

博士論文

Studies on FeCl₃-Mediated Synthesis of C₆₀ Derivatives
and Dumbbell-shaped C₁₂₀

(塩化第二鉄を用いた C₆₀ 誘導体および
ダンベル型 C₁₂₀ の合成に関する研究)

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INDEX

1. Introduction	-3-
1.1 The Background of Fullerene	-3-
1.2 Production of Fullerenes	-4-
1.3 Purification of [60]Fullerene	-4-
1.4 Synthesis of Fullerene Derivatives	-5-
1.5 Aim of the Thesis	-6-
References and Notes	-7-
2. FeCl ₃ -mediated quantitative conversion of C ₆₀ to polyarylated fullerenes	-8-
2.1 Introduction	-8-
2.2 FeCl ₃ -mediated Quantitative Conversion of C ₆₀ to Polyarylated Fullerenes Containing C ₆₀ (C ₆ H ₄ Cl) ₅ Cl	-10-
2.3 Investigation of Reaction Conditions	-12-
2.4 FeCl ₃ -mediated Synthesis of Polyarylated Fullerenes Containing C ₆₀ (C ₆ H ₄ X) ₅ Cl	-12-
2.5 Proposed Reaction Mechanisms	-13-
2.6 Conclusion	-15-
Experimental Section	-16-
References and Notes	-23-
3. FeCl ₃ -mediated Synthesis of Fulleranyl Esters as Low-LUMO Acceptors for Organic Photovoltaic Devices	-26-
3.1 Introduction	-26-
3.2 Synthesis and Characterization of Fulleranyl Esters	-27-
3.3 Scope and Limitation	-30-
3.4 Reaction Mechanisms	-31-
3.5 Preparation and Characterization of Low-LUMO Fullerenes	-34-
3.6 OPV Performance	-36-
3.7 Conclusion	-37-
Experimental Section	-38-
References and Notes	-81-
Appendix	-84-

4. FeCl ₃ -Mediated Retro-Reactions of Fullerene Derivatives to C ₆₀	-88-
4.1 Introduction	-88-
4.2 Retro-Reaction of Diels–Alder Adduct of [60]Fullerene	-89-
4.3 Retro-Reaction of PCBM	-92-
4.4 Conclusion	-95-
Experimental Section	-96-
References and Notes	-97-
5. Solution-Phase Synthesis of Dumbbell-Shaped C ₁₂₀ by FeCl ₃ -Mediated Dimerization of C ₆₀	-99-
5.1 Introduction	-99-
5.2 Synthesis of Dumbbell-shaped C ₁₂₀	-100-
5.3 Reaction Conditions	-101-
5.4 Proposed Reaction Mechanisms	-104-
5.5 Remarks on Our Approach through Fullerene Cation	-106-
5.6 Conclusion	-106-
Experimental Section	-107-
References and Notes	-108-
6. Conclusion	-110-
List of Publications	-112-
Acknowledgements	-114-

1. Introduction

1.1 The Background of Fullerene

Buckminsterfullerene (C_{60} , [60]fullerene) is soccer-ball-shaped (I_h -symmetry) with 12 pentagons and 20 hexagons. [60]fullerene was discovered by Richard Smalley, Robert Curl, James Heath, Sean O'Brien, and Harold Kroto at Rice University in 1985.¹ Fullerenes have a huge variety of properties, such as aromaticity, solubility, superconductivity, electron acceptability, HIV medicine, and so on, thus [60]fullerene is expected to be a standard nanomaterial in the next generation (Figure 1-1).² However, fullerene materials have held a drawback for industrial application. Pure [60]fullerene is still expensive as compared with common industrial chemicals due to difficulty of efficient production and purification.

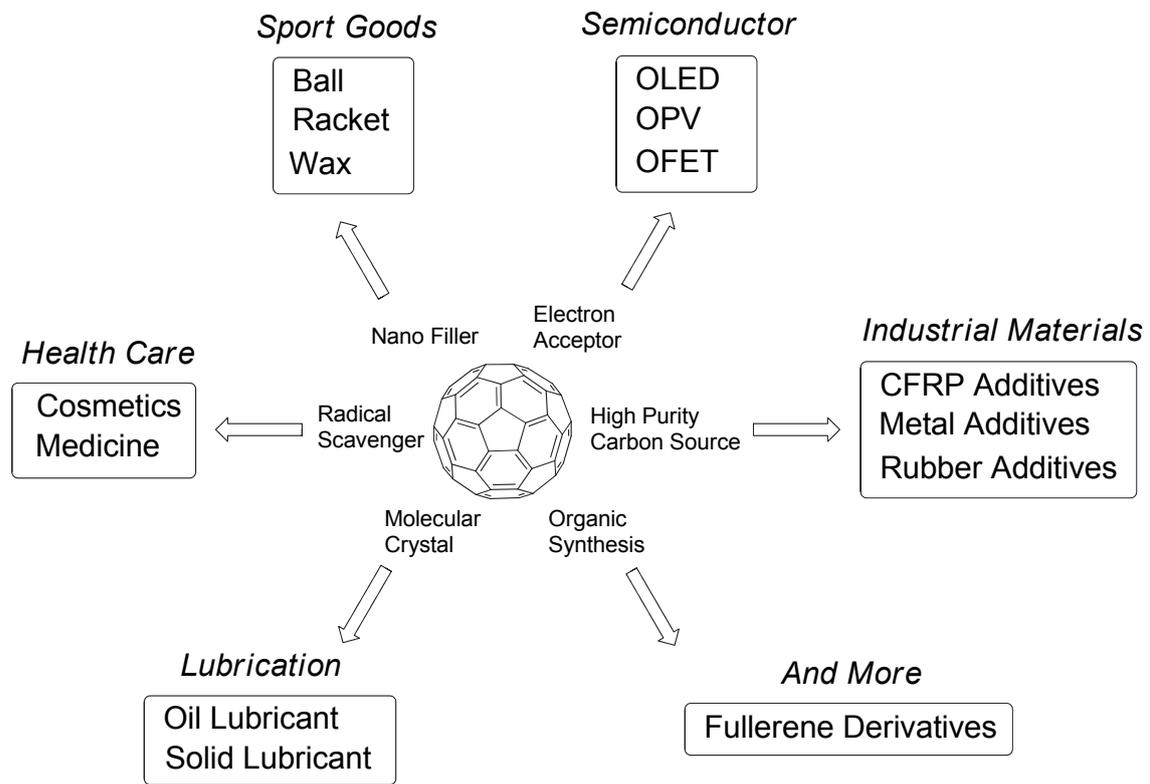


Figure 1-1. Fullerene applications

1.2 Production of Fullerenes

Although fullerenes used to be produced by arc heating of graphite around the world, this batch process is difficult to scale up. Hence, a new synthetic method developed for industrialization. Howard et al. have reported a combustion method for fullerene production, this procedure is stable for continuous process and easy to scale up.³

A large-scale facility that has a capacity to produce tons of fullerenes per year has been operating since 2003.⁴ As a result, parent fullerene (mixed fullerene) became much more affordable due to mass production.

1.3 Purification of [60]Fullerene

Since fullerenes are produced as a mixture containing [60]fullerene (C_{60}), [70]fullerene (C_{70}), and higher fullerenes ($C_{>70}$), the separation of [60]fullerene from other isomers is crucial. Two fundamental technologies are known for [60]fullerene purification: chromatography⁵ and separation through the formation of inclusion complexes,⁶ both of which can be modified to achieve effective separation on a laboratory scale.

However, the former requires large amounts of stationary and mobile phases, and this procedure is difficult to scale up. The latter requires high-cost host compounds and involves intricate operations (Figure 1-3). Therefore, both methods are unsuitable for large-scale [60]fullerene separation.

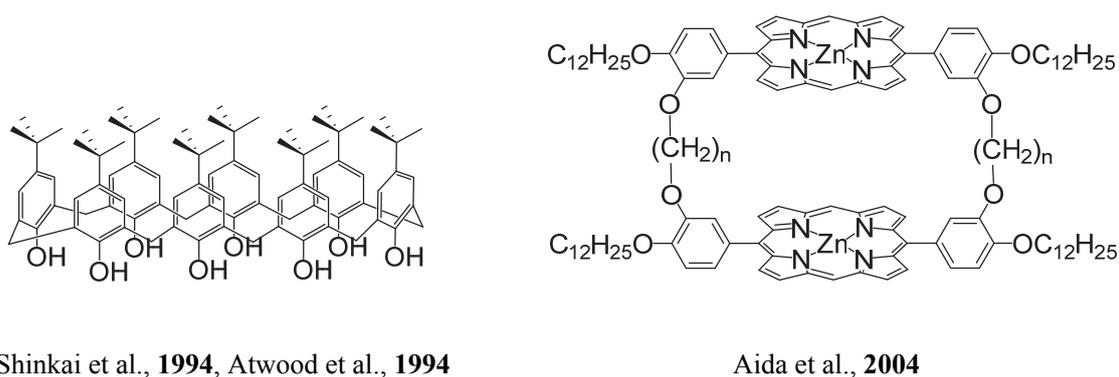
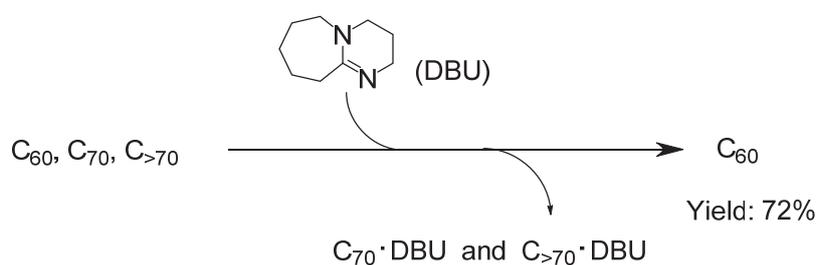


Figure 1-2. Host molecules for complexation with C_{60}

Nagata et al. developed a facile and efficient purification procedure for separating one kilogram of [60]fullerene from a fullerene mixture using base including amidine structure (N=C–N), such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).⁷ Compared to the conventional methods, their method is efficient, low-cost, and can be easily scaled up, because the separation procedure requires only mild conditions such as ambient temperature, commercially available materials, and conventional unit operations.

Scheme 1-1. Purification of [60]fullerene from a fullerene mixture using DBU



1.4 Synthesis of Fullerene Derivatives

Various organic synthetic methodologies are applicable to fullerenes as well as common organic compounds. Fullerene derivatives are expected to be highly-functional and multifunctional material for those substituents and solubility. Although many synthetic methods for derivatization of [60]fullerene have been developed to date⁸, there has been little research into the facile and economical synthesis of fullerene derivatives (i.e., polyhydroxylation⁹ and hydroarylation¹⁰). Facile synthetic methods are craved for advancement of fullerene industry.

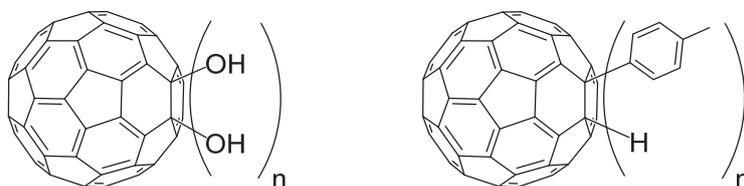


Figure 1-3. Inexpensive fullerene derivatives

1.5 Aim of the Thesis

The aim of this thesis is to develop facile and versatile synthetic method for various fullerene derivatives without using particular reagents and equipment. To achieve the purpose, I focused attention on the reactivity of Iron(III)chloride (FeCl_3). Inexpensive FeCl_3 is widely applicable to various organic syntheses due to the diversity.¹¹ FeCl_3 plays an important role as a Lewis acid or oxidant in the organic reaction. Therefore, I anticipate that various reactions of fullerene take place using FeCl_3 . I have investigated FeCl_3 -mediated polyarylation of C_{60} (Chapter 2), synthesis of fullerenyl esters (Chapter 3), retro-reactions of fullerene derivatives to C_{60} (Chapter 4), and solution-phase dimerization of C_{60} (Chapter 5) in this thesis.

In addition, Iron is an abundant element in the earth's crust, therefore, it is environmentally-friendly. From the viewpoint of a ubiquitous element strategy, development of FeCl_3 -mediated synthesis possesses high academic values.

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2. FeCl₃-mediated quantitative conversion of C₆₀ to polyarylated fullerenes[†]

2.1 Introduction

A concise and low-cost procedure for producing fullerene derivatives has an important aspect in fullerene industries as mentioned in Chapter 1. Development of a simple and low-cost procedure for producing fullerene derivatives is important for their commercial production. Although several low-cost methods for production¹ and purification² of parent fullerenes have been developed to date, there has been little research into the economical synthesis of C₆₀ derivatives.³ The most costly process for production of fullerene derivatives is generally isolation and purification of the target compound from a product mixture containing multi-adducts. However, in some cases for industrial-scale processes, an inexpensive product mixture itself is also important. For instance, product mixtures such as polyarylated fullerene (C₆₀Ar_nR₂; n = 8 and 10; R = H and alkyl groups), polyhydroxylated fullerene (C₆₀(OH)_n; n > 8), polyaminated fullerenes, and mixture of PCBM have been utilized to photoresist materials for extreme-UV lithography,⁴ proton conductors for fuel cells,⁵ optical limiting materials,⁶ and electron-acceptors in organic photovoltaic cells.⁷ On these applications, chemical modification is a tool to tune the electronic properties and solubility of fullerene derivatives mixtures. As functional polymers with polydispersities have been used generally, fullerene derivative mixtures have been also employed as functional materials. Note that such inexpensive modified fullerenes mixtures have been often adopted, rather than expensive single products in industry.

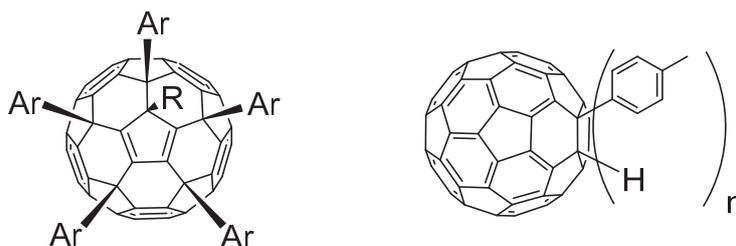


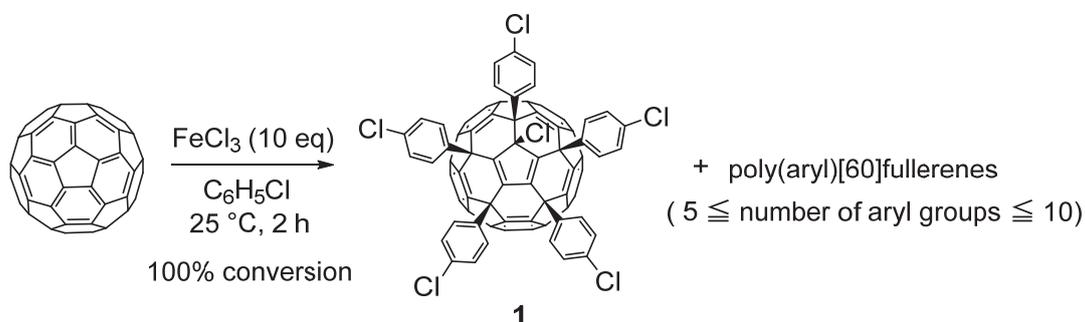
Figure 2-1. Arylated[60]fullerenes

Among fullerene derivatives, arylated[60]fullerenes as shown in Figure2-1 are interesting materials not only in organic chemistry but also in nanoscale materials science. Penta(aryl)[60]fullerenes, in particular, have shown many fascinating physical and chemical properties as reported by Nakamura and coworkers.⁸ However, expensive organometallic reagents (i.e., Grignard reagents) are normally used in the arylation of C₆₀,⁹ therefore, this synthetic method has still held a drawback for industrial

large-scale applications. On the other hand, Friedel–Crafts arylation reactions of fullerenes using Lewis acids have been reported since 1990s.¹⁰ Although the AlCl_3 -mediated Friedel–Crafts reaction is the simplest method for the synthesis of arylated fullerene derivatives, it is difficult to introduce only aryl groups to the C_{60} core because hydrogenation also proceeds in parallel with arylation.¹⁰ The use of inexpensive FeCl_3 for the Friedel–Crafts reactions in the presence of bromine has been also attempted.¹¹ In this investigation toluene and xylene were used as substrates, but products characterization was not sufficient likely because of severely complex mixtures of the products. The most problematic thing is a remaining C_{60} , which tends to block a way to the purpose.

I report a new class of method, that is, inexpensive FeCl_3 -mediated polyarylation of C_{60} by using aryl halides with a facile synthetic procedure in this chapter. The reaction of C_{60} with chlorobenzene in the presence of FeCl_3 yielded a mixture of arylated products ($5 \leq \text{number of aryl groups} \leq 10$) containing penta(aryl)[60]fullerenes up to 29% yield (Scheme 2-1). Although the product is a mixture, the conversion of C_{60} is almost quantitative. This convenient fullerene-modification method will produce industrially useful materials at low cost.

Scheme 2-1. Inexpensive functionalization of C_{60} with FeCl_3 and aryl halides



2.2 FeCl₃-mediated Quantitative Conversion of C₆₀ to Polyarylated Fullerenes Containing C₆₀(C₆H₄Cl)₅Cl (**1**)

The main advantage of the present reaction is a facile and inexpensive procedure as well as almost quantitative conversion of fullerene. A mixture of [60]fullerene (501 mg) and FeCl₃ (1.13 g, 10.0 equiv.) in chlorobenzene (25 mL) was stirred at 25 °C for 2 h, yielding a mixture of products containing the pentaadduct C₆₀(C₆H₄Cl)₅Cl (**1**) and various other polyarylated fullerene derivatives. Figure 2-1 shows an HPLC trace for this product mixture: a peak at the retention time of 14.5 min was assigned to compound **1** by its characteristic UV-vis spectrum.^{9e} Compounds with retention time less than about 14 min in Figure 2-2 are polyarylated products (number of aryl groups > 5). Notably, there is no peak for the starting material C₆₀ (retention time = ca. 18 min).

Atmospheric pressure photoionization mass spectrometry (APPI-MS) revealed the existence of compound **1**, as well as hepta-, octa-, and deca-adducts.¹² This reaction represents an inexpensive 100%-conversion reaction that can provide a polyarylated fullerene mixture. Although this is the purpose of the research, I did separation of **1** for structural characterization and further discussion. Preparative HPLC separation of **1** from the product mixture using a Cosmosil Buckyprep column (Nacalai Tesque) afforded pure compound **1** in 25% isolated yield (Table 2-1, entry 1). Pure product **1** was characterized by ¹H and ¹³C NMR and combustion analysis. The structure of **1** was determined unambiguously by X-ray crystallographic analysis (Figure 2-3) of a single crystal, obtained by slow diffusion of methanol into a solution of **1** in toluene. The chlorine atom is accommodated in the space surrounded by five aryl groups. Because of positional disorder of the chlorine atom on the five-membered ring of the cyclopentadiene moiety, I was not able to discuss the bond length between the chlorine and carbon atoms.

Table 2-1. FeCl₃-mediated multiarylation reaction of C₆₀

Entry	Substrate	Solvent	Conversion of C ₆₀	Main Product (yield)
1	C ₆ H ₅ Cl	C ₆ H ₅ Cl	100%	C ₆₀ (C ₆ H ₄ Cl) ₅ Cl (25%)
2	C ₆ H ₅ Cl	CH ₂ Cl ₂	87%	C ₆₀ (C ₆ H ₄ Cl) ₅ Cl (10%)
3	C ₆ H ₅ Cl	CHCl ₃	89%	C ₆₀ (C ₆ H ₄ Cl) ₅ Cl (12%)
4	C ₆ H ₅ Cl	1,1,2,2-tetrachloroethane	95%	C ₆₀ (C ₆ H ₄ Cl) ₅ Cl (29%)
5	C ₆ H ₅ Br	1,1,2,2-tetrachloroethane	95%	C ₆₀ (C ₆ H ₄ Br) ₅ Cl (23%)

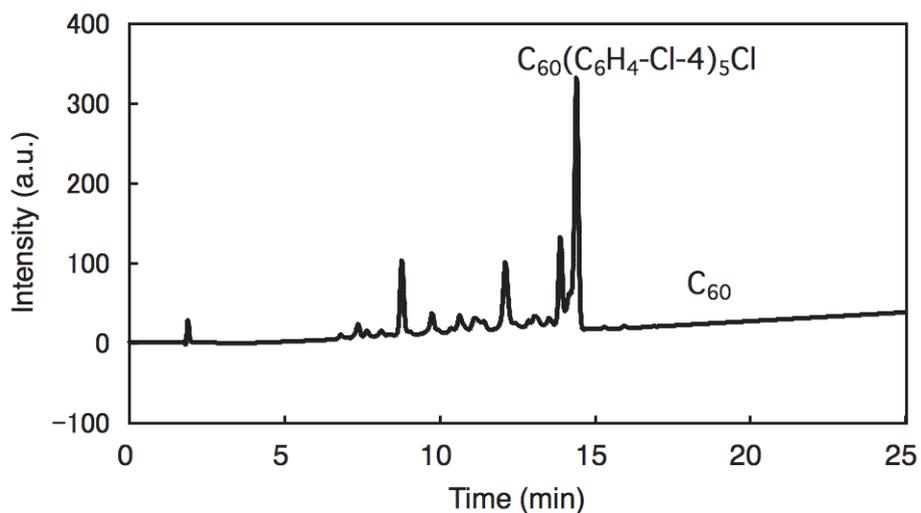


Figure 2-2. HPLC trace for the product mixture containing **1**. Peaks at the retention time less than about 14 min represent multiple-adducts bearing more than five aryl groups. Conditions: YMC-Pack ODS-AM, 5 micron, 4.6 x 150 mm. Linear methanol/toluene gradient from 25% to 55% toluene over 25 min; flow rate: 1.0 mL/min.

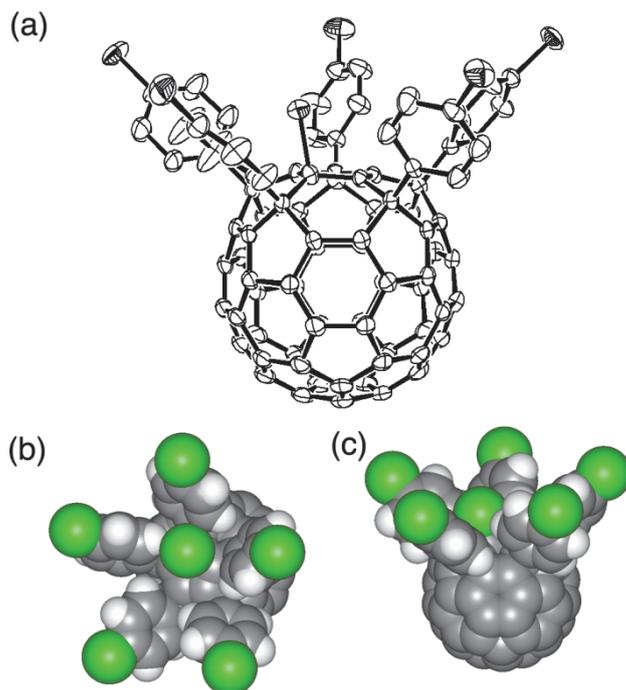


Figure 2-3. Crystal structure of **1**·(C₆H₅CH₃). (a) ORTEP drawing with thermal ellipsoids at 30% probability. Solvent molecules found in the unit cell and disordered chlorine atoms are omitted for clarity. (b), (c) Space-filling models.

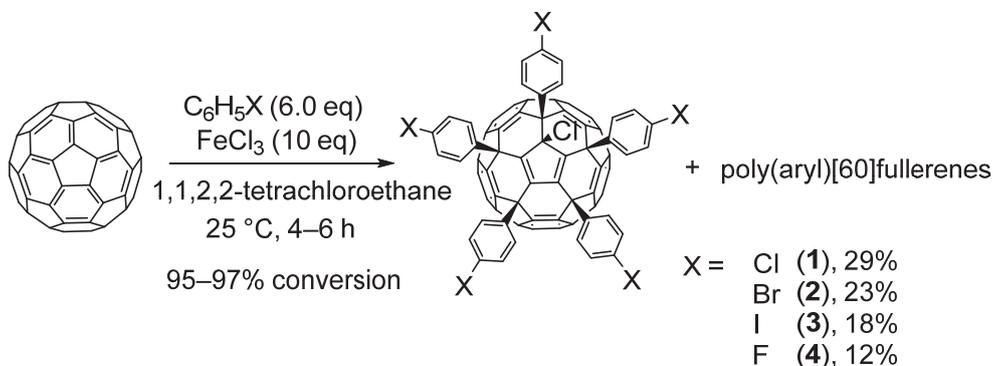
2.3 Investigation of Reaction Conditions

I next investigated the scope and limitations of this reaction. When toluene, *p*-xylene, 1,2,4-trimethylbenzene, or anisole were used in place of chlorobenzene, the reaction proceeded slowly to afford trace amounts of hydroarylated products and remaining C₆₀ (ca. 30%).^{10b} Other Lewis acids were tested; FeCl₂, FeBr₃, ZnCl₂, AlCl₃, BF₃·Et₂O, RuCl₃, CeCl₃·7H₂O, TiCl₄, NiCl₂, and CoCl₂ all gave poor results. Only FeBr₃ gave 10% conversion of C₆₀, but the product was a complex mixture of unidentifiable products. Hence, I found this reaction system only works with halogenated benzenes and FeCl₃. I surmise that not only Lewis acidity but also strong electron accepting ability to oxidize the fullerene part is necessary for this reaction (*vide infra*).

2.4 FeCl₃-mediated Synthesis of Polyarylated Fullerenes Containing C₆₀(C₆H₄X)₅Cl (1–4)

I then focused on reaction systems using different organic solvents (Scheme 2-2). The amount of chlorobenzene was reduced from solvent scale to 6 molar equivalents with respect to C₆₀. The use of chlorinated solvents such as CH₂Cl₂, CHCl₃, and 1,1,2,2-tetrachloroethane gave good C₆₀ conversion (Table 3-1, entries 2–4). In particular, 1,1,2,2-tetrachloroethane was a preferred solvent, because it dissolves C₆₀ and does not have an aromatic moiety that takes part in the Friedel–Crafts reaction. The advantage of this method is that the amount of substrate can be controlled. In fact, decreasing the substrate, this reaction system gave better yield (29%) of the penta-adduct product and less of the multi (hepta, octa, and deca)-adduct products. Brominated, iodinated, and fluorinated benzenes also successfully reacted in 1,1,2,2-tetrachloroethane to give excellent C₆₀ conversion (Table 2-1, entries 5–7). Products 2–4 (Scheme 2-2) contain the chlorine atoms on the cyclopentadienyl moiety of the C₆₀ core; it is likely that this chlorine atom comes from FeCl₃. These chlorinated fullerene derivatives have already been reported,¹³ and are known to have unique electrochemical properties.¹⁴ However, the synthesis required many steps and started from C₆₀Cl₆.^{15,16} or penta-(organo)[60]fullerenes.¹⁷ The present method involves a one-step synthesis without a complex procedure.

Scheme 2-2. Functionalization of C_{60} with $FeCl_3$ and halogenated benzene in 1,1,2,2-tetrachloroethane



Among halogenated benzenes, chlorinated benzene gave the best result in this reaction due to electronegativity. The reason for low yield of product **4** would be the increase the rate of polyarylation (number of aryl groups > 5).

2.5 Proposed Reaction Mechanisms

Finally, I propose two reaction mechanisms of this reaction. One is a hydroarylation–oxidation mechanism, while the other is an electron transfer mechanism. As for the former mechanism (Scheme 2-3), at first, similar to the $AlCl_3$ -mediated Friedel–Crafts reaction of C_{60} ,^{10, 18} hydroarylation of C_{60} occurs in the presence of $FeCl_3$ to produce an arylhydrofullerene, $C_{60}ArH$. This hydroarylated product is oxidized by $FeCl_3$ to afford an arylfullerene cation,^{19,20} $C_{60}Ar^+$, which undergoes second Friedel–Crafts reaction to give a diarylfullerene, $C_{60}Ar_2$.²¹ The same reaction proceeds on $C_{60}Ar_2$ to give pentaarylated fullerene cation, $C_{60}Ar_5^+$, which is chlorinated to yield $C_{60}Ar_5Cl$. Further reactions can occur at the pentaarylchloro[60]fullerene to give polyarylated products bearing more than five aryl groups.

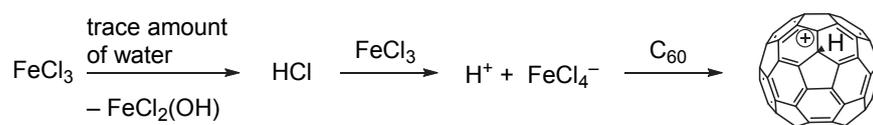
The latter proposed mechanism is rather daring (Scheme 2-4) from the view point of oxidation potentials of C_{60} and $FeCl_3$.²² I hypothesized that $FeCl_3$ mediate formation of fullerene radical cation. When it comes to $C_{60}^{+\cdot}$ formation, Fukuzumi et al. have reported that Fe^{3+} -exchanged zeolite generates a fullerene radical cation.²³ Single electron transfer occurs from C_{60} to $FeCl_3$ to generate fullerene radical cation. This step is actually chlorination of fullerene to afford ClC_{60}^{\cdot} , but the generated chlorinated compound can undergoes de-chlorination by $FeCl_3$ affording fullerene radical cation. This active species can take part in the Friedel–Crafts reaction to afford arylfullerene radical, ArC_{60}^{\cdot} . Oxidation of this radical species by $FeCl_3$ generates the cation to proceed the Friedel–Crafts

reaction.

