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Single-step synthesis of pentaaryl-monohydro[60]fullerenes through fivefold addition of organocopper reagent to C_{60}

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Abstract

The reaction of an organocopper reagent ($ArMgBr/CuBr{\cdot}SMe_2$) with C_{60} was optimized for the fivefold addition forming a novel Cp-type ligand precursor 1,4,11,15,30-pentaaryl-2-hydro[60]fullerene ($C_{60}Ar_5H$, **1**), where Ar stands for Ph, 4-$CF_3C_6H_4$, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-BuC_6H_4, 4-PhC_6H_4, and 1-naphthyl groups. Under the optimized conditions, a large quantity (8.90 g) of $C_{60}Ph_5H$ has been synthesized in a single operation. © 2000 Elsevier Science S.A. All rights reserved.

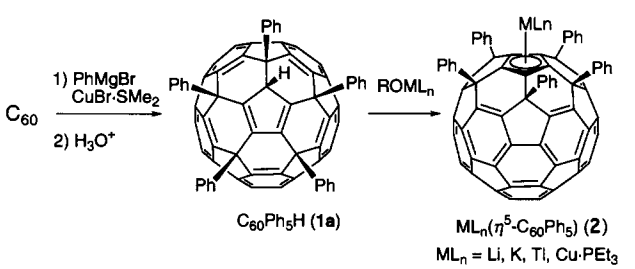
Keywords: Fullerene; Organocopper reagent; Multiple addition; Cyclopentadiene; Cp ligand

1. Introduction

The three-dimensional reactive polyene system of fullerene will serve as a platform for nano-scale molecular architectures, if multiple-site functionalization is achieved with high regio- and stereoselectivities. To this goal, we have developed and reported previously, the fivefold addition of an organocopper reagent to C_{60} (Scheme 1 **1a**) [1]. Thus, an organocopper reagent which was prepared in situ from PhMgBr and $CuBr{\cdot}SMe_2$ adds regioselectively to the [5]radialene partial structure in C_{60} and gives, after aqueous work up, 1,4,11,15,30-pentaphenyl-2-hydro[60]fullerene ($C_{60}Ph_5H$, **1a**) [2] in a quantitative yield.

Salient features of this new fullerene derivative reside not only in its concave crown-like structure created by the five aromatic rings, but also in the properties as a cyclopentadiene, which is embedded in the spherical carbon network of C_{60}. The cyclopentadiene moiety is electronically connected with the bottom 50 π-electron polyene system through endohedral homoconjugation as revealed by ab initio MO calculations and electrochemical measurements [3]. Upon treatment with a metal alkoxide (LiO′Bu, KO′Bu, TlOEt, $CuOEt{\cdot}PEt_3$), the cyclopentadiene **1** has been converted into the corresponding metal cyclopentadienides $ML_n(\eta^5\text{-}C_{60}Ph_5)$ (**2**, ML_n = Li, K, Tl, $Cu{\cdot}PEt_3$) [1a]. These compounds are the first fullerene–metal complexes involving η^5-fullerene–metal bonding.

In the present paper, we report the full details of the synthesis of the new ligand molecules $C_{60}Ar_5H$ (**1a–g**) through the fivefold organocopper addition as applied for various aryl groups of different electronic and steric properties. The method optimized for a large-scale preparation gave **1a** of 98% HPLC purity in a quantity as large as 8.90 g in a single operation.



Scheme 1. Synthesis of pentahaptofullerene–metal complexes through fivefold organocopper addition.

