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One-Pot Sequential Synthesis of Acetoxylated [60]Fullerene Derivatives

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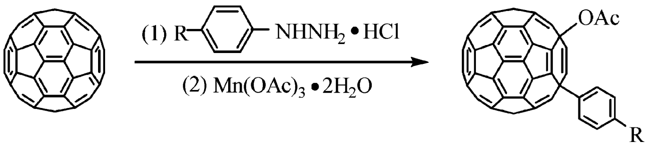
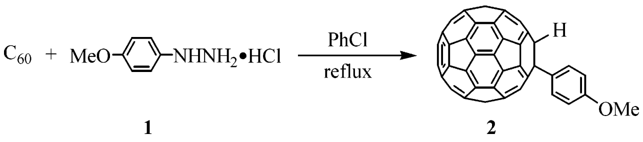


The reaction of [60]fullerene with 4-substituted phenylhydrazine hydrochlorides in refluxing chlorobenzene under aerobic conditions afforded 1-(4-substituted phenyl)-1,2-dihydro[60]fullerenes, which could be subsequently oxidized to 1-acetoxyl-4-aryl-1,4-dihydro[60]fullerenes by manganese(III) acetate dihydrate in one pot. The transformation of $ArC_{60}-H$ to $ArC_{60}-OAc$ has been realized with $Mn(OAc)_3 \cdot 2H_2O$ for the first time.

[60]Fullerene derivatives have been proven to be attractive compounds due to their outstanding properties and may have promising applications in life science and material sciences.[1] The commonly used strategies for fullerene functionalizations include nucleophilic reactions, radical reactions, and [2 + 1], [2 + 2], [3 + 2], and [4 + 2] cycloadditions.[2] Compared with the widely investigated interaction of fullerenes with amines,[3] reports on the reactions of hydrazines with fullerenes have been relatively rare. One example is that anhydrous hydrazine has been used for the reduction of C_{60} to produce hydrogenated fullerenes.[4] Previous work on aromatic hydrazines in fullerene chemistry has been focused mainly on the synthesis of hydrazones, which reacted with C_{60} to give pyrazolino[60]fullerenes.[5] In addition, they were utilized very recently in the regioselective reactions with cage-opened diketone derivatives of C_{60} for ring expansion.[6] These reactions proceeded with unusual migration of two hydrogen atoms from hydrazine to the fullerene cage accompanied by a carbon−carbon bond scission of the fullerene skeleton and afforded fullerene derivatives having a methylene carbon and a phenylhydrazone group along the orifice.[6] The lack of the report on the reactions of phenylhydrazines with C_{60} itself prompted us to explore these reactions. Unexpectedly, 1-aryl-1,2-dihydro[60]fullerenes ($C_{60}HAr$) were obtained from the reaction of C_{60} with phenylhydrazine hydrochlorides.

SCHEME 1. Preparation of Adduct 2



Manganese(III) acetate dihydrate ($Mn(OAc)_3 \cdot 2H_2O$) has been most commonly used in the generation of carbon-centered radicals from various carbonyl compounds in organic synthesis.[7] Recently, we investigated radical reactions between C_{60} and active methylene compounds mediated by $Mn(OAc)_3 \cdot 2H_2O$ and obtained novel 1,4-adducts, 1,16-adducts of C_{60}, and singly bonded fullerene dimers.[8] Therefore, we attempted the reaction of the obtained $C_{60}HAr$ with $Mn(OAc)_3 \cdot 2H_2O$ and found that 1-aryl-1,2-dihydro[60]fullerenes could be transformed to 1-acetoxyl-4-aryl-1,4-dihydro[60]fullerenes. Further investigation revealed that the acetoxylated fullerenes could also be formed in one pot by the direct oxidation of the reaction mixture of C_{60} and phenylhydrazine hydrochlorides with $Mn(OAc)_3 \cdot 2H_2O$. To the best of our knowledge, we are not aware of any report on the synthesis of $C_{60}HAr$ by the reaction of C_{60} with phenylhydrazine hydrochloride derivatives and the acetoxylation of $C_{60}HAr$ by $Mn(OAc)_3 \cdot 2H_2O$. Herein, we describe this one-pot methodology for fullerene acetoxylation.

