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Novel Functionalizations of [60]Fullerene-Fused Lactones

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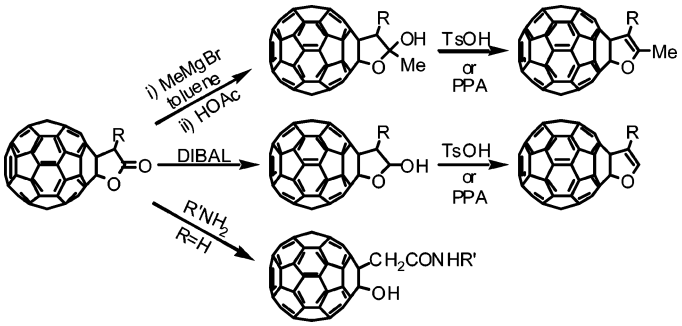

Reactions of [60]fullerene-fused lactones with methylmagnesium bromide and diisobutylaluminum hydride afforded rare fullerene hemiketals and hemiacetals, which were dehydrated by *p*-toluenesulfonic acid monohydrate or polyphosphonic acid to the corresponding [60]fullerene-fused dihydrofurans. Thus obtained alkyl-substituted and especially unsubstituted [60]fullerene-fused dihydrofurans are difficult to prepare by other methods. The unsubstituted [60]fullerene-fused lactone could react with aliphatic amines to give fullerols.

Introduction

Due to the availability of fullerenes in a macroscopic amount, various effective methods for fullerene functionalizations to prepare a plethora of fullerene derivatives have been discovered.[1] However, there is a demand to develop more protocols to obtain fullerene derivatives with some desired specific structures. For example, the simplest unsubstituted fullerene-fused dihydrofuran remains elusive, and only one fullerene hemiacetal derivative has been reported until today.[2] The formation of an acetal, hemiketal, or ketal moiety in fullerene functionalizations is still underexploited.[3]

Free radical reactions are of great interest and are important methodologies to functionalize fullerenes.[4] Recently, we have successfully applied manganese(III) acetate dihydrate ($Mn(OAc)_3 \cdot 2H_2O$) to the free radical reactions of [60]fullerene (C_{60}) to give a diversity of fullerene products.[5] The $Mn(OAc)_3 \cdot 2H_2O$-mediated reactions of C_{60} with various active methylene compounds, aromatic methyl ketones, and β-enamino carbonyl compounds afforded 1,4-adducts and 1,16-adducts of C_{60},[5a,b] singly bonded fullerene dimers,[5a] C_{60}-fused dihydrofuran

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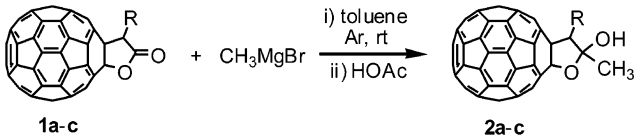
SCHEME 1. Preparation of Fullerene Hemiketals 2a−c



1a-c **2a-c**

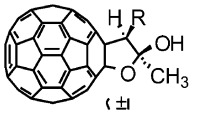
1a, **2a**: R = H; **1b**, **2b**: R = CH_3; **1c**, **2c**: R = Ph

derivatives,[5c] methanofullerenes,[5a,c] and C_{60}-fused pyrroline derivatives.[5e] Interestingly, ArC_{60}−H could be transformed into ArC_{60}−OAc by $Mn(OAc)_3 \cdot 2H_2O$.[5d] We have recently reported the preliminary result for the preparation of C_{60}-fused lactones mediated by $Mn(OAc)_3 \cdot 2H_2O$ and the novel reductive ring opening of the lactone moiety by Grignard reagents.[6] In continuation of our interest in fullerene chemistry,[5−7] herein we describe further functionalizations of C_{60}-fused lactones with methylmagnesium bromide (CH_3MgBr), diisobutylaluminum hydride (DIBAL-H), and aliphatic amines (RCH_2NH_2) to obtain fullerene hemiketals, fullerene hemiacetals, and fullerols. The hemiketals and hemiacetals can be further transformed into C_{60}-fused dihydrofurans by dehydration.

