of the C(sp^3)–H bond. The signal at 172.02 ppm is assigned to the cationic carbon, which is close to the shifts reported for analogous carbons (174.9 ppm for CH_2ClCCl_2–C_{60}^+ and 174.67 ppm for $(EtO)_2P(O)CH_2$–C_{60}^+).[11,14] Bulk trifluoromethanesulfonate anions generated from the combination of TfOH and *o*-chloranil might help stabilization of the in situ-formed fullerenyl cation. It is worthy to note that **1b** remains insoluble in Komatsu reported mixed acid system (4:1 H_2SO_4 and CF_3SO_3H)[11] after 24-hour magnetic stirring at the room temperature, and no arylation product were observed even upon addition of arenes, finally the recovered compound is intact **1b**, revealing that common $RC_{60}H$ can't be transformed into the corresponding fullerenyl cation according to the reported conditions[11].

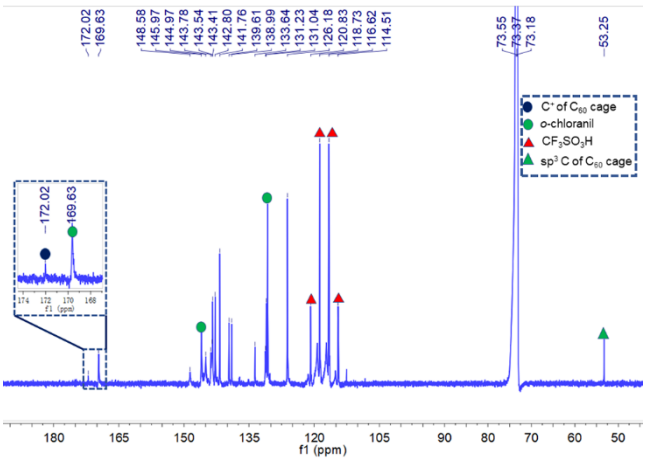


Figure 4. ^{13}C NMR spectrum of the cationic species in *o*-chloranil-TfOH. (rt, 150MHz, $C_2D_2Cl_4$) The signal of *o*-chloranil is marked with green dot; that of CF_3SO_3H is marked with red triangle; that of the characteristic carbocation and sp^3 carbon on the C_{60} cage are marked with deep-blue dot and green triangle respectively.

To determine whether the fullerenyl cation is generated by a direct heterolytic cleavage of a C(sp^3)–H bond in the one-step synthesis of 1,4-di(organo)fullerenes, electron paramagnetic resonance (EPR) spectroscopy[17] and radical-inhibition studies were conducted. The EPR spectrum of **1a**, *o*-chloranil and TfOH exhibited a distinct signal at g = 2.005 (Table S2 and Figure S22). This signal confirmed that fullerenyl radicals or radical cations are generated in the present coupling reaction. Additionally, when 3 equiv of butylated hydroxytoluene (BHT) was added as a radical scavenger,[18] the coupling reaction was completely suppressed, and the starting $RC_{60}H$ was completely recovered (Figure S23), which also confirmed that a radical process is involved in this reaction.

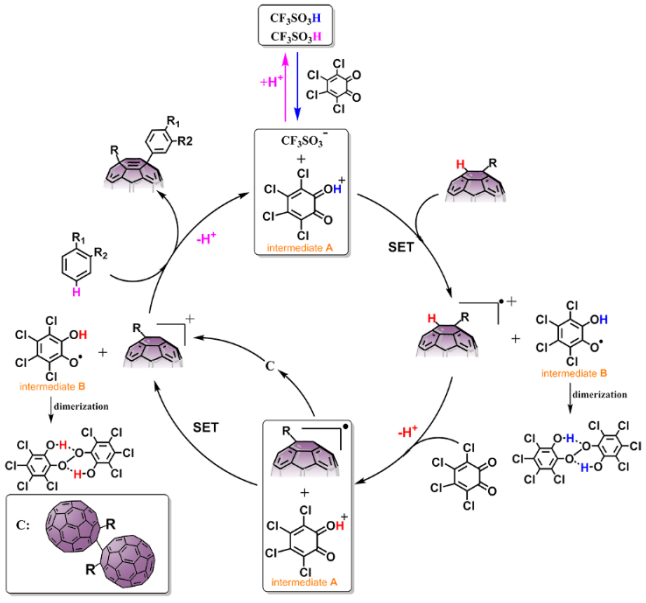


Figure 5. Proposed mechanism for the TfOH-catalyzed oxidative arylation of organo(hydro)fullerenes.

Based on the confirmed coexistence of radical and cation as well as the features of Friedel-Crafts-type reactions in the one-step synthesis of 1,4-di(organo)fullerenes, a possible oxidative arylation mechanism via a fullerenyl cation as the key reaction intermediate was proposed (Figure 5). In the presence of catalytic TfOH, a small portion of the *o*-chloranil is readily protonated to form highly oxidative intermediate **A**. Then, induced by oxidation with intermediate **A**, $RC_{60}H$ can lose one electron to generate RH–$C_{60}^{\bullet+}$ and intermediate **A** itself is reduced to radical intermediate **B**. After losing an electron, the C(sp^3)–H bond of RH–$C_{60}^{\bullet+}$ is wakened, the hydrogen cation of RH–$C_{60}^{\bullet+}$ can be abstracted by *o*-chloranil to form intermediate **A**.[19] Then the newly formed intermediate **A** can oxidize the formed fullerenyl radical to afford the key fullerenyl cation intermediate and intermediate **B**. Alternatively, the fullerenyl radical can dimerize, producing fullerene dimer **C**,[20] and **C** can be cleaved to generate the key fullerenyl cation according to previous reports.[11, 21] Finally, the in situ formed R–C_{60}^{+} and the arenes undergo a Friedel-Crafts-type reaction to give the desired coupling products and protons to turn over the TfOH catalytic cycle. Regioselective attack of the fullerenyl cation by the arene at the 4-position might be due to steric effects. Notably, the signal of dimeric radical **B** is indeed observed in the HRMS spectrum of the coupling product mixture, as shown in Figure S24. The proposed mechanism reasonably explains the high coupling efficiency and the need for more than two equivalents of oxidants in the present oxidative coupling.