4-Methoxyphenylhydrazine hydrochloride (**1**) was first chosen to react with C_{60}. The reaction was found to proceed well in refluxing chlorobenzene and gave 1-(4-methoxyphenyl)-1,2-dihydro[60]fullerene (**2**) in 37% yield (95% on the basis of consumed C_{60}) after reflux for 20 h (Scheme 1).

The absorption at 434 nm in the UV−vis spectrum of **2** is characteristic of a [60]fullerene monoadduct with a 1,2-addition pattern. The MALDI-TOF mass spectrum of **2** gave *m/z* 827 (M − 1) as the base peak. The ^1H NMR spectrum of **2** displayed a singlet at 6.70 ppm for the proton connecting to the fullerene core besides those

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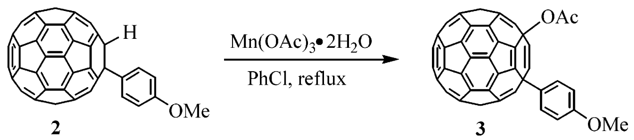
SCHEME 2. Preparation of Acetoxylated Fullerene 3



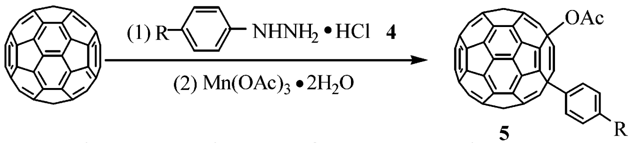
signals for the 4-methoxyphenyl group. The ^{13}C NMR spectrum of **2** displayed 5 peaks at 158.45, 139.56, 127.87, 114.50, and 54.65 ppm for the 4-methoxyphenyl carbons, 28 peaks between 154 and 134 ppm integrated as the 58 sp^2 carbons of the fullerene cage, and 2 peaks at 66.40 and 63.02 ppm for the 2 fullerenyl sp^3 carbons, fully consistent with its C_s symmetry.

Compound **2** was then treated with $Mn(OAc)_3$·$2H_2O$ in order to see if further functionalization could occur. It was satisfactory to find that refluxing a mixture of **2** and 6 equiv of $Mn(OAc)_3$·$2H_2O$ for 2 h in chlorobenzene gave 1-acetoxyl-4-(4-methoxyphenyl)-1,4-dihydro[60]fullerene (**3**) in 50% yield (93% on the basis of consumed **2**) (Scheme 2).

Detailed spectral characterization of **3** revealed that an acetoxy moiety was introduced to the fullerene core in a 1,4-addition pattern. The typical broad absorption around 442 nm in the UV−vis spectrum of **3** was diagnostic of a 1,4-adduct of C_{60}. The ^1H NMR spectrum of **3** showed two singlets at 2.41 and 3.89 ppm for the acetyl methyl and methoxy groups, respectively, and two doublets at 8.14 and 7.14 ppm for four protons of the benzene ring. The ^{13}C NMR spectrum of **3** exhibited 5 peaks at 159.79, 131.56, 128.78, 115.39, and 55.89 ppm for the 4-methoxyphenyl carbons, 2 peaks at 169.29 and 21.63 ppm for the acetoxy carbons, 49 peaks between 154 and 137 ppm integrating as the 58 sp^2 carbons of the C_{60} skeleton, and 2 peaks at 77.78 and 60.72 ppm for the 2 sp^3 carbons of the C_{60} cage linked to the aryl group and the acetoxy group, respectively, indicating that **3** has C_1 symmetry. Notably, the resonance (77.78 ppm) of the sp^3 carbon of the fullerene core connected to the acetoxy group in **3** is close to that (ca. 80 ppm) bound to an alkoxy or alkylperoxy group in other 1,4-adducts[9] but seems to be obviously shifted upfield compared with that (ca. 90 ppm) linked to ester groups in 1,2-adducts of C_{60}.[10] The sp^3 carbons of the C_{60} cage were observed to be shifted upfield over 10 ppm for a 1,4-adduct relative to those for the corresponding 1,2-adduct.[9b,11] The IR spectrum of **3** showed characteristic absorption of the acetoxy group at 1753 cm^{-1}, and those peaks at 1430, 1179, 585, and 526 cm^{-1} for the C_{60} skeleton. The MALDI-TOF MS of **3** displayed a strong peak at *m/z* 827 due to the loss of the acetoxy group.