Results and Discussion

We previously reported that the reactions of C_{60}-fused lactones with Grignard reagents in tetrahydrofuran gave unexpectedly the reductive ring-opened products, probably due to the initiation of an electron-transfer process between the C_{60} skeleton and the Grignard reagent.[6] The attempt to obtain the corresponding hemiketals or tertiary alcohols with a Grignard reagent in tetrahydrofuran failed. However, we later found that the desired fullerene hemiketals could be produced when toluene was chosen as the solvent. Lactones **1a**−**c** reacted instantaneously with methylmagnesium bromide (CH_3MgBr) in toluene at room temperature and gave fullerene hemiketals **2a**−**c** after quenching with acetic acid (Scheme 1).

The identity of hemiketals **2a**−**c** was fully established by MS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV−vis spectra. The negative APCI MS of hemiketal **2a** showed the molecular ion at *m*/*z* 794. In the ^{1}H NMR spectrum of hemiketal **2a**, the two methylene protons were split as two AB doublets at 3.62 and 3.84 ppm with J = 12.5 Hz due to the adjacent chiral center. In the ^{13}C NMR spectrum of hemiketal **2a**, the peak for the hemiketal carbon appeared at 104.89 ppm, and the chemical shifts for the two sp^3-carbons of the C_{60} skeleton (97.87 and 68.35 ppm) were close to those of lactones **1a**.[6] Forty-six peaks including some overlapped ones for the 58 sp^2-carbons of the C_{60} moiety were observed in the range of 134−157 ppm, consistent with the C_1 symmetry of its molecular structure. While hemiketal **2a** was a single pure product, careful examination of the ^{1}H NMR spectra of hemiketals **2b** and **2c** revealed



2b: R = CH_3; **2c**: R = Ph

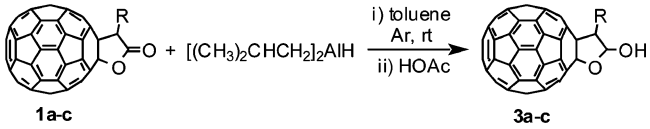
FIGURE 1. The structure for the *cis* isomers of hemiketals **2b** and **2c**.

TABLE 1. Yields, *cis*/*trans* Isomer Ratio, and Recovered Lactones for the Preparation of Hemiketals 2a−c

hemiketal	R	yield[a] (%)	*cis*/*trans*[b]	recovered lactone (%)
2a	H	75		19
2b	CH_3	41	>95/5	54
2c	Ph	42	90/10	38

[a] Total isolated yield including both *cis* and *trans* isomers. [b] The *cis*/*trans* ratio was determined by the ^{1}H NMR spectrum.

SCHEME 2. Preparation of Fullerene Hemiacetals 3a−c



1a-c **3a-c**

1a, **3a**: R = H; **1b**, **3b**: R = CH_3; **1c**, **3c**: R = Ph

that a minor isomer also coexisted. The predominant isomer of hemiketals **2b** and **2c** was determined as the *cis* isomer (Figure 1) by their NOESY spectra. The exclusive formation of the *cis* isomer can be understood by the fact that attack of the carbonyl group by CH_3MgBr is preferred from the less hindered side of the lactone moiety. The attempt to separate out the minor *trans* isomer through column chromatography was unsuccessful.

The yields and *cis*/*trans* isomer ratio along with recovered lactones for the reactions of C_{60}-fused lactones **1a**−**c** with CH_3MgBr in toluene for 5 min are listed in Table 1.