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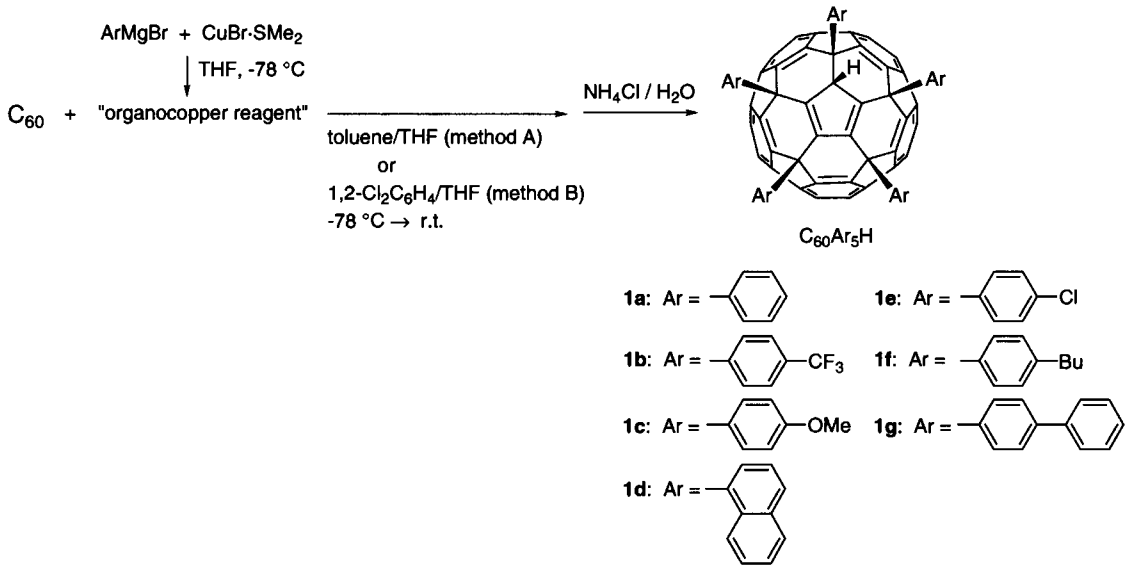

Scheme 2. Fivefold addition of organocopper reagent to C_{60}.

2. Results and discussion

In contrast to the monoaddition reactions of the Grignard and organolithium reagents to C_{60} [4], an organocopper reagent prepared in situ from PhMgBr and CuBr·SMe_2 exhibited unusual reactivity, giving a fivefold addition product $C_{60}Ph_5H$ (**1a**) (Scheme 2). The efficiency of the fivefold addition and selectivity of the reaction depend on the amount and ratio of the Grignard reagent and the copper(I) salt. Results of the HPLC analysis (Buckyprep column (Nacalai Tesque Co., 4.6 × 250 mm), 7:3 toluene–*i*-PrOH, 350 nm detection) of the organocopper reaction are summarized in Table 1. Reaction of C_{60} with eight equivalents of PhMgBr and one equivalent of CuBr·SMe_2 (1:8:1 C_{60}–PhMgBr–CuBr·SMe_2) in toluene–THF at room temperature (r.t.) for 10 min formed **1a** in 2% HPLC yield along with a trace of monoadduct $C_{60}PhH$ ($< 1\%$) and several unidentified products (18%), leaving 80% of C_{60} unreacted (Table 1, entry 1). Standing the reaction mixture for 1 h resulted in the disappearance of the peak of **1a** and led to the formation of a complex mixture (data not shown). The selectivity for the fivefold addition could be improved by increasing the amount of CuBr·SMe_2 rather than that of the Grignard reagent. As shown in Table 1, entry 2, the reaction with six equivalents of PhMgBr and three equivalents of CuBr·SMe_2 for 18 h gave **1a** in 25% yield with 28% C_{60} conversion. The product distribution did not change when the reaction stood at r.t. for a prolonged period. The conversion of C_{60} was increased to 97% by using 20 equivalents of PhMgBr and ten equivalents of CuBr·SMe_2, giving **1a** in 88% HPLC yield (Table 1, entry 3). Next, we re-examined the ratio of the Grignard reagent and CuBr·SMe_2, and found that the fivefold addition proceeds smoothly and very cleanly when the ratio is 1:1. As shown in Table 1, entry 4, the reaction with 16 equivalents each of PhMgBr and CuBr·SMe_2 led to completion within 40 h and formed **1a** quantitatively ($> 99\%$ by HPLC). The reaction of 330 mg (0.458 mmol) of C_{60} afforded 496 mg (94%) of **1a** as an orange amorphous solid. The reaction is so clean that the product obtained after aqueous work up, followed by removal of biphenyl through hexane washing and drying in vacuo, gave an analytically pure product.