Further investigation revealed that **3** could be obtained in a one-pot process by the direct oxidation of the reaction mixture of C_{60} and hydrazine **1** with $Mn(OAc)_3$·$2H_2O$. Thus, a mixture of C_{60} and 3 equiv of **1** was refluxed in chlorobenzene for 20 h; then, 9 equiv of $Mn(OAc)_3$·$2H_2O$ was added, and the reaction was continued under reflux for another 2 h. After the usual workup, 1,4-adduct **3** was isolated in 21% yield (54% on the basis of reacted C_{60}). This one-pot procedure could be successfully extended to other phenylhydrazine hydrochlorides **4a**, **4b**, and **4c** and afforded the corresponding acetoxylated fullerene derivatives **5a**, **5b**, and **5c** under the same conditions (Scheme 3).

SCHEME 3. One-Pot Synthesis of Acetoxylated Fullerenes 5



4a, **5a**: R = H; **4b**, **5b**: R = CH_3; **4c**, **5c**: R = Cl

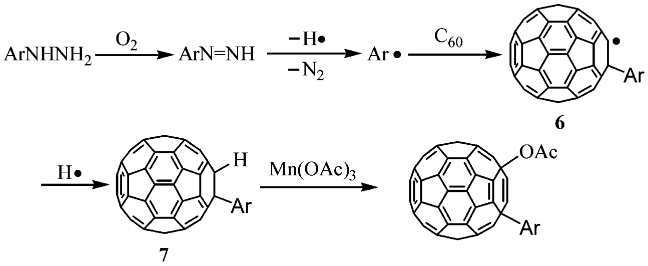
TABLE 1. Yields of 5 along with Recovered C_{60} for the One-Pot Acetoxylation of the Reaction Mixtures of C_{60} and 4 with $Mn(OAc)_3$·$2H_2O$

substrate	product	yield (%)[a]	recovered C_{60} (%)
4a	**5a**	33 (72)	54
4b	**5b**	36 (61)	41
4c	**5c**	32 (73)	56

[a] Refers to isolated yield; the yield in parentheses was based on consumed C_{60}.

The yields of adducts **5** along with recovered C_{60} for the one-pot acetoxylation of the reaction mixtures of C_{60} and phenylhydrazines **4** with $Mn(OAc)_3$·$2H_2O$ are summarized in Table 1. Compounds **5a**−**c** were also fully characterized by MALDI-TOF MS, ^1H NMR, ^{13}C NMR, IR, and UV−vis spectral data and exhibited spectral patterns similar to those of adduct **3**.

SCHEME 4. Proposed Mechanism for the Formation of Acetoxylated Fullerenes



The aryl radicals can be generated from phenylhydrazine hydrochlorides by various oxidizing agent such as oxygen, metal oxides, lead tetraacetate, and copper(II) salts.[12] In our present methodology, formation of adducts **3** and **5** likely proceeds through the addition to C_{60} of an aryl radical generated in situ from the phenylhydrazine derivative by oxidation via oxygen[12] to produce the fullerene radical **6**, followed by hydrogen abstraction to form adduct **7**, which is subsequently oxidized by $Mn(OAc)_3$·$2H_2O$ to afford acetoxylated fullerene **3**/**5** (Scheme 4).

To obtain further information on the reaction mechanism, we examined the reaction of phenylhydrazine

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hydrochloride in refluxing chlorobenzene in the absence of C_{60}. Phenylation of chlorobenzene occurred when the reaction was carried out under aerial conditions. Three chlorobiphenyl isomers were obtained, and the isomer distribution determined by GC-MS was ortho 55%, meta 26%, and para 19%. The isomer ratio is close to that from the reaction of cholorobenzene with phenyl radical obtained by other oxidizing agents.[12a,b] Furthermore, carrying out the reaction under a nitrogen atmosphere did not afford any chlorobiphenyls. This result suggests that aerial oxygen plays a key role in the oxidation of phenylhydrazine to produce a phenyl radical, which then reacts with chlorobenzene to give chlorobiphenyl isomers. When C_{60} is present, the aryl radical prefers to attack C_{60} and results in the formation of **7**. In control experiments, when $Mn(OAc)_3 \cdot 2H_2O$ was replaced by AcOH or Ac_2O under the same aerial conditions, **5a** could not be formed. In addition, the oxidation of **7** by $Mn(OAc)_3 \cdot 2H_2O$ could also be achieved under a nitrogen atmosphere. These results indicate that the introduction of the acetoxy group is not due to the oxidation by either O_2/AcOH or O_2/Ac_2O (AcOH or Ac_2O might exist in reagent $Mn(OAc)_3 \cdot 2H_2O$). $Mn(OAc)_3 \cdot 2H_2O$ has been employed for the acetoxylations of enones and aromatic ketones.[13] The reaction is thought to proceed through the formation of a Mn(III) enolate, which loses Mn(II) upon one-electron oxidation to give the corresponding α'-keto radical; the resultant tertiary radical is prone to further oxidation by another equivalent of $Mn(OAc)_3$ to provide the acetoxylated product.[13] However, in our case, a Mn(III) enolate intermediate should not be formed. Although the detailed mechanism for the transformation of $ArC_{60}-H$ to $ArC_{60}-OAc$ is not clear right now, a radical process might be involved in the oxidation step.