Nucleophilic additions are among the earliest observed reactions in fullerene chemistry. Addition of Grignard or lithium reagents to the C=C bonds of C_{60} is an attractive synthetic method for fullerene functionalizations.[1] However, CH_3MgBr did not add to C_{60} under our conditions, reflecting the higher reactivity of the lactone moiety compared to that of the C=C bonds of C_{60}. In addition, hemiketals **2a**−**c** could not react with another molecule of CH_3MgBr to afford the corresponding tertiary alcohols even in the presence of a large excess of the Grignard reagent or by increasing the reaction temperature and extending the reaction time. The choice of noncoordinating toluene replacing tetrahydrofuran as the solvent was very important to obtain fullerene hemiketals **2a**−**c** because it could retard the competing electron-transfer process between the C_{60} moiety and CH_3MgBr.

Encouraged by the successful preparation of fullerene hemiketals from C_{60}-fused lactones **1a**−**c** and CH_3MgBr, we explored the reactions of lactones **1a**−**c** with diisobutylaluminum hydride (DIBAL-H) hoping to obtain fullerene hemiacetals. To our satisfaction, treatment of lactones **1a**−**c** with DIBAL-H at room temperature led to formation of fullerene hemiacetals **3a**−**c** immediately (Scheme 2).

The yields and *cis*/*trans* isomer ratio along with recovered lactones for the reactions of C_{60}-fused lactones **1a**−**c** with DIBAL-H in toluene for 5 min are listed in Table 2.

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TABLE 2. Yields, *cis*/*trans* Isomer Ratio, and Recovered Lactones for the Preparation of Hemiacetals 3a−c

hemiacetal	R	yield[a] (%)	*cis*/*trans*[b]	recovered lactone (%)
3a	H	93		trace
3b	CH_3	81	78/22	15
3c	Ph	76	42/58	trace

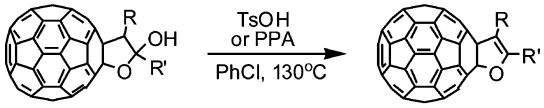
[a] Total isolated yield including both *cis* and *trans* isomers. [b] The *cis*/*trans* ratio was determined by the ^{1}H NMR spectrum.

As can be seen from Table 2, the yields for the hemiacetals **3a**−**c** were very high. Compound **3a** was reported as one of the products from the photochemical reaction of C_{60} with triethylamine in air-saturated solution.[2] Nevertheless, the yield was quite low, that is, 6−10% yield on the basis of reacted C_{60}. Obviously, our protocol provides a better alternative access to product **3a** in much higher yield. The structure of hemiacetal **3a** was confirmed by comparison of its spectral data with those reported previously.[2] For hemiacetals **3b** and **3c**, both *cis* and *trans* isomers were observed. The *cis* and *trans* isomers of **3b** and **3c** were also inseparable by column chromatography, and their ratios were determined by the integrals in the ^{1}H NMR spectra. The coupling constants for the methine protons on the tetrahydrofuran ring in the *trans* isomers with similar structural moieties are usually smaller and even close to zero.[8] Therefore, the isomer with smaller coupling constants for the methine protons was assigned as the *trans* isomer. The poorer stereoselectivity of **3b**,**c** relative to that of **2b,c** needs further investigation. In contrast with all other cases, the *trans* isomer of **3c** was formed preferentially, though the exact reason is still unknown. Similar to hemiketals **2a**−**c**, no further reaction of hemiacetals **3a**−**c** by another molecule of DIBAL-H was achieved.