To better understand the single electron oxidation to form RH–$C_{60}^{\bullet+}$ and the subsequent hydrogen abstraction process, DFT calculations were employed. The calculated Mulliken charges suggest that electron transfer from $RC_{60}H$ to intermediate **A** to form RH–$C_{60}^{\bullet+}$ is favorable (Table S4). Detailed analysis of the transition state of the subsequent hydrogen abstraction step shows that the Mulliken charge of the reactive hydrogen atom is 0.383, while its spin density is only 0.048, indicating that the reactive hydrogen atom is abstracted as a positive ion (proton) rather than as a free radical (Table S5).

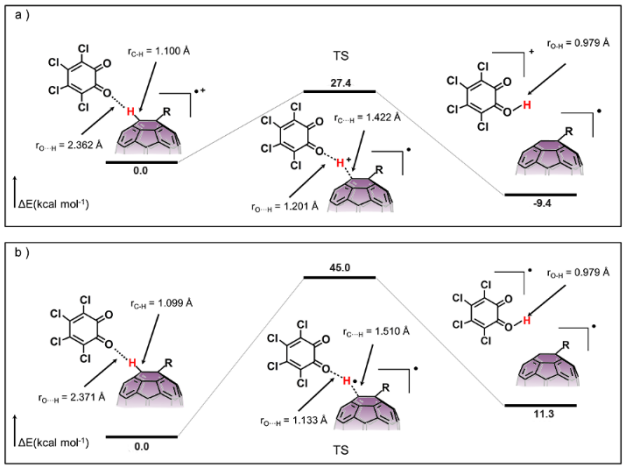


Figure 6. The reaction energy barrier of two possible reaction pathways calculated at the M06-2X/6-31G (d,p) level.

Additionally, a possible homolytic cleavage of the C(sp^3)-H bond of $RC_{60}H$ is revealed energetically unfavorable. The estimated reaction energy barrier of the hydrogen cation abstraction step (RH–$C_{60}^{\bullet+}$ + *o*-chloranil → R–$C_{60}^{\bullet}$ + **A**) is around 27.4 kcal/mol as shown in Figure 6a, by comparison, that of hydrogen radical abstraction step is up to 45.0

kcal/mol (Figure 6b). Therefore, the DFT calculations support the proposed SET transfer to form RH–$C_{60}^{\bullet+}$ followed by a proton abstraction process.

In summary, the first direct oxidative arylation of C(sp^3)–H in common $RC_{60}H$ generating symmetrical or unsymmetrical 1,4-di(organo)fullerenes has been efficiently realized by using a new combination of catalytic TfOH and stoichiometric *o*-chloranil as well as arenes. Unexpectedly, the in situ formed fullerenyl cation intermediate has been confirmed by the ^{13}C NMR spectroscopy of a mixture of $RC_{60}H$, *o*-chloranil and TfOH. In addition, the new strategy successfully solves the challenges associated with the production of stable R–C_{60}^{+} cation species from common $RC_{60}H$ compounds without any coordination of an R group. The proposed mechanism assumes that protonated *o*-chloranil is the crucial oxidant species for the indirect heterolytic cleavage of the C(sp^3)–H bond of $RC_{60}H$, forming the key fullerenyl cation.

EXPERIMENTAL SECTION

General conditions: Unless otherwise noted, all solvents including *o*-dichlorobenzene(*o*-DCB) and reactants (Benzene, Anisole, Toluene and Chlorobenzene, Benzoic acid, 2-methoxy-, methyl ester) were dried with P_2O_5 (Phosphorus pentoxide) over night, then distilled. Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of nitrogen in flame-dried glassware with standard vacuum-line techniques. All reactions that require heating were heated by oil bath. All work-up and purification procedures were carried out with reagent-grade solvents in air.

Preparative recycling HPLC was performed with a Shimadzu LC-20AT instrument equipped with a 5PPB column (10 mm × 250 mm, COSMOSIL). High-resolution mass spectra (HRMS) were obtained from a microTOF-QII (Atmospheric Pressure Chemical Ionization time-of-flight mass spectrometry, APCI-TOF-MS) and a Bruker instrument. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE III 500 MHz (^1H 500 MHz, ^{13}C 125 MHz) spectrometer and a Bruker AVANCE III 600 MHz (^1H 600 MHz, ^{13}C 150 MHz) spectrometer. Chemical shifts for ^1H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.0 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, quin = quintet, sex = sextet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

Organo(hydro)fullerenes synthesis

1-methyl-4-hydro [60] fullerene (1a) A two-neck 500-mL glass round flask containing a magnetic stirring bar was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this flask were added C_{60} (720 mg, 1 mmol), CH_3MgBr (2 M in THF) (1.5 mL, 3 mmol), DMF (2.3 mL, 30 mmol), *o*-DCB (180 mL). This mixture was mixed for 5 min. Then, the mixture was evaporated and the residue was dissolved by100 mL toluene. The solution was subjected to preparative recycling HPLC equipped with a Buckyprep column (eluent: toluene/ isopropanol = 7/3) to afford **1a** (390.1 mg, 53%). C_{60} was recovered in 40% (288.0 mg). Data of compound **1a**: ^1H NMR (500 MHz, $CDCl_3/CS_2$ = 1:2) δ 3.32 (s, 3H) δ 6.45 (s, 1H). HRMS: (APCI-TOF, negative) m/z calcd for $C_{61}H_4$ [M]$^-$: 736.0313, found 736.0324.