Among various oxygenated fullerene derivatives, the most studied ones have been fullerenols, epoxidated fullerenes, and alkoxylated and alkylperoxylated fullerene derivatives.[2,9] Acyloxylated fullerenes are rare compared to the above-mentioned oxygen-rich fullerene derivatives. Zhdankin and co-workers carried out the reaction of C_{60} with (diacetoxy)iodobenzene and obtained $C_{60}(OAc)_4$ for which the structure has not been well established.[14] The only two known fullerenyl esters were obtained by the esterifications of 1-cyano-2-hydroxy-1,2-dihydro[60]fullerene[10] that was formed by ring opening of [60]fullereno-[1,2-*d*]isoxazole, which needed to be prepared by the addition of either fulminic acid or *N*-silyloxynitrone to C_{60}.[15] In our protocol, acetoxylated fullerene derivatives could be prepared in one pot by heating the reaction mixtures of C_{60} and phenylhydrazine hydrochloride derivatives in chlorobenzene, followed by treating with $Mn(OAc)_3 \cdot 2H_2O$. The current one-pot acetoxylation of C_{60} provided a novel route to fullerene derivatives with an ester group directly attached to the fullerene cage. The transformation of $ArC_{60}-H$ to $ArC_{60}-OAc$ has been realized with $Mn(OAc)_3 \cdot 2H_2O$ for the first time.

Experimental Section

Synthesis of 1-(4-Methoxyphenyl)-1,2-dihydro[60]fullerene 2. A mixture of C_{60} (28.8 mg, 0.04 mmol) and 4-methoxyphenylhydrazine hydrochloride (20.9 mg, 0.12 mmol) was refluxed in chlorobenzene (15 mL) for 20 h. After removal of chlorobenzene in vacuo and separation on a silica gel column with CS_2 as the eluent, adduct **2** (12.3 mg, 37%) was obtained along with recovered C_{60} (17.6 mg, 61%): ^1H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, J = 8.8 Hz, 2H), 7.24 (d, J = 8.8 Hz, 2H), 6.70 (s, 1H), 3.97 (s, 3H); ^{13}C NMR (75 MHz, CS_2-CDCl_3 with $Cr(acac)_3$ as a relaxation agent, all 2C unless indicated) δ 158.45 (1C, aryl *C*), 153.20, 151.70, 146.58 (1C), 146.35 (1C), 145.92, 145.49, 145.44, 145.29, 145.27, 145.00, 144.89, 144.61, 144.58, 144.49, 144.46, 143.74, 143.65, 142.37, 141.66 (4C), 141.40, 141.12 (4C), 141.06, 140.74, 140.67, 139.56 (1C, aryl *C*), 139.39, 139.33, 135.41, 134.77, 127.87 (aryl *C*), 114.50 (aryl *C*), 66.40 (1C, sp^3-C of C_{60}), 63.02 (1C, sp^3-C of C_{60}), 54.65 (1C, OCH_3); FT-IR (KBr) υ_{max} (cm^{-1}) 2947, 2922, 2828, 1610, 1506, 1460, 1428, 1299, 1251, 1215, 1179, 1113, 1032, 963, 903, 838, 823, 807, 792, 767, 747, 702, 646, 585, 566, 552, 527, 476; MS (MALDI-TOF) *m/z* 827 ($M^- - 1$); UV-vis ($CHCl_3$) λ_{max} nm (log ϵ) 256 (5.11), 309 (4.61), 434 (3.63), 702 (2.54).