The hydroxy group of the hemiketals **2a**−**c** and hemiacetals **3a**−**c** has the potential for many further functionalizations, such as esterification, etherification, and dehydration, to attain various fullerene derivatives that incorporate with desired specific structure units. Electron-withdrawing group, such as carbonyl and aryl groups, were usually attached to the olefinic carbons in the reported C_{60}-fused dihydrofurans, which were commonly prepared from the reactions of C_{60} with β-keto esters, β-diketones, or aromatic methyl ketones in the presence of a base or metal oxidant.[4e,5c,9] However, alkyl-substituted C_{60}-fused dihydrofurans have not appeared in the literature. We conjectured that our synthesized hemiketals **2a**−**c** and hemiacetals **3a**−**c** should be the excellent precursors. To our delight, we found that *p*-toluenesulfonic acid monohydrate (TsOH·H_2O) and polyphosphoric acid (PPA) could efficiently cause the dehydration of hemiketals **2a**−**c** and hemiacetals **3a**−**c** to give the corresponding C_{60}-fused dihydrofuran derivatives **4a**−**f** (Scheme 3).

The yields and reactions times for the formation of products **4a**−**f** from the dehydration reactions of hemiketals **2a**−**c** and hemiacetals **3a**−**c** in the presence of TsOH and PPA are summarized in Table 3.

SCHEME 3. Dehydration of Hemiketals 2a−c and Hemiacetals 3a−c



4a-f

4a: R = H, R' = CH_3; **4b**: R = CH_3, R' = CH_3;
4c: R = Ph, R' = CH_3; **4d**: R = H, R' = H;
4e: R = CH_3, R' = H; **4f**: R = Ph, R' = H

TABLE 3. Yields and Reaction Times for the Dehydration Reactions of Hemiketals 2a−c and Hemiacetals 3a−c by TsOH and PPA

product	acid	time (h)	yield (%)	recovered **2** or **3** (%)
4a	TsOH	2	64	35
	PPA	0.5	99	trace
4b	TsOH	1	86	12
	PPA	0.5	96	trace
4c	TsOH	1	98	trace
	PPA	0.5	98	trace
4d	TsOH	2	trace	trace
	PPA	1	91	trace
4e	TsOH	2	89	9
	PPA	4	96	trace
4f	TsOH	1	98	trace
	PPA	6	84	15

The presence of TsOH or PPA proved to be crucial for the success of the dehydrations, with no formation of **4a**−**f** in their absence. It can be seen from Table 3 that PPA generally performed better than TsOH for the dehydration process except for the formation of **4f**. Both *cis* and *trans* isomers of hemiketals **2b**,**c** and hemiacetals **3b**,**c** could be dehydrated to give the dihydrofuran derivatives. For the dehydration of **3a**, TsOH afforded some unknown products rather than the desired **4d**. However, PPA was successful for the preparation of the simplest and unsubstituted C_{60}-fused dihydrofuran **4d**, which might be difficult to be obtained by any other route.

Compounds **4a**−**f** were fully characterized by their MS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV−vis spectra. In the ^{13}C NMR spectra of compounds **4a**−**f**, the two sp^3-carbons of the C_{60} cage were located at 98.37−101.67 and 71.79−76.12 ppm, and the observation of two half-intensity peaks and no more than 29 lines for the sp^2-carbons of the C_{60} skeleton was consistent with their C_s molecular symmetries. The ^{13}C NMR spectral patterns of compounds **4a**−**f** were similar to those of other C_{60}-fused dihydrofurans.[4e,5c,9]

In order to open the lactone moiety of compounds **1a**−**c**, we examined the reactions of **1a**−**c** with benzylamine and allylamine. The reactions of lactone **1a** with benzylamine and allylamine in chlorobenzene at 30−35 °C produced the ring-opened fullerols **5a** and **5b** in 43 and 38% yield, respectively (Scheme 4).

The identities of fullerols **5a** and **5b** were established by their MS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV−vis spectra. In the ^{1}H NMR spectra of **5a** and **5b** in CS_2/DMSO-d_6, the hydroxy and amide protons appeared in a very downfield region (at ca. 9 ppm). The C_s symmetry of **5a** and **5b** was supported by their ^{13}C NMR spectral data. The peaks at about 171 ppm in their ^{13}C NMR spectra and the absorptions at around 1630 cm^{-1} in their FT-IR spectra indicated the presence of an amide group.