The reaction conditions thus optimized (method A) could successfully be applied to the synthesis of various pentaaryl-monohydro[60]fullerenes (**1b**–**d**) bearing aromatic groups with different electronic and steric properties. Results are summarized in Table 2. Substitution at the *para* position of PhMgBr with an electron-withdrawing CF_3 group caused significant acceleration of the reaction (Table 2, entry 1). The reaction was again very clean, affording the pentaarylation product $C_{60}(4\text{-}CF_4\text{–}C_6H_4)_5H$ (**1b**) in a quantitative yield. On the other hand, the substitution with the electron-donating MeO

Table 1
Reaction of PhMgBr–CuBr·SMe_2 with C_{60} (optimization of reaction conditions) [a]

Run	Equivalent to C_{60}		Time [b]	HPLC intensity ratio (%)	
	PhMgBr	CuBr·SMe_2		C_{60}	**1a**
1	8	1	10 min	80	2
2	6	3	18 h	72	25
3	20	10	144 h	3	88
4	16	16	44 h	0	100

[a] Reaction was carried out in toluene–THF.
[b] Reaction time at r.t.

Table 2
Fivefold organocopper addition to C_{60} with various aryl Grignard reagents (method A) [a]

Run	ArMgBr	Time [b] (h)	HPLC intensity ratio (%)	
			C_{60}	**1**
1	4-$CF_3C_6H_4$MgBr	18	0	100 (**1b**)
2	4-$MeOC_6H_4$MgBr	72	3	87 (**1c**)
3	(1-Naph)MgBr	72	0	91 (**1d**)

[a] Reaction was carried out in toluene–THF. Ratio = 1:1 ArMgBr–CuBr·SMe_2.
[b] Reaction time at r.t.

group retarded the reaction. In this case, the reaction stopped at 97% conversion of C_{60} and gave C_{60}(4-$MeOC_6H_4$)H (**1c**) in 87% HPLC yield along with small amounts of unidentified side products (10%). The reaction of an organocopper reagent from (1-naphthyl)magnesium bromide, which is sterically more demanding than that from PhMgBr, led to completion within 72 h to give the fivefold addition product C_{60}(1-Naph)$_5$H (**1d**) of 91% HPLC purity.

By using 1,2-dichlorobenzene as solvent instead of toluene, the concentration of substrates could be increased about three times, and hence the reaction time of the fivefold addition was dramatically reduced (method B). With 15 equivalents each of the Grignard reagent and CuBr·SMe_2, the reaction was completed within 2 h in all cases examined, which include the reactions with PhMgBr, 4-$CF_3C_6H_4$MgBr, 4-ClC_6H_4MgBr, 4-$MeOC_6H_4$MgBr, 4-BuC_6H_4MgBr, 4-PhC_6H_4MgBr. Results of the preparative experiments are summarized in Table 3. The low yield observed for C_{60}(4-$BuC_6H_4)_5$H (**1e**) (Table 3, entry 6) is due to the loss during the hexane precipitation/washing of the product because of the high solubility of **1e** in hexane. The use of 1,2-dichlorobenzene is also beneficial for a large-scale preparation. Under essentially the same conditions, we could obtain 8.90 g of $C_{60}Ph_5H$ (**1a**) with 98% HPLC purity in 95% chemical yield in a single operation (Table 3, entry 2).

3. Conclusions

The Cp-type ligand precursors **1** that can be used for the synthesis of pentahaptofullerene–metal complexes **2** were synthesized in one step by the fivefold addition of the organocopper reagent (1:1 ArMgBr–CuBr·SMe_2) to C_{60}. This synthetic method is versatile and very efficient, providing the compounds with various aryl groups in high yields and in large quantities. Studies to extend this method to the synthesis of alkyl, alkenyl, and alkynyl derivatives are in progress in our laboratory.

4. Experimental

4.1. Synthesis of $C_{60}Ph_5H$ (1a)

4.1.1. Method A

A solution of 330 mg (0.458 mmol) of C_{60} in 150 ml of toluene was cooled to −78°C. The solution was transferred through a cannula over 15 min to a magnetically stirred mixture of an organocopper reagent prepared from PhMgBr (0.94 M in THF, 7.81 ml, 7.33 mmol) and CuBr·SMe_2 (1.51 g, 7.35 mmol) in 7.8 ml of THF at −78°C. The resulting dark green suspension was gradually warmed to −20°C over 3 h. At this point, the purple color of the supernatant disappeared completely (quenching an aliquot of the colorless supernatant with NH_4Cl solution resulted in complete recovery of C_{60}, suggesting that the solid materials are C_{60}–copper complexes). The mixture was then allowed to warm to 25°C. While stirring was continued at this temperature, the progress of the reaction was monitored by HPLC. After 2 h stirring at r.t., the color of the solid became bright wine red, the supernatant being

Table 3
Fivefold organocopper addition to C_{60} with various aryl Grignard reagents (method B) [a]