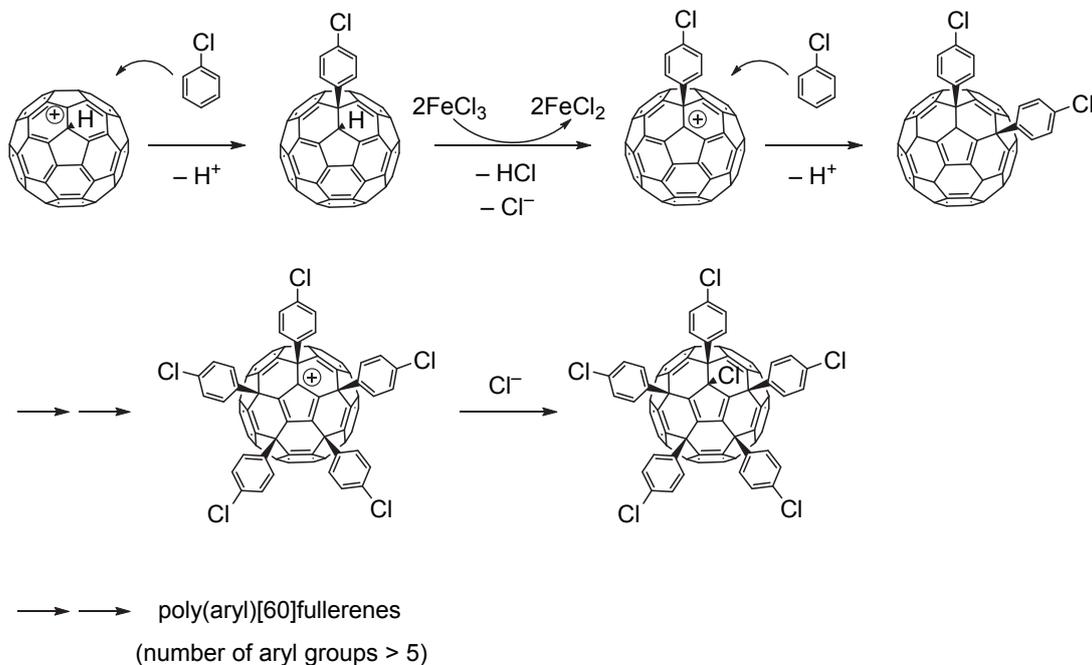
On both reaction mechanisms, I think oxidation ability of FeCl_3 plays an important role to proceed this reaction. In addition, halogenated aryl groups as well as chlorinated solvents seem to stabilize a key intermediate, arylfullerene cation C_{60}Ar^+ , which has been shown by Kitagawa et al.¹⁹

Scheme 2-3. Proposed reaction mechanism: hydroarylation and oxidation mechanism

(a) Generation of hydrofullerene cation

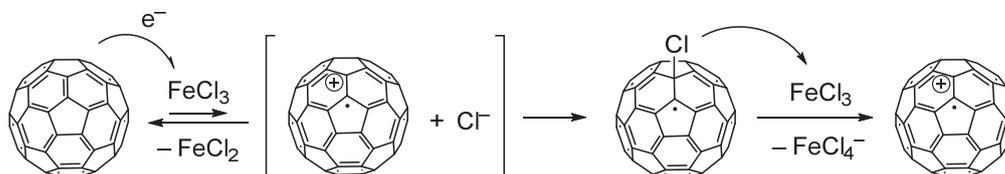


(b) Friedel-Crafts reaction

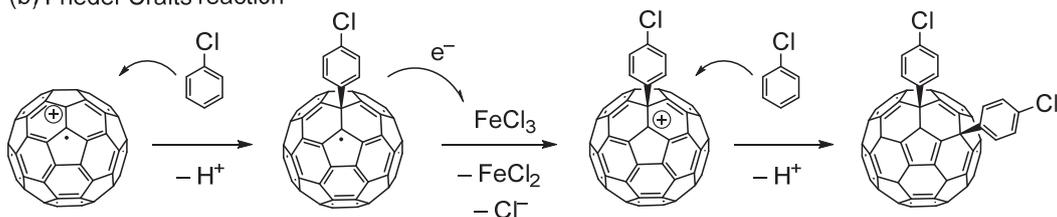


Scheme 2-4. Proposed reaction mechanism: electron transfer mechanism

(a) Generation of fullerene radical cation



(b) Friedel-Crafts reaction



2.6 Conclusion

I have described a new FeCl_3 -mediated polyarylation of C_{60} , which produces in quantitative conversion a polyarylated fullerene mixture containing pentaaryl(chloro)[60]fullerenes in up to 29% yield and polyarylated product having more than five aryl groups. This simple, low-cost method could be applied to industrial-scale production. The successful use of FeCl_3 in this method is of particular interest from the viewpoint of a ubiquitous element strategy that avoids the use of rare metals and expensive noble metals.

Experimental Section

General

All reactions were carried out under argon or nitrogen atmosphere. Analytical gradient reversed-phase HPLC was performed on an Agilent 1200 series instrument equipped with an ODS column (YMC-Pack ODS-AM, 5 micron, 4.6 x 150 mm). All runs used linear gradients of methanol (solvent A) and toluene (solvent B). The gradient ran from 25% B up to 55% B over 25 min. Flow rate was 1.0 mL/min and routine UV detection was performed at 290 nm. All ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-AL 400 NMR spectrometer system. NMR spectra are reported in part per million from internal tetramethylsilane (δ 0.00 ppm) for ^1H NMR and from CDCl_3 (δ 77.00 ppm) for ^{13}C NMR. Mass spectra were measured with Agilent1100LC/MS (APPI, Negative mode) equipped on an ODS column (YMC-Pack ODS-AM). Preparative HPLC was performed on a Buckyprep column (Nacalai Tesque Inc., 20 mm x 250 mm) using toluene/methanol (7/3) as eluent (flow rate: 10 mL/min, detected at 290 nm with an UV spectrometer, Shimadzu SPD-6AV).

Materials

Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Sigma-Aldrich Co., Wako Pure Chemical Industries, or other commercial suppliers and used after appropriate purification. [60]Fullerene (99.5%) was purchased from Frontier Carbon Corporation. Iron(III)chloride was purchased from Wako Pure Chemical Industries and used as received.

Synthesis of 1

To a mixture of C_{60} (501 mg, 0.70 mmol) and iron(III) chloride (1.13 g, 6.97 mmol) was added chlorobenzene (25 mL) at room temperature. After stirred for 2 hours, the reaction mixture was quenched with water (0.5 mL). The resulting solution was passed through a pad of silica gel (eluent: toluene) and the volatiles were removed with rotary evaporator. The crude product contained the desired penta-adduct **1** mainly, and small amounts of polyarylated products as analyzed by HPLC (YMC-Pack ODS-AM) as shown in Figure 2-4. Purification with HPLC (Buckyprep column, Nacalai Tesque Inc., 4.6 mm ID x 250 mm, monitored at 308 nm, eluent: toluene/methanol = 7/3) gave the title compound $\text{C}_{60}(\text{C}_6\text{H}_4\text{-Cl-4})_5\text{Cl}$ as orange powder (228 mg, 25%). ^1H NMR (400 MHz, CDCl_3): δ 7.02–7.08 (m, 4H, C_6H_4), 7.23 (d, J = 8.8 Hz, 4H, C_6H_4), 7.30 (d, J = 8.8 Hz, 4H, C_6H_4), 7.40–7.49 (m, 4H, C_6H_4), 7.61–7.80 (m, 4H, C_6H_4); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 57.28 (2C,

$\text{sp}^3\text{-C}_{60}$), 59.96 (2C, $\text{sp}^3\text{-C}_{60}$), 62.65 (1C, $\text{sp}^3\text{-C}_{60}$), 75.85(1C, C($\text{sp}^3\text{-C}_{60}$)-Cl), 128.06 (1C, $\text{C}_6\text{H}_4\text{Cl}$), 128.94 (4C, $\text{C}_6\text{H}_4\text{Cl}$), 129.00 (4C, $\text{C}_6\text{H}_4\text{Cl}$), 129.36 (4C, $\text{C}_6\text{H}_4\text{Cl}$), 129.49 (4C, $\text{C}_6\text{H}_4\text{Cl}$), 130.85 (2C, $\text{C}_6\text{H}_4\text{Cl}$), 133.90 (2C, $\text{C}_6\text{H}_4\text{Cl}$), 134.33 (2C, $\text{C}_6\text{H}_4\text{Cl}$), 134.36 (2C, $\text{C}_6\text{H}_4\text{Cl}$), 134.99 (2C, $\text{C}_6\text{H}_4\text{Cl}$), 136.50 (2C, $\text{C}_6\text{H}_4\text{Cl}$), 141.13 (2C), 142.58 (2C), 142.62 (2C), 142.86 (1C, $\text{C}_6\text{H}_4\text{Cl}$), 143.01 (2C), 143.34 (2C), 143.36 (2C), 144.12 (2C), 144.18 (2C), 144.28 (2C), 144.44 (2C), 144.56 (2C), 144.71 (2C), 145.75 (2C), 146.95 (2C+1C), 147.09 (2C), 148.00 (1C), 148.07 (2C), 148.43 (2C), 148.53 (2C), 148.54 (6C), 148.57 (2C), 149.41 (2C), 150.26 (2C), 153.19 (2C), 155.81 (2C); APPI-MS (-): calcd for $\text{C}_{90}\text{H}_{20}\text{Cl}_5$ ($\text{M} - \text{Cl}^-$): 1278.4; found, 1279.0; Anal. Calcd for $\text{C}_{90}\text{H}_{20}\text{Cl}_6$, C 82.28; H, 1.53. Found: C 81.90; H, 1.66.

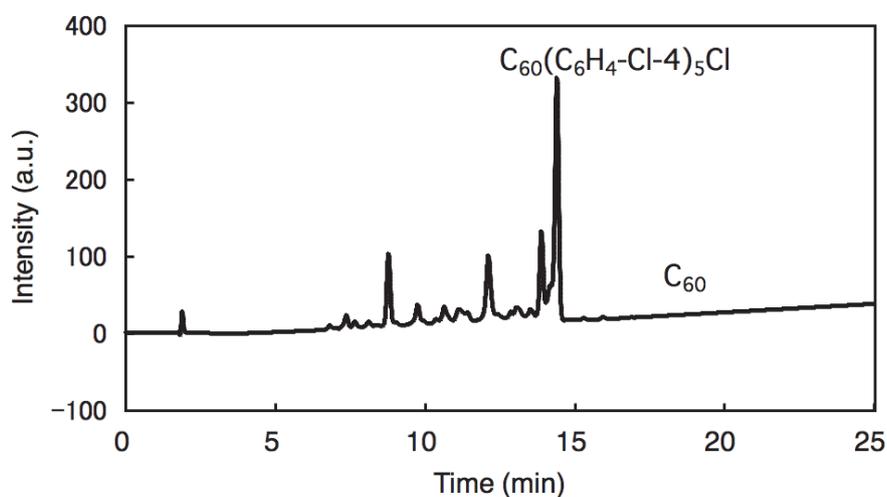


Figure 2-4. HPLC chart for the synthesis of **1**

Alternative Synthetic Method using Solvent

To a mixture of C_{60} (500mg, 0.70 mmol) and iron(III) chloride (1.13 g, 6.97 mmol) was added 1,1,2,2-tetrachloroethane (25 mL) followed by chlorobenzene (470 mg, 4.18 mmol) at room temperature. After stirred for 4 hours, the reaction mixture was quenched with water (0.5 mL). The resulting solution was passed through a pad of silica gel (eluent: toluene) and the volatiles were removed with rotary evaporator. The crude product contained the desired-penta adduct **1** mainly, and small amounts of polyarylated products as well as a trace amount of unreacted C_{60} as analyzed by HPLC (YMC-Pack ODS-AM) as shown in Figure 2-5. Purification with HPLC (Buckyprep column, Nacalai Tesque Inc., 4.6 mm ID x 250 mm, monitored at 308 nm, eluent: toluene/methanol = 7/3) gave compound **1** as orange powder (265 mg, 29%).

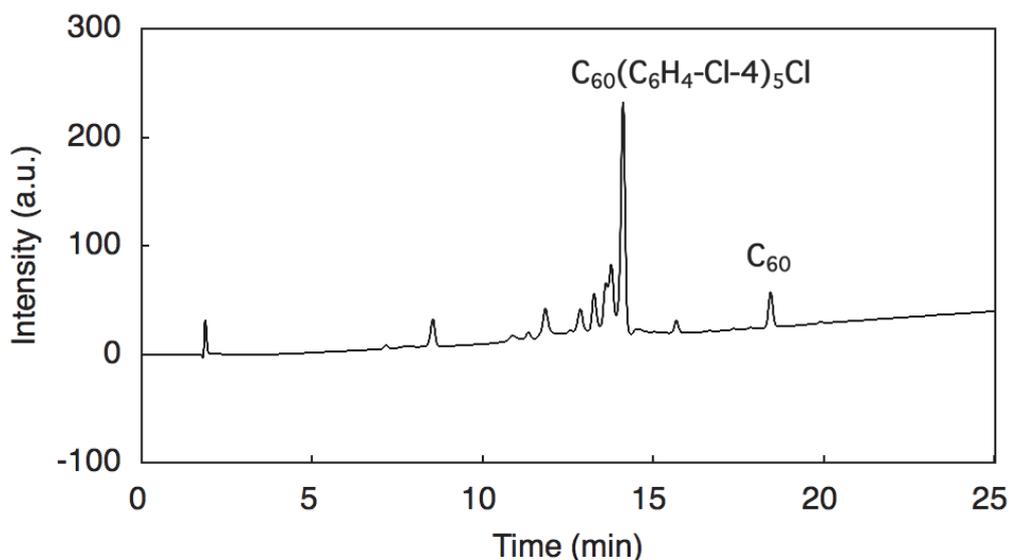


Figure 2-5. HPLC chart for the synthesis of **1** in 1,1,2,2-tetrachloroethane

Synthesis of **2**

To a mixture of C_{60} (500mg, 0.70 mmol) and iron(III) chloride (1.13 g, 6.97 mmol) was added 1,1,2,2-tetrachloroethane (25 mL) followed by bromobenzene (650 mg, 4.14 mmol) at room temperature. After stirred for 6 hours, the reaction mixture was quenched with water (0.5 mL). The resulting solution was passed through a pad of silica gel (eluent: toluene) and the volatiles were removed with rotary evaporator. The crude product contained the desired penta adduct **2** mainly, and small amounts of polyarylated products as well as a trace amount of unreacted C_{60} as analyzed by HPLC (YMC-Pack ODS-AM) as shown in Figure 2-6. Purification with HPLC (Buckyprep column, Nacalai Tesque Inc., 4.6 mm ID x 250 mm, monitored at 308 nm, eluent: toluene/methanol = 7/3) gave compound **2** as orange powder (245 mg, 23%). 1H NMR (400 MHz, $CDCl_3$): δ 6.97 (d, J = 8.8 Hz, 2H, C_6H_4), 7.22 (d, J = 8.8 Hz, 2H, C_6H_4), 7.39 (s, 8H, C_6H_4), 7.44 (d, J = 8.4 Hz, 4H, C_6H_4), 7.70 (d, J = 8.4 Hz, 4H, C_6H_4); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 57.53 (2C, sp^3-C_{60}), 60.18 (2C, sp^3-C_{60}), 62.88 (1C, sp^3-C_{60}), 75.78 (1C, $C(sp^3-C_{60})-Cl$), 129.83 (4C, C_6H_4Br), 129.92 (4C, C_6H_4Br), 130.74 (2C, C_6H_4Br), 131.19 (2C, C_6H_4Br), 131.29 (2C, C_6H_4Br), 132.04 (4C, C_6H_4Br), 132.10 (4C, C_6H_4Br), 134.14 (4C, C_6H_4Br), 135.54 (2C, C_6H_4Br), 137.32 (2C, C_6H_4Br), 142.65 (2C), 142.75 (2C), 142.93 (2C), 143.45 (2C), 143.48 (2C), 144.20 (2C), 144.26 (2C), 144.40 (2C), 144.52 (2C), 144.73 (2C), 144.84 (2C), 145.86 (2C), 147.10 (2C+1C), 147.23 (2C), 148.14 (1C), 148.33 (2C), 148.39 (2C), 148.57 (2C), 148.67 (6C), 148.71 (2C), 149.23 (2C), 150.40 (2C), 153.07 (2C), 155.90 (2C); APPI-MS (-): calcd for $C_{90}H_{20}Br_5$ (M - Cl): 1500.6; found, 1500.6; Anal. Calcd for $C_{90}H_{20}Br_5Cl$, C 70.37; H, 1.31. Found: C 70.36; H, 1.36.

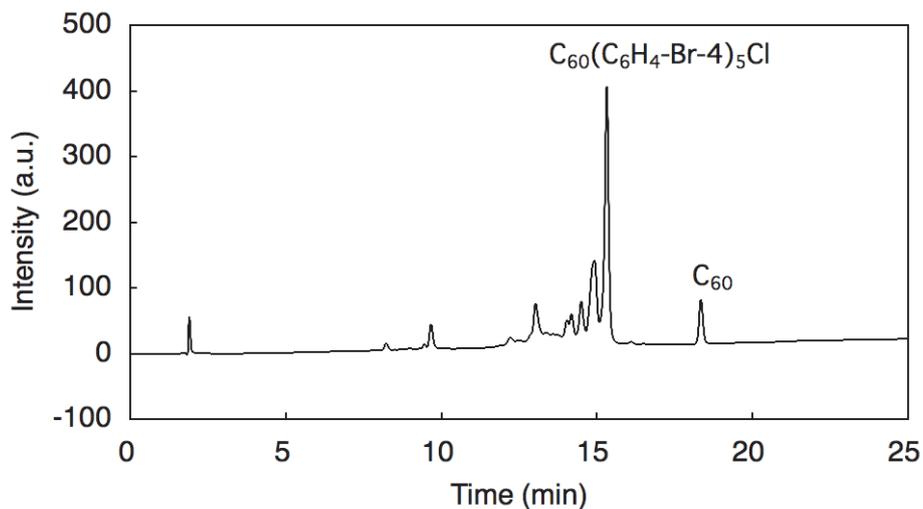


Figure 2-6. HPLC chart for the synthesis of **2** in 1,1,2,2-tetrachloroethane

Synthesis of **3**

To a mixture of C_{60} (501 mg, 0.70 mmol) and iron(III) chloride (1.13 g, 6.97 mmol) was added 1,1,2,2-tetrachloroethane (25 mL) followed by iodobenzene (850 mg, 4.17 mmol) at room temperature. After stirred for 4 hours, the reaction mixture was quenched with water (0.5 mL). The resulting solution was passed through a pad of silica gel (eluent: toluene) and the volatiles were removed with rotary evaporator. The crude product contained the desired penta adduct **3** mainly, and small amounts of polyarylated products as well as a trace amount of unreacted C_{60} as analyzed by HPLC (YMC-Pack ODS-AM) as shown in Figure 2-7. Purification with HPLC (Buckyprep column, Nacalai Tesque Inc., 4.6 mm ID x 250 mm, monitored at 308 nm, eluent: toluene/methanol = 7/3) gave compound **3** as orange powder (221 mg, 18%). ^1H NMR (400 MHz, CDCl_3): δ 6.83 (d, $J = 8.8$ Hz, 2H, C_6H_4), 7.26 (d, $J = 8.8$ Hz, 4H, C_6H_4), 7.42 (d, $J = 8.8$ Hz, 4H, C_6H_4), 7.54–7.60 (m, 8H, C_6H_4), 7.64 (d, $J = 8.8$ Hz, 4H, C_6H_4); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 57.63 (2C, $\text{sp}^3\text{-C}_{60}$), 60.27 (2C, $\text{sp}^3\text{-C}_{60}$), 62.99 (1C, $\text{sp}^3\text{-C}_{60}$), 75.67 (1C, $\text{C}(\text{sp}^3\text{-C}_{60})\text{-Cl}$), 130.01 (4C, $\text{C}_6\text{H}_4\text{I}$), 130.10 (4C, $\text{C}_6\text{H}_4\text{I}$), 131.52 (2C, $\text{C}_6\text{H}_4\text{I}$), 136.56 (2C, $\text{C}_6\text{H}_4\text{I}$), 137.11 (2C, $\text{C}_6\text{H}_4\text{I}$), 137.98 (4C, $\text{C}_6\text{H}_4\text{I}$), 138.04 (4C, $\text{C}_6\text{H}_4\text{I}$), 142.62 (2C), 142.67 (2C), 142.74 (2C), 142.92 (8C, $\text{C}_6\text{H}_4\text{I}$), 143.14 (2C), 143.42 (2C), 144.17 (2C), 144.25 (2C), 144.37 (2C), 144.51 (2C), 144.72 (2C), 144.83 (2C), 145.82 (2C), 147.10 (2C+1C), 147.23 (2C), 147.73 (1C), 148.20 (2C), 148.38 (2C), 148.55 (2C), 148.66 (6C), 148.70 (2C), 149.44 (2C), 150.37 (2C), 153.39 (2C), 155.85 (2C); APPI-MS (–): calcd for $\text{C}_{90}\text{H}_{20}\text{I}_5$ (M – Cl): 1735.6; found, 1734.6; Anal. Calcd for $\text{C}_{90}\text{H}_{20}\text{I}_5\text{Cl}$, C 61.03; H, 1.14. Found: C 61.02; H, 0.65.

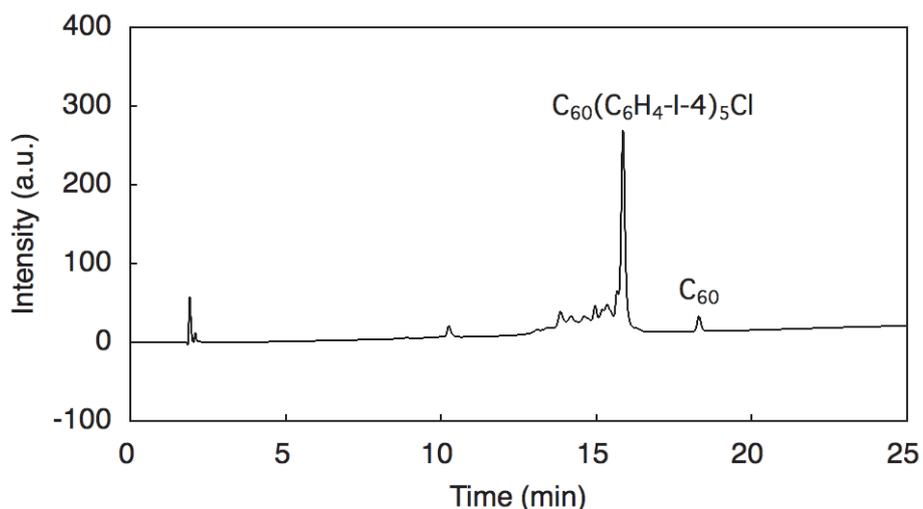


Figure 2-7. HPLC chart for the synthesis of **3** in 1,1,2,2-tetrachloroethane

Synthesis of **4**

To a mixture of C_{60} (502 mg, 0.70 mmol) and iron(III) chloride (1.14 g, 7.03 mmol) was added 1,1,2,2-tetrachloroethane (25 mL) followed by fluorobenzene (402 mg, 4.18 mmol) at room temperature. After stirred for 4 hours, the reaction mixture was quenched with water (0.5 mL). The resulting solution was passed through a pad of silica gel (eluent: toluene) and the volatiles were removed with rotary evaporator. The crude product contained the desired penta adduct **4** mainly, and small amounts of polyarylated products as well as a trace amount of unreacted C_{60} as analyzed by HPLC (YMC-Pack ODS-AM) as shown in Figure 2-8. Purification with HPLC (Buckyprep column, Nacalai Tesque Inc., 4.6 mm ID x 250 mm, monitored at 308 nm, eluent: toluene/methanol = 7/3) gave compound **4** as orange powder (103 mg, 12%). ^1H NMR (400 MHz, CDCl_3): δ 6.80–6.85 (m, 2H, C_6H_4), 6.99–7.09 (m, 8H, C_6H_4), 7.13–7.17 (m, 2H, C_6H_4), 7.56–7.59 (m, 4H, C_6H_4), 7.87–7.90 (m, 4H, C_6H_4); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 57.39 (2C, $\text{sp}^3\text{-C}_{60}$), 60.06 (2C, $\text{sp}^3\text{-C}_{60}$), 62.78 (1C, $\text{sp}^3\text{-C}_{60}$), 77.17 (1C, $\text{C}(\text{sp}^3\text{-C}_{60})\text{-Cl}$), 115.04 (2C, $C_6H_4\text{F}$), 115.72 (4C, $C_6H_4\text{F}$), 115.95 (4C, $C_6H_4\text{F}$), 129.93 (4C, $C_6H_4\text{F}$), 130.05 (4C, $C_6H_4\text{F}$), 130.09 (4C, $C_6H_4\text{F}$), 131.40 (2C, $C_6H_4\text{F}$), 131.48 (2C, $C_6H_4\text{F}$), 132.64 (2C, $C_6H_4\text{F}$), 134.22 (2C, $C_6H_4\text{F}$), 142.91 (4C), 143.28 (2C), 143.62 (2C), 143.70 (2C), 144.20 (2C), 144.26 (2C), 144.41 (2C), 144.51 (2C), 144.82 (2C), 144.95 (2C), 146.16 (2C), 147.15 (2C), 147.28 (2C+1C), 147.76 (2C), 148.15 (1C), 148.23 (2C), 148.40 (2C), 148.61 (2C), 148.69 (6C), 148.72 (2C), 149.87 (2C), 150.68 (2C), 153.42 (2C), 156.28 (2C); APPI-MS (-): calcd for $C_{90}H_{20}F_5$ (M – Cl $^-$): 1196.1; found, 1196.1; Anal. Calcd for $C_{90}H_{20}F_5Cl$, C 87.77; H, 1.64. Found: C 88.07; H, 1.17.

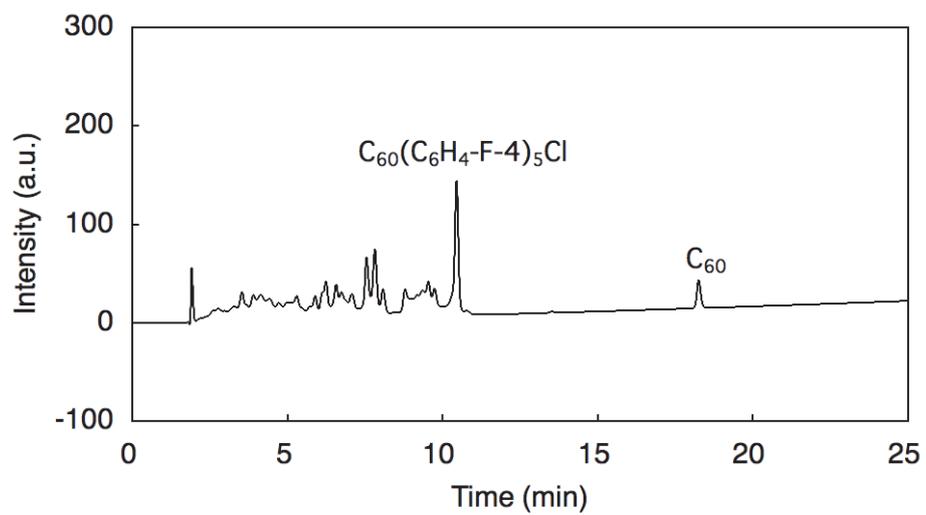


Figure 2-8. HPLC chart for the synthesis of **4** in 1,1,2,2-tetrachloroethane

Table 2-2. Crystal and refinement data for **1**

Empirical formula	$C_{60}(C_6H_4Cl)_5Cl \cdot C_7H_8$
Formula weight	1405.89
Temperature	293(2) K
Radiation	MoK α ($\lambda = 0.71073$ Å)
Crystal system	Triclinic
Space group	<i>P</i> -1
Unit cell dimensions	$a = 14.5009(18)$ Å
	$b = 16.212(2)$ Å
	$c = 14.5134(18)$ Å
	$\alpha = 97.198(2)^\circ$
	$\beta = 99.991(2)^\circ$
	$\gamma = 86.541(2)^\circ$
V (Å ³)	3331.0(7)
Z	2
Density ρ calc (g·cm ⁻³)	1.402
Absorption coefficient (mm ⁻¹)	0.312
F(000)	1424
Crystal dimensions (mm ³)	0.3 · 0.25 · 0.2
range for data collection	$4.08 \leq \theta \leq 26.37^\circ$
Index ranges	$-13 \leq h \leq 18$
	$-17 \leq k \leq 20$
	$-18 \leq l \leq 15$
Reflections collected / unique	19536 / 13280 ($R_{\text{int}} = 0.0356$)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6183 / 0 / 288
Goodness-of-fit on F^2	1.102
Final <i>R</i> indices [$I > 2\sigma(I)$] ^{a), b)}	$R1 = 0.1051$, $wR2 = 0.2953$
<i>R</i> indices (all data) ^{a), b)}	$R1 = 0.1994$, $wR2 = 0.3703$
Largest diff. peak and hole (e·Å ⁻³)	1.099 / -0.548

^{a)} $\Sigma(|Fo| - |Fc|) / \Sigma|Fo|$

^{b)} $wR2 = [\Sigma\omega(|Fo|^2 - |Fc|^2)^2 / \Sigma(\omega Fo^4)]^{1/2}$

References and Notes

† The contents of this chapter have already been published in the following paper. Hashiguchi, M.; Watanabe, K.; Matsuo, Y. *Org. Biomol. Chem.* **2011**, *9*, 6417–6421.

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3. FeCl₃-mediated Synthesis of Fullereryl Esters as Low-LUMO Acceptors for Organic Photovoltaic Devices[†]

3.1 Introduction

Organic photovoltaic (OPV) devices using fullerene derivatives as electron-acceptors are expected to be one of the ubiquitous energy sources in the future.¹ To date, various fullerene derivatives, as typified by [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM)², have been developed for OPV applications, and a power conversion efficiency of more than 9% has been attained.³ For the advancement of fullerene-based electron-acceptors, various synthetic methodologies, for example, dimethyl formamide (DMF)-assisted monoaddition⁴ and silylmethyl-fullerene cation-utilized cyclopropanation⁵ reactions, have been developed to create high-performance materials for efficient OPV devices. Development of methodology for fullerene-functionalization can certainly open up opportunities for research in this field.

In general, design guidelines on creating fullerene acceptors are based on raising LUMO levels to obtain a higher open-circuit voltage (V_{OC}) for OPV devices.⁶ These have been realized by introducing electron-donating groups⁷ and decreasing fullerene π -systems^{5,6,8}, to decrease the electron affinity of the fullerene core. On the other hand, the lowering of LUMO levels of fullerenes is also a respected strategy. Low bandgap polymers⁹, which were recently introduced for OPV application, have low LUMO levels that tend to require low-LUMO fullerenes for efficient charge separation. Although obtaining high-LUMO fullerenes is relatively straightforward, since the addition of carbon functional groups to fullerene generally raises LUMO levels, the approach towards low-LUMO fullerenes is rather limited. Only a few low-LUMO fullerenes such as azafulleroid and fullerene ketolactams have been investigated for OPV devices.¹⁰ Further investigations on low-LUMO fullerenes are awaited to expand upon this field of research.