1-phenyl-4-hydro [60] fullerene (1b) A two-neck 25-mL glass round flask containing a magnetic stirring bar was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this flask were added C_{60} (43.2 mg, 60 μmol), potassium phenyltrifluoroborate (16.6 mg, 90 μmol), $[Rh(cod)(MeCN)_2]BF_4$ (2.2 mg, 6 μmol), *o*-DCB (7.2 mL), H_2O (1.8 mL). This mixture was stirred at 60 °C for 12 h in the oil bath, the mixture was cooled to room temperature. Then the mixture was evaporated and the residue was dissolved by 50 mL toluene and subjected to preparative recycling HPLC equipped with 5PPB column (eluent: toluene) to afford **1b** (20.1 mg, 42 %) as dark brown solid. Data of compound **1b**: ^1H NMR (500 MHz, $CDCl_3/CS_2$ = 1:2) δ 8.49-8.51 (d, J = 8, 2H), δ 7.80-7.84 (d, J_1 = 12 Hz, J_2 = 8 Hz, 2H), δ 7.62-7.65 (m, 1H), δ 6.79 (s, 1H). HRMS: (APCI-TOF, negative) m/z calcd for $C_{66}H_6$ [M]$^-$: 798.0469, found 798.0471.

General Procedure for TfOH-Catalyzed Reaction of 1a and 1b with Aromatic Compounds. A two-neck 10-mL glass round flask containing a magnetic stirring bar was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this flask were added **1a** or **1b** (20 μmol), *o*-chloranil (12.3 mg, 50 μmol), dry *o*-DCB (2.0 mL), and then **2a-2e** (200 μmol) under a stream of nitrogen. To the reaction mixture was added TfOH (0.1 M solution in *o*-DCB, 20 μL, 2 μmol) and then the mixture was stirred at 100 °C in the oil bath. After cooling to room temperature, the mixture was evaporated and the residue was dissolved by 15 mL toluene. The solution was passed through a pad of silica gel with copious washings with toluene (~20 mL). The filtrate was concentrated and subjected to preparative recycling HPLC equipped with a 5PPB column (eluent: toluene) to afford **3a-3e** and **4a-4e**.

1-methyl-4-phenyl [60] fullerene (3a) Following the general procedure, the reaction of **1a** (14.7 mg, 20 μmol) with *o*-chloranil (12.3 mg, 50 μmol), **2a** (200 μmol) and TfOH (0.1 M solution in *o*-DCB, 20 μL, 2 μmol) at 100 °C stirring for 10 h afforded **3a** (13.0 mg ,80%). **^1H NMR** (500 MHz, $CDCl_3/CS_2$ = 1:2) δ 2.8 (s, 3H), δ 7.55-7.58 (m, 1H), δ 7.68-7.71 (m, 2H), δ 8.34-8.36 (m, 2H). **^{13}C {^1H} NMR** (150 MHz, $CDCl_3/CS_2$ = 1:2) δ 37.4 (1C CH_3), 54.5 (1C $C_{60}CH_3$), 61.7 (1C $C_{60}Ph$), 119.2 (1C C60), 124.1 (1C C60)，127.37 (2C C_6H_5), 128.42 (1C C_6H_5), 129.8 (2C C_6H_5), 129.96 (2C C_{60}), 130.01 (2C C_{60}), 137.5 (1C C_{60}), 137.9 (1C C_{60}), 138.9 (1C C_{60}), 139.0 (1C C_{60}), 140.2 (1C C_6H_5), 141.1 (1C C_{60}), 141.2 (1C C_{60}), 142.1 (1C C_{60}), 142.3 (1C C_{60}), 142.5 (1C C_{60}), 142.66 (2C C_{60}), 142.72 (1C C_{60}), 142.8 (1C C_{60}), 142.9 (1C C_{60}), 143.25 (1C C_{60}), 143.28 (1C C_{60}),143.29 (1C C_{60}), 143.31 (1C C_{60}), 143.37 (1C C_{60}), 143.88 (1C C_{60}), 144.06 (1C C_{60}), 144.15 (1C C_{60}), 144.26 (1C C_{60}), 144.34 (1C C_{60}), 144.38 (1C C_{60}), 144.44 (1C C_{60}), 144.5 (2C C_{60}), 144.8 (2C C_{60}), 145.00 (1C C_{60}), 145.04 (1C C_{60}), 145.3 (2C C_{60}), 145.6 (1C C_{60}), 145.7 (1C C_{60}), 147.01 (1C C_{60}), 147.03 (1C C_{60}), 147.06 (1C C_{60}), 147.08 (1C C_{60}), 147.13 (1C C_{60}), 147.14 (1C C_{60}), 147.2 (1C C_{60}), 147.3 (1C C_{60}), 148.2 (1C C_{60}), 148.7 (1C C_{60}), 148.77 (1C C_{60}), 148.81 (1C C_{60}), 150.7 7(1C C_{60}), 152.9 (1C C_{60}), 157.1 (1C C_{60}), 158.4 (1C C_{60}). **HRMS**: (APCI-TOF, negative) m/z calcd for $C_{67}H_8$ [M]$^-$: 812.0621, found 812.0637.