Run	ArMgBr (equivalent to C_{60})	C_{60} (g)	Time [b] (h)	Yield of **1** [c] (%)	Purity of **1** [d] (%)
1	PhMgBr (15)	1.00	2	99.5 (**1a**)	>99
2	PhMgBr (25)	6.07	24	95 (**1a**)	98
3	4-$CF_3C_6H_4$MgBr (12) [e]	0.20	2	99 (**1b**)	>99
4	4-$MeOC_6H_4$MgBr (16)	0.10	2	99 (**1c**)	96
5	4-ClC_6H_4MgBr (15)	0.20	2	99.6 (**1d**)	95
6	4-BuC_6H_4MgBr (15)	0.20	2	41 (**1e**)	95
7	4-PhC_6H_4MgBr (15)	0.20	2	99.8 (**1f**)	>99

[a] Reaction was carried out in 1,2-dichlorobenzene–THF. Ratio = 1:1 ArMgBr–CuBr·SMe_2, unless otherwise noted.
[b] Reaction time at r.t.
[c] Isolated yield of **1** with a purity indicated in the next column.
[d] Intensity ratio (350 nm) in the HPLC analysis of the isolated product.
[e] Ratio = 1:12:15 C_{60}–ArMgBr–CuBr·SMe_2.

red in color. The reaction was completed in 2 days and was quenched with NH_4Cl solution. The mixture was separated into two phases, and the aqueous phase was extracted with toluene three times. The combined organic phase was washed with brine, dried by passing through a pad of Na_2SO_4, and evaporated. The remaining powder was washed with hexane ($\times 4$) to remove biphenyl (100% of theory, 776 mg), and dried in vacuo to afford 496 mg (94%) of $C_{60}Ph_5H$: 99% purity on HPLC analysis; ^{1}H-NMR (400 MHz, $CDCl_3$) [2] δ 7.79 (m, 4H), 7.59 (m, 4H), 7.42–7.14 (m, 17H), 5.30 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$–CS_2) [2] δ 155.59 (2C), 151.81 (2C), 151.66 (2C), 150.82 (2C), 148.36 (2C), 148.32 (2C), 148.26 (2C), 147.98 (2C), 147.84 (2C), 147.63 (2C + 1C), 147.34 (2C), 147.19 (2C), 146.76 (2C), 146.67 (2C), 146.48 (1C), 145.68 (2C), 145.36 (2C), 145.18 (2C), 144.89 (2C + 1C), 144.09 (2C), 144.02 (2C), 143.94 (4C), 143.86 (2C), 143.80 (2C), 143.23 (2C), 142.89 (2C), 138.95 (2C), 138.80 (2C), 128.58 (4C), 128.51 (2C), 128.25 (4C), 127.79 (4C), 127.59 (4C), 127.41 (2C), 127.29 (2C), 127.14 (2C), 126.86 (1C), 62.76 (2C), 60.44 (2C), 58.44 (1C), 58.34 (1C); UV–vis (1.9×10^{-5} M in CH_2Cl_2) 258 (ε 95 000), 273 (ε 92 000), 350 (ε 26 000), 390 (ε 13 000), 442 (ε 4900), 470 (ε 4200) nm (M^{-1} cm^{-1}); FAB MS m/z 1106 [M^+], 720 [C_{60}]; Anal. Calc. for $C_{90}H_{26}\cdot(C_6H_5CH_3)_{0.5}$: C, 97.38; H, 2.62. Found: C, 7.04; H 2.87%. The ^{13}C-NMR data agree almost exactly with those in Ref. [2] (measured in CS_2, $CDCl_3$ for lock signal) except in a region around 144 ppm, where, in our own measurement (in $CDCl_3$–CS_2 mixture), there appears to be a substantial shift of the signal at 143.77 ppm ([2]) causing coincidence with the signal at 143.94 ppm.