To lower the LUMO levels of fullerenes, electron-withdrawing groups, such as the cyano group, are installed on fullerene.¹¹⁻¹³ Another approach involves attaching electronegative atoms such as oxygen on fullerene to increase the electron affinity of the fullerene core. Various oxygen-attached fullerene derivatives such as hydroxylfullerenes,¹⁴ alkoxyfullerenes,¹⁵ peroxidized fullerenes,¹⁶ 1,3-dioxolane fullerenes,¹⁷ fullerooxazoles,¹⁸ fullerene isoxazolines,¹⁹ fused furanylfullerenes,²⁰ had already been reported. Among these, fullereryl esters²¹ are considered to be the most suitable for OPV application: these compounds bear electron-withdrawing ester moieties and exhibit high solubility in organic solvents.

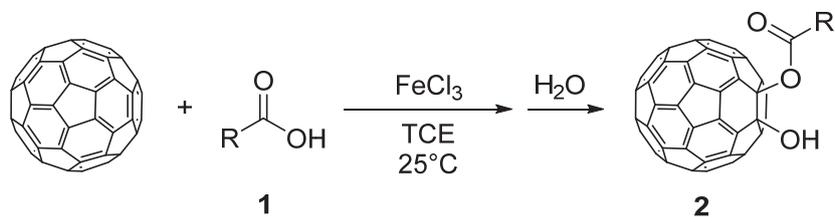
For fullereryl esters, only the synthesis of acetoxyated fullerenes and C₆₀-fused lactones have been reported in literature.^{14d,14h,14i,19c,21} These compounds have been synthesized through one-pot reactions with (diacetoxy)iodobenzene,^{21a} Mn(OAc)₃·2H₂O, or Pd(OAc)₄.^{21c,d,e} However, general synthetic methodology to obtain fullereryl esters with broad substrate scope has not been realized so far.

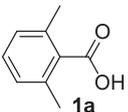
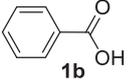
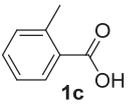
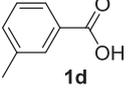
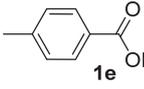
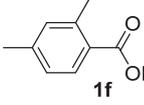
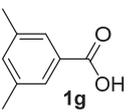
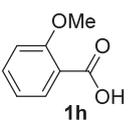
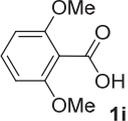
Herein I report facile one-pot syntheses of hydroxyfullereryl esters C₆₀(OCOR)(OH) by using versatile carboxylic acids and inexpensive iron trichloride (FeCl₃). This reaction proceeds under mild conditions, and possesses substrate diversity catering to both aromatic and aliphatic carboxylic acids. The hydroxyl functionality can be utilized to obtain a diester derivative C₆₀(OCOAr)(OCOPh) (Ar = 2,6-xylyl) and a siloxyl derivative C₆₀(OCOAr)(OSiMe₃). This approach allows us to obtain low-LUMO fullerenes, which will attract special attention for use with low-LUMO donors in OPV application.

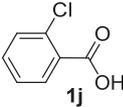
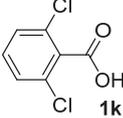
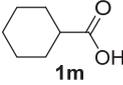
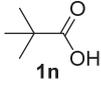
3.2 Synthesis and Characterization of Fullereryl Esters

Treatment of C₆₀ with 2,6-dimethylbenzoic acid (**1a**, 10 equiv.) in the presence of FeCl₃ (20 equiv.) in 1,1,2,2-tetrachloroethane (TCE) at 25 °C for 4 hours, produced 1-hydroxy-2-{2,6-dimethylphenylcarbonyloxy}[60]fullerene (hydroxyfullereryl 2,6-dimethylbenzoate), C₆₀(OCOC₆H₃Me₂-2,6) (**2a**) in 68% isolated yield (Table 3-1, entry 1). Aromatic organic solvents such as toluene and xylene, often used in the synthesis of fullerene derivatives, were found to be unsuitable for this reaction. The use of toluene and xylene causes a side reaction, hydroarylation²², which is mediated by Lewis acidic FeCl₃. This will in turn lead to a decrease in the chemical yield of the desired product. Therefore, TCE was chosen instead as the solvent for this reaction, since it did not have any aromatic component, and it could dissolve the starting material C₆₀. This reaction afforded almost quantitative conversion of C₆₀ upon stirring at room temperature for 4–8 hours. As shown in Figure 3-1, product **2a** was obtained as the main product. Possible side products in this reaction were diadducts and multiadducts. Although numerous side products were formed due to the inevitable formation of regiochemical isomers of diadducts and multiadducts, the absolute amount obtained for each side product was very small. The drawback of this reaction was the need for a large excess of substrates and FeCl₃; maximum selectivity was obtained when 10 equiv. of carboxylic acid and 20 equiv. of FeCl₃ were used. Nevertheless, this reaction is highly applicable to industrial production because of the relative low cost of both substrate and iron trichloride as compared to C₆₀.

Table 3-1. Reaction conditions and yields for the reaction of C₆₀ with carboxylic acids **1a–n** in the presence of FeCl₃^a



carboxylic acids 1	reaction time (h)	conv. of C ₆₀ (%) ^b	HPLC area ratio (%) ^b	yield of 2 (%) ^c
	4	95	79	68
	8	95	49	14
	8	96	49	28
	7	95	49	25
	7	96	51	24
	8	97	56	30
	8	96	44	22
	8	–	–	– ^d
	8	–	–	– ^d

	5	91	54	35
	8	–	–	– ^d
	4	90	64	29
	6	76	54	21
	8	52	32	10

^a All reactions were performed under a nitrogen atmosphere with a molar ratio of C₆₀:FeCl₃:**1** = 1:20:10.

^b Conversion of C₆₀ and selectivity of product formation were determined by HPLC analysis. ^c Isolated yield. ^d No reaction.

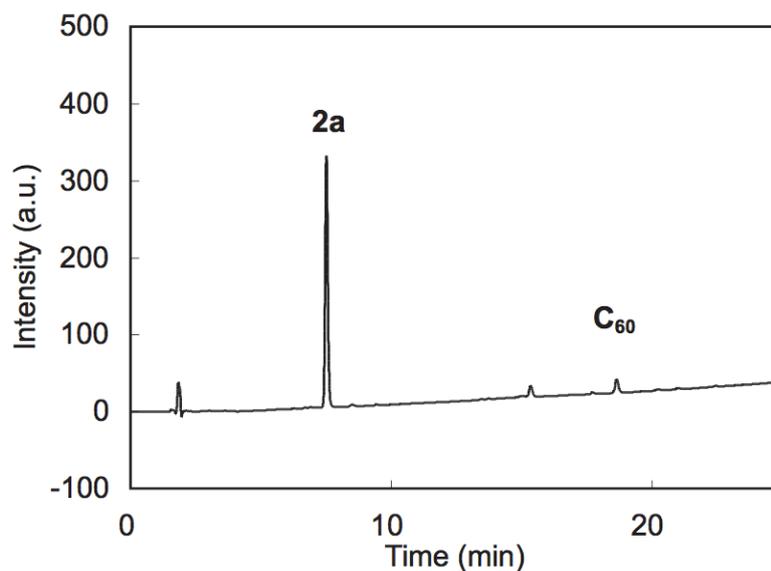


Figure 3-1. HPLC trace for the product mixture containing **2a**. Conditions: ODS column, 3 micron, 4.6 x 150 mm. Linear methanol/toluene gradient from 25% to 55% toluene over 25 min; flow rate: 1.0 mL/min.

Product **2a** can be purified with either silica-gel column chromatography or HPLC separation. Purified compound **2a** was characterized with ^1H and ^{13}C NMR, IR, electrospray ionization (ESI)-mass spectroscopic analysis, and elemental analysis. The structure of **2a** was determined unambiguously by X-ray crystallographic analysis of its single crystal, which was obtained by slow evaporation of a CS_2 solution of **2a** (Figure 3-2). It was elucidated from the X-ray structure that the arylcarbonyloxy group and the hydroxyl group were added to C_{60} in a 1,2-addition pattern. However, these two addends were positionally disordered in the unit cells. Therefore, exact bond lengths between the oxygen atoms and the fullerene carbon atoms could not be determined.

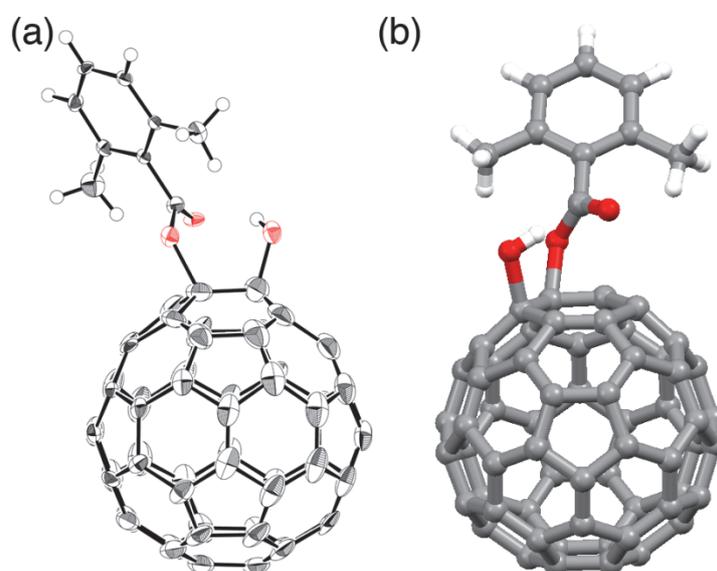


Figure 3-2. Crystal structure of **2a**·0.5 CS_2 . (a) ORTEP drawing with thermal ellipsoids at 30% probability. Solvent molecules found in the unit cell and disordered oxygen atoms are omitted for clarity. (b) Ball-and-stick model. Note that the position of the hydrogen atom of the hydroxyl group is not accurate because it has not been optimized.

3.3 Scope and Limitation

The scope and limitation of the reaction is illustrated in Table 3-1. The reaction was applicable to both aromatic and aliphatic carboxylic acids, though the latter type gave lower yields. Non-substituted benzoic acid (**1b**) showed similar reactivity to **1a** (conversion of C_{60} = 95%), but comparatively low selectivity, to produce the corresponding fullerenyl ester **2b** (14% yield, entry 2). I postulate that the poor selectivity was caused by the coordination of FeCl_3 to the carbonyl group of the substrate. Another potential reason for this low yield would be the side reaction between a possible cationic fullerene intermediate (vide infra) and non-substituted aryl groups. There had been

many reports on reactions of fullerene cations with aryl groups in literature^{14i,22a,d,23}. Mono-methylated benzoic acids **1c**, **1d**, **1e**, gave corresponding fullereryl esters **2c**, **2d**, **2e**, in chemical yields of 24–28%. For di-methylated benzoic acids, 2,4-dimethylbenzoic acid (**1f**) afforded a 30% yielding reaction, while 3,5-dimethylbenzoic acid (**1g**) gave a comparatively lower yield of 22%. 2-methoxybenzoic acid (**1h**) and 2,6-dimethoxybenzoic acid (**1i**) did not produce any fullereryl ester, most likely due to coordination of FeCl₃ to the methoxy groups. 2-Chlorobenzoic acid (**1j**) gave the second best result (35% yield), but 2,6-dichlorobenzoic acid (**1k**) did not yield any fullereryl ester at all. The lack of reaction with **1k** could be attributed to the steric bulkiness of its two chlorine atoms. Aliphatic carboxylic acids **1l**, **1m**, **1n**, reacted with C₆₀ under the same conditions to produce fullereryl esters **2l**, **2m**, **2n**, respectively. Among these three substrates, pivalic acid (**1n**) gave the lowest yield. This is likely due to the steric hindrance that was present in **1n** as well.

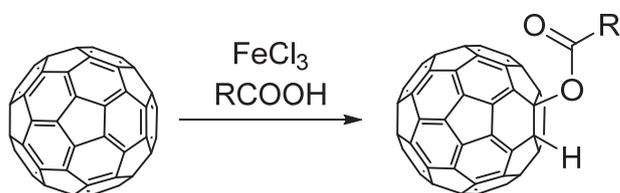
Attempts to use aldehydes such as benzaldehyde and esters such as ethyl benzoate, in place of carboxylic acids, were unsuccessful when similar reaction conditions were used. Although Wang et al. had previously reported a Fe(ClO₄)₃-mediated addition of aldehydes and esters to fullerene^{17e}, it seemed that FeCl₃ was not suitable for this purpose. In addition, we attempted the reaction using other Lewis acids, oxidants, and iron complexes (AlCl₃, RuCl₃, BF₃·Et₂O, CuCl₂, FeCl₂, ZnCl₂, Fe(acac)₃, and Fe(ClO₄)₃) in place of FeCl₃, but we also could not obtain the desired fullereryl esters from their respective carboxylic acids. Therefore, this reaction was found to be specific for FeCl₃ and carboxylic acids only.

3.4 Reaction Mechanisms

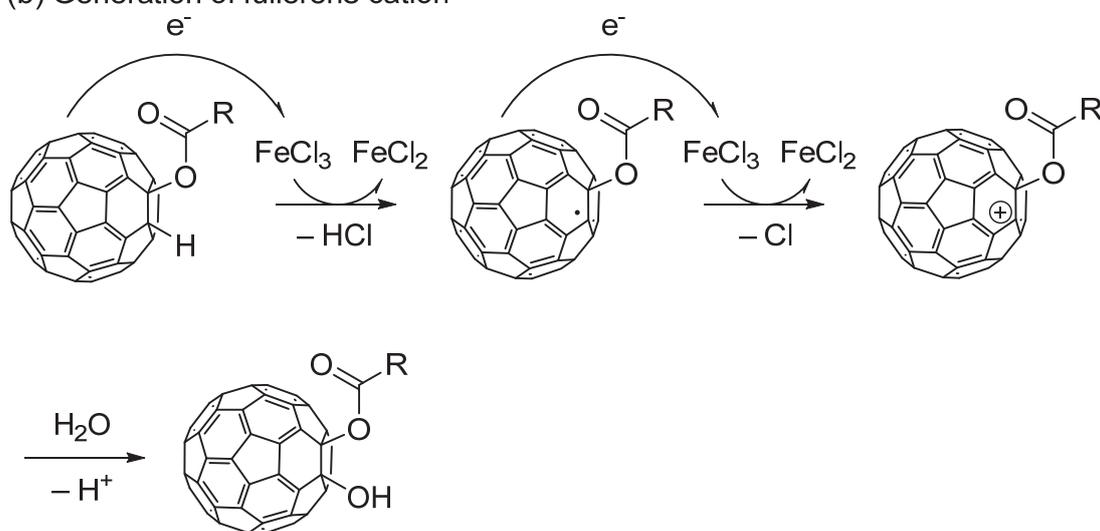
Next, we will discuss the reaction mechanisms involved in this reaction. The simple reaction mechanism described below is proposed based on the assumption that fullerene behaves like an olefin. Komeyama had previously reported a FeCl₃-catalyzed addition of carboxylic acids to olefins²⁴. Applying this concept to fullerene functionalization, the first step would be the formation of a (carbonyloxy)hydrofullerene intermediate (Scheme 3-1a). Next, the hydrogen atom on fullerene is oxidized by FeCl₃ to give a (carbonyloxy)fullerene cation, which is then hydroxylated upon H₂O treatment to produce (carbonyloxy)(hydroxy)fullerene (Scheme 3-1b). Fullerene cations were known to be stabilized by halogen atoms of halogenated solvents such as chloroform^{14e,23d,e}. For this reaction, it is hypothesized that TCE and the oxygen atoms of the carbonyl moiety on the intermediates helped to stabilize the fullerene cations. However, it is difficult to elucidate the reasons behind the selective formation of a monoadduct (Figure 3-1) using this mechanism. C₆₀ has 30 olefinic components, thus multiadducts should be formed.

Scheme 3-1. Proposed reaction mechanism via (carbonyloxy)hydrofullerene intermediates

(a) Formation of fullereryl ester



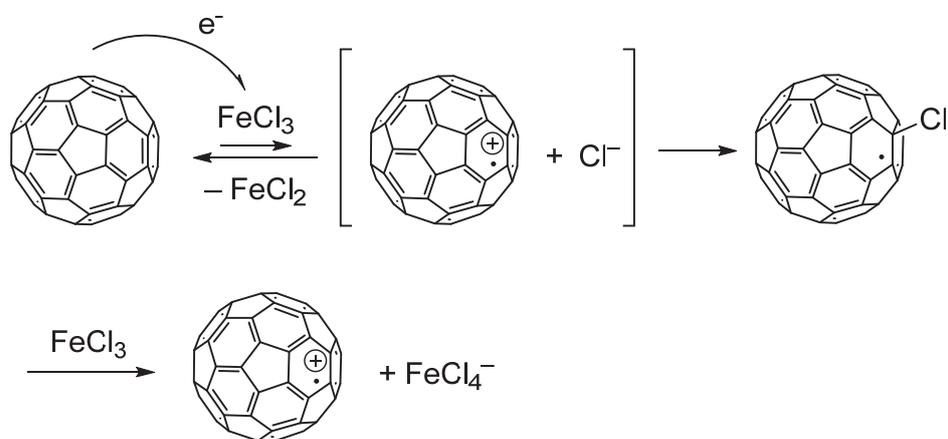
(b) Generation of fullerene cation



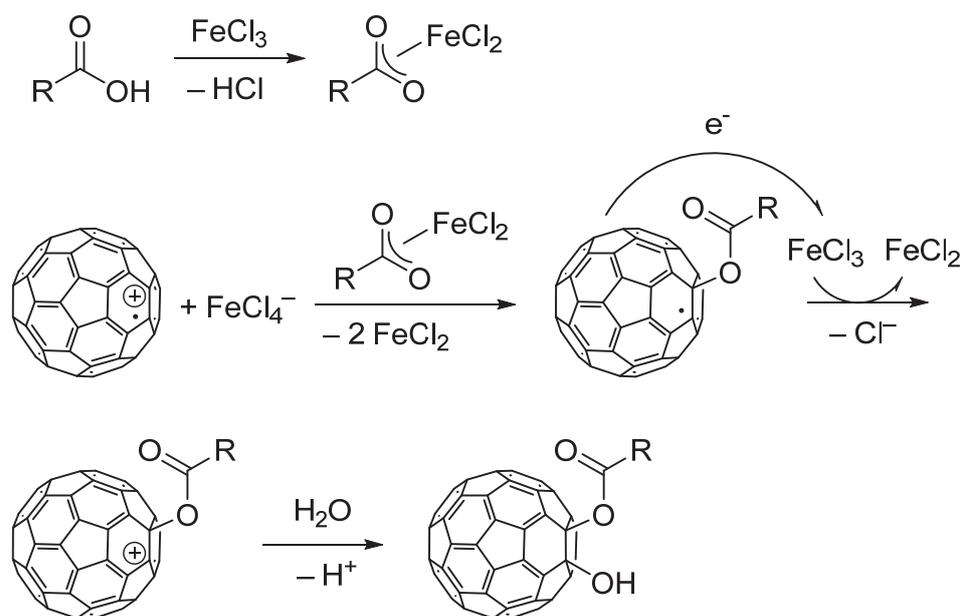
Therefore, I propose another plausible mechanism involving a single electron transfer (SET) event from C₆₀ to FeCl₃ to generate a C₆₀ radical cation (Scheme 3-2a)^{22d} transition state as noted in Chapter 2. A subsequent chlorination forms ClC₆₀[•], which in turn undergoes de-chlorination in the presence of FeCl₃ to give a fullerene radical cation. This active species reacts with carboxylic acids or possible iron carboxylate complexes to form a fullerene–oxygen bond, affording (RCO₂)C₆₀[•] (Scheme 4-2b). Oxidation of this radical species by FeCl₃ generates a cation (RCO₂)C₆₀⁺, which is hydroxylated upon H₂O treatment, thereby completing the reaction. The key to this reaction mechanism is the formation of the fullerene radical cation. Considering the oxidation potential of C₆₀ and the reduction potential of FeCl₃,²⁵ it is thermodynamically unfavorable for the oxidation of C₆₀ by FeCl₃. However, coordination of C₆₀ to FeCl₃ might alter the oxidation and reduction potentials, thus leading to a favorable reaction.

Scheme 3-2. Proposed reaction mechanism via fullerene radical cation

(a) Generation of fullerene radical cation



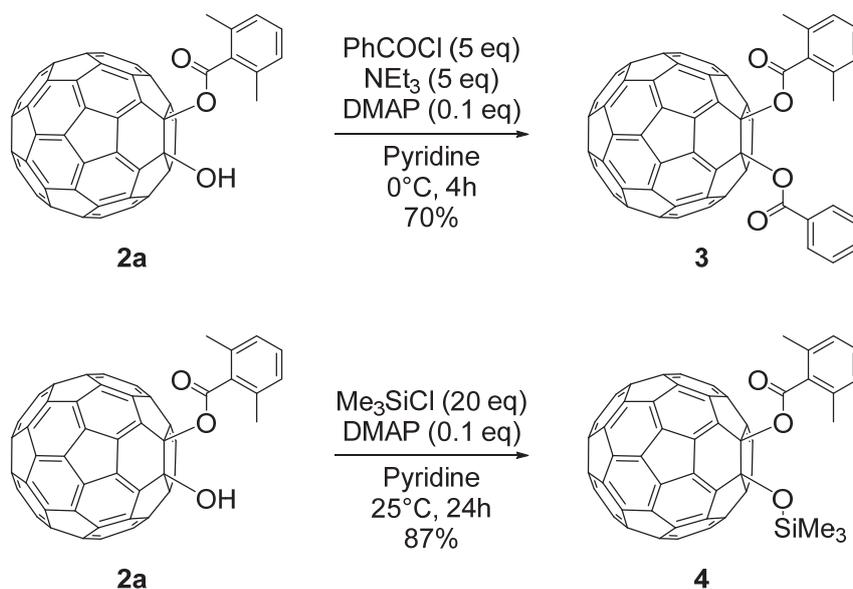
(b) Formation of fullereryl ester



3.5 Preparation and Characterization of Low-LUMO Fullerenes

Next, I performed functional group transformations on the hydroxyl groups of **2a**. Electrochemical studies of **2a** showed its irreversible reduction/oxidation process due to the presence of the hydroxyl group. Masking the hydrogen atom of the hydroxyl group is thus necessary to obtain an electrochemically stable fullerene-based electron acceptor for application in OPV devices. Syntheses of fullerene ethers and esters from fullerenols is generally straightforward.^{14h)} Treatment of fullereneol **2a** with benzoic acid chloride (5 equiv.), in the presence of diethyl amine (5 equiv.) and dimethylaminopyridine (DMAP, 0.1 equiv.) in pyridine at 0 °C for 4 hours, produced a diester derivative **3** in 70% yield. A siloxyl derivative **4** was also obtained in 87% yield via the reaction of fullereneol **2a** with trimethylsilyl chloride (20 equiv.), in the presence of DMAP (0.1 equiv.) in pyridine at 25 °C for 24 hours. Compounds **3** and **4** were characterized via ¹H NMR, ¹³C NMR, IR, ESI-MS, elemental analysis, and X-ray crystallography (Figure 3-3).

Scheme 3-3. Synthesis of compounds **3** and **4**



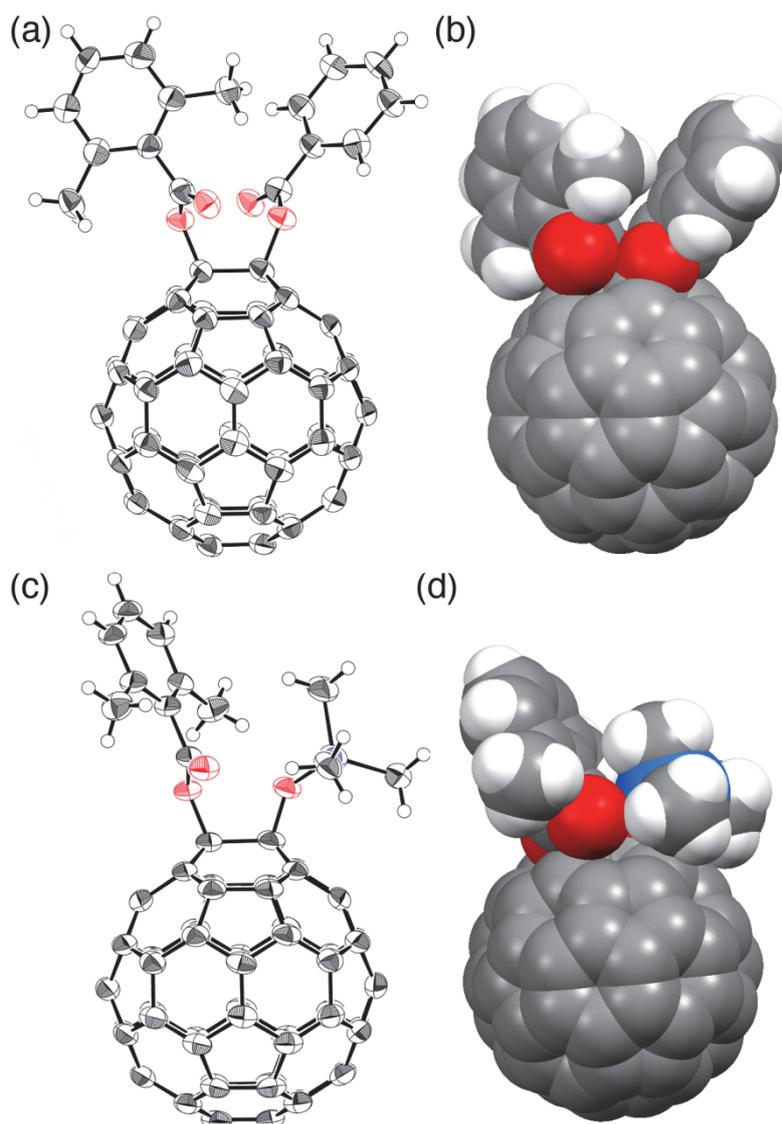


Figure 3-3. Crystal structures of **3**·CS₂ and **4**. (a) ORTEP drawing of **3** with thermal ellipsoids at 30% probability. (b) Space-filling model showing the side view of **3**. (c) ORTEP drawing of **4** with thermal ellipsoids at 30% probability. (d) Space-filling model showing the side view of **4**.

Electrochemical studies were performed on **3** and **4** to determine the LUMO levels of the compounds (Table 3-2). Both compounds **3** and **4** exhibited reversible reductive waves, as observed in the measurements. The first reduction potential for both **3** and **4** in 1,2-dichlorobenzene was -1.12 V vs Fc/Fc⁺. The LUMO level was formally calculated to be -3.68 eV. This value is rather similar to the LUMO level of C₆₀ (-3.70 eV, estimated from electrochemical measurement in 1,2-dichlorobenzene), but lower than that of PCBM (-3.62 eV). The two electron-withdrawing groups attached to each fullerene molecule confer large electron affinities and low LUMO levels to

products **3** and **4**. These compounds are considered to be rare; they possess low-LUMO levels similar to C₆₀, while at the same time they exhibit a much higher solubility than C₆₀.

Table 3-2. Reduction potentials and LUMO levels for **3** and **4** in comparison with C₆₀ and PCBM ^a

Compound	$E_{1/2}^{\text{red}}$ (V vs Fc/Fc ⁺)			LUMO level (eV) ^b
	E_1	E_2	E_3	
C₆₀	-1.10	-1.49	-1.95	-3.70
3	-1.12	-1.50	-1.98	-3.68
4	-1.12	-1.49	-1.95	-3.68
PCBM	-1.18	-1.56	-2.07	-3.62

^a Potentials in V vs a ferrocene/ferrocenium (Fc/Fc⁺) couple were measured by cyclic voltammetry in 1,2-Cl₂C₆H₄ solution containing Bu₄N⁺PF₆⁻ (0.1 M) as a supporting electrolyte at 25 °C with a scan rate of 0.1 Vs⁻¹. Glassy carbon, platinum wire, and Ag/Ag⁺ electrodes were used as the working, counter, and reference electrodes, respectively. ^b Estimated using the following equation: LUMO level = - (4.8 + $E_{1/2}^{\text{red1}}$) eV.²⁶

3.6 OPV Performance

OPV fabrication and measurement are achieved by Mr. Naoki Obata and Mr. Kee Sheng Yeo in Matuo Labo (See Appendix)

3.7 Conclusion

I have demonstrated the facile synthetic methodology to introduce two electron-withdrawing groups to fullerene, to obtain fullerene electron-acceptors that have low LUMO levels. The synthesis relies on FeCl₃-mediated introduction of carbonyloxyl groups by using carboxylic acids. Inexpensive FeCl₃ is used for this reaction, and the reaction proceeds under mild conditions. Although there are some limitations (protection of 2,6-substituents is necessary; coordination of oxygen-containing groups is prohibited) on the carboxylic acid substrates employed due to the use of Lewis acidic FeCl₃, it has been observed that both aromatic and aliphatic carboxylic acids are compatible with this reaction. Even though there is the drawback of using a large excess of reagents, the products are still considered cost-competitive because of the inherent low cost of the reagents (FeCl₃ and carboxylic acids), as compared to the high cost of fullerenes or that of expensive noble metal catalysts that are employed in some fullerene functionalization reactions.

Fullerenyl esters such as compounds **3** and **4** are representative of soluble low-LUMO electron acceptors for application in solution-processed OPV devices, and the present study had displayed their performance in standard bulk heterojunction devices. Efficiencies of these devices were low because of low V_{OC} derived from the low LUMO levels. Nevertheless, the use of low-LUMO acceptors gives the opportunity to employ a wider range of donor materials, especially those with low LUMO levels. Further molecular design and optimization of the organic components (i.e. phenyl groups) of the fullerenyl esters is necessary to achieve high efficiencies in OPV devices.