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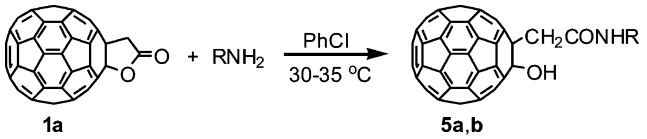
SCHEME 4. Preparation of Fullerols 5a and 5b



1a **5a,b**

5a: R = CH_2Ph, **5b**: R = $CH_2CH{=}CH_2$

The sp^3-carbon of the C_{60} skeleton attached to the hydroxy group was located at about 86 ppm in the ^{13}C NMR spectra of **5a** and **5b**, pretty close to that in other fullerols.[10]

Higher reaction temperature led to lower yields because of the reversibility of the reactions, which was confirmed by the fact that, even though **5a** and **5b** were stable at room temperature, lactone **1a** was obtained when they were heated above 50 °C. Unfortunately, lactones **1b** and **1c** could not react with benzylamine and allylamine, probably due to the unfavored steric interactions of substituted phenyl and methyl groups and reversibility of the addition reaction. The reactions of **1a** with other amines were also examined. While a primary amine such as butamine afforded a poor result, secondary amines and aromatic amines could not cleave the lactone moiety.

Conclusion

Further functionalizations of C_{60}-fused lactones **1a**−**c** with CH_3MgBr and DIBAL-H in toluene at ambient temperature led to the formation of scarce fullerene hemiketals **2a**−**c** and fullerene hemiacetals **3a**−**c**. Dehydrations of the obtained hemiketals and hemiacetals by TsOH or PPA resulted in the generation of C_{60}-fused dihydrofurans **4a**−**f** including the unsubstituted and simplest C_{60}-fused dihydrofuran **4d**, which would be difficult to be obtained by known fullerene chemistry. Reactions of unsubstituted lactone **1a** with benzylamine and allylamine afforded lactone-opened fullerols **5a** and **5b**.

Experimental Section

Preparation of Fullerene Hemiketals 2a−c. Lactone **1a** (**1b** or **1c**, 0.025 mmol) was dissolved in freshly distilled dry toluene (20 mL) with the aid of sonication, and then the resulting solution was deoxygenated with argon for 10 min. To the solution was added methylmagnesium bromide (50 μL × 3.00 M in diethyl ether, 0.15 mmol), and the reaction mixture was stirred at room temperature under argon atmosphere for less than 5 min and then acidified with acetic acid (0.4 mL). After the solvent was evaporated in vacuo, the residue was separated on a silica gel column with carbon disulfide/toluene as the eluent to afford unreacted lactone and hemiketal **2a** (**2b** or **2c**).

2a: ^1H NMR (300 MHz, CS_2/*o*-$C_6D_4Cl_2$) δ 3.84 (d, J = 12.5 Hz, 1H), 3.62 (d, J = 12.5 Hz, 1H), 2.92 (br s, 1H), 2.03 (s, 3H); ^{13}C NMR (75 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 156.48, 155.63, 152.24, 149.40, 147.11, 146.45, 145.43, 145.39, 145.34 (2C), 145.23, 145.14, 145.11 (2C), 145.00, 144.97, 144.95, 144.84, 144.70, 144.69, 144.58, 144.47, 144.42, 144.24 (3C), 144.22 (2C), 143.97 (2C), 143.86, 143.49, 142.09, 142.05, 141.74 (2C), 141.68 (2C), 141.65, 141.62, 141.38, 141.33 (2C), 141.30, 141.26 (2C), 141.00 (2C), 140.87, 140.64, 139.10, 138.91, 138.52 (2C), 137.75, 137.04, 136.77, 134.48, 104.89, 97.87 (sp^3-*C* of C_{60}), 68.35 (sp^3-*C* of C_{60}), 52.57, 25.50; FT-IR ν/cm^{-1} (KBr) 2921 (m), 2851 (w), 1505 (m), 1427 (m), 1380 (w), 1218 (m), 1180 (m), 1109 (s), 999 (s), 885 (s), 767 (m), 593 (w), 574 (m), 556 (w), 524 (s); UV−vis ($CHCl_3$) λ_{max}/nm (log ϵ) 256 (4.88), 312 (4.39), 427 (3.26), 693 (2.43); MS (APCI) *m*/*z* 794 (M^-).