4.1.2. Method B (1 g scale)

At −78°C, 21 ml of 1.0 M solution of PhMgBr in THF (21.0 mmol) was added to a suspension of 4.30 g (20.9 mmol) of CuBr·SMe_2 in 50 ml of THF. The mixture was stirred for 5 min. A solution of 1.00 g (1.40 mmol) of C_{60} in 100 ml of 1,2-$Cl_2C_6H_4$ was added over 5 min. After completion of the addition, the mixture was warmed to 25°C with a water bath and was stirred for 2 h. The reaction was quenched by adding 2 ml NH_4Cl (aq.). After dilution with 100 ml of toluene, the mixture was dried over Na_2SO_4, and filtered through a pad of silica gel. Volatile materials were removed under reduced pressure on a rotary evaporator, and then most of 1,2-Cl_2–C_6H_4 was removed under vacuum to leave a thick solution of **1a** in 1,2-Cl_2–C_6H_4. Upon addition of hexane, an amorphous orange solid was precipitated. The precipitates were collected by suction, washed several times with hexane, and dried in vacuo to give 1.53 g (99.5% yield, >99% HPLC purity) of **1a**.

4.1.3. Method B (6 g scale)

In a 1 l two-neck flask was placed 6.07 g (8.43 mmol) of C_{60} and a stirring bar. The flask was purged with nitrogen. To this flask 420 ml of 1,2-dichlorobenzene was added and stirred. The resulting deep purple solution was degassed in vacuo.

In a 2 l three-neck round-bottom flask equipped with a three-way stop cock, a septum rubber and a stop cock, was placed 42.9 g (208.6 mmol) of CuBr·SMe_2 and a stirring bar. At r.t., 240 ml of THF was added to CuBr·SMe_2. The mixture was cooled to −78°C and treated with 214 ml (207.6 mmol) of a 0.97 M solution of PhMgBr in THF. The resulting yellow suspension was stirred at −78°C for 20 min. Then the solution of C_{60} in 1,2-dichlorobenzene was transferred through a cannula over a period of 25 min. After stirring at −78°C for 15 min, the cooling bath was replaced with a water bath (26°C). While stirring was continued at r.t., the progress of reaction was monitored by HPLC. The HPLC analysis indicated that the consumption of C_{60} was stopped within 24 h at 98% conversion. At r.t., 800 ml of NH_4Cl (sat. aq.) was added to the mixture and stirred for several minutes. The mixture was extracted three times with toluene. The combined extracts were dried over Na_2SO_4, and passed through a short column of silica gel. The column was washed with toluene. Toluene and other volatile materials were removed by a rotary evaporator to leave a red 1,2-dichlorobenzene solution containing **1a** and biphenyl. Most of 1,2-dichlorobenzene was removed under vacuum to leave orange amorphous solid. The solid was washed several times with hexane to give 8.90 g (95%) of $C_{60}Ph_5H$ (**1a**). The HPLC analysis showed 98% intensity for **1a** and 2% for C_{60}. The ^{1}H-NMR spectrum indicated the content of 1,2-dichlorobenzene is less than 1%.

4.2. Synthesis of $C_{60}(4\text{-}CF_3C_6H_4)_5H$ (1b)

Prepared from a 1.07 M solution of 4-$CF_3C_6H_4MgBr$ in THF by both methods A and B: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.87–7.85 (m, 5H), 7.62–7.60 (m, 10H), 7.44–7.42 (m, 5H), 5.19 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$–CS_2) δ 154.69, 151.70, 150.64, 149.69, 149.11, 148.57, 148.53, 148.32, 148.04 (overlapping two signals), 147.90, 147.87, 147.77, 147.40, 146.72, 146.63, 146.44, 146.20, 146.11, 144.70, 144.60 (overlapping two signals), 144.30, 144.27, 144.13, 144.08, 144.03, 143.97, 143.41, 142.64, 142.37, 142.18, 125.7–125.5 (m, overlapping two quartet, 6C), 125.39 (q, $J_{C-F} = 3.72$ Hz, 4C), 62.55, 60.09, 58.14, 57.97. Six quartet signals corresponding to CF_3 and CF_3–C carbons were not detected because of their low intensities; APCI MS (LC MS, 7:3 toluene–*i*-PrOH) 1446 [M^+].

4.3. Synthesis of $C_{60}(4\text{-}MeOC_6H_4)_5H$ (1c)

Prepared from a 0.92 M solution of 4-$MeOC_6H_4MgBr$ in THF by both methods A and B:

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.57 (d, $J = 8.79$ Hz, 4H), 7.36 (d, $J = 8.79$ Hz, 4H), 7.15 (d, $J = 8.79$ Hz, 4H), 6.78 (d, $J = 8.79$ Hz, 2H), 6.62 (d, $J = 8.79$ Hz, 4H), 6.57 (d, $J = 8.79$ Hz, 2H); ^{13}C-NMR measurement was unsuccessful because of the low solubility of **1c** in common NMR solvents.