Experimental Section

General Considerations and Materials

All reactions were carried out under nitrogen atmosphere. Analytical gradient reversed-phase HPLC was performed with an ODS column (3 micron, 4.6 x 150 mm). All runs used linear gradients of methanol (solvent A) and toluene (solvent B). The gradient ran from 25% B up to 55% B over 25 min. Flow rate was 1.0 mL/min and routine UV detection was performed at 290 nm. NMR spectra are reported in part per million from CDCl₃ (δ 7.24 ppm for ¹H NMR and δ 77.00 ppm for ¹³C NMR). Mass spectra were measured with ESI-mass spectrometer (Negative mode) equipped on an ODS column. Preparative HPLC was performed on a Buckyprep column (20 mm x 250 mm) using toluene/2-propanol (9/1 or 8/2) as eluent (flow rate: 10 mL/min, detected at 290 nm with an UV spectrometer). Unless otherwise noted, materials were used as received from commercial suppliers.

1-Hydroxy-9-(2,6-Dimethylbenzoyloxy)-1,9-Dihydro(C₆₀-I_h)[5,6]fullerene (2a)

To a mixture of C₆₀ (500 mg, 0.69 mmol) and 2,6-dimethylbenzoic acid (1.04 g, 6.9 mmol) in 1,1,2,2-tetrachloroethane (25 mL) at 25 °C, FeCl₃ (2.25 g, 14 mmol) was added. After stirring for 4 h, an adequate amount of water was added to quench the reaction. The product was extracted with toluene (200 mL). The organic layer was washed with distilled water, and solvent was evaporated. Purification of the product was performed by preparative HPLC separation (Buckyprep column, eluent: toluene/2-propanol = 9/1) to obtain the title compound (415 mg, 68% isolated yield, analytically pure) as black crystals. ¹H NMR (400 MHz, CDCl₃/CS₂): δ 2.74 (s, 6H, CH₃), 5.28 (s, 1H, OH), 7.18 (d, *J* = 7.6 Hz, 2H, Ar), 7.33 (t, *J* = 7.6 Hz, 1H, Ar); ¹³C NMR (100 MHz, CDCl₃/CS₂): δ 20.73 (2C, CH₃), 84.87 (1C, C₆₀OH), 89.34 (1C, C₆₀OCOAr), 128.02 (2C, Ar), 130.17 (1C, Ar), 132.06 (1C, Ar), 136.16 (2C, Ar), 136.25 (2C, C₆₀), 138.38 (2C, C₆₀), 139.14 (2C, C₆₀), 139.57 (2C, C₆₀), 141.19 (2C, C₆₀), 141.21 (2C, C₆₀), 141.36 (2C, C₆₀), 141.42 (2C, C₆₀), 142.06 (2C, C₆₀), 142.16 (2C, C₆₀), 142.33 (2C, C₆₀), 142.46 (4C, C₆₀), 144.20 (2C, C₆₀), 144.41 (2C, C₆₀), 144.71 (2C, C₆₀), 144.84 (2C, C₆₀), 145.05 (4C, C₆₀), 145.27 (2C, C₆₀), 145.78 (2C, C₆₀), 145.96 (2C, C₆₀), 145.99 (2C, C₆₀), 146.02 (2C, C₆₀), 146.32 (2C, C₆₀), 146.35 (2C, C₆₀), 147.11 (2C, C₆₀), 148.34 (1C, C₆₀), 148.43 (1C, C₆₀), 150.74 (2C, C₆₀), 172.08 (1C, C₆₀OCOAr); FT-IR (KBr): 3527 (m), 2922 (w), 1716 (s), 1265 (s), 1242 (s), 1111 (m), 1065 (s), 1036 (m), 984 (m), 768 (m), 698 (m), 526 (s) cm⁻¹; ESI-MS (-): *m/z* calcd for C₆₉H₉O₃ (M - H⁺): 885.8; found, 885.8; Anal. Calcd for C₆₉H₁₀O₃: C, 93.45; H, 1.14. Found: C, 93.21; H, 1.48.

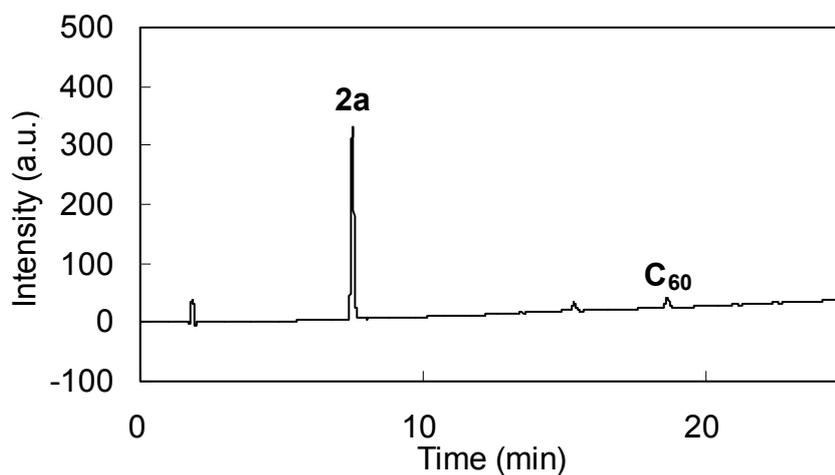
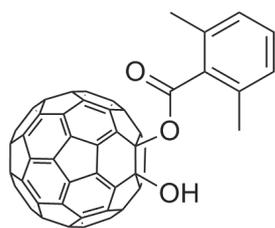


Figure 3-4. HPLC chart for the synthesis of **2a**



2a

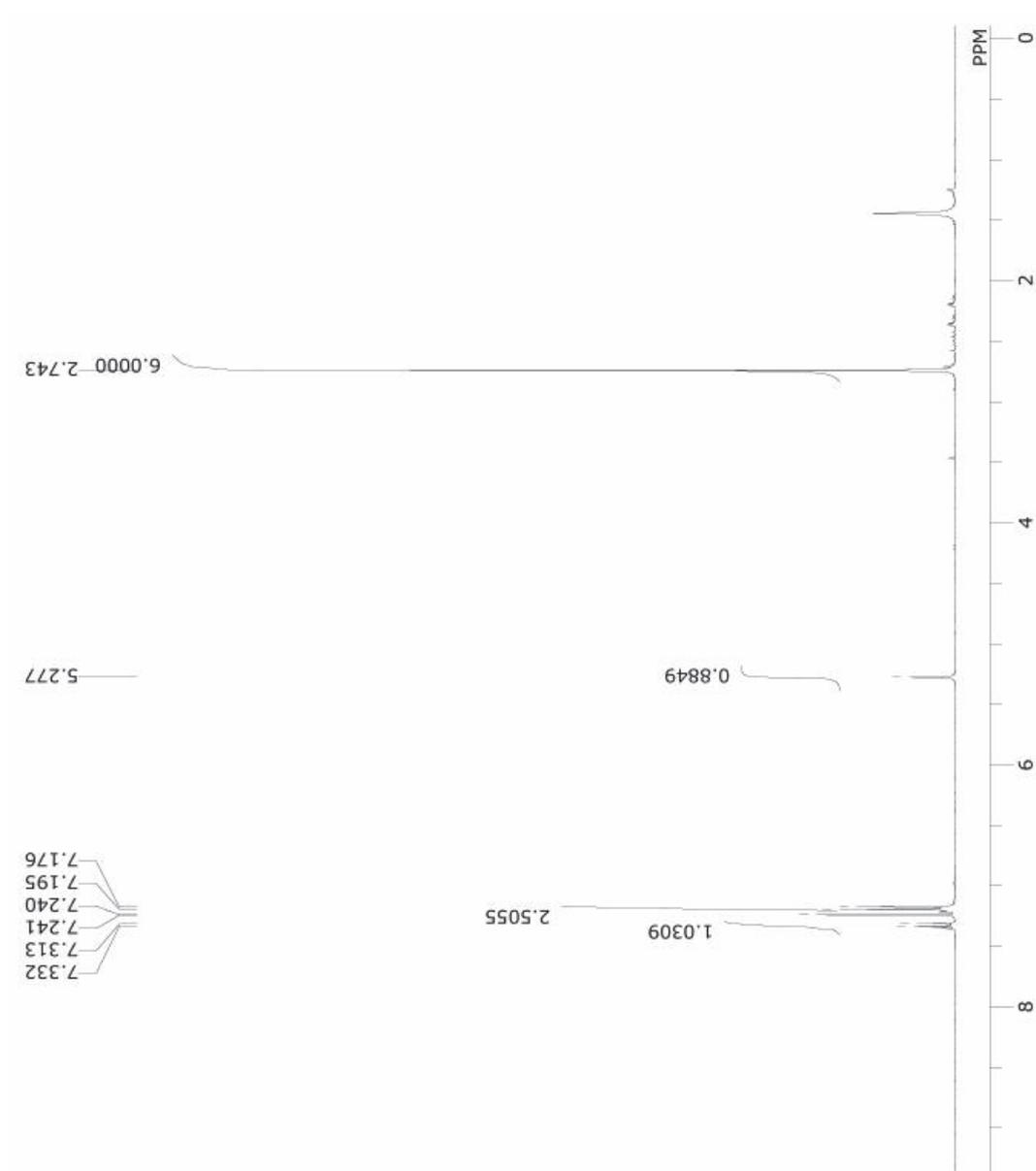
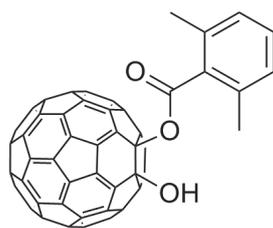


Figure 3-5. ^1H NMR spectrum of **2a** in $\text{CS}_2\text{-CDCl}_3$



2a

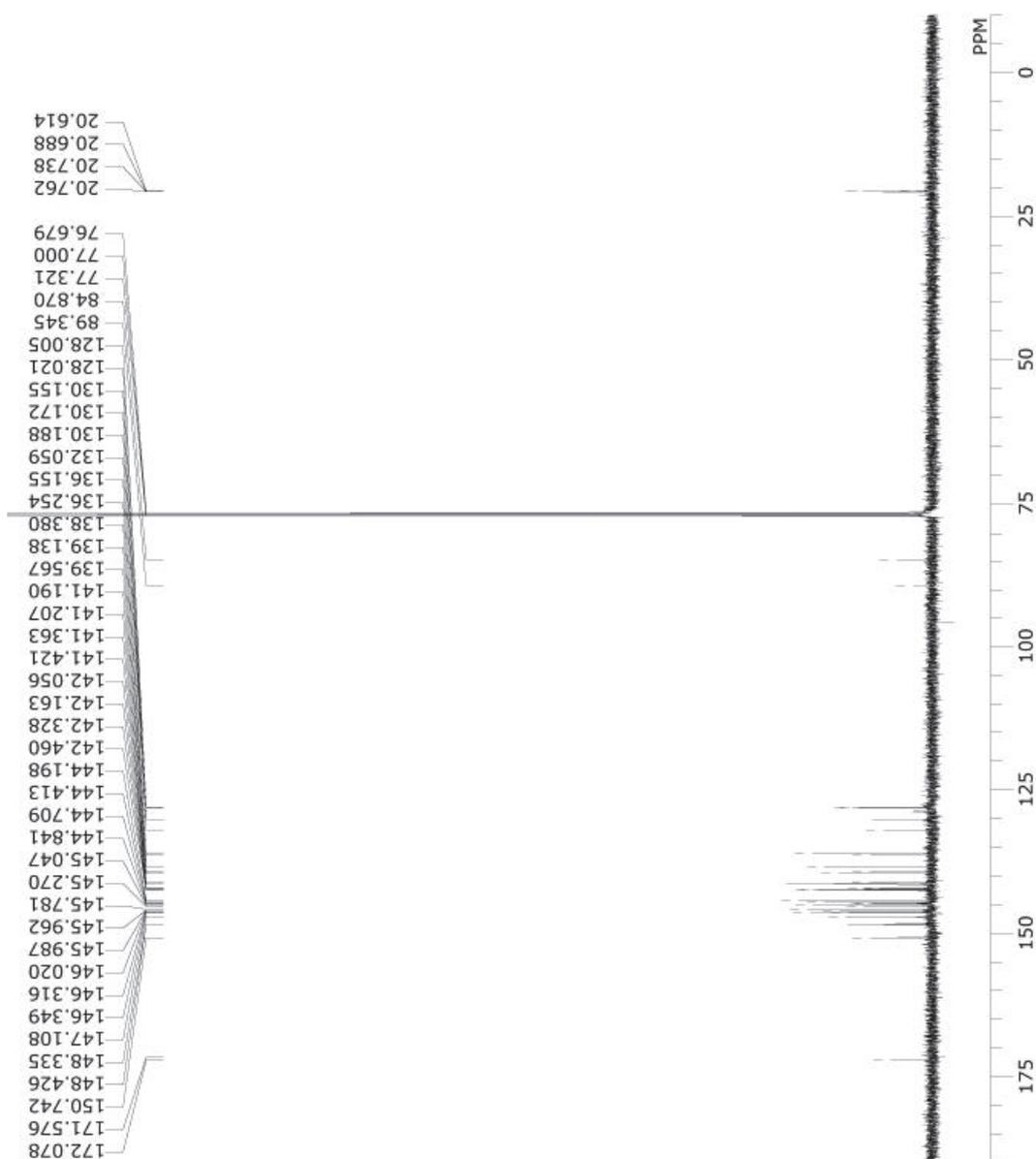


Figure 3-6. ^{13}C NMR spectrum of **2a** in $\text{CS}_2\text{-CDCl}_3$

1-Hydroxy-9-Benzoyloxy-1,9-Dihydro(C₆₀-I_h)[5,6]fullerene (2b)

To a mixture of C₆₀ (500 mg, 0.69 mmol) and benzoic acid (854 mg, 6.9 mmol) in 1,1,2,2-tetrachloroethane (25 mL) at 25 °C, FeCl₃ (2.25 g, 14 mmol) was added. After stirring for 8 h, an adequate amount of water was added to quench the reaction. The product was extracted with toluene (200 mL). The organic layer was washed with distilled water, and solvent was evaporated. Purification of the product was performed by preparative HPLC separation (Buckyprep column, eluent: toluene/2-propanol = 9/1) to obtain the title compound (84 mg, 14% isolated yield, analytically pure) as black crystals. ¹H NMR (400 MHz, CDCl₃/CS₂): δ 5.23 (s, 1H, OH), 7.63 (t, *J* = 7.8 Hz, 2H, Ph), 7.74 (t, *J* = 7.6 Hz, 1H, Ar), 8.51 (d, *J* = 7.8 Hz, 2H, Ar); ¹³C NMR (100 MHz, CDCl₃/CS₂): δ 84.99 (1C, C₆₀OH), 89.11 (1C, C₆₀OCOPh), 128.56 (2C, Ph), 129.13 (1C, Ph), 130.40 (2C, Ph), 133.82 (1C, Ph), 136.27 (2C, C₆₀), 138.43 (2C, C₆₀), 139.00 (2C, C₆₀), 139.51 (2C, C₆₀), 141.17 (2C, C₆₀), 141.21 (2C, C₆₀), 141.35 (2C, C₆₀), 141.40 (2C, C₆₀), 142.06 (2C, C₆₀), 142.16 (2C, C₆₀), 142.30 (2C, C₆₀), 142.44 (4C, C₆₀), 144.43 (2C, C₆₀), 144.45 (2C, C₆₀), 144.71 (2C, C₆₀), 144.87 (2C, C₆₀), 145.01 (4C, C₆₀), 145.29 (2C, C₆₀), 145.76 (2C, C₆₀), 145.95 (2C, C₆₀), 145.97 (2C, C₆₀), 146.06 (2C, C₆₀), 146.31 (2C, C₆₀), 146.34 (2C, C₆₀), 147.31 (2C, C₆₀), 148.32 (1C, C₆₀), 148.43 (1C, C₆₀), 150.87 (2C, C₆₀), 169.08 (1C, C₆₀OCOPh); FT-IR (KBr): 3512 (m), 1705 (s), 1273 (s), 1090 (s), 1066 (m), 991 (m), 708 (m), 526 (s) cm⁻¹; ESI-MS (-): *m/z* calcd for C₆₇H₅O₃ (M - H⁺): 857.8; found, 858.0; Anal. Calcd for C₆₇H₆O₃: C, 93.71; H, 0.70. Found: C, 93.56; H, 0.50.

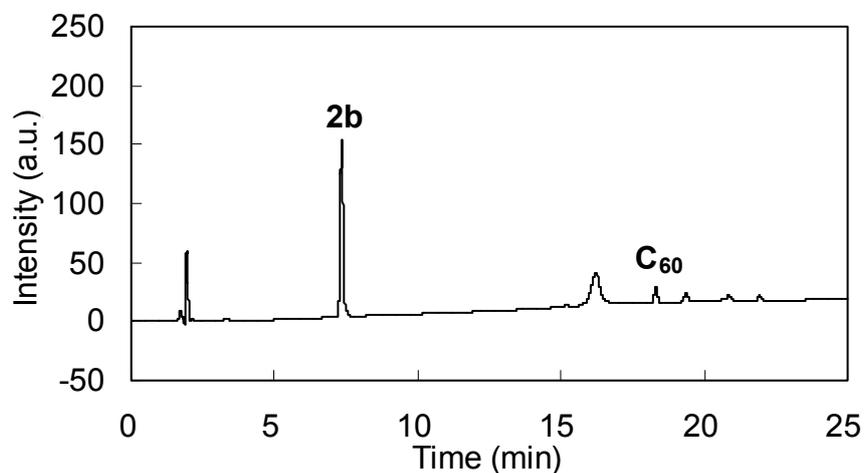
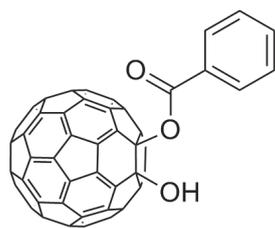


Figure 3-7. HPLC chart for the synthesis of **2b**



2b

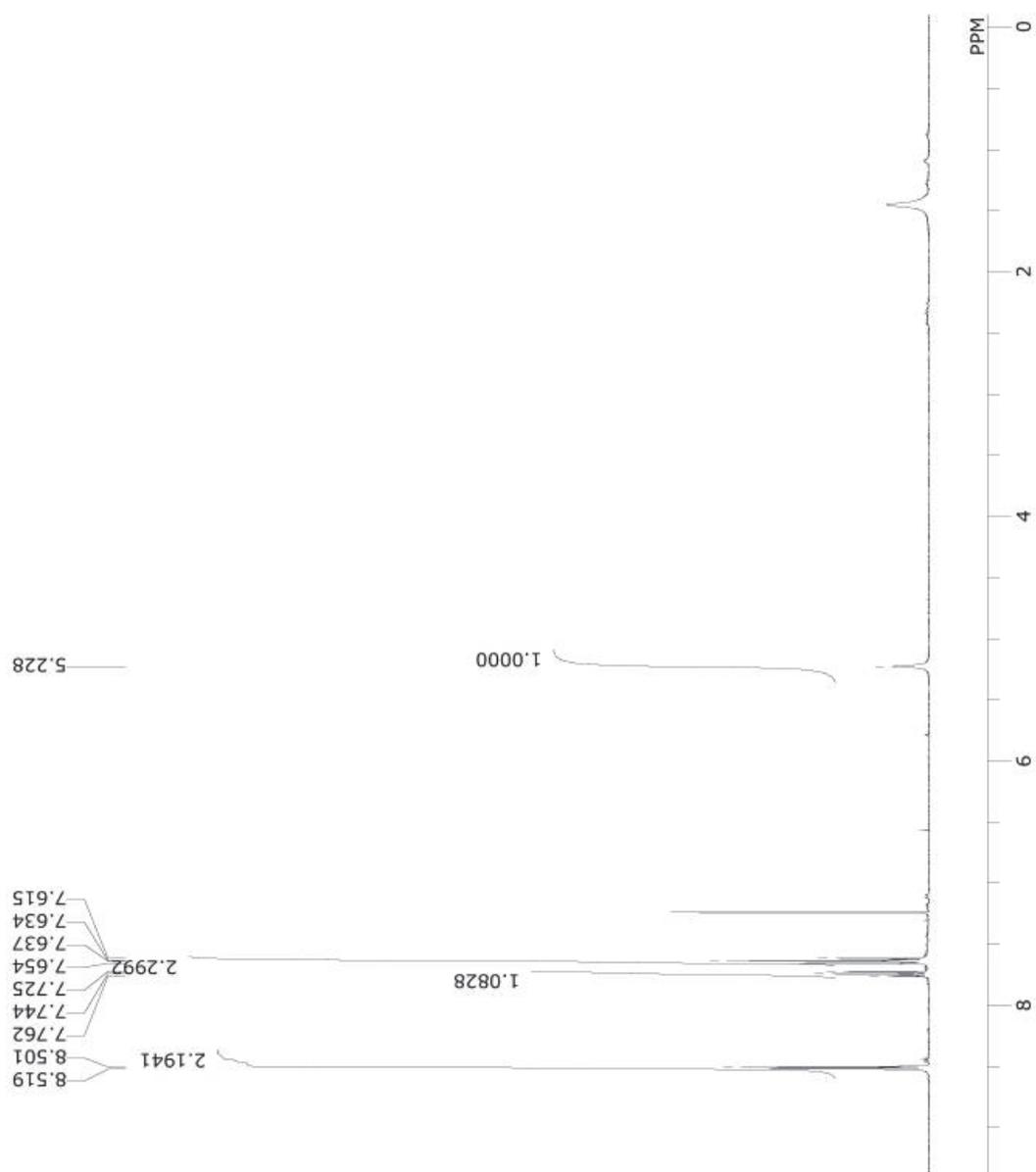
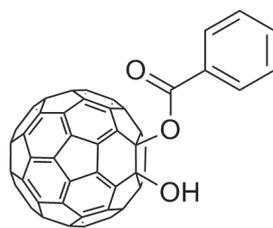


Figure 3-8. ^1H NMR spectrum of **2b** in $\text{CS}_2\text{-CDCl}_3$



1-Hydroxy-9-(2-Methylbenzoyl)oxy-1,9-Dihydro(C₆₀-I_h)[5,6]fullerene (2c)

To a mixture of C₆₀ (500 mg, 0.69 mmol) and 2-toluic acid (944 mg, 6.9 mmol) in 1,1,2,2-tetrachloroethane (25 mL) at 25 °C, FeCl₃ (2.25 g, 14 mmol) was added. After stirring for 8 h, an adequate amount of water was added to quench the reaction. The product was extracted with toluene (200 mL). The organic layer was washed with distilled water, and solvent was evaporated. Purification of the product was performed by preparative HPLC separation (Buckyprep column, eluent: toluene/2-propanol = 9/1) to obtain the title compound (168 mg, 28% isolated yield, analytically pure) as black crystals. ¹H NMR (400 MHz, CDCl₃/CS₂): δ 2.96 (s, 3H, CH₃), 5.27 (s, 1H, OH), 7.42–7.45 (m, 2H, Ar), 7.57 (t, *J* = 7.6 Hz, 1H, Ar), 8.48 (d, *J* = 6.8 Hz, 1H, Ar); ¹³C NMR (100 MHz, CDCl₃/CS₂): δ 22.58 (1C, CH₃), 84.95 (1C, C₆₀OH), 88.98 (1C, C₆₀OCOAr), 128.58 (1C, Ar), 128.25 (1C, Ar), 131.74 (1C, Ar), 131.93 (1C, Ar), 133.01 (1C, Ar), 136.30 (2C, C₆₀), 138.40 (1C, Ar), 138.40 (2C, C₆₀), 139.04 (2C, C₆₀), 139.48 (2C, C₆₀), 141.19 (2C, C₆₀), 141.23 (2C, C₆₀), 141.33 (2C, C₆₀), 141.38 (2C, C₆₀), 142.04 (2C, C₆₀), 142.14 (2C, C₆₀), 142.30 (2C, C₆₀), 142.43 (4C, C₆₀), 144.40 (2C, C₆₀), 144.42 (2C, C₆₀), 144.69 (2C, C₆₀), 144.87 (2C, C₆₀), 145.00 (2C, C₆₀), 145.01 (2C, C₆₀), 145.28 (2C, C₆₀), 145.75 (2C, C₆₀), 145.94 (2C, C₆₀), 145.95 (2C, C₆₀), 146.02 (2C, C₆₀), 146.29 (2C, C₆₀), 146.32 (2C, C₆₀), 147.47 (2C, C₆₀), 148.31 (1C, C₆₀), 148.40 (1C, C₆₀), 150.87 (2C, C₆₀), 169.94 (1C, C₆₀OCOAr); FT-IR (KBr): 3496 (m), 2924 (w), 1703 (s), 1252 (s), 1111 (m), 1065 (s), 1036 (m), 987 (m), 735 (m), 526 (s) cm⁻¹; ESI-MS (-): *m/z* calcd for C₆₈H₇O₃ (M - H⁺): 871.8; found, 871.7; Anal. Calcd for C₆₈H₈O₃: C, 93.58; H, 0.92. Found: C, 93.25; H, 0.77.

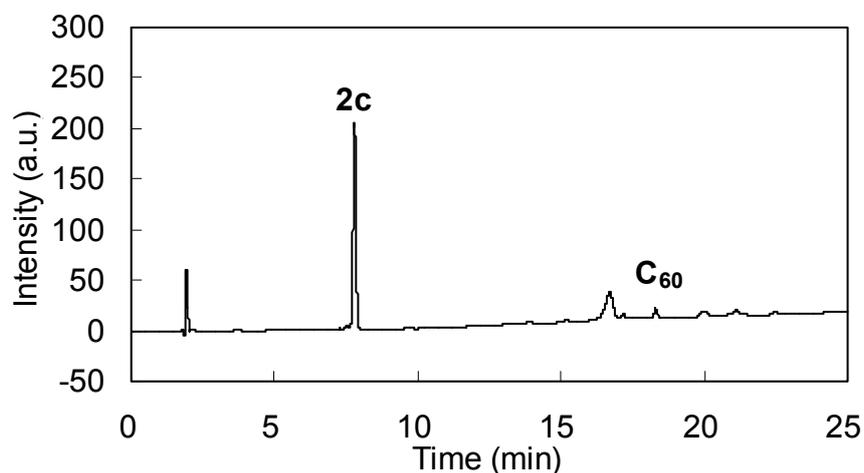
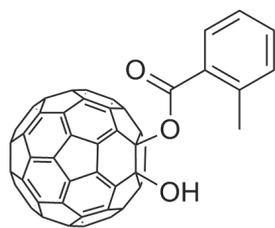


Figure 3-10. HPLC chart for the synthesis of 2c



2c

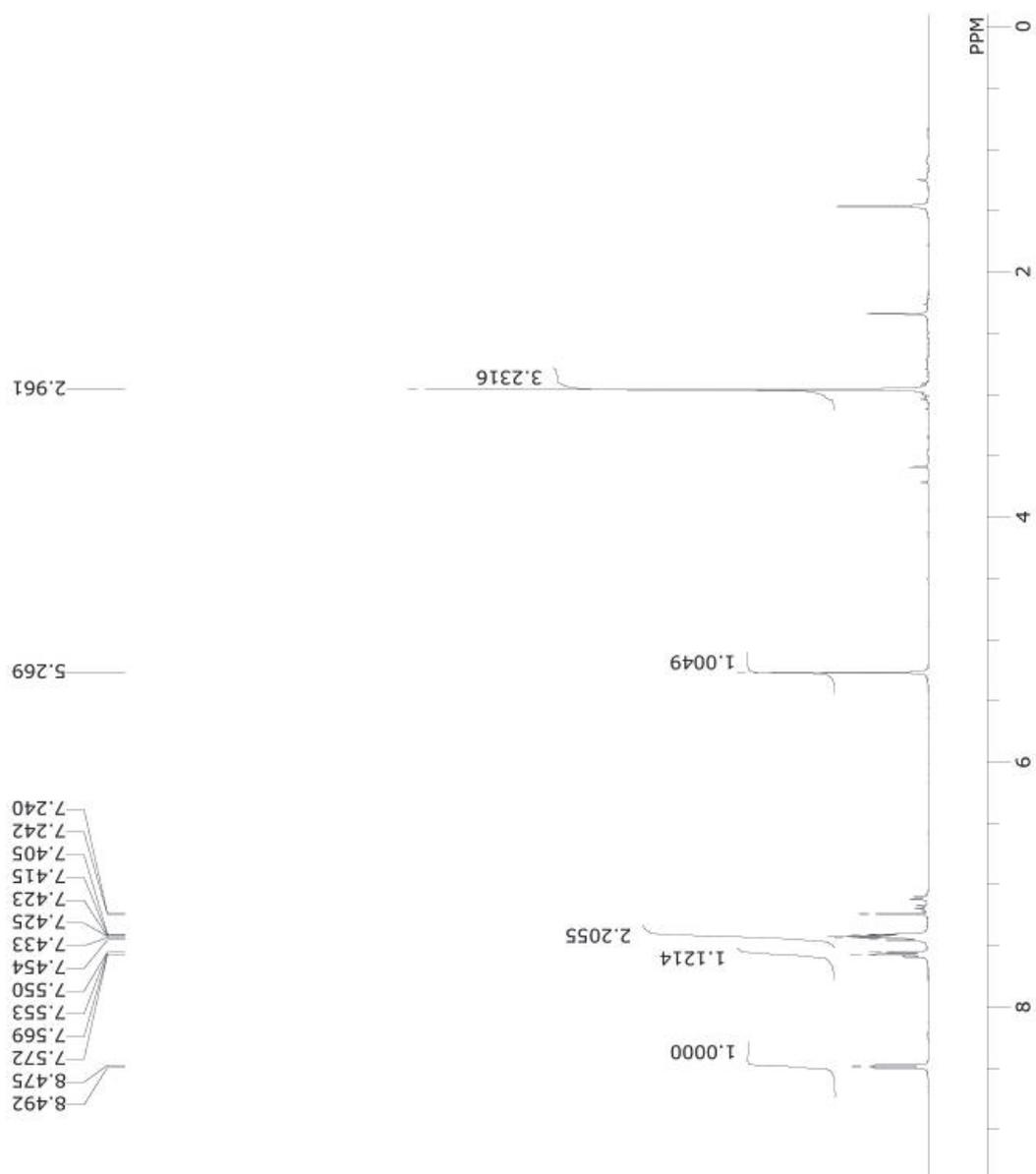
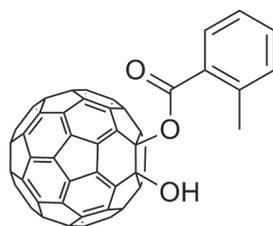