Preparation of Fullerene Hemiacetals 3a−c. Lactone **1a** (**1b** or **1c**, 0.025 mmol) was dissolved in freshly distilled dry toluene (20 mL) with the aid of sonication, and then the resulting solution was deoxygenated by argon for 10 min. After the DIBAL-H (150 μL × 1.00 M in toluene, 0.15 mmol) was added, the reaction mixture was stirred at room temperature under argon atmosphere for less than 5 min and then acidified with acetic acid (0.4 mL). After the solvent was evaporated in vacuo, the residue was separated on a silica gel column with toluene/carbon disulfide as the eluent to afford unreacted lactone and fullerene hemiacetal **3a** (**3b** or **3c**).

3a: ^1H NMR (300 MHz, CS_2/*o*-$C_6D_4Cl_2$) δ 6.42 (d, J = 3.9 Hz, 1H), 3.85 (d, J = 12.6 Hz, 1H), 3.76 (dd, J = 12.6, 3.9 Hz, 1H), 3.28 (br s, 1H); ^{13}C NMR (75 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 156.29, 155.49, 151.84, 149.11, 147.12, 146.47, 145.47, 145.41, 145.37, 145.36, 145.27, 145.15, 145.14, 145.12, 145.01, 145.00, 144.94, 144.92, 144.68, 144.66, 144.60, 144.45, 144.39, 144.30, 144.28 (2C), 144.25, 144.23, 143.94 (2C), 143.86, 143.51, 142.11, 142.07, 141.78 (2C), 141.73, 141.72, 141.69, 141.67, 141.40, 141.37, 141.34 (2C), 141.30, 141.26, 141.06, 141.03, 141.00, 140.68, 139.15, 139.00, 138.65, 138.59, 137.27, 136.83, 136.54, 134.52, 97.88, 97.69 (sp^3-*C* of C_{60}), 66.95 (sp^3-*C* of C_{60}), 48.75; FT-IR ν/cm^{-1} (KBr) 2920 (m), 2850 (w), 1506 (s), 1461 (w), 1426 (s), 1336 (w), 1210 (w), 1170 (m), 1103 (m), 1046 (s), 1016 (s), 980 (s), 940 (s), 880 (w), 763 (w), 574 (w), 555 (w), 525 (s); UV−vis ($CHCl_3$) λ_{max}/nm (log ϵ) 256 (5.08), 313 (4.57), 427 (3.42), 693 (2.41); MS (APCI) *m*/*z* 780 (M^-).

Dehydration of Hemiketals 2a−c and Hemiacetals 3a−c with TsOH·H_2O or PPA. The mixture of a chosen compound **2a** (**2b**, **2c**, **3a**, **3b**, or **3c**, 0.025 mmol) and TsOH·H_2O (9.6 mg, 0.05 mmol) or PPA (170 mg, 0.50 mmol) was dissolved in chlorobenzene (20 mL), and then the resulting solution was stirred in an oil bath preset at 130 °C. The reaction was monitored by TLC and stopped at the desired time. After the solvent was evaporated in vacuo, the residue was separated on a silica gel column with carbon disulfide as the eluent to afford C_{60}-fused dihydrofuran derivative **4a** (**4b**, **4c**, **4d**, **4e**, or **4f**) and, if any, unreacted hemiketal or hemiacetal.