1-methyl-4-(4-methoxyphenyl) [60] fullerene (3b) and 1-methyl-4-(2-methoxyphenyl) [60] fullerene (3b') Following the

general procedure, the reaction of **1a** (14.7 mg, 20 μmol) with *o*-chloranil (12.3 mg, 50 μmol), **2b** (200 μmol) and TfOH (0.1 M solution in *o*-DCB, 20 μL, 2 μmol) at 100 °C stirring for 5h afforded **3b** and **3b'** (14.1mg ,84%).**^{1}H NMR** (500 MHz, $CDCl_3/CS_2$ = 1:2) of **3b**: δ 2.79 (s, 3H), δ 3.98 (s, 3H), δ 7.18-7.21 (m, 2H), δ 8.22-8.25 (m, 2H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3/CS_2$ = 1:2) of **3b**: δ 37.4 (1C CH_3), 54.5 (1C OMe), 55.3 (2C C_{60}), 115.2 (2C C_6H_4), 128.5 (2C C_6H_4), 129.97 (1C C_{60}), 130.02 (1C C_{60}), 133.2 (1C C_{60}), 137.4 (1C C_{60}), 137.9 (1C C_{60}), 138.9 (1C C_{60}), 140.0 (1C C_{60}), 141.1 (1C C_6H_4), 142.1 (1C C_{60}), 142.5 (2C C_{60}), 142.66 (1C C_{60}), 142.74 (1C C_{60}), 142.83 (1C C_{60}), 142.84 (1C C_{60}), 143.23 (1C C_{60}), 143.28 (1C C_{60}), 143.29 (2C C_{60}), 143.31 (2C C_{60}), 143.37 (1C C_{60}), 143.9 (1C C_{60}), 144.08 (2C C_{60}), 144.10 (1C C_{60}), 144.15 (1C C_{60}), 144.30 (1C C_{60}), 144.35 (1C C_{60}), 144.41 (1C C_{60}), 144.48 (1C C_{60}), 144.50 (2C C_{60}), 144.52 (1C C_{60}), 144.54 (1C C_{60}), 144.55 (2C C_{60}), 144.7 (1C C_{60}), 145.0 (1C C_{60}), 145.2 (1C C_{60}), 145.3 (1C C_{60}), 145.6 (1C C_{60}), 145.68 (1C C_{60}), 147.01 (2C C_{60}), 147.02 (1C C_{60}), 147.06 (1C C_{60}), 147.08 (1C C_{60}), 147.14 (1C C_{60}), 147.2 (1C C_{60}), 147.3 (1C C_{60}), 148.3 (1C C_{60}), 148.6 (1C C_{60}), 148.8 (2C C_{60}), 151.0 (1C C_{60}), 152.9 (1C C_{60}), 157.3 (2C C_{60}), 158.4 (1C C_{60}), 159.7 (1C C_6H_4). **HRMS** of **3b**: (APCI-TOF, negative) m/z calcd for $C_{68}OH_{10}$ [M]$^-$:842.0732, found 842.0725. **HRMS** of **3b'**: (APCI-TOF, negative) m/z calcd for $C_{68}OH_{10}$ [M]$^-$: 842.0732, found 842.0714.

1-methyl-4-(4-methyl-phenyl) [60] fullerene (3c) Following the general procedure, the reaction of **1a** (14.7 mg, 20 μmol) with *o*-chloranil (12.3 mg, 50 μmol), **2c** (200 μmol) and TfOH (0.1 M solution in *o*-DCB, 20 μL, 2 μmol) at 100 °C stirring for 8 h afforded **3c** (12.8 mg, 78%).**^{1}H NMR** (500 MHz, $CDCl_3/CS_2$ = 1:2) δ 2.57 (s, 3H), δ 2.79 (m, 1H), δ 7.49 (d, *J* = 10 Hz, 2H), δ 8.21 (d, *J* = 10 Hz, 2H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3/CS_2$ = 1:2) δ 21.6 (1C CH_3), 28.2 (1C CH_3), 54.5 (1C $C_{60}CH_3$), 61.4 (1C C_{60}Ph), 127.3 (2C C_6H_4), 130.5 (2C C_6H_4), 137.5 (1C C_{60}), 137.9 (2C C_{60}), 138.1 (1C C_6H_4), 138.2 (1C C_{60}), 138.9 (1C C_{60}), 139.0 (1C C_{60}), 141.2 (1C C_{60}), 142.1 (1C C_{60}), 142.3 (1C C_{60}), 142.5 (1C C_{60}), 142.66 (1C C_{60}), 142.73 (2C C_{60}), 142.8 (2C C_{60}), 143.2 (1C C_{60}), 143.26 (1C C_{60}), 143.28 (2C C_{60}), 143.3 (1C C_{60}), 143.4 (1C C_{60}), 143.92 (1C C_{60}), 144.08 (1C C_{60}), 144.09 (1C C_{60}), 144.15 (1C C_{60}), 144.26 (1C C_{60}), 144.30 (1C C_{60}), 144.35 (1C C_{60}), 144.39 (1C C_{60}), 144.50 (2C C_{60}), 144.52 (2C C_{60}), 144.54 (1C C_{60}), 144.8 (1C C_{60}), 144.95 (1C C_{60}), 145.00 (1C C_{60}), 145.05 (1C C_{60}), 145.22 (1C C_{60}), 145.25 (1C C_{60}), 146.99 (1C C_{60}), 147.08 (2C C_{60}), 147.10 (1C C_{60}), 147.13 (1C C_{60}), 147.17 (1C C_{60}), 147.22 (1C C_{60}), 147.3 (1C C_{60}), 148.3 (1C C_{60}), 148.67 (1C C_{60}), 148.75 (1C C_{60}), 148.78 (1C C_{60}), 150.9 (1C C_{60}), 152.9 (2C C_{60}), 157.3 (2C C_{60}), 158.44 (1C C_6H_4). **HRMS**: (APCI-TOF, negative) m/z calcd for $C_{68}H_{10}$ [M]$^-$: 826.0782, found 826.0748.