Figure 3-11. ^1H NMR spectrum of **2c** in $\text{CS}_2\text{-CDCl}_3$



2c

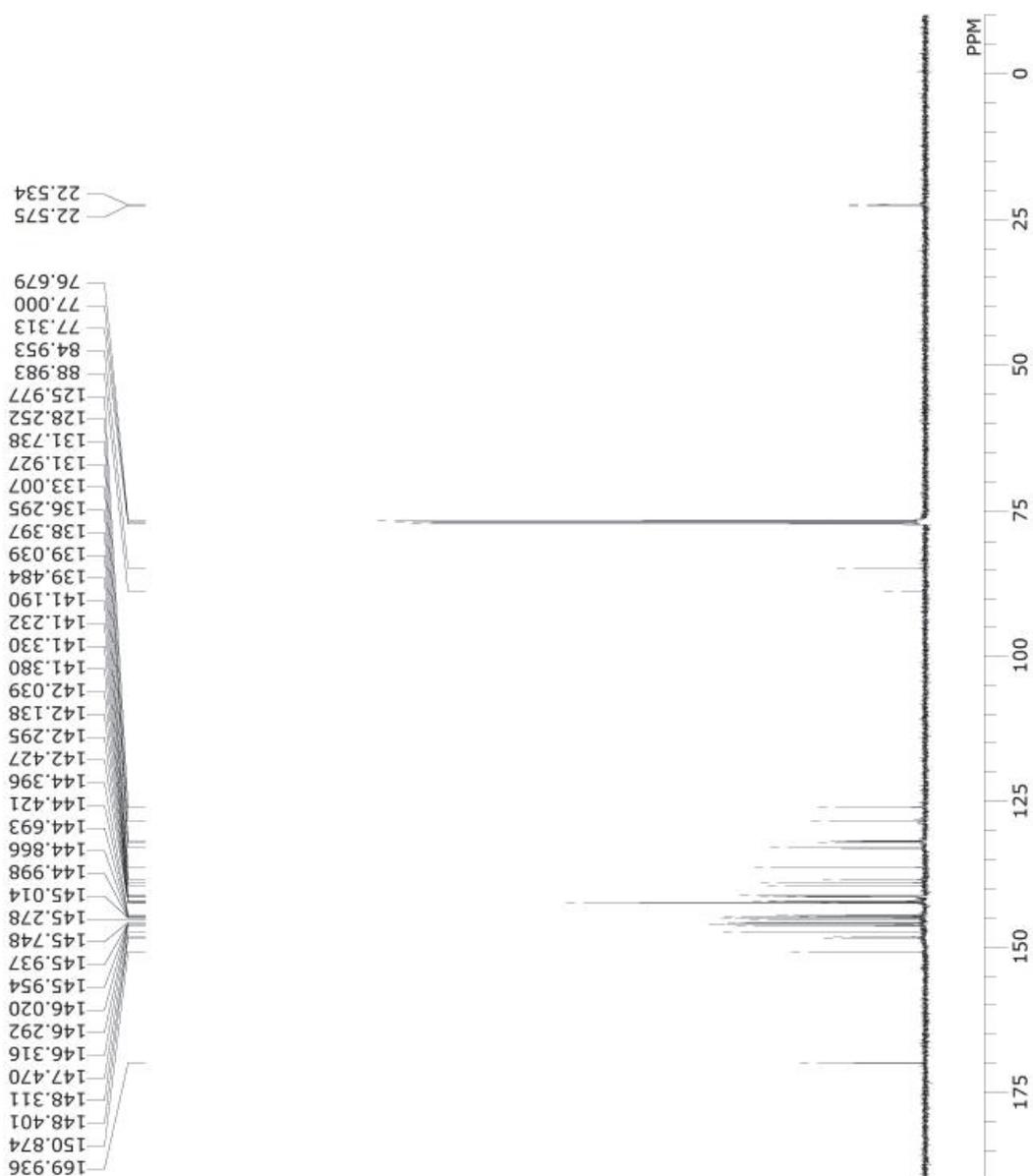


Figure 3-12. ^{13}C NMR spectrum of **2c** in $\text{CS}_2\text{-CDCl}_3$

1-Hydroxy-9-(3-Methylbenzoyl)oxy-1,9-Dihydro(C₆₀-I_h)[5,6]fullerene (2d)

To a mixture of C₆₀ (501 mg, 0.70 mmol) and 3-toluic acid (947 mg, 7.0 mmol) in 1,1,2,2-tetrachloroethane (25 mL) at 25 °C, FeCl₃ (2.25 g, 14 mmol) was added. After stirring for 8 h, an adequate amount of water was added to quench the reaction. The product was extracted with toluene (200 mL). The organic layer was washed with distilled water, and solvent was evaporated. Purification of the product was performed by preparative HPLC separation (Buckyprep column, eluent: toluene/2-propanol = 9/1) to obtain the title compound (150 mg, 25% isolated yield, analytically pure) as black crystals. ¹H NMR (400 MHz, CDCl₃/CS₂): δ 2.56 (s, 3H, CH₃), 5.26 (s, 1H, OH), 7.49–7.55 (m, 2H, Ar), 8.30 (d, *J* = 7.6 Hz, 1H, Ar), 8.32 (s, 1H, Ar); ¹³C NMR (100 MHz, CDCl₃/CS₂): δ 21.46 (1C, CH₃), 84.99 (1C, C₆₀OH), 89.04 (1C, C₆₀OCOAr), 127.64 (1C, Ar), 128.50 (1C, Ar), 129.02 (1C, Ar), 130.92 (1C, Ar), 134.64 (1C, Ar), 136.27 (2C, C₆₀), 138.27 (2C, C₆₀), 138.41 (1C, Ar), 138.98 (2C, C₆₀), 139.48 (2C, C₆₀), 141.17 (2C, C₆₀), 141.20 (2C, C₆₀), 141.33 (2C, C₆₀), 141.37 (2C, C₆₀), 142.05 (2C, C₆₀), 142.14 (2C, C₆₀), 142.29 (2C, C₆₀), 142.42 (4C, C₆₀), 144.41 (2C, C₆₀), 144.45 (2C, C₆₀), 144.69 (2C, C₆₀), 144.88 (2C, C₆₀), 145.00 (2C, C₆₀), 145.01 (2C, C₆₀), 145.28 (2C, C₆₀), 145.74 (2C, C₆₀), 145.94 (2C, C₆₀), 146.04 (2C, C₆₀), 146.29 (2C, C₆₀), 146.33 (2C, C₆₀), 147.36 (2C, C₆₀), 148.30 (2C, C₆₀), 148.41 (1C, C₆₀), 150.90 (1C, C₆₀), 169.29 (1C, C₆₀OCOAr); FT-IR (KBr): 3512 (m), 2912 (w), 1701 (s), 1277 (s), 1192 (s), 1101 (m), 1036 (s), 999 (m), 742 (m), 526 (s) cm⁻¹; ESI-MS (-): *m/z* calcd for C₆₈H₇O₃ (M - H⁺): 871.8; found, 871.8; Anal. Calcd for C₆₈H₈O₃: C, 93.58; H, 0.92. Found: C, 93.51; H, 1.11.

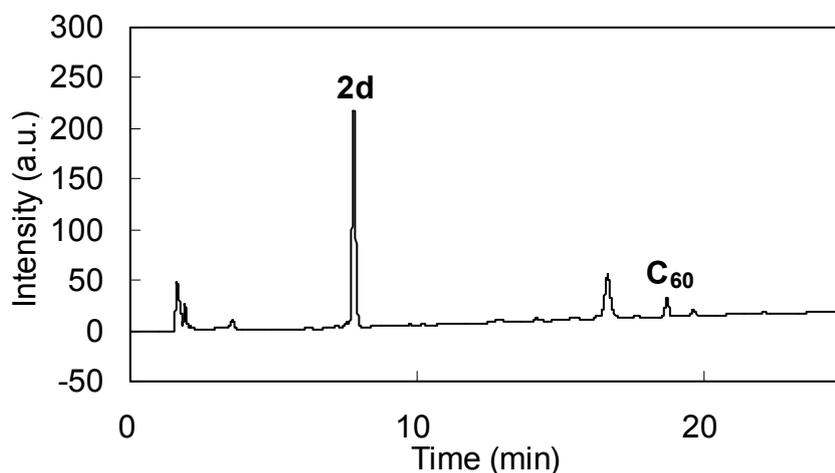
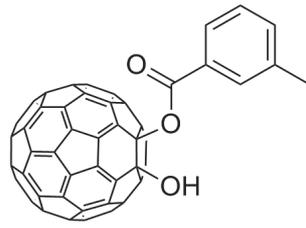


Figure 3-13. HPLC chart for the synthesis of **2d**



2d

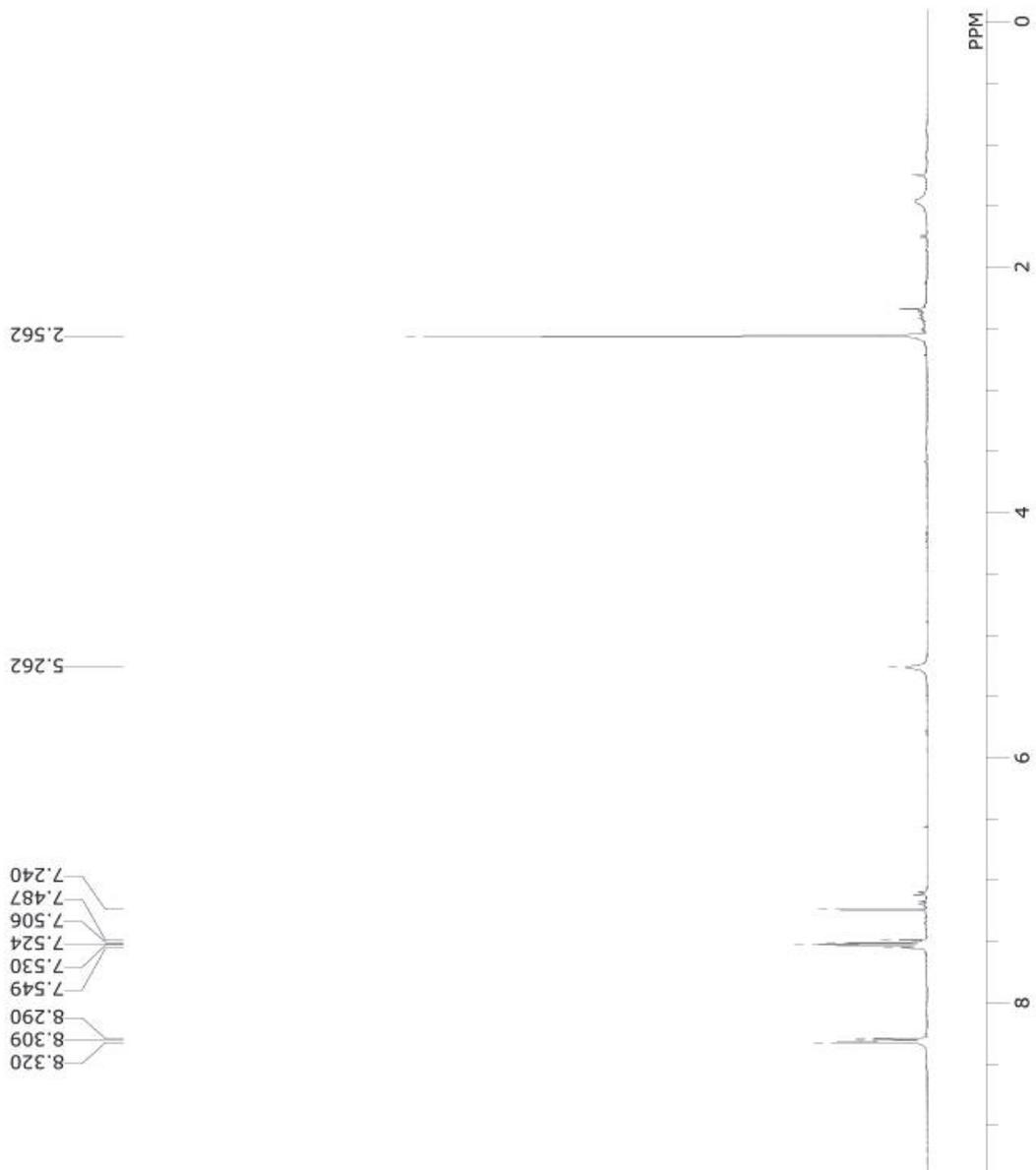
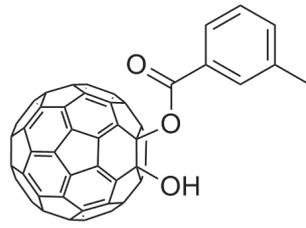


Figure 3-14. ^1H NMR spectrum of **2d** in $\text{CS}_2\text{-CDCl}_3$



2d

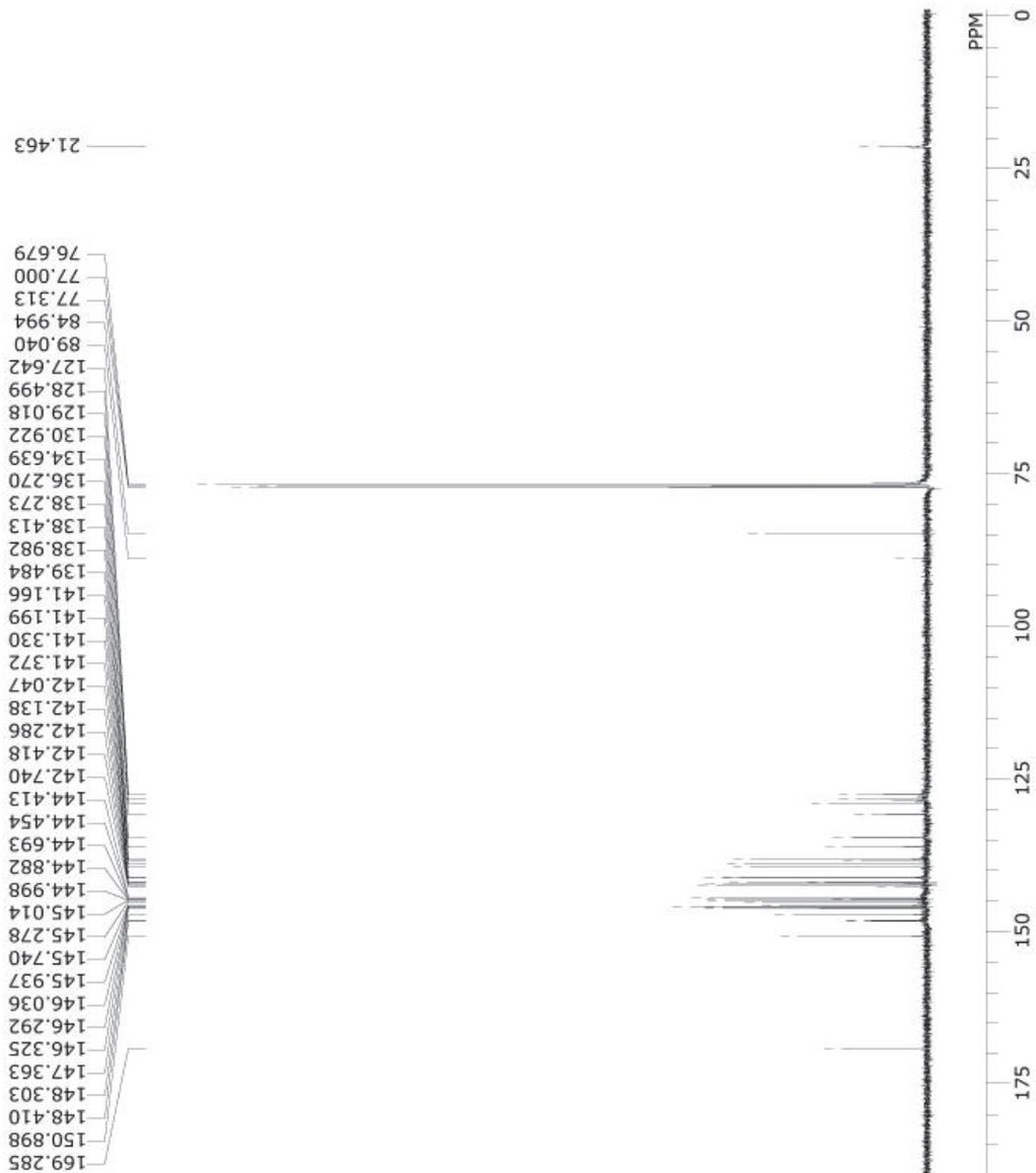


Figure 3-15. ^{13}C NMR spectrum of **2d** in $\text{CS}_2\text{-CDCl}_3$

1-Hydroxy-9-(4-Methylbenzoyl)oxy-1,9-Dihydro(C₆₀-I_h)[5,6]fullerene (2e)

To a mixture of C₆₀ (501 mg, 0.70 mmol) and 4-toluic acid (948 mg, 7.0 mmol) in 1,1,2,2-tetrachloroethane (25 mL) at 25 °C, FeCl₃ (2.24 g, 14 mmol) was added. After stirring for 7 h, an adequate amount of water was added to quench the reaction. The product was extracted with toluene (200 mL). The organic layer was washed with distilled water, and solvent was evaporated. Purification of the product was performed by preparative HPLC separation (Buckyprep column, eluent: toluene/2-propanol = 9/1) to obtain the title compound (146 mg, 24% isolated yield, analytically pure) as black crystals. ¹H NMR (400 MHz, CDCl₃/CS₂): δ 2.55 (s, 3H, CH₃), 5.29 (s, 1H, OH), 7.42 (d, *J* = 8.4 Hz, 2H, Ar), 8.39 (d, *J* = 8.4 Hz, 2H, Ar); ¹³C NMR (100 MHz, CDCl₃/CS₂): δ 22.41 (1C, CH₃), 85.85 (1C, C₆₀OH), 89.45 (1C, C₆₀OCOAr), 126.77 (1C, Ar), 129.74 (2C, Ar), 130.96 (2C, Ar), 136.70 (2C, C₆₀), 138.84 (2C, C₆₀), 139.42 (2C, C₆₀), 139.93 (1C, Ar), 139.93 (2C, C₆₀), 141.61 (2C, C₆₀), 141.64 (2C, C₆₀), 141.76 (2C, C₆₀), 141.81 (2C, C₆₀), 142.49 (2C, C₆₀), 142.58 (2C, C₆₀), 142.73 (2C, C₆₀), 142.86 (4C, C₆₀), 144.86 (2C, C₆₀), 144.90 (2C, C₆₀), 145.14 (2C, C₆₀), 145.33 (2C, C₆₀), 145.44 (4C, C₆₀), 145.72 (2C, C₆₀), 146.18 (2C, C₆₀), 146.37 (2C, C₆₀), 146.39 (2C, C₆₀), 146.46 (2C, C₆₀), 146.73 (2C, C₆₀), 146.77 (2C, C₆₀), 147.87 (2C, C₆₀), 148.75 (1C, C₆₀), 148.85 (1C, C₆₀), 151.37 (2C, C₆₀), 169.70 (1C, C₆₀OCOAr); FT-IR (KBr): 3506 (m), 2912 (w), 1701 (s), 1610 (m), 1275 (s), 1178 (m), 1092 (s), 1034 (m), 989 (m), 748 (m), 526 (s) cm⁻¹; ESI-MS (-): *m/z* calcd for C₆₈H₇O₃ (M - H⁺): 871.8; found, 871.8; Anal. Calcd for C₆₈H₈O₃: C, 93.58; H, 0.92. Found: C, 93.35; H, 1.08.

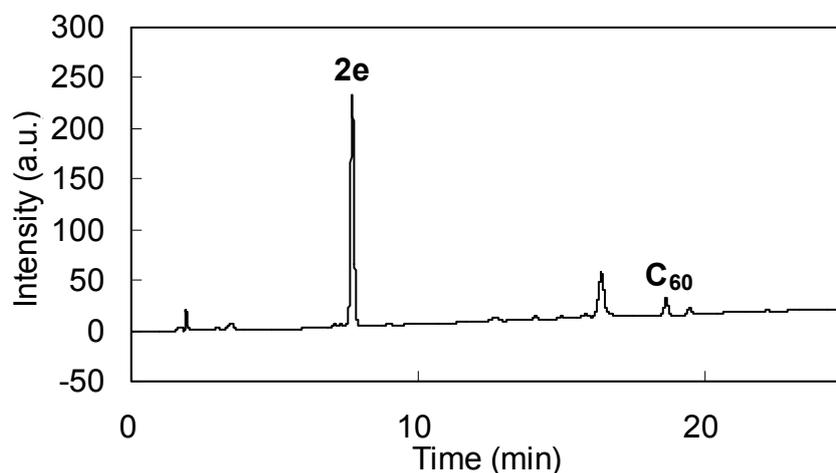
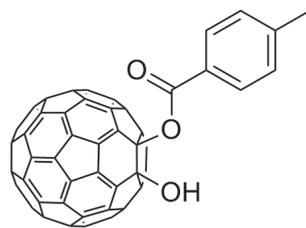


Figure 3-16. HPLC chart for the synthesis of 2e



2e

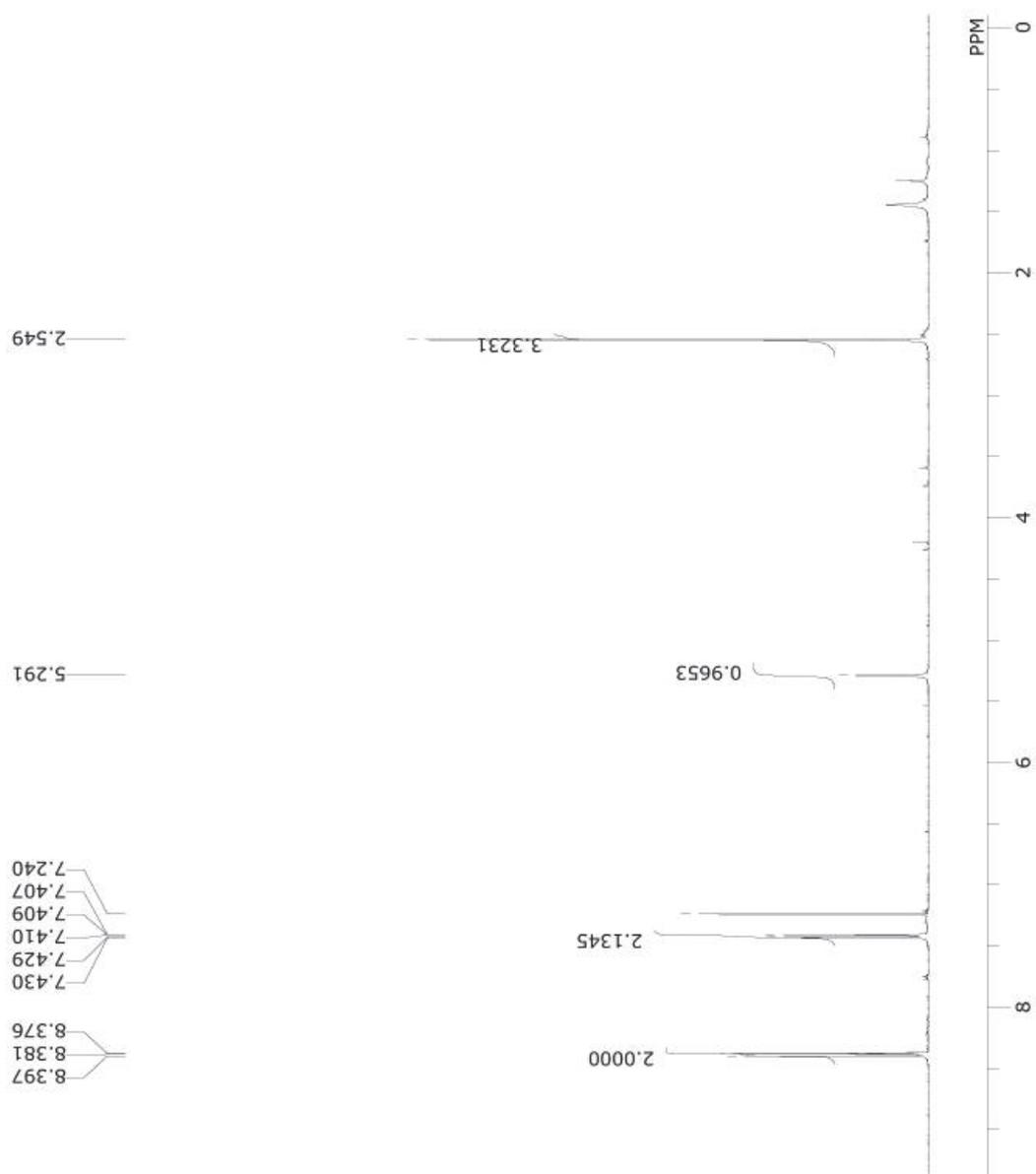
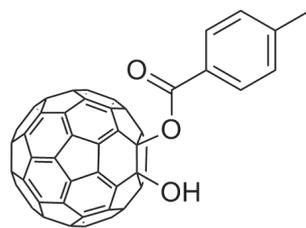


Figure 3-17. ^1H NMR spectrum of **2e** in $\text{CS}_2\text{-CDCl}_3$



2e

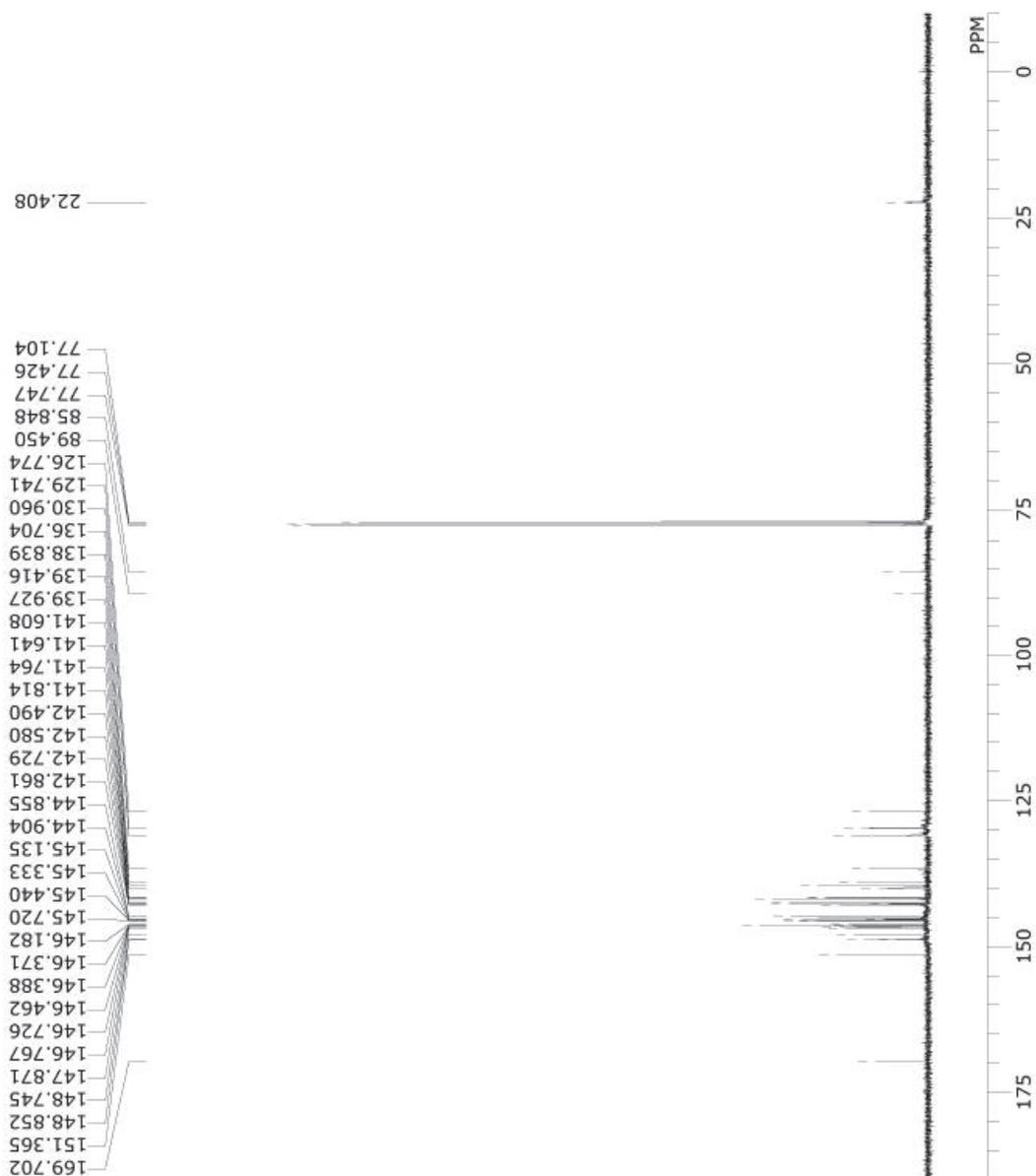


Figure 3-18. ¹³C NMR spectrum of **2e** in CS₂-CDCl₃

1-Hydroxy-9-(2,4-Dimethylbenzoyloxy)-1,9-Dihydro(C₆₀-I_h)[5,6]fullerene (2f)

To a mixture of C₆₀ (502 mg, 0.70 mmol) and 2,4-dimethylbenzoic acid (1.03 g, 6.9 mmol) in 1,1,2,2-tetrachloroethane (25 mL) at 25 °C, FeCl₃ (2.25 g, 14 mmol) was added. After stirring for 8 h, an adequate amount of water was added to quench the reaction. The product was extracted with toluene (200 mL). The organic layer was washed with distilled water, and solvent was evaporated. Purification of the product was performed by preparative HPLC separation (Buckyprep column, eluent: toluene/2-propanol = 9/1) to obtain the title compound (185 mg, 30% isolated yield, analytically pure) as black crystals. ¹H NMR (400 MHz, CDCl₃/CS₂): δ 2.48 (s, 3H, CH₃), 2.92 (s, 3H, CH₃), 5.27 (s, 1H, OH), 7.18–7.22 (m, 2H, Ar), 8.40 (d, *J* = 7.6 Hz, 1H, Ar); ¹³C NMR (100 MHz, CDCl₃/CS₂): δ 21.74 (1C, CH₃), 22.80 (1C, CH₃), 85.04 (1C, C₆₀OH), 88.92 (1C, C₆₀OCOAr), 125.05 (1C, Ar), 126.75 (1C, Ar), 127.97 (1C, Ar), 128.72 (1C, Ar), 133.34 (1C, Ar), 134.83 (1C, Ar), 136.32 (2C, C₆₀), 138.41 (2C, C₆₀), 139.01 (2C, C₆₀), 139.51 (2C, C₆₀), 141.24 (2C, C₆₀), 141.36 (2C, C₆₀), 141.41 (2C, C₆₀), 141.53 (2C, C₆₀), 142.07 (2C, C₆₀), 142.17 (2C, C₆₀), 142.32 (2C, C₆₀), 142.45 (4C, C₆₀), 144.46 (4C, C₆₀), 144.73 (2C, C₆₀), 144.95 (2C, C₆₀), 145.03 (2C, C₆₀), 145.05 (2C, C₆₀), 145.33 (2C, C₆₀), 145.77 (2C, C₆₀), 145.96 (2C, C₆₀), 145.98 (2C, C₆₀), 146.04 (2C, C₆₀), 146.33 (2C, C₆₀), 146.35 (2C, C₆₀), 147.64 (2C, C₆₀), 148.34 (1C, C₆₀), 148.43 (1C, C₆₀), 150.99 (2C, C₆₀), 170.04 (1C, C₆₀OCOAr); FT-IR (KBr): 3518 (m), 2918 (w), 1695 (s), 1612 (m), 1432 (m), 1296 (s), 1259 (s), 1142 (m), 1065 (s), 1038 (s), 993 (m), 769 (m), 526 (s) cm⁻¹; ESI-MS (-): *m/z* calcd for C₆₉H₉O₃ (M - H⁺): 885.8; found, 886.0; Anal. Calcd for C₆₉H₁₀O₃: C, 93.45; H, 1.14. Found: C, 93.68; H, 1.03.