Synthesis of 1-Acetoxy-4-(4-methoxyphenyl)-1,4-dihydro-[60]fullerene 3. A mixture of **2** (16.6 mg, 0.02 mmol) and $Mn(OAc)_3 \cdot 2H_2O$ (32.2 mg, 0.12 mmol) was refluxed for 2 h in chlorobenzene (10 mL). After removal of chlorobenzene in vacuo and separation on a silica gel column with CS_2 as the eluent, 1-acetoxyl-4-(4-methoxyphenyl)-1,4-dihydro[60]fullerene (**3**) (8.9 mg, 50%) was obtained together with unreacted **2** (7.7 mg, 46%): ^1H NMR (300 MHz, CS_2−acetone-d_6) δ 8.14 (d, J = 8.8 Hz, 2H), 7.14 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, CS_2−acetone-d_6 with $Cr(acac)_3$ as a relaxation agent, all 1C unless indicated) δ 169.29 (OO*C*CH_3), 159.79 (aryl *C*), 153.97, 153.56, 152.40, 148.85, 148.23, 147.29, 147.08 (2C), 146.93, 146.83, 146.80 (2C), 146.64 (2C), 146.30, 145.71, 145.63, 145.51, 145.43, 145.18, 144.88, 144.85, 144.57, 144.50, 144.17, 144.12 (2C), 144.04 (4C), 143.95, 143.82, 143.75, 143.59, 143.39, 143.24, 143.21, 143.09, 142.94, 142.89 (2C), 142.78, 142.64, 142.60, 142.45, 142.42, 142.31 (2C), 142.16, 142.09, 141.96, 140.83, 140.56, 139.80, 138.60, 137.97, 137.43, 131.56 (aryl *C*), 128.78 (2C, aryl *C*), 115.39 (2C, aryl *C*), 77.78 (sp^3-*C* of C_{60}), 60.72 (sp^3-*C* of C_{60}), 55.89 (OCH_3), 21.63 (OOC*C*H_3); FT-IR (KBr) υ_{max} (cm^{-1}) 2954, 2922, 2860, 1753, 1508, 1459, 1430, 1363, 1300, 1251, 1219, 1179, 1079, 1035, 1010, 989, 933, 890, 824, 628, 585, 526; MS (MALDI-TOF) *m/z* 827 (M^- − OAc); UV-vis ($CHCl_3$) λ_{max} nm (log ϵ) 209 (5.26), 257 (5.08), 328 (4.54), 442 (3.80).

Typical Procedure for One-Pot Synthesis of Acetoxylated 1,4-Adduct 3/5. A mixture of C_{60} (28.8 mg, 0.04 mmol) and phenylhydrazine hydrochloride **1/4** (0.12 mmol) was refluxed in chlorobenzene (15 mL) for 20 h; $Mn(OAc)_3 \cdot 2H_2O$ (96.5 mg, 0.36 mmol) was then added, and heating under reflux was continued for 2 h. After evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel using CS_2 as the eluent to afford **3/5** and unreacted C_{60}.

5a: ^1H NMR (300 MHz, CS_2−DMSO-d_6) δ 8.20 (d, J = 7.3 Hz, 2H), 7.60 (t, J = 7.3 Hz, 2H), 7.47 (t, J = 7.3 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, CS_2−DMSO-d_6, all 1C unless indicated) δ 167.65 (OO*C*CH_3), 152.37, 151.80, 150.76, 147.58, 146.97, 145.97, 145.79, 145.77, 145.68, 145.57 (3C), 145.42, 145.39, 145.30, 145.04, 144.46, 144.26 (2C), 144.17, 143.92, 143.66, 143.59, 143.29, 143.27, 142.87, 142.83, 142.81, 142.78, 142.74 (2C), 142.67, 142.56, 142.47, 142.34, 142.12, 141.97, 141.92, 141.79, 141.72, 141.63, 141.61, 141.52, 141.46, 141.37, 141.16, 141.12, 141.01, 140.98, 140.89, 140.82, 140.66, 139.62, 139.31, 138.47, 138.28 (aryl *C*), 137.56, 136.78, 136.26, 128.57 (2C, aryl *C*), 127.39 (aryl *C*), 126.30 (2C, aryl *C*), 76.53 (sp^3-*C* of C_{60}), 59.94 (sp^3-*C* of C_{60}), 20.19 (OOC*C*H_3); FT-IR (KBr) υ_{max} (cm^{-1}) 2922, 2859, 1754, 1492, 1461, 1428, 1364, 1218, 1188, 1126, 1078, 1031, 1009, 989, 932, 734, 691, 629, 584, 559, 527; MS (MALDI-TOF) *m/z* 797 (M^- − OAc); UV-vis ($CHCl_3$) λ_{max} nm (log ϵ) 209 (5.43), 258 (4.96), 328 (4.49), 444 (3.82).