1-methyl-4-(2-methoxybenzoate) [60] fullerene (3d) Following the general procedure, the reaction of **1a** (14.7 mg, 20 μmol) with *o*-chloranil (12.3 mg, 50 μmol), **2d** (200 μmol) and TfOH (0.1 M solution in *o*-DCB, 20 μL, 2 μmol) at 100 °C stirring for 12 h. After cooling to room temperature, the mixture was evaporated and the residue was dissolved by 5 mL CS_2. The solution was passed through a silica gel (eluent: CS_2: Dichloromethane = 10:1) and afforded **3d** (14.8 mg, 82%). **^{1}H NMR** (500 MHz, $CDCl_3/CS_2$ = 1:2) δ 2.75 (s, 3H), 3.90 (s, 3H), 4.00 (s, 3H), δ 7.23-7.25 (d, *J* = 10 Hz, 1H), δ 8.36-8.48 (dd, J_1 = 5 Hz J_2 =10 Hz, 1H), δ 8.60-8.61 (d, *J* = 5 Hz, 1H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3/CS_2$ = 1:2) δ 36.0 (1C CH_3), 52.1 (1C COOMe), 54.5 (1C $C_{60}CH_3$), 56.2 (1C OMe), 60.5 (1C C_{60}Ph), 113.1 (1C C_6H_4), 121.3 (1C C_6H_4), 125.5 (1C C_{60}), 128.4 (1C C_{60}), 129.1 (1C C_{60}), 129.99 (2C C_{60}), 130.04 (2C C_{60}), 130.7 (1C C_6H_4), 132.1 (1C C_6H_4), 133.0 (1C C_{60}), 137.6 (1C C_{60}), 137.9 (1C C_{60}), 139.1 (1C C_{60}), 141.2 (1C C_{60}), 142.1 (1C C_{60}), 142.3 (1C C_{60}), 142.55 (1C C_{60}), 142.67 (1C C_{60}), 142.70 (1C C_{60}), 142.75 (1C C_{60}), 142.83 (1C C_{60}), 142.9 (1C C_{60}), 143.28 (1C C_{60}), 143.32 (1C C_6H_4), 143.34 (1C C_{60}), 143.4 (2C C_{60}), 143.8 (1C C_{60}), 144.1 (1C C_{60}), 144.2 (2C C_{60}), 144.3 (1C C_{60}), 144.37 (1C C_{60}), 144.38 (2C C_{60}), 144.5 (1C C_{60}), 144.6 (2C C_{60}), 144.7 (1C C_{60}), 145.0 (1C C_{60}), 145.26 (1C C_{60}), 145.31 (1C C_{60}), 145.66 (1C C_{60}), 145.72 (1C C_{60}), 146.9 (1C C_{60}), 147.0 (1C C_{60}), 147.1 (1C C_{60}), 147.2 (1C C_{60}), 147.3 (1C C_{60}), 147.6 (1C C_{60}), 148.2 (1C C_{60}), 148.6 (1C C_{60}), 148.7 (1C C_{60}), 148.8 (1C C_{60}), 150.5 (1C C_{60}), 152.9 (1C C_{60}), 156.5 (1C C_{60}), 158.4 (1C C_{60}), 159.1 (1C C_{60}), 166.8 (1C C_6H_4), 174.4 (1C COOMe). **HRMS**: (APCI-TOF, negative) m/z calcd for $C_{70}O_3H_{12}$ [M]$^-$: 900.0783, found 900.0774.