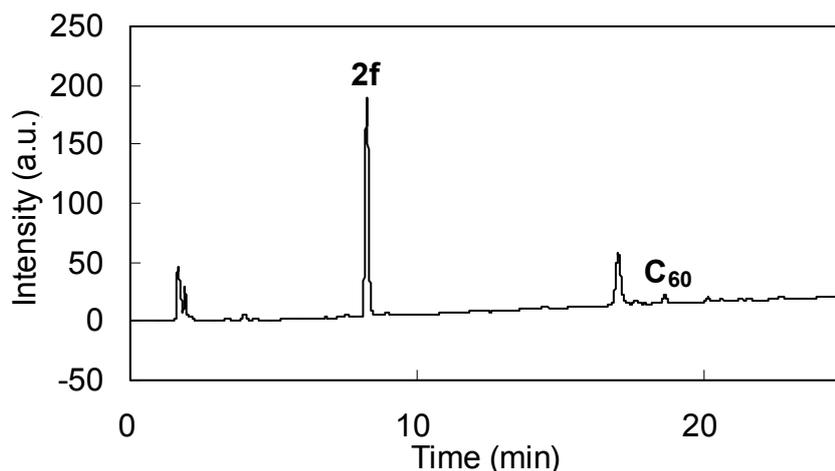
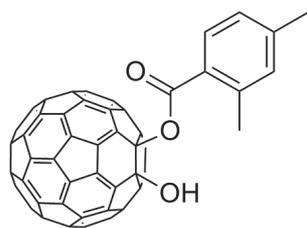


Figure 3-19. HPLC chart for the synthesis of 2f



2f

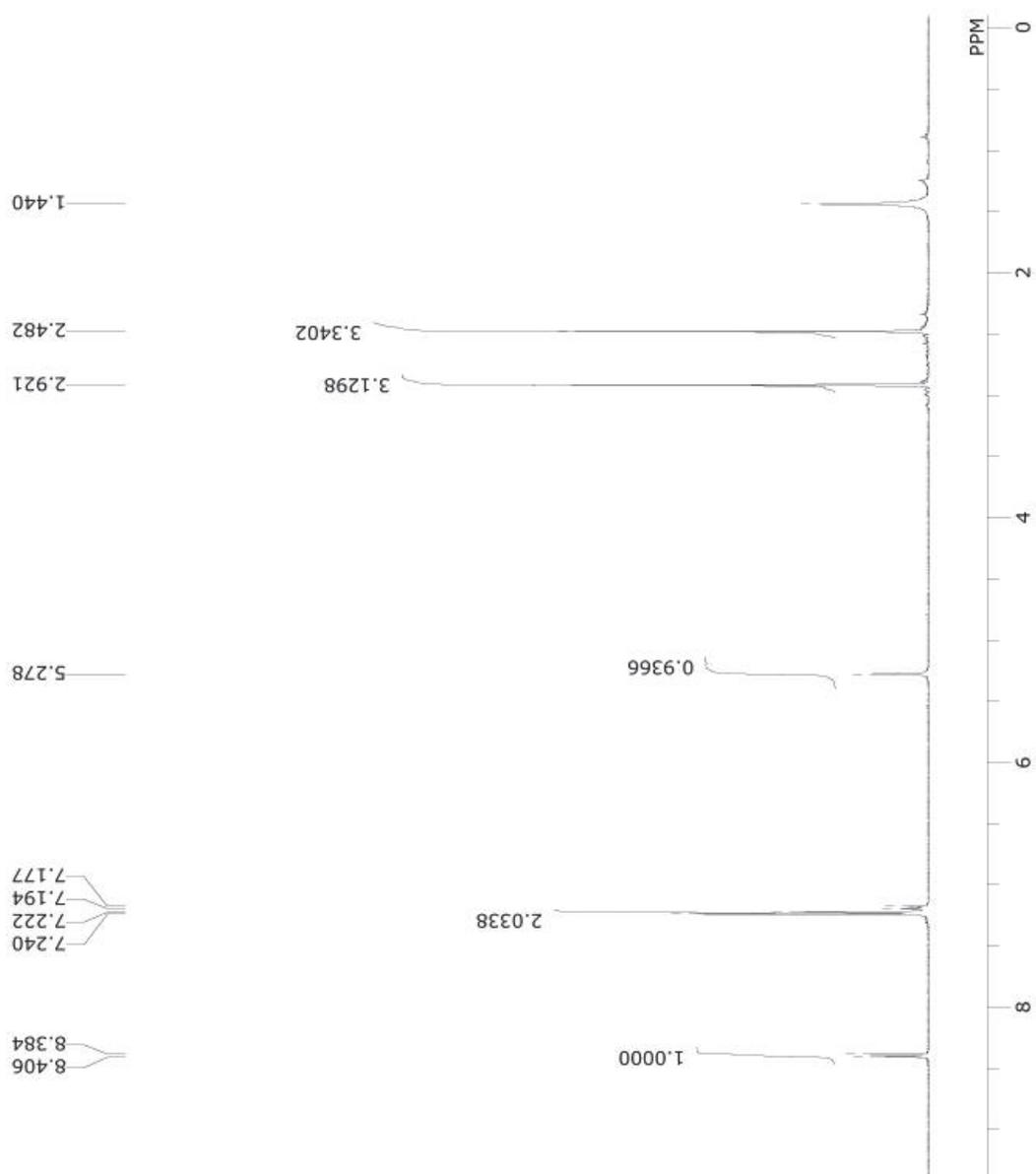
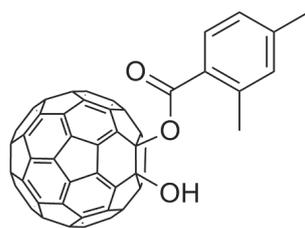


Figure 3-20. ¹H NMR spectrum of **2f** in CS₂-CDCl₃



2f

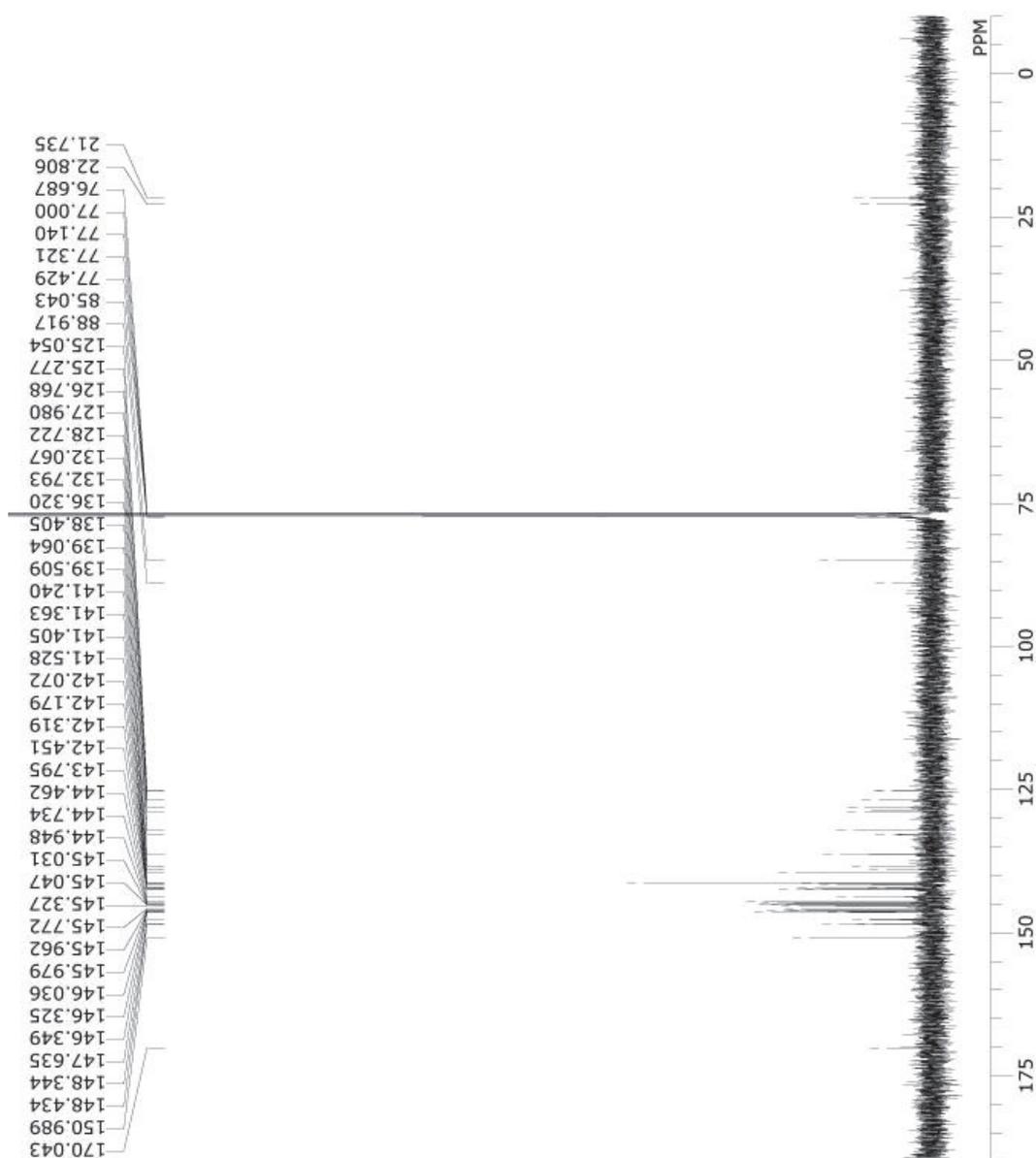


Figure 3-21. ¹³C NMR spectrum of **2f** in CS₂-CDCl₃

1-Hydroxy-9-(3,5-Dimethylbenzoyloxy)-1,9-Dihydro(C₆₀-I_h)[5,6]fullerene (2g)

To a mixture of C₆₀ (500 mg, 0.69 mmol) and 3,5-dimethylbenzoic acid (1.03 g, 6.9 mmol) in 1,1,2,2-tetrachloroethane (25 mL) at 25 °C, FeCl₃ (2.25 g, 14 mmol) was added. After stirring for 8 h, an adequate amount of water was added to quench the reaction. The product was extracted with toluene (200 mL). The organic layer was washed with distilled water, and solvent was evaporated. Purification of the product was performed by preparative HPLC separation (Buckyprep column, eluent: toluene/2-propanol = 9/1) to obtain the title compound (134 mg, 22% isolated yield, analytically pure) as black crystals. ¹H NMR (400 MHz, CDCl₃/CS₂): δ 2.51 (s, 6H, CH₃), 5.30 (s, 1H, OH), 7.35 (s, 1H, Ar), 8.12 (s, 2H, Ar); ¹³C NMR (100 MHz, CDCl₃/CS₂): δ 21.36 (2C, CH₃), 85.01 (1C, C₆₀OH), 88.99 (1C, C₆₀OCOAr), 128.22 (2C, Ar), 128.91 (1C, Ar), 135.62 (1C, Ar), 136.28 (2C, C₆₀), 138.17 (2C, C₆₀), 138.41 (2C, Ar), 138.98 (2C, C₆₀), 139.48 (2C, C₆₀), 141.17 (2C, C₆₀), 141.20 (2C, C₆₀), 141.33 (2C, C₆₀), 141.37 (2C, C₆₀), 142.06 (2C, C₆₀), 142.14 (2C, C₆₀), 142.29 (2C, C₆₀), 142.43 (4C, C₆₀), 144.42 (2C, C₆₀), 144.48 (2C, C₆₀), 144.69 (2C, C₆₀), 144.90 (2C, C₆₀), 145.00 (2C, C₆₀), 145.01 (2C, C₆₀), 145.29 (2C, C₆₀), 145.74 (2C, C₆₀), 145.95 (4C, C₆₀), 146.03 (2C, C₆₀), 146.29 (2C, C₆₀), 146.33 (2C, C₆₀), 147.43 (2C, C₆₀), 148.31 (1C, C₆₀), 148.41 (1C, C₆₀), 150.92 (2C, C₆₀), 169.52 (1C, C₆₀OCOAr); FT-IR (KBr): 3525 (m), 2912 (w), 1701 (s), 1311 (s), 1209 (s), 1111 (m), 1036 (m), 1009 (m), 527 (s) cm⁻¹; ESI-MS (-): *m/z* calcd for C₆₉H₉O₃ (M - H⁺): 885.8; found, 886.1; Anal. Calcd for C₆₉H₁₀O₃: C, 93.45; H, 1.14. Found: C, 93.08; H, 0.86.

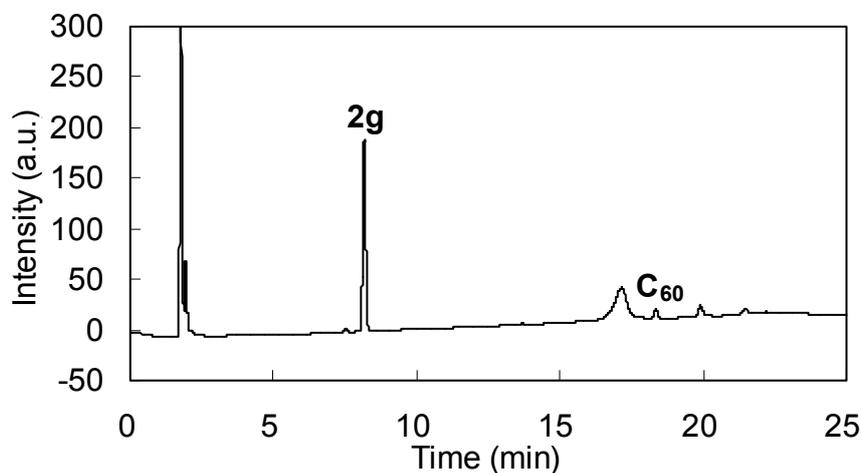


Figure 3-22. HPLC chart for the synthesis of 2g

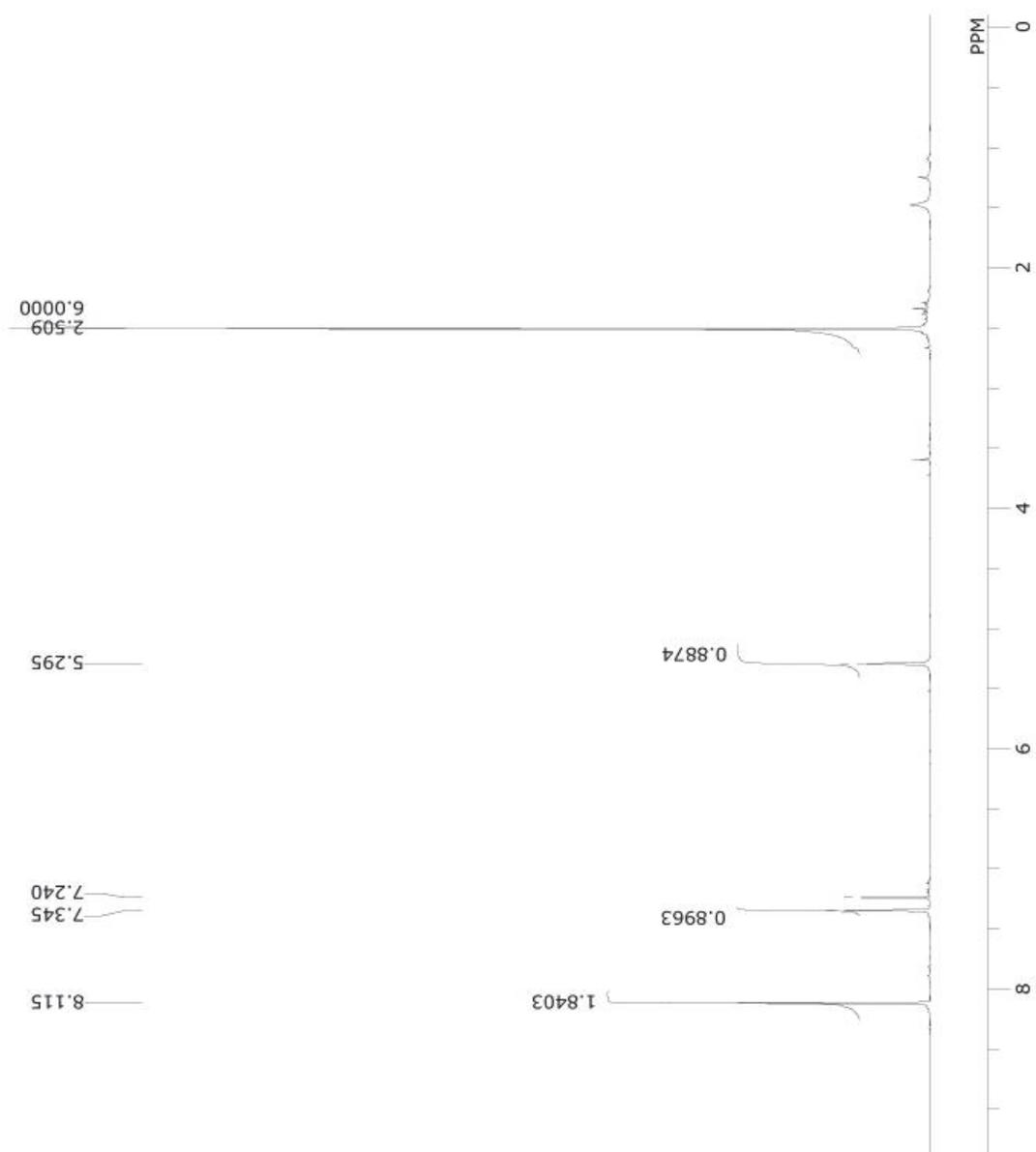
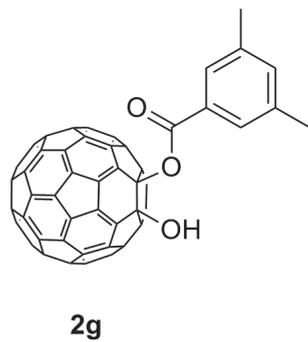


Figure 3-23. ¹H NMR spectrum of **2g** in CS₂-CDCl₃

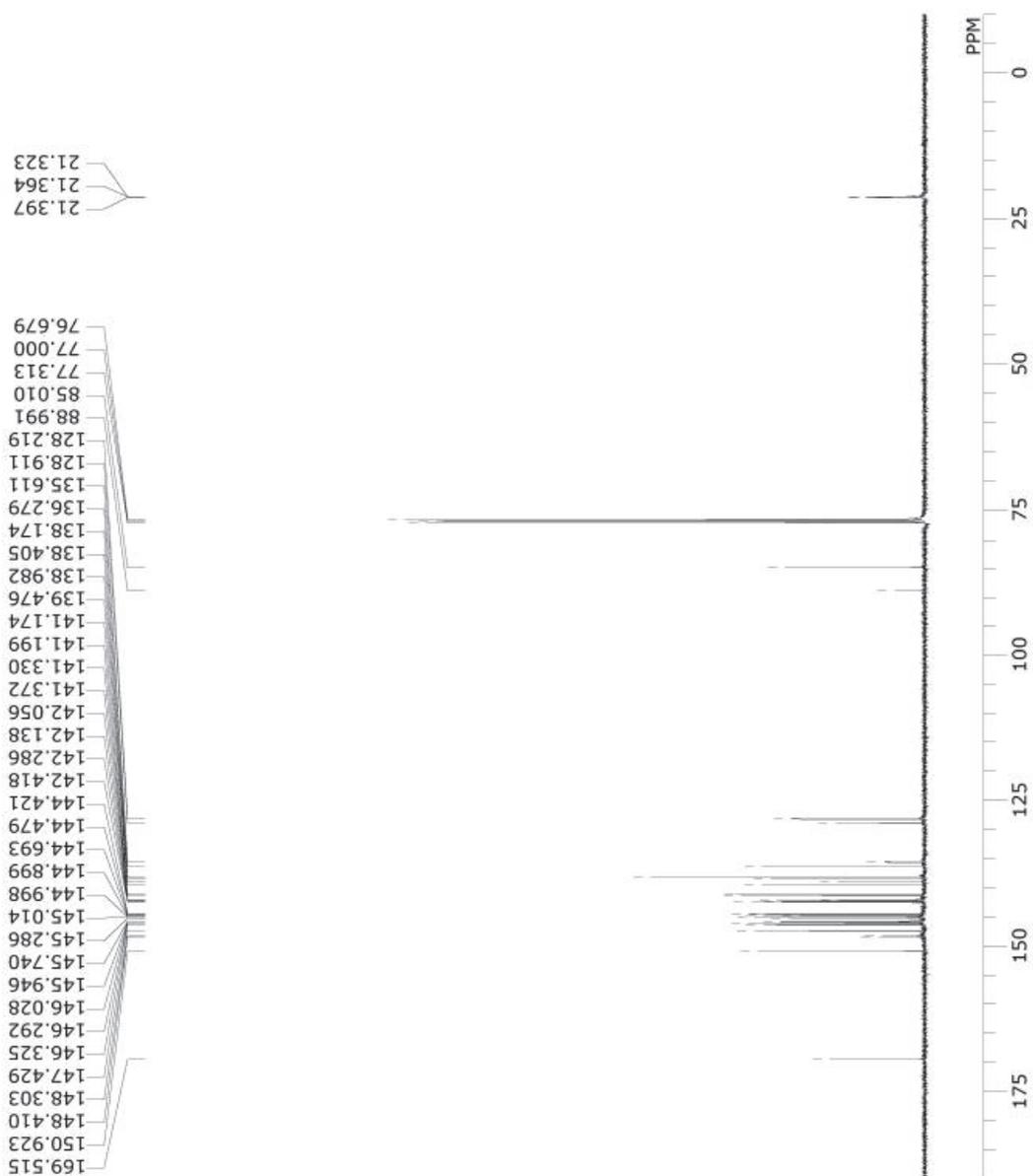
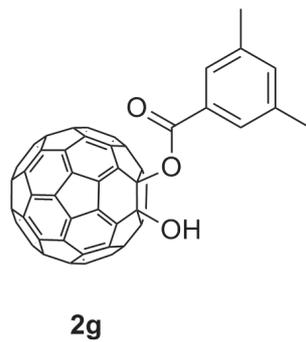


Figure 3-24. ^{13}C NMR spectrum of **2g** in $\text{CS}_2\text{-CDCl}_3$

1-Hydroxy-9-(2-Chlorobenzoyloxy)-1,9-Dihydro(C₆₀-I_h)[5,6]fullerene (2j)

To a mixture of C₆₀ (502 mg, 0.70 mmol) and 2-chlorobenzoic acid (1.09 g, 7.0 mmol) in 1,1,2,2-tetrachloroethane (25 mL) at 25 °C, FeCl₃ (2.25 g, 14 mmol) was added. After stirring for 5 h, an adequate amount of water was added to quench the reaction. The product was extracted with toluene (200 mL). The organic layer was washed with distilled water, and solvent was evaporated. Purification of the product was performed by preparative HPLC separation (Buckyprep column, eluent: toluene/2-propanol = 9/1) to obtain the title compound (216 mg, 35% isolated yield, analytically pure) as black crystals. ¹H NMR (400 MHz, CDCl₃/CS₂): δ 5.19 (s, 1H, OH), 7.51–7.55 (m, 1H, Ar), 7.61–7.63 (m, 2H, Ar), 8.42 (d, *J* = 7.6 Hz, 1H, Ar); ¹³C NMR (100 MHz, CDCl₃/CS₂): δ 85.46 (1C, C₆₀OH), 89.43 (1C, C₆₀OCOAr), 126.65 (1C, Ar), 128.85 (1C, Ar), 131.31 (1C, Ar), 132.44 (1C, Ar), 133.34 (1C, Ar), 134.83 (1C, Ar), 136.33 (2C, C₆₀), 138.45 (2C, C₆₀), 139.05 (2C, C₆₀), 139.52 (2C, C₆₀), 141.16 (2C, C₆₀), 141.19 (2C, C₆₀), 141.37 (2C, C₆₀), 141.41 (2C, C₆₀), 142.07 (2C, C₆₀), 142.15 (2C, C₆₀), 142.31 (2C, C₆₀), 142.44 (2C, C₆₀), 142.45 (2C, C₆₀), 144.40 (2C, C₆₀), 144.42 (2C, C₆₀), 144.69 (2C, C₆₀), 144.80 (2C, C₆₀), 145.02 (2C, C₆₀), 145.04 (2C, C₆₀), 145.28 (2C, C₆₀), 145.78 (2C, C₆₀), 145.98 (4C, C₆₀), 146.08 (2C, C₆₀), 146.32 (2C, C₆₀), 146.34 (2C, C₆₀), 147.04 (2C, C₆₀), 148.34 (1C, C₆₀), 148.43 (1C, C₆₀), 150.65 (2C, C₆₀), 167.53 (1C, C₆₀OCOAr); FT-IR (KBr): 3529 (m), 1718 (s), 1435 (m), 1294 (s), 1248 (s), 1109 (s), 1043 (s), 987 (m), 742 (m), 526 (s) cm⁻¹; ESI-MS (-): *m/z* calcd for C₆₇H₄ClO₃ (M - H⁺): 882.2; found, 892.0; Anal. Calcd for C₆₇H₅ClO₃: C, 90.09; H, 0.56. Found: C, 89.99; H, 0.51.