5b: ^1H NMR (300 MHz, CS_2−acetone-d_6) δ 8.08 (d, J = 8.8 Hz, 2H), 7.41 (d, J = 8.8 Hz, 2H), 2.48 (s, 3H), 2.39 (s, 3H); ^{13}C

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NMR (75 MHz, CS_2−acetone-d_6, all 1C unless indicated) δ 169.73 (OO*C*CH_3), 154.09, 153.52, 152.46, 149.02, 148.39, 147.44, 147.24 (2C), 147.10, 147.00 (2C), 146.94, 146.82, 146.77, 146.47, 145.88, 145.77, 145.68, 145.59, 145.35, 145.06, 145.03, 144.73, 144.68, 144.32, 144.28, 144.26, 144.20 (4C), 144.16, 143.99, 143.91, 143.76, 143.56, 143.39 (2C), 143.25, 143.12, 143.05 (2C), 142.94, 142.83, 142.77, 142.59 (2C), 142.45 (2C), 142.32, 142.26, 142.10, 141.01, 140.73, 139.96, 138.85, 138.26 (aryl *C*), 138.15, 137.62, 136.91 (aryl *C*), 130.77 (2C, aryl *C*), 127.73 (2C, aryl *C*), 77.97 (sp^3-*C* of C_{60}), 61.21 (sp^3-*C* of C_{60}), 21.79, 21.75; FT-IR (KBr) υ_{max} (cm^{-1}) 2947, 2921, 2852, 1754, 1509, 1460, 1427, 1364, 1314, 1266, 1219, 1188, 1120, 1079, 1043, 1010, 990, 932, 891, 819, 771, 732, 628, 601, 584, 561, 526; MS (MALDI-TOF) *m/z* 811 (M^- − OAc); UV−vis ($CHCl_3$) λ_{max} nm (log ϵ) 209 (5.34), 257 (5.04), 328 (4.58), 440 (3.95).

5c: ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.17 (d, *J* = 8.7 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, CS_2−DMSO-d_6, all 1C unless indicated) δ 167.80 (OO*C*CH_3), 151.87, 151.52, 150.34, 147.68, 147.11, 146.02, 145.89, 145.79, 145.74, 145.68 (2C), 145.55, 145.52, 145.50, 145.33, 145.17, 144.54, 144.38, 144.30, 144.20, 144.03, 143.82, 143.65, 143.37, 143.35, 142.92 (2C), 142.90, 142.85, 142.82, 142.80, 142.75, 142.58, 142.54, 142.44, 142.21, 142.08, 141.90, 141.86 (2C), 141.74, 141.70, 141.63 (2C), 141.51, 141.26, 141.20, 141.10, 141.04, 140.99, 140.90, 140.63, 139.77, 139.42, 138.45, 137.95, 137.01 (aryl *C*), 136.94, 136.44, 133.48 (aryl *C*), 128.82 (2C, aryl *C*), 127.94 (2C, aryl *C*), 76.54 (sp^3-*C* of C_{60}), 59.28 (sp^3-*C* of C_{60}), 19.77 (OOC*C*H_3); IR (KBr) υ_{max} (cm^{-1}) 2921, 2852, 1755, 1722, 1704, 1564, 1547, 1488, 1463, 1427, 1365, 1263, 1218, 1094, 1014, 990, 934, 895, 840, 823, 584, 528; MS (MALDI-TOF) *m/z* 831 (M^- − OAc); UV−vis ($CHCl_3$) λ_{max} nm (log ϵ) 209 (5.36), 260 (4.99), 328 (4.51), 442 (3.76).

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