1-methyl-4-(4-chloro-phenyl) [60] fullerene (3e) Following the general procedure, the reaction of **1a** (14.7 mg, 20 μmol) with *o*-chloranil (12.3 mg, 50 μmol), **2e** (200 μmol) and TfOH (0.1 M solution in *o*-DCB, 20 μL, 2 μmol) at 100 °C stirring for 24 h afforded **3e** (13.4 mg, 79%).**^{1}H NMR** (500 MHz, $CDCl_3/CS_2$ = 1:2) δ 2.8 (s, 3H), δ 7.65-7.68 (m, 2H), δ 8.32 - 8.31 (m, 2H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3/CS_2$ = 1:2) δ 30.5(1C CH_3), 51.8 (1C $C_{60}CH_3$), 52.6 (1C C_{60}Ph), 125.7 (1C C_{60}), 126.8 (2C C_6H_4), 128.0 (2C C_6H_4), 128.7 (1C C_{60}), 132.79 (1C C_{60}), 135.60 (1C C_{60}), 135.96 (1C C_{60}), 136.76 (1C C_{60}), 137.3 (1C C_{60}), 137.7 (2C C_{60}), 139.4 (1C C_{60}), 140.2 (1C C_{60}), 140.4 (1C C_{60}), 140.6 (1C C_{60}), 140.7 (1C C_{60}), 140.8 (1C C_{60}), 140.9 (1C C_{60}), 141.0 (1C C_{60}), 141.38 (2C C_{60}), 141.40 (1C C_6H_4), 141.44 (1C C_{60}), 141.8 (1C C_{60}), 142.17 (1C C_{60}), 142.18 (1C C_{60}), 142.20 (2C C_{60}), 142.30 (1C C_{60}), 142.35 (1C C_{60}), 142.39 (1C C_{60}), 142.42 (1C C_{60}), 142.47 (1C C_{60}), 142.51 (1C C_{60}), 142.59 (1C C_{60}), 142.60 (1C C_{60}), 142.7 (1C C_{60}), 142.8 (1C C_{60}), 143.02 (1C C_{60}), 143.05 (1C C_{60}), 143.3 (2C C_{60}), 143.4 (2C C_{60}), 143.7 (1C C_{60}), 143.8 (1C C_{60}), 144.9 (1C C_{60}), 145.11 (1C C_{60}), 145.13 (1C C_6H_4), 145.14 (1C C_{60}), 145.2 (1C C_{60}), 145.3 (1C C_{60}), 145.4 (1C C_{60}), 145.6 (1C C_{60}), 146.2 (1C C_{60}), 146.6 (1C C_{60}), 146.85 (1C C_{60}), 146.92 (1C C_{60}), 148.2 (1C C_{60}), 154.5 (1C C_{60}), 156.3 (1C C_{60}). **HRMS**: (APCI-TOF, negative) m/z calcd for $C_{67}ClH_7$ [M]$^-$: 846.0246, found 846.0233.

1,4-bisphenyl [60] fullerene (4a) Following the general procedure, the reaction of **1b** (15.8 mg, 20 μmol) with *o*-chloranil (12.3 mg, 50 μmol), **2a** (200 μmol) and TfOH (0.1 M solution in *o*-DCB, 20 μL, 2 μmol) at 100 °C stirring for 6 h afforded **4a** (15.0 mg, 86%).**^{1}H NMR** (500 MHz, $CDCl_3/CS_2$ = 1:2) δ 7.48-7.51 (m, 2H), δ 7.54-7.57 (m, 4H), δ 8.14-8.16 (m, 4H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3/CS_2$ = 1:2) δ 61.9 (2C C_{60}C), 127.7 (4C C_6H_5), 128.4 (2C C_6H_5), 129.6 (4C C_6H_5), 137.6 (2C C_{60}), 139.0 (2C C_{60}), 140.5 (2C C_{60}), 142.3 (2C C_{60}), 142.4 (2C C_{60}), 142.7 (2C C_{60}), 142.8 (2C C_{60}), 142.9 (2C C_{60}), 143.34 (2C C_{60}), 143.36 (2C C_{60}), 143.4 (2C C_{60}), 144.0 (2C C_{60}), 144.1 (2C C_6H_5), 144.4 (2C C_{60}), 144.46 (2C C_{60}), 144.52 (2C C_{60}), 144.6 (2C C_{60}), 144.9 (2C C_{60}), 145.0 (2C C_{60}), 145.3 (2C C_{60}), 145.3 (2C C_{60}), 145.8(2C C_{60}), 147.0 (2C C_{60}), 147.10 (2C C_{60}), 147.2 (2C C_{60}), 147.3 (2C C_{60}), 148.6 (2C C_{60}), 148.8 (2C C_{60}), 151.1 (2C C_{60}) 156.7 (2C C_{60}). **HRMS**: (APCI-TOF, negative) m/z calcd for $C_{72}H_{10}$ [M]$^-$: 874.0783, found 874.0782.