4.4. Synthesis of C_{60}(1-naphthyl)$_5$H (**1d**)

Prepared from a 0.70 M solution of 1-naphthylmagnesium bromide in THF by method A: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.57 (d, $J = 8.30$ Hz, 2H), 9.19 (d, $J = 8.78$ Hz, 2H), 8.68 (d, $J = 8.30$ Hz, 1H), 8.35 (d, $J = 7.33$ Hz, 2H), 8.28 (d, $J = 6.84$ Hz, 2H), 7.90 (d, $J = 7.82$ Hz, 2H), 7.76 (d, $J = 7.81$ Hz, 2H), 7.66–7.19 (m, 17H), 7.09 (m, 2H), 6.96 (m, 1H), 6.63 (m, 1H), 5.98 (s, 1H), 5.16 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$–CS_2) δ 157.80, 154.52, 153.86, 153.45, 149.16, 148.96, 148.83, 148.77, 148.57, 148.55, 148.41, 148.16, 147.97, 147.66, 147.60, 147.57, 146.32, 145.98, 145.83, 145.75, 145.00, 144.49 (overlapping, two peaks), 143.62, 143.44, 143.39, 142.03, 138.67, 135.15, 134.70, 134.56, 133.72, 133.32, 132.47, 132.31, 130.53, 130.27, 129.81, 129.68, 129.62, 129.60, 129.50, 129.18, 128.76, 128.57, 126.51, 126.49, 126.33, 126.25, 125.92, 125.63, 125.19 (overlapping, two peaks), 125.07, 124.97, 124.68, 124.53, 124.00, 63.79, 62.93, 60.04, 59.96.

4.5. Synthesis of C_{60}(4-ClC_6H_4)$_5$H (**1e**)

Prepared from a 1.25 M Et_2O solution of 4-ClC_6H_4MgBr by method B: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70 (d, $J = 8.4$ Hz, 4H), 7.50 (d, $J = 8.4$ Hz, 4H), 7.36 (d, $J = 8.4$ Hz, 4H), 7.27 (d, $J = 8.4$ Hz, 2H), 7.22 (d, $J = 8.4$ Hz, 4H), 7.18 (d, $J = 8.4$ Hz, 2H), 5.20 (s, 1H); ^{13}C-NMR measurement was unsuccessful because of low solubility of **1e** in $CDCl_3$.

4.6. Synthesis of C_{60}(4-BuC_6H_4)$_5$H (**1f**)

Prepared from a 1.28 M solution of 4-BuC_6H_4MgBr in THF by method B: ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.65 (d, $J = 8.1$ Hz, 4H), 7.47 (d, $J = 7.8$ Hz, 4H), 7.30 (d, $J = 8.4$ Hz, 2H), 7.11 (d, $J = 7.8$ Hz, 4H), 6.97 (d, $J = 8.1$ Hz, 4H), 6.90 (d, $J = 8.4$ Hz, 2H), 5.22 (s, 1H), 2.8–2.5 (m, 10H), 1.8–1.4 (m, 10H), 1.4–1.2 (m, 10H), 1.0–0.8 (m, 15H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 156.11, 152.41, 152.28, 151.70, 148.49, 148.45, 148.44, 148.16, 148.02, 147.85, 147.51, 146.98, 146.88, 146.68, 146.13, 145.86, 145.62, 145.33, 144.41, 144.14, 144.04, 143.92, 143.84, 143.74, 143.01, 142.92, 142.04, 141.78, 141.55, 137.06, 137.01, 128.91, 128.77, 128.58, 128.53, 128.10, 127.95, 127.86, 127.56, 63.03, 60.81, 58.77, 58.68, 35.28, 35.22, 35.19, 33.61, 33.50, 22.39, 22.24, 22.18, 21.56, 14.13, 14.11, 14.05.

4.7. Synthesis of C_{60}(4-PhC_6H_4)$_5$H (**1g**)

Prepared from a 1.25 M solution of 4-PhC_6H_4MgBr in THF by method B: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.91 (d, $J = 8.4$ Hz, 4H), 7.75 (d, $J = 8.4$ Hz, 4H), 7.7–7.3 (m, 37H), 5.45 (s, 1H); ^{13}C-NMR measurement was unsuccessful because of low solubility of **1g** in $CDCl_3$.

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