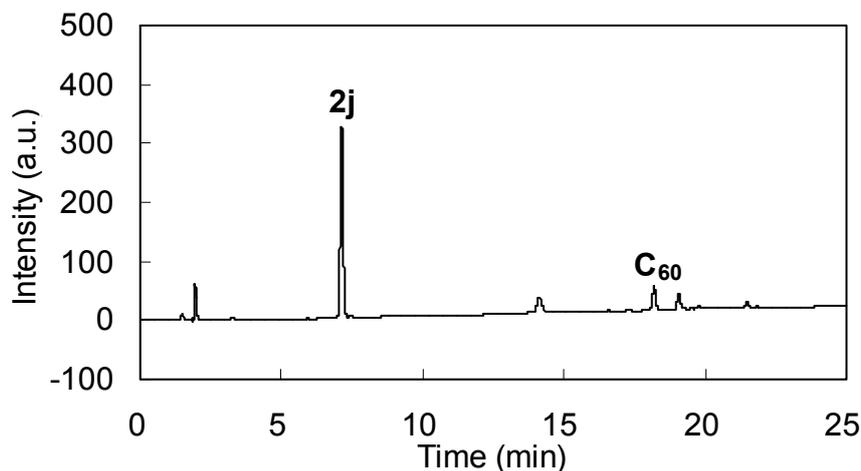
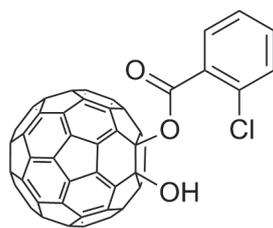


Figure 3-25. HPLC chart for the synthesis of 2j



2j

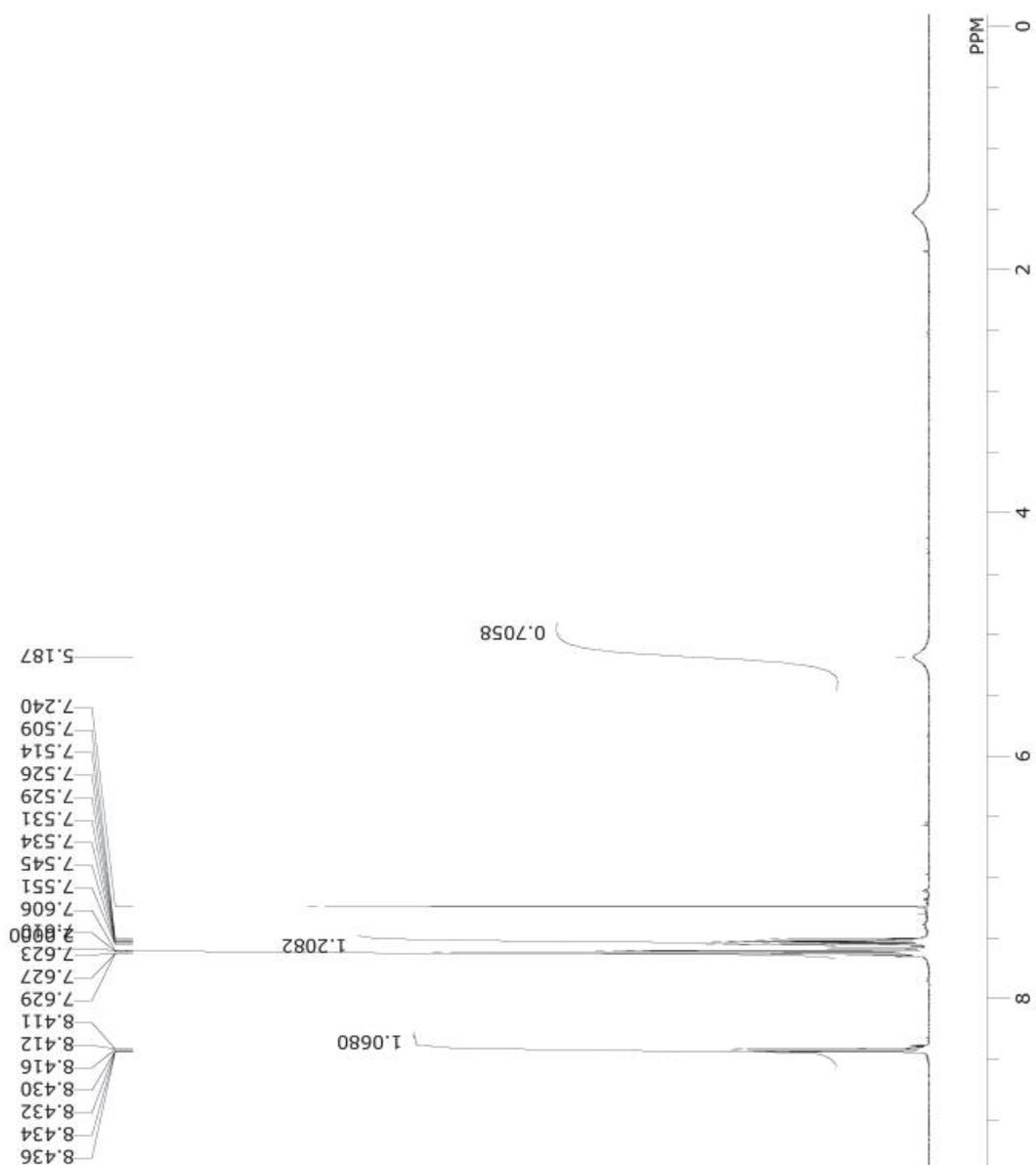
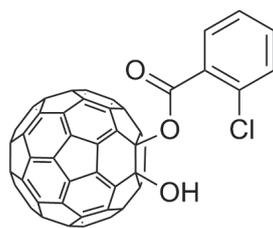


Figure 3-26. ¹H NMR spectrum of **2j** in CS₂-CDCl₃



2j

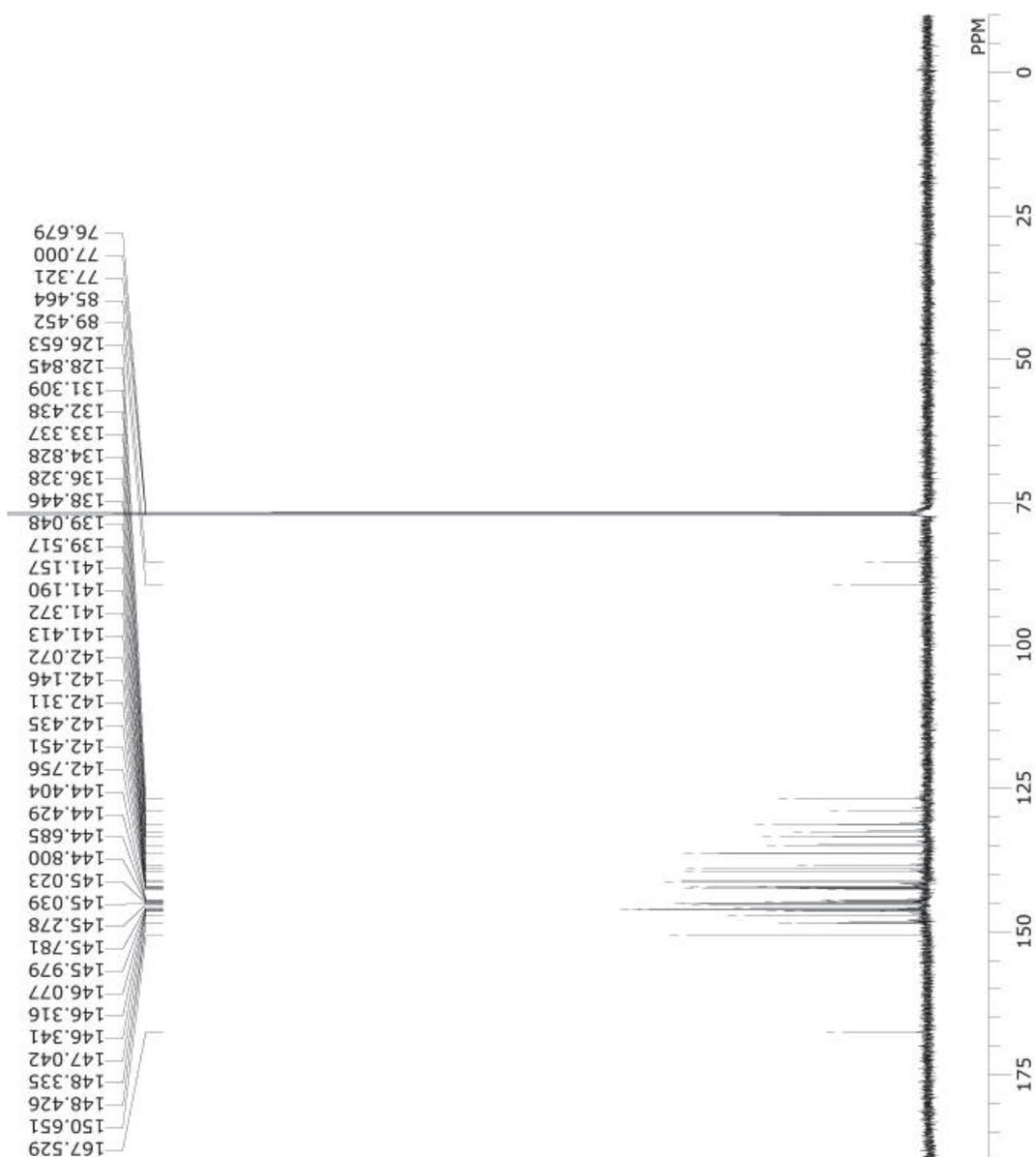


Figure 3-27. ¹³C NMR spectrum of **2j** in CS₂-CDCl₃

1-Hydroxy-9-Acetoxy-1,9-Dihydro(C₆₀-I_h)[5,6]fullerene (2I)

To a mixture of C₆₀ (503 mg, 0.70 mmol) and acetic acid (420 mg, 7.0 mmol) in 1,1,2,2-tetrachloroethane (25 mL) at 25 °C, FeCl₃ (2.26 g, 14 mmol) was added. After stirring for 4 h, an adequate amount of water was added to quench the reaction. The product was extracted with toluene (200 mL). The organic layer was washed with distilled water, and solvent was evaporated. Purification of the product was performed by preparative HPLC separation (Buckyprep column, eluent: toluene/2-propanol = 9/1) to obtain the title compound (160 mg, 29% isolated yield, analytically pure) as black crystals. ¹H NMR (400 MHz, CDCl₃/CS₂): δ 2.69 (s, 3H, CH₃), 4.99 (s, 1H, OH); FT-IR (KBr): 3514 (m), 2918 (w), 1726 (s), 1429 (m), 1360 (m), 1228 (s), 1138 (m), 1101 (m), 1001 (s), 949 (m), 526 (s) cm⁻¹; ESI-MS (-): *m/z* calcd for C₆₂H₃O₃ (M - H⁺): 795.7; found, 796.0; Anal. Calcd for C₆₂H₄O₃: C, 93.47; H, 0.51. Found: C, 93.27; H, 0.49. ¹³C NMR spectra could not be obtained because of low solubility in common organic solvents.

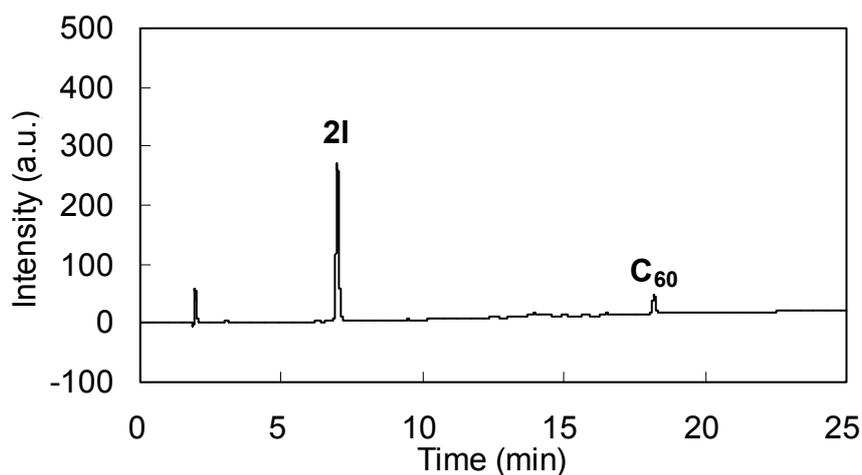
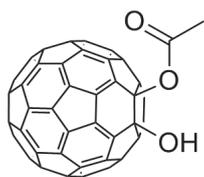


Figure 3-28. HPLC chart for the synthesis of 2I



21

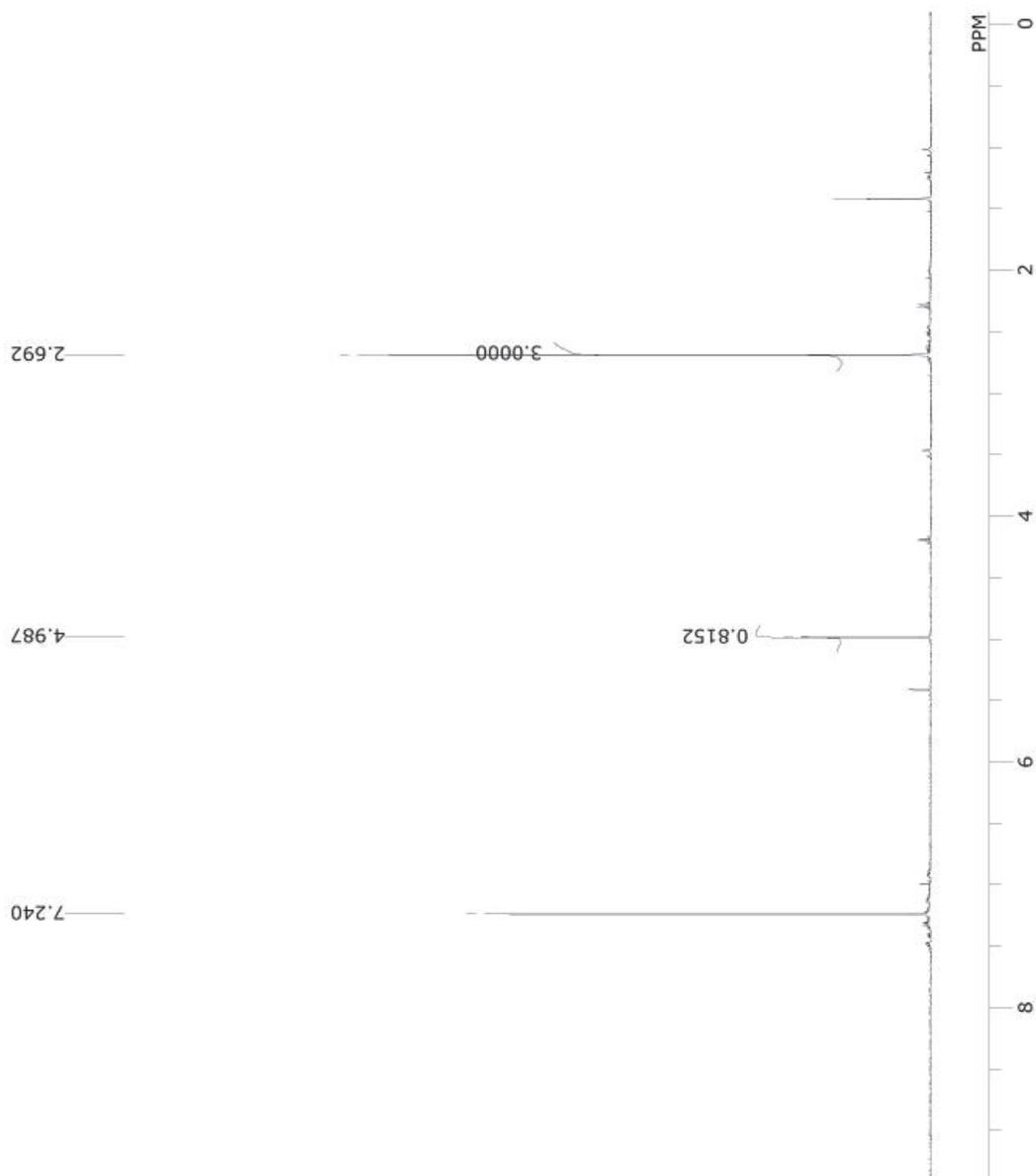


Figure 3-29. ^1H NMR spectrum of **21** in $\text{CS}_2\text{-CDCl}_3$

1-Hydroxy-9-Cyclohexanecarboxyloxy-1,9-Dihydro(C₆₀-I_h)[5,6]fullerene (2m)

To a mixture of C₆₀ (500 mg, 0.69 mmol) and cyclohexanecarboxylic acid (890 mg, 6.9 mmol) in 1,1,2,2-tetrachloroethane (25 mL) at 25 °C, FeCl₃ (2.25 g, 14 mmol) was added. After stirring for 6 h, an adequate amount of water was added to quench the reaction. The product was extracted with toluene (200 mL). The organic layer was washed with distilled water, and solvent was evaporated. Purification of the product was performed by preparative HPLC separation (Buckyprep column, eluent: toluene/2-propanol = 9/1) to obtain the title compound (124 mg, 21% isolated yield, analytically pure) as black crystals. ¹H NMR (400 MHz, CDCl₃/CS₂): δ 1.42–1.56 (m, 3H, C₆H₁₁), 1.73–2.05 (m, 4H, C₆H₁₁), 2.34–2.49 (m, 3H, C₆H₁₁), 2.94–2.99 (m, 1H, C₆H₁₁), 5.05 (s, 1H, OH); ¹³C NMR (100 MHz, CDCl₃/CS₂): δ 25.81 (2C, C₆H₁₁), 26.11 (1C, C₆H₁₁), 29.48 (2C, C₆H₁₁), 43.97 (1C, C₆H₁₁), 84.71 (1C, C₆₀OH), 88.42 (1C, C₆₀OCOC₆H₁₁), 123.26 (1C, C₆₀), 136.24 (1C, C₆₀), 137.78 (1C, C₆₀), 137.94 (1C, C₆₀), 138.20 (1C, C₆₀), 139.01 (1C, C₆₀), 139.18 (1C, C₆₀), 139.29 (1C, C₆₀), 139.45 (1C, C₆₀), 141.14 (1C, C₆₀), 141.17 (1C, C₆₀), 141.31 (1C, C₆₀), 141.36 (1C, C₆₀), 141.56 (1C, C₆₀), 141.64 (1C, C₆₀), 141.75 (1C, C₆₀), 141.83 (1C, C₆₀), 141.92 (1C, C₆₀), 141.97 (1C, C₆₀), 142.02 (1C, C₆₀), 142.12 (1C, C₆₀), 142.29 (1C, C₆₀), 142.33 (1C, C₆₀), 142.36 (1C, C₆₀), 142.38 (1C, C₆₀), 142.42 (1C, C₆₀), 144.23 (1C, C₆₀), 144.34 (1C, C₆₀), 144.41 (1C, C₆₀), 144.45 (1C, C₆₀), 144.64 (1C, C₆₀), 144.68 (1C, C₆₀), 144.75 (2C, C₆₀), 144.83 (1C, C₆₀), 144.98 (1C, C₆₀), 145.01 (1C, C₆₀), 145.25 (1C, C₆₀), 145.72 (1C, C₆₀), 145.75 (1C, C₆₀), 145.82 (1C, C₆₀), 145.92 (1C, C₆₀), 145.95 (2C, C₆₀), 146.02 (1C, C₆₀), 146.13 (1C, C₆₀), 146.28 (2C, C₆₀), 146.30 (2C, C₆₀), 147.12 (1C, C₆₀), 147.50 (1C, C₆₀), 147.90 (1C, C₆₀), 148.30 (1C, C₆₀), 148.39 (1C, C₆₀), 148.65 (1C, C₆₀), 150.79 (2C, C₆₀), 178.85 (1C, C₆₀OCOC₆H₁₁); FT-IR (KBr): 3525 (m), 2926 (m), 2848 (m), 1718 (s), 1448 (m), 1126 (m), 1036 (s), 1016 (s), 526 (s) cm⁻¹; ESI-MS (-): *m/z* calcd for C₆₇H₁₁O₃ (M - H⁺): 863.8; found, 864.0; Anal. Calcd for C₆₇H₁₂O₃: C, 93.05; H, 1.40. Found: C, 92.66; H, 1.08.

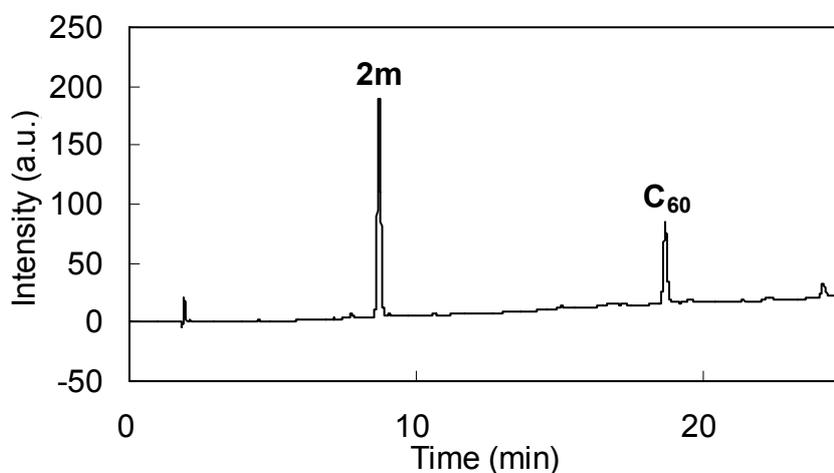
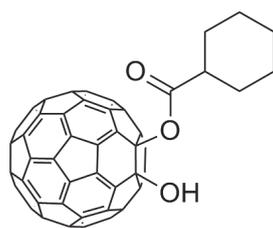


Figure 3-30. HPLC chart for the synthesis of 2m



2m

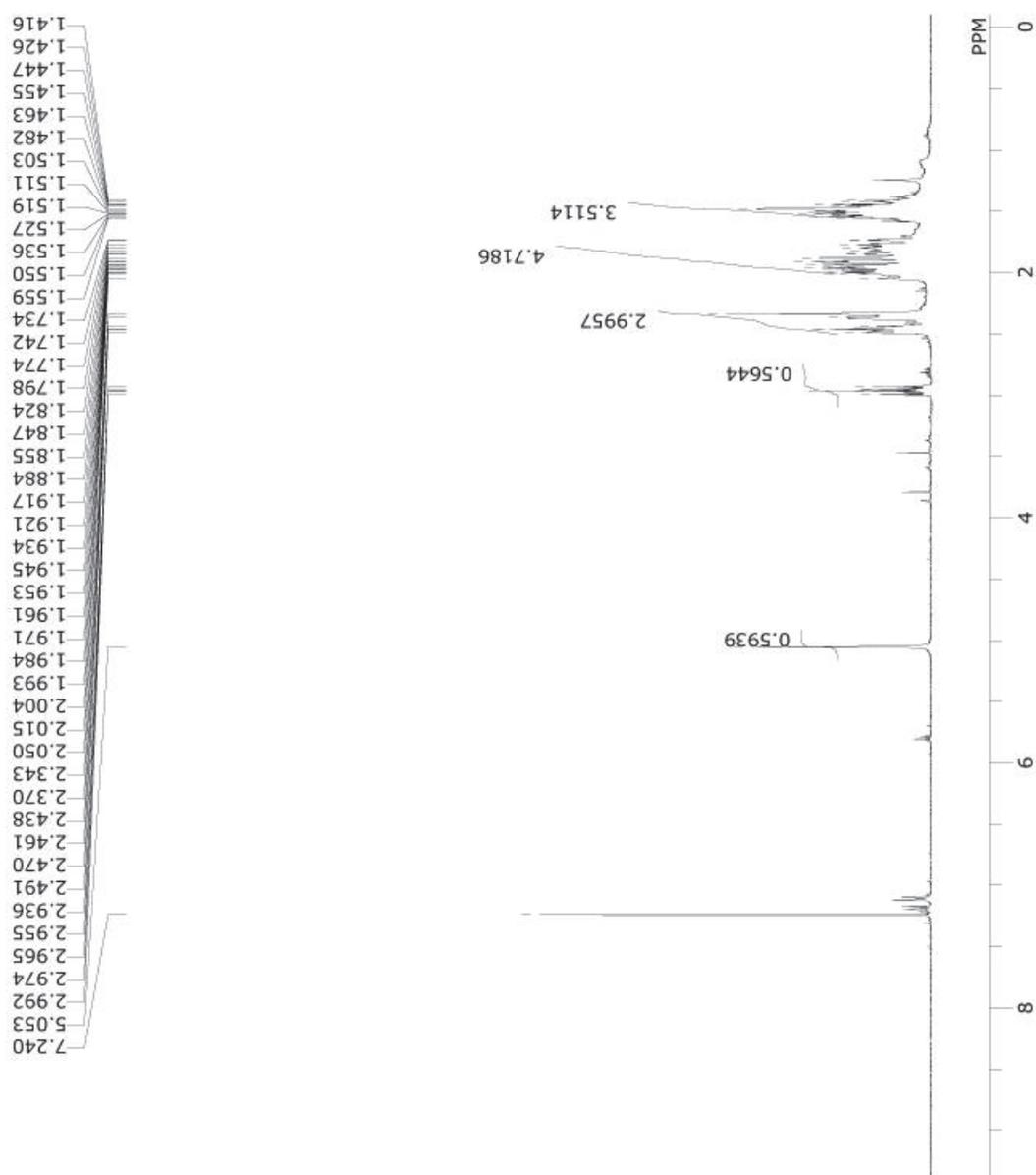
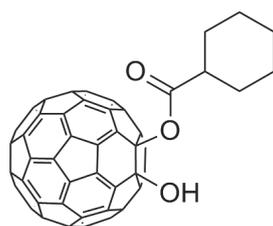


Figure 3-31. ^1H NMR spectrum of **2m** in $\text{CS}_2\text{-CDCl}_3$



2m

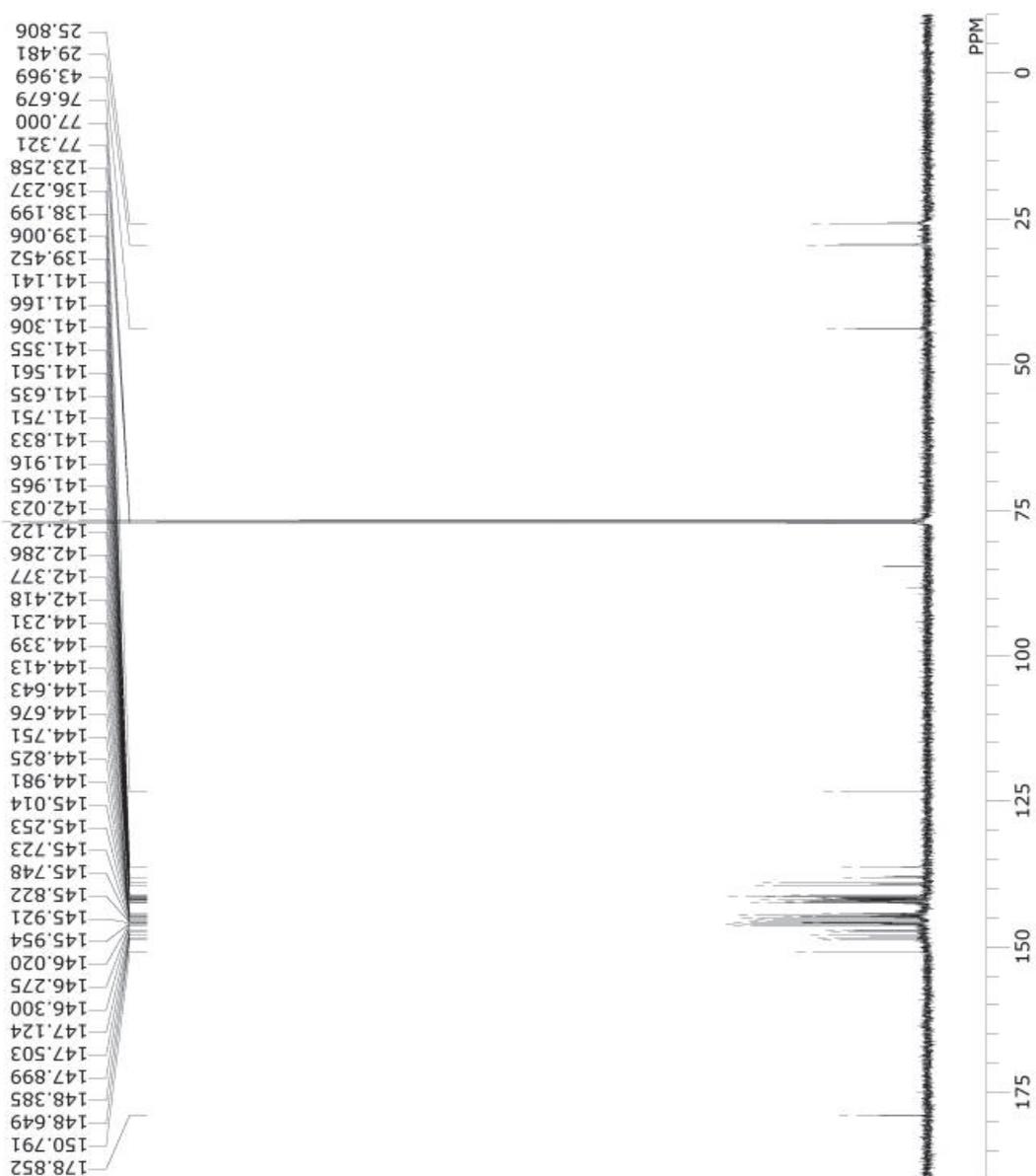


Figure 3-32. ^{13}C NMR spectrum of 2m in $\text{CS}_2\text{-CDCl}_3$

1-Hydroxy-9-(*tert*-Butylcarbonyl)oxy-1,9-Dihydro(C₆₀-I_h)[5,6]fullerene (2n)

To a mixture of C₆₀ (501 mg, 0.70 mmol) and pivalic acid (712 mg, 7.0 mmol) in 1,1,2,2-tetrachloroethane (25 mL) at 25 °C, FeCl₃ (2.25 g, 14 mmol) was added. After stirring for 8 h, an adequate amount of water was added to quench the reaction. The product was extracted with toluene (200 mL). The organic layer was washed with distilled water, and solvent was evaporated. Purification of the product was performed by preparative HPLC separation (Buckyprep column, eluent: toluene/2-propanol = 9/1) to obtain the title compound (59 mg, 10% isolated yield, analytically pure) as black crystals. ¹H NMR (400 MHz, CDCl₃/CS₂): δ 1.64 (s, 9H, ^tBu), 5.02 (s, 1H, OH); ¹³C NMR (100 MHz, CDCl₃/CS₂): δ 38.67 (3C, CH₃), 39.87 (1C, C(CH₃)₃), 84.76 (1C, C₆₀OH), 88.44 (1C, C₆₀OCO^tBu), 125.33 (1C, C₆₀), 135.60 (1C, C₆₀), 137.77 (1C, C₆₀), 137.89 (1C, C₆₀), 138.27 (1C, C₆₀), 139.02 (1C, C₆₀), 139.16 (1C, C₆₀), 139.28 (1C, C₆₀), 139.44 (1C, C₆₀), 141.12 (1C, C₆₀), 141.14 (1C, C₆₀), 141.29 (1C, C₆₀), 141.34 (1C, C₆₀), 141.55 (1C, C₆₀), 141.62 (1C, C₆₀), 141.77 (1C, C₆₀), 141.81 (1C, C₆₀), 141.90 (1C, C₆₀), 141.95 (1C, C₆₀), 142.00 (1C, C₆₀), 142.11 (1C, C₆₀), 142.26 (1C, C₆₀), 142.30 (1C, C₆₀), 142.34 (1C, C₆₀), 142.36 (1C, C₆₀), 142.39 (1C, C₆₀), 144.22 (1C, C₆₀), 144.31 (1C, C₆₀), 144.39 (1C, C₆₀), 144.42 (1C, C₆₀), 144.61 (1C, C₆₀), 144.66 (1C, C₆₀), 144.72 (1C, C₆₀), 144.73 (1C, C₆₀), 144.80 (1C, C₆₀), 144.96 (1C, C₆₀), 144.99 (1C, C₆₀), 145.23 (1C, C₆₀), 145.71 (1C, C₆₀), 145.72 (1C, C₆₀), 145.80 (1C, C₆₀), 145.81 (1C, C₆₀), 145.90 (1C, C₆₀), 145.92 (1C, C₆₀), 145.95 (1C, C₆₀), 146.01 (2C, C₆₀), 146.12 (1C, C₆₀), 146.26 (1C, C₆₀), 146.28 (1C, C₆₀), 147.03 (1C, C₆₀), 147.41 (1C, C₆₀), 147.88 (1C, C₆₀), 148.29 (1C, C₆₀), 148.37 (1C, C₆₀), 148.61 (1C, C₆₀), 150.77 (2C, C₆₀), 181.35 (1C, C₆₀OCO^tBu); FT-IR (KBr): 3525 (m), 2964 (m), 1718 (m), 1479 (m), 1460 (m), 1431 (m), 1396 (m), 1363 (m), 1279 (m), 1124 (s), 1084 (m), 1005 (s), 783 (m), 526 (s) cm⁻¹; ESI-MS (-): *m/z* calcd for C₆₅H₉O₃ (M - H⁺): 837.8; found, 838.1; Anal. Calcd for C₆₅H₁₀O₃: C, 93.08; H, 1.20. Found: C, 93.22; H, 1.06.