1-phenyl-4-(4-methoxyphenyl) [60] fullerene (4b) and 1-phenyl-4-(2-methoxyphenyl) [60] fullerene (4b') Following the general procedure, the reaction of **1b** (15.8 mg, 20 μmol) with *o*-chloranil (12.3 mg, 50 μmol), **2b** (200 μmol) and TfOH (0.1 M solution in *o*-DCB, 20 μL, 2 μmol) at 100 °C stirring for 6 h afforded **4b** and **4b'** (17.4 mg, 96%). **^{1}H NMR** (500 MHz, $CDCl_3/CS_2$ = 1:2) of **4b**: δ 8.14 - 8.16 (d, *J* = 10 Hz, 2H), 8.01 - 8.03 (d, *J* = 10 Hz, 2H), 7.55 - 7.58 (m, 2H), 7.48 - 7.51 (m, 2H), 7.04 - 7.06 (d, *J* = 10 Hz, 2H), 3.93(S, 3H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3/CS_2$ = 1:2) of **4b**: δ 55.26 (1C OMe), 61.3 (1C C_{60}C), 61.8 (1C C_{60}C), 114.9 (2C C_6H_4), 127.7 (2C C_6H_5), 128.4 (1C C_6H_5), 128.8 (2C C_6H_5), 129.6 (2C C_6H_4), 132.6 (1C C60), 137.6 (1C C60), 138.96 (1C C60), 139.03 (1C C60), 137.5 (1C C60), 140.6 (1C C60), 141.2 (1C C60), 142.3 (1C C60), 142.43 (1C C60), 142.45 (1C C60), 142.7 (2C C60), 142.8 (2C C60), 143.0 (1C C60), 143.3 (1C C60), 143.3 (2C C60), 143.36 (1C C60), 143.38 (2C C60), 144.0 (1C C60), 144.09 (1C C60), 144.12 (1C C60), 144.17 (2C C60), 144.18 (2C C60), 144.39 (1C C60), 144.43 (1C C60), 144.45 (1C C60), 144.49 (1C C60), 144.53 (2C C60), 144.6 (1C C60), 144.92 (2C C60), 145.04 (1C C60), 145.1 (1C C60), 145.2 (1C C60), 145.3 (1C C60), 145.6 (1C C60), 145.7 (1C C_6H_5), 147.01 (1C C60), 147.02 (2C C60), 147.05 (1C C60), 147.1 (1C C60), 147.17 (2C C60), 147.28 (1C C60), 147.30 (1C C_6H_4), 148.6 (1C C60), 148.7 (1C C60), 148.82 (1C C60), 148.84 (1C C60), 151.0 (1C C60), 151.4 (1C C60), 156.7 (1C C60), 157.0 (1C C60), 159.6 (1C C_6H_4). **HRMS** for **4b**: (APCI-TOF, negative) m/z calcd for $C_{73}OH_{12}$ [M]$^-$: 904.0888, found 904.0894. **HRMS** for **4b'**: (APCI-TOF, negative) m/z calcd for $C_{73}OH_{12}$ [M]$^-$: 904.0888, found 904.0895.

1-phenyl-4-(4-methyl-phenyl) [60] fullerene (4c) Following the general procedure, the reaction of **1b** (15.8 mg, 20 μmol) with *o*-chloranil (12.3 mg, 50 μmol), **2c** (200 μmol) and TfOH (0.1 M solution in *o*-DCB, 20 μL, 2 μmol) at 100 °C stirring for 12 h afforded **4c** (15.2 mg, 86%).**^{1}H NMR** (500 MHz, $CDCl_3/CS_2$ = 1:2) δ 2.52 (S, 3H), δ 7.345 (d, J = 5Hz, 2H), δ 7.48-7.51 (m, 1H), δ 7.55-7.58 (m, 2H), δ 7.99-8.01 (m, 2H), δ 8.14-8.16 (m, 2H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3/CS_2$ = 1:2) δ 21.6 (1C CH_3). 61.6 (1C C_{60}C), 61.8 (1C C_{60}C), 127.6 (2C C_6H_3), 127.7 (2C C_6H_3), 128.4 (1C C_6H_5), 129.6 (2C C_6H_4), 130.2 (2C C_6H_4), 137.5 (1C C60), 137.60 (1C C60), 137.64 (1C C60), 138.0 (1C C_6H_4), 138.97 (1C C60), 139.06 (1C C60), 140.6 (2C C60), 141.2 (2C C60), 142.3 (1C C60), 142.4 (2C C60), 142.7 (2C C60), 142.8 (2C C60), 142.9 (1C C60), 143.31 (1C C60), 143.34 (2C C60), 143.35 (1C C60), 143.38 (1C C_6H_4), 144.02 (1C C60), 144.07 (1C C60), 144.1 (1C C60), 144.2 (1C C_6H_5), 144.39 (1C C60), 144.42 (1C C60), 144.47 (1C C60), 144.49 (1C C60), 144.53 (2C C60), 144.55 (1C C60), 144.56 (1C C60), 144.9 (2C C60), 145.0 (1C C60), 145.1 (1C C60), 145.2 (1C C60), 145.3 (1C C60), 145.5 (1C C60), 145.7 (2C C60), 147.0 (2C C60)1, 147.10 (1C C60), 147.11 (2C C60), 147.2 (1C C60), 147.3 (2C C60), 148.6 (1C C60), 148.7 (1C C60), 148.8 (1C C60), 151.0 (1C C60), 151.3 (1C C60), 156.8 (1C C60),157.0 (2C C60). **HRMS**: (APCI-TOF, negative) m/z calcd for $C_{73}H_{12}$ [M]$^-$: 888.0939, found 888.0960.