4a: ^1H NMR (300 MHz, CS_2/DMSO-d_6) δ 5.81 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, CS_2/DMSO-d_6 with $Cr(acac)_3$ as relaxation reagent) (all 2C unless indicated) δ 155.36 (1C), 149.05, 146.85 (1C), 146.12 (1C), 145.07, 144.91, 144.85, 144.79, 144.72, 144.55, 143.98, 143.96, 143.95 (4C), 143.94, 143.83, 143.28, 143.13, 141.77, 141.73, 141.49, 141.46, 141.12, 140.99, 140.95, 140.70, 140.50, 139.32, 138.56, 136.11, 134.53, 100.88 (1C, sp^3-*C* of C_{60}), 98.96 (1C), 72.92 (1C, sp^3-*C* of C_{60}), 13.18 (1C); FT-IR ν/cm^{-1} (KBr) 2921 (m), 2852 (w), 1507 (s), 1466 (w), 1429 (m), 1375 (w), 1276 (w), 1182 (w), 1127 (w), 1044 (w), 1005 (w), 981 (w), 940 (w), 726 (w), 600 (w), 575 (w), 525 (s); UV−vis ($CHCl_3$) λ_{max}/nm (log ϵ) 255 (5.00), 315 (4.49), 427 (3.35), 693 (2.52); MS (APCI) *m*/*z* 776 (M^-).

Preparation of Fullerols 5a and 5b. After lactone **1a** (19.5 mg, 0.025 mmol) was dissolved with chlorobenzene (15 mL), benzylamine or allylamine (0.5 mmol) was added, and the reaction mixture was stirred at 30−35 °C for 15 h. The resulting solution was directly separated on a silica gel column with CS_2/$CHCl_3$ as the eluent, and fullerol **5a** (9.6 mg, 43%) or **5b** (8.0 mg, 38%) was obtained along with unreacted lactone **2a** (43 and 35%, respectively). All operations were conducted at <40 °C.

5a: ^1H NMR (300 MHz, CS_2/DMSO-d_6) δ 9.37 (s, 1H), 9.27 (t, J = 5.7 Hz, 1H), 7.29−7.13 (m, 5H), 4.54 (d, J = 5.7 Hz, 2H), 4.50 (s, 2H); ^{13}C NMR (75 MHz, CS_2/DMSO-d_6 with $Cr(acac)_3$ as relaxation reagent) (all 2C unless indicated) δ 171.10 (1C, *C*ONH), 154.84, 153.05, 147.05 (1C), 146.57 (1C), 145.20 (4C), 144.90, 144.82, 144.73, 144.60, 144.58, 144.12, 144.04 (4C), 144.11, 143.72, 143.45, 141.67, 141.32, 141.28, 141.12, 141.08, 140.89, 140.61, 140.58, 139.94, 138.52, 138.15, 137.39 (1C, aryl *C*), 135.23, 134.88, 127.44 (aryl *C*), 126.96 (aryl *C*), 126.19 (1C, aryl *C*), 86.60

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(1C, sp^3-*C* of C_{60}), 63.07 (1C, sp^3-*C* of C_{60}), 44.25 (1C), 42.71 (1C); FT-IR ν/cm^{-1} (KBr) 3449 (s), 2920 (w), 2851 (w), 1637 (s), 1510 (s), 1451 (w), 1423 (m), 1181 (w), 1158 (w), 1105 (m), 1034 (s), 1002 (w), 775 (w), 696 (s), 590 (w), 575 (m), 561 (w), 526 (s); UV−vis ($CHCl_3$) λ_{max}/nm (log ϵ) 254 (4.88), 314 (4.25), 430 (3.10), 693 (2.30); MS (APCI) *m*/*z* 884 (M^- − 1).

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Supporting Information Available: Spectral data for products **2b**, **2c**, **3b**, **3c**, **4b**−**f**, and **5b**; NMR spectra of products **2a**−**c**, **3a**−**c**, **4a**−**f**, **5a**, and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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