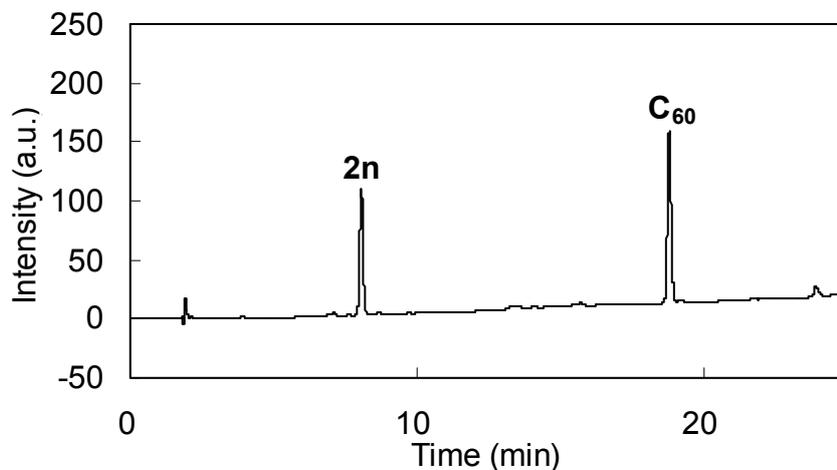
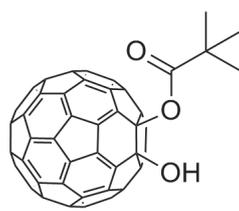


Figure 3-33. HPLC chart for the synthesis of 2n



2n

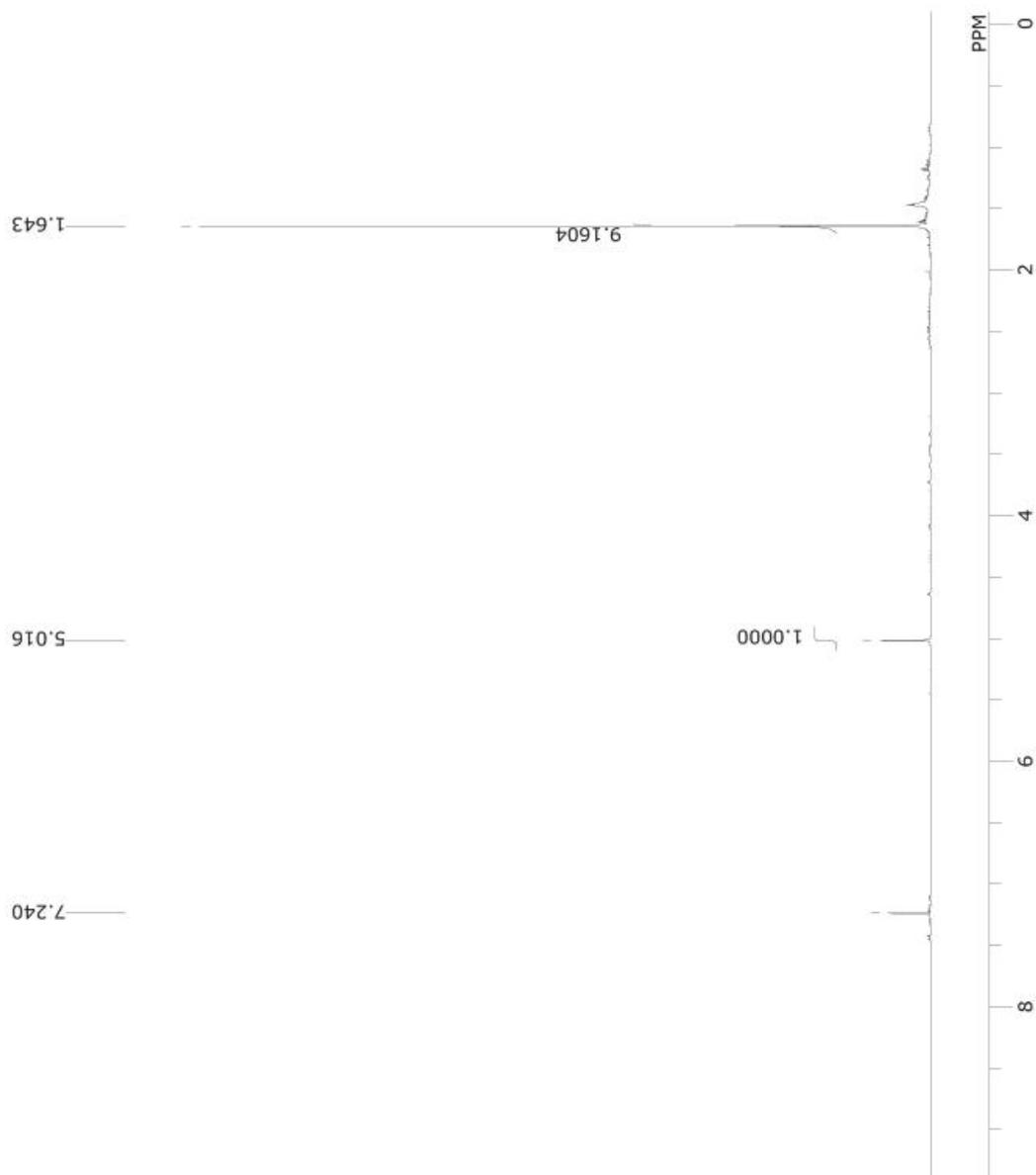
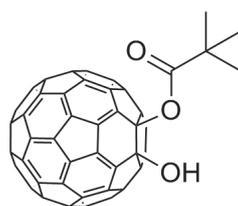


Figure 3-34. ^1H NMR spectrum of **2n** in $\text{CS}_2\text{-CDCl}_3$



2n

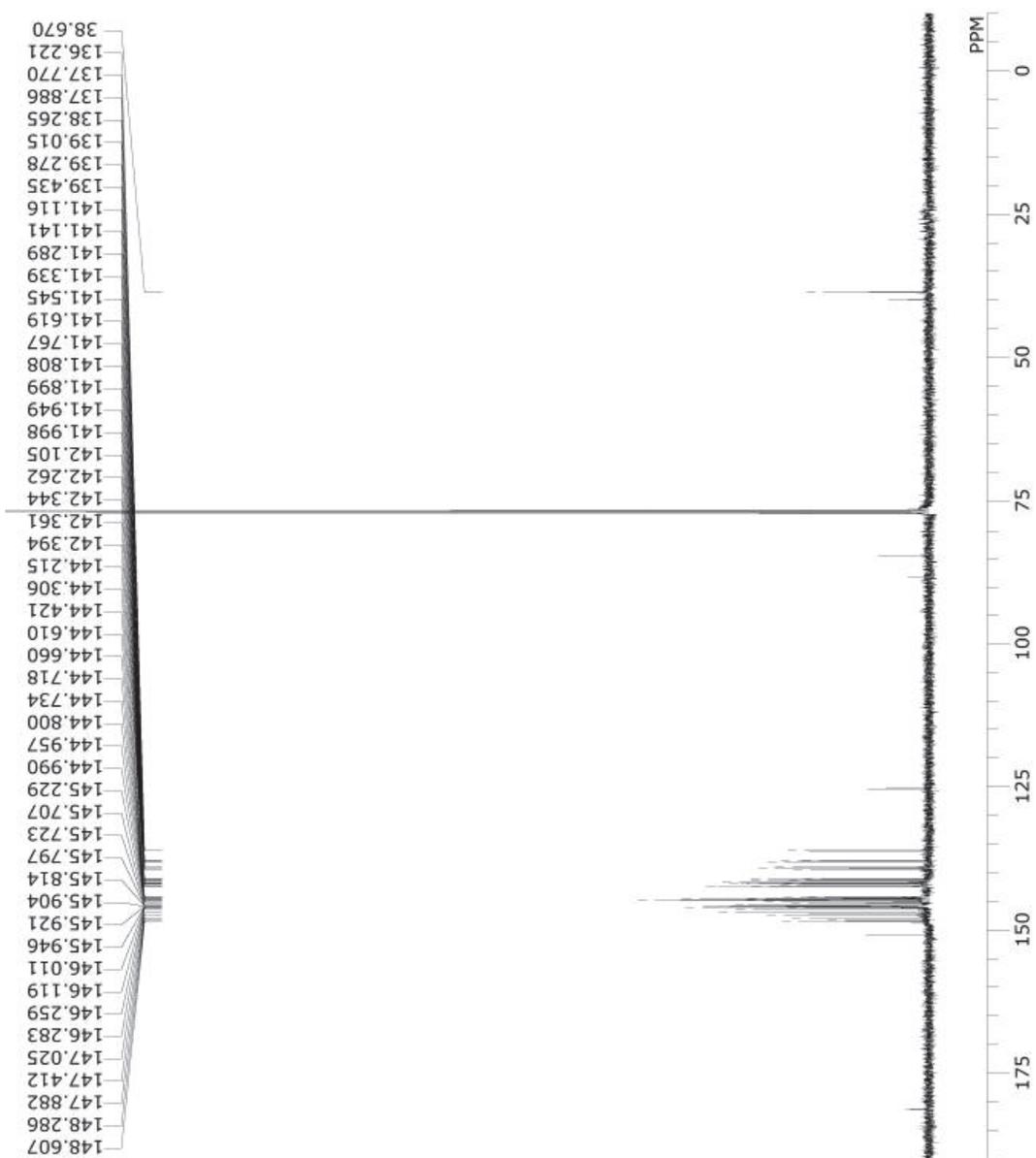


Figure 3-35. ^{13}C NMR spectrum of **2n** in $\text{CS}_2\text{-CDCl}_3$

1-Benzoyloxy-9-(2,6-Dimethylbenzoyloxy)-1,9-Dihydro(C₆₀-I_h)[5,6]fullerene (3)

To a mixture of compound **2a** (100 mg, 0.11 mmol) and benzoyl chloride (0.065 mL, 0.56 mmol) in pyridine (5.0 mL) at 0 °C, triethylamine (0.079 mL, 0.56 mmol) and 4-dimethylaminopyridine (1.38 mg, 0.011 mmol) were added. After the reaction mixture was stirred for 4 h, the solution was quenched with water. The product was extracted with toluene (40 mL). The organic layer was washed with distilled water, and solvent was evaporated. Purification of the product was performed by preparative HPLC separation (Buckyprep column, eluent: toluene/2-propanol = 8/2) to obtain the title compound (78 mg, 70% isolated yield, analytically pure) as black crystals. ¹H NMR (400 MHz, CDCl₃/CS₂): δ 2.41 (s, 6H, CH₃), 6.94 (d, *J* = 7.6 Hz, 2H, Ar), 7.16 (t, *J* = 7.8 Hz, 1H, Ar), 7.50 (t, *J* = 7.8 Hz, 2H, Ph), 7.65 (t, *J* = 7.6 Hz, 1H, Ph), 8.29 (d, *J* = 8.0 Hz, 2H, Ph); ¹³C NMR (100 MHz, CDCl₃/CS₂): δ 21.14 (2C, CH₃), 88.10 (1C, C₆₀OCOAr), 88.50 (1C, C₆₀OCOAr), 128.02 (4C, Ar), 128.24 (2C, Ar), 129.60 (1C, C₆₀), 130.07 (2C, Ar), 130.78 (1C, C₆₀), 133.19 (2C, Ar), 133.17 (2C, Ar), 138.50 (1C, C₆₀), 138.64 (1C, C₆₀), 138.85 (2C, C₆₀), 139.14 (2C, C₆₀), 140.89 (2C, C₆₀), 140.94 (2C, C₆₀), 141.34 (2C, C₆₀), 141.39 (2C, C₆₀), 142.15 (2C, C₆₀), 142.22 (2C, C₆₀), 142.39 (2C, C₆₀), 142.41 (2C, C₆₀), 142.58 (1C, C₆₀), 142.76 (1C, C₆₀), 144.40 (2C, C₆₀), 144.54 (2C, C₆₀), 144.60 (2C, C₆₀), 144.63 (2C, C₆₀), 144.97 (2C, C₆₀), 145.01 (2C, C₆₀), 145.36 (2C, C₆₀), 145.91 (2C, C₆₀), 145.93 (2C, C₆₀), 145.95 (4C, C₆₀), 146.34 (4C, C₆₀), 147.37 (2C, C₆₀), 147.50 (2C, C₆₀), 148.32 (2C, C₆₀), 165.72 (1C, C₆₀OCOAr), 167.57 (1C, C₆₀OCOAr); FT-IR (KBr): 2922 (w), 1741 (s), 1423 (m), 1263 (s), 1232 (s), 1180 (m), 1065 (s), 978 (m), 769 (m), 706 (m), 526 (s) cm⁻¹; ESI-MS (-): *m/z* calcd for C₇₆H₁₄O₄ (M⁻): 990.9; found, 990.5; Anal. Calcd for C₇₆H₁₄O₄: C 92.12; H, 1.42. Found: C 92.40; H, 1.10.

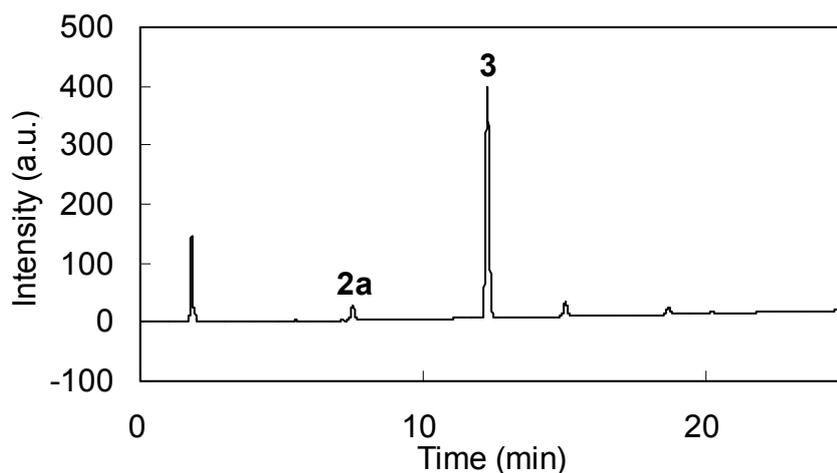


Figure 3-36. HPLC chart for the synthesis of **3**

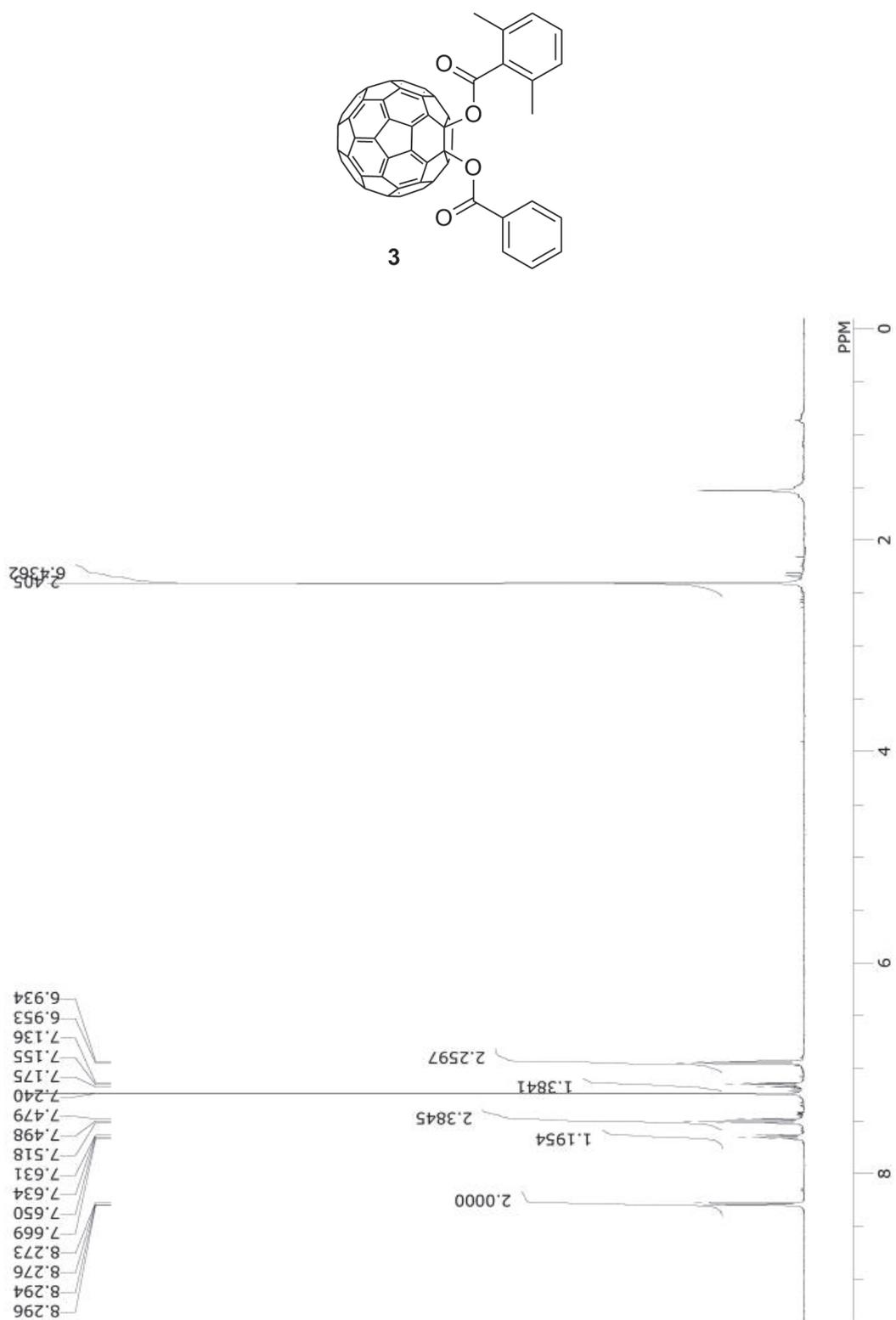


Figure 3-37. ¹H NMR spectrum of **3** in CS₂-CDCl₃

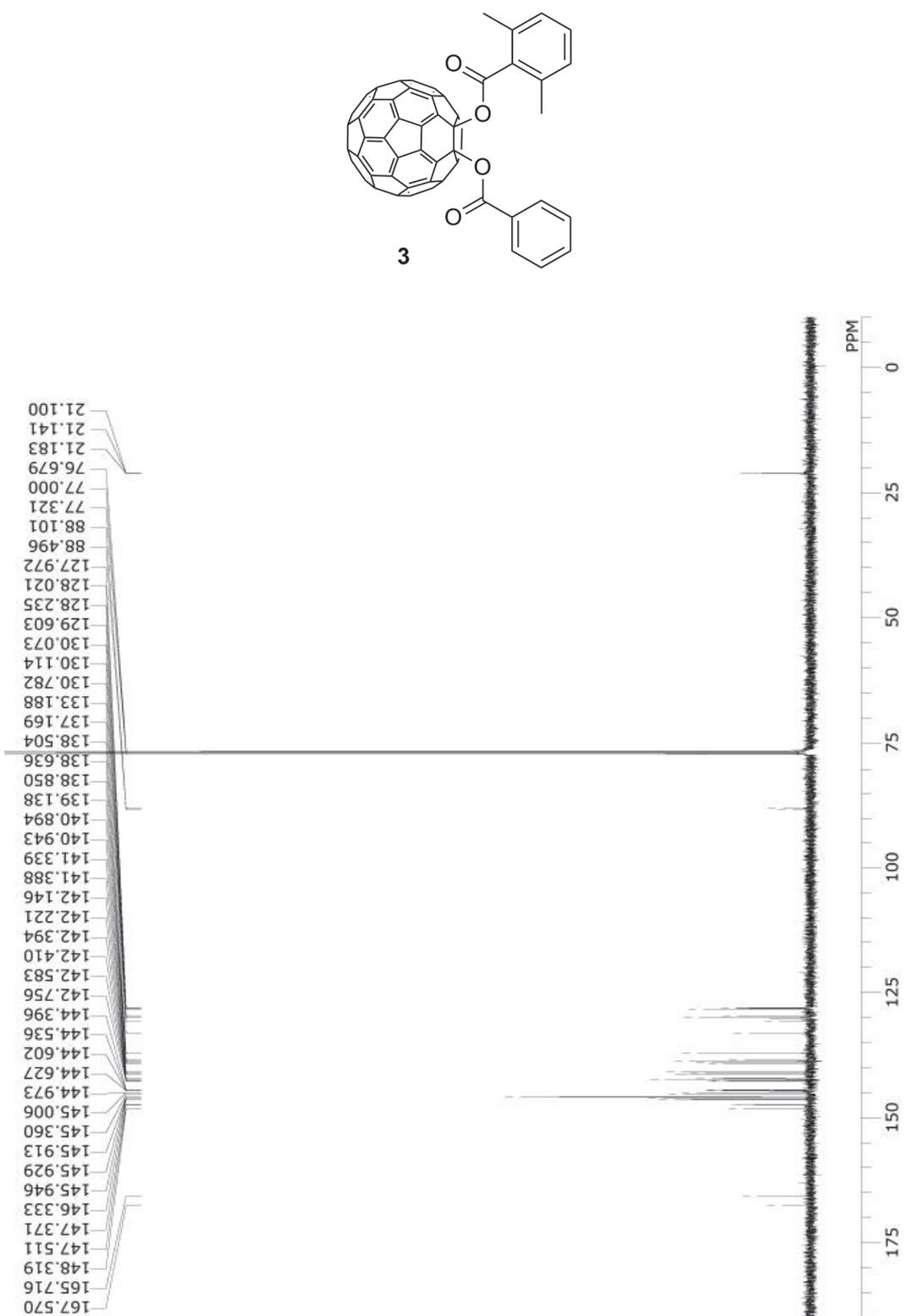


Figure 3-38. ¹³C NMR spectrum of **3** in CS₂-CDCl₃

1-Trimethylsilyloxy-9-(2,6-Dimethylbenzoyl)oxy-1,9-Dihydro(C₆₀-I_h)[5,6]fullerene (4)

To a mixture of compound **2a** (100 mg, 0.11 mmol) and trimethylsilyl chloride (0.195 mL, 2.3 mmol) in pyridine (5.0 mL) at 25 °C, 4-dimethylaminopyridine (1.40 mg, 0.011 mmol) was added. After the reaction mixture was stirred for 24 h, the solution was quenched with water. The product was extracted with toluene (40 mL). The organic layer was washed with distilled water, and solvent was evaporated. Purification of the product was performed by preparative HPLC separation (Buckyprep column, eluent: toluene/2-propanol = 8/2) to obtain the title compound (94 mg, 87% isolated yield, analytically pure) as black crystals. ¹H NMR (400 MHz, CDCl₃/CS₂): δ 0.47 (s, 9H, Si(CH₃)₃), 2.90 (s, 6H, CH₃), 7.26 (d, *J* = 7.6 Hz, 2H, Ar), 7.39 (t, *J* = 8.0 Hz, 1H, Ar); ¹³C NMR (100 MHz, CDCl₃/CS₂): δ 2.83 (3C, Si(CH₃)₃), 23.05 (2C, ArCH₃), 85.89 (1C, C₆₀OSi(CH₃)₃), 89.12 (1C, C₆₀OCOAr), 129.09 (2C, Ar), 129.09 (1C, C₆₀), 130.08 (1C, C₆₀), 130.68 (2C, Ar), 136.63 (2C, Ar), 138.13 (2C, C₆₀), 138.80 (1C, C₆₀), 139.03 (1C, C₆₀), 139.35 (2C, C₆₀), 141.12 (2C, C₆₀), 141.31 (2C, C₆₀), 141.32 (2C, C₆₀), 141.37 (2C, C₆₀), 142.07 (2C, C₆₀), 142.09 (2C, C₆₀), 142.33 (2C, C₆₀), 142.42 (2C, C₆₀), 142.55 (1C, C₆₀), 142.76 (1C, C₆₀), 144.41 (2C, C₆₀), 144.48 (2C, C₆₀), 144.59 (2C, C₆₀), 144.66 (2C, C₆₀), 144.94 (2C, C₆₀), 144.97 (2C, C₆₀), 145.41 (2C, C₆₀), 145.67 (2C, C₆₀), 145.83 (2C, C₆₀), 145.92 (2C, C₆₀), 145.95 (2C, C₆₀), 146.25 (2C, C₆₀), 146.28 (2C, C₆₀), 148.28 (1C, C₆₀), 148.38 (1C, C₆₀), 148.94 (2C, C₆₀), 150.43 (2C, C₆₀), 166.98 (1C, C₆₀OCOAr); FT-IR (KBr): 2654 (w), 2922 (w), 1734 (s), 1464 (m), 1419 (m), 1252 (s), 1236 (s), 1113 (s), 1070 (s), 997 (m), 872 (s), 843 (s), 769 (m), 698 (m), 526 (s) cm⁻¹; ESI-MS (-): *m/z* calcd for C₇₂H₁₈O₃Si (M⁻): 959.0; found, 959.0; Anal. Calcd for C₇₂H₁₈O₃Si: C, 90.17; H, 1.89. Found: C, 90.52; H, 1.66.

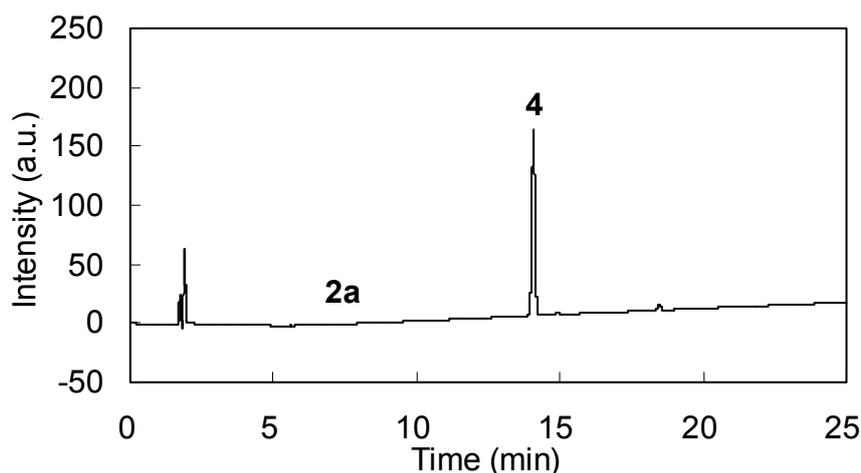


Figure 3-39. HPLC chart for the synthesis of **4**

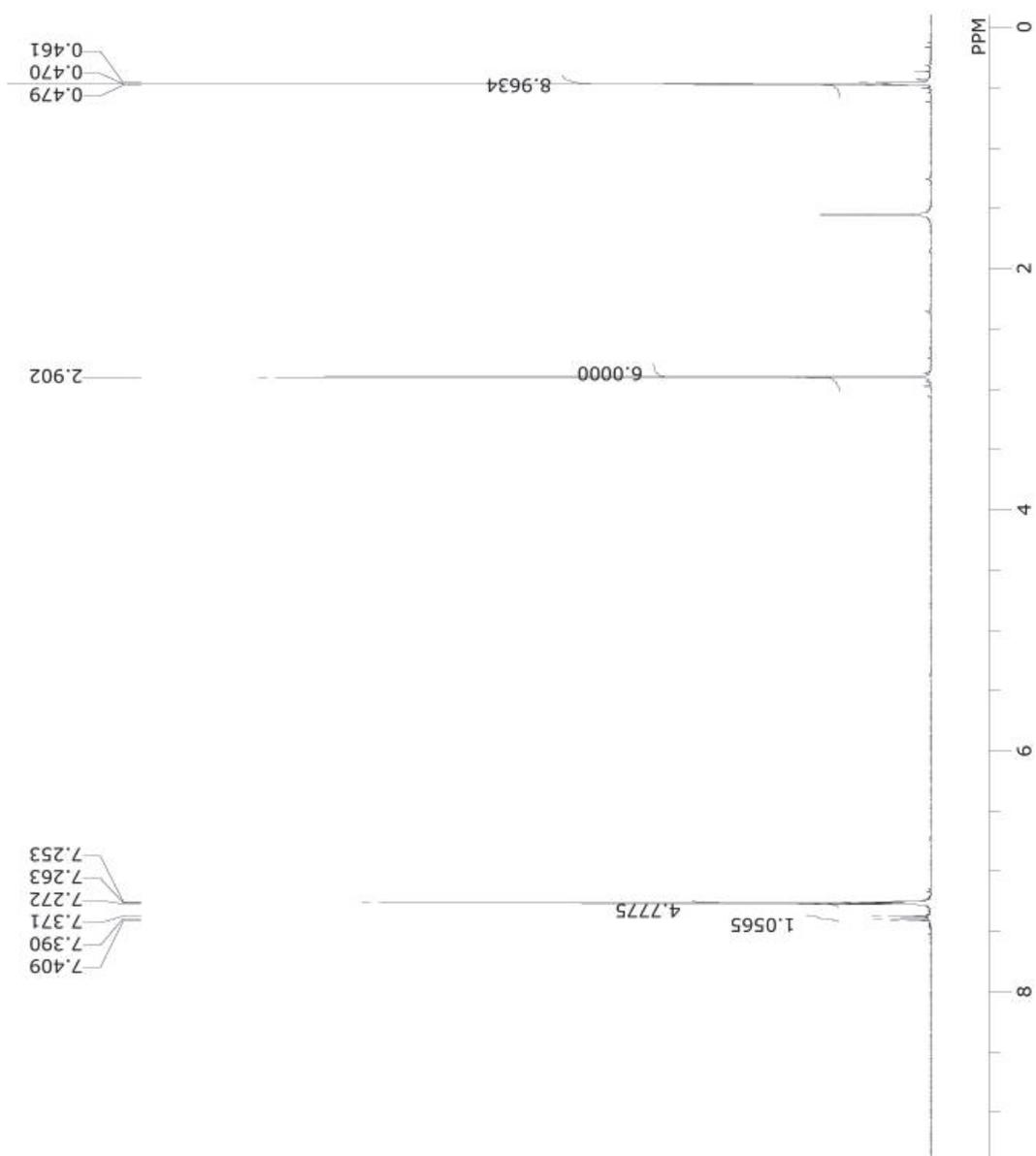
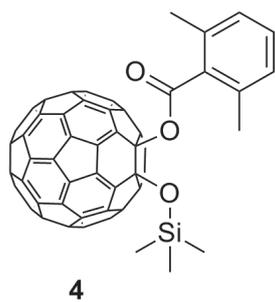


Figure 3-40. ¹H NMR spectrum of 4 in CS₂-CDCl₃