1-phenyl-4-(2-methoxybenzoate) [60] fullerene (4d) Following the general procedure, the reaction of **1b** (15.8 mg, 20 μmol) with *o*-chloranil (12.3 mg, 50 μmol), **2d** (200 μmol) and TfOH (0.1 M solution in *o*-DCB, 20 μL, 2 μmol) at 100 °C stirring for 12 h. After cooling to room temperature, the mixture was evaporated and the residue was dissolved by 5 mL CS_2. The solution was passed through a silica gel (eluent: CS_2:/CH_2Cl_2 = 10:1) and afforded **4d** (16.7 mg, 86%). **^{1}H NMR** (500 MHz, $CDCl_3/CS_2$ = 1:2) δ 3.90 (s, 3H), δ 4.03 (s, 3H), δ 7.15 (d, *J* = 5 Hz, 1H), δ 7.49-7.52 (m, 1H), δ 7.57-7.60 (m, 2H), δ 8.16-8.18 (m, 2H), δ 8.22 (dd, J_1 = 5 Hz, J_2 =10 Hz, 1H), δ 8.46 (d, *J* = 2.5 Hz, 2H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3/CS_2$ = 1:2) δ 52.1 (1C COOOMe), 54.5 (1C C_{60}C), 56.2 (1C OMe), 60.5 (1C C_{60}C), 121.3 (1C C_6H_5), 125.5 (1C C_6H_3), 128.4 (1C C_6H_3), 129.1 (1C C_6H_3), 129.99 (2C C60), 130.04 (2C C60), 130.6 (2C C_6H_5), 132.1 (2C C_6H_5), 133.0 (1C C_6H_3), 137.6 (1C C60), 137.9 (1C C60), 138.7 (1C C60), 139.1 (1C C60), 141.2 (1C C60), 142.1 (1C C60), 142.3 (1C C60), 142.55 (1C C60), 142.67 (1C C60), 142.70 (1C C60), 142.75 (1C C60), 142.83 (1C C60), 142.86 (1C C60), 143.28 (1C C60), 143.32 (2C C_{60}0), 143.34 (1C C60), 143.4 (1C C60), 143.8 (1C C_6H_5), 144.1 (1C C60), 144.12 (1C C60), 144.13 (1C C60), 144.2 (1C C60), 144.34 (1C C60), 144.37 (1C C60), 144.38 (1C C60), 144.39 (1C C_6H_3), 144.4 (1C C60), 144.5 (1C C60), 144.6 (2C C60), 144.7 (1C C60), 144.97 (1C C60), 145.00 (1C C60), 145.2 (1C C60), 145.3 (1C C60), 145.66 (1C C60), 145.72 (1C C60), 146.9 (1C C60), 147.02 (1C C60), 147.04 (1C C60), 147.07 (1C C60), 147.09 (1C C60), 147.15 (1C C60), 147.25 (1C C60), 147.34 (1C C60), 147.5 (1C C60), 148.2 (1C C60), 148.5 (1C C60), 148.77 (1C C60), 148.83 (1C C60), 150.5 (1C C60), 152.9 (1C C60), 156.5 (1C C60), 158.4 (1C C60), 159.1 (1C C60), 165.8 (1C C_6H_3), 174.4 (1C $COOCH_3$). **HRMS**: (APCI-TOF, negative) m/z calcd for $C_{75}O_3H_{14}$ [M]$^-$: 962.0943, found 962.0934.

1-phenyl-4-(4-chloro-phenyl) [60] fullerene (4e) Following the general procedure, the reaction of **1b** (15.8 mg, 20 μmol) with *o*-chloranil (12.3 mg, 50 μmol), **2e** (200 μmol) and TfOH (0.1 M solution in *o*-DCB, 20 μL, 2 μmol) at 100 °C stirring for 24 h afforded **4e** (11.3 mg, 62%).**^{1}H NMR** (500 MHz, $CDCl_3/CS_2$ = 1:2) δ 7.50-7.54 (m, 3H), δ 7.57-7.61 (m, 2H), δ 8.05-8.09 (m, 2H), δ 8.13-8.13 (m, 2H). **^{13}C {^{1}H} NMR** (150 MHz, $CDCl_3/CS_2$ = 1:2) δ 61.1 (1C C_{60}C), 61.8 (1C C_{60}C), 119.2 (1C C60), 124.0 (1C C_6H_5), 125.5 (1C C60), 127.6 (2C C_6H_5), 128.4 (2C C_6H_4), 128.6 (1C C60), 129.0 (2C C_6H_5), 129.1 (1C C_6H_4), 129.7 (2C C_6H_4), 129.99 (1C C60), 130.04 (1C C60), 134.7 (1C C60), 137.5 (1C C60), 137.7 (1C C60), 138.87 (1C C60), 139.07 (1C C60), 139.2 (1C C60), 140.4 (1C C60), 141.3 (1C C60), 142.2 (1C C60), 142.4 (1C C60), 142.5 (1C C60), 142.66 (1C C60), 142.70 (1C C60), 142.8 (1C C60), 143.0 (1C C60), 143.38 (1C C_6H_4), 143.40 (1C C_6H_5), 143.9 (1C C60), 144.07 (1C C60), 144.15 (2C C60), 144.21 (1C C60), 144.25 (1C C60), 144.29 (1C C60), 144.31 (1C C60), 144.36 (1C C60), 144.44 (1C C60), 144.49 (1C C60), 144.51 (1C C60), 144.57 (1C C60), 144.60 (1C C60), 144.7 (1C C60), 144.87 (1C C60), 144.89 (1C C60), 144.98 (1C C60), 145.27 (1C C60), 145.35 (1C C60), 145.6 (1C C60), 145.8 (1C C60), 146.9 (1C C60), 147.00 (1C C60), 147.06 (2C C60), 147.17 (1C C60), 147.20 (1C C60), 147.33 (1C C60), 147.35 (1C C60), 148.39 (1C C60), 148.6 (1C C60), 148.9 (1C C60), 149.0 (1C C60), 150.6 (1C C60), 151.0 (1C C60), 156.0 (1C C60), 156.7 (1C C60). **HRMS**: (APCI-TOF, negative) m/z calcd for $C_{72}ClH_9$ [M]$^-$: 908.0393, found 908.0407.

ASSOCIATED CONTENT

Supporting Information

Experimental section including ^{1}H and ^{13}C NMR spectra and X-ray crystallography data, CIF files and computation data.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This research was supported by the National Natural Science Foundation of China (21771152, 2172100121, 21390390, 51572231, 21701134, 2170010228), the 973 Program of China (2015CB932301) and the Fundamental Research Funds for the Central Universities (20720170028, 20720160084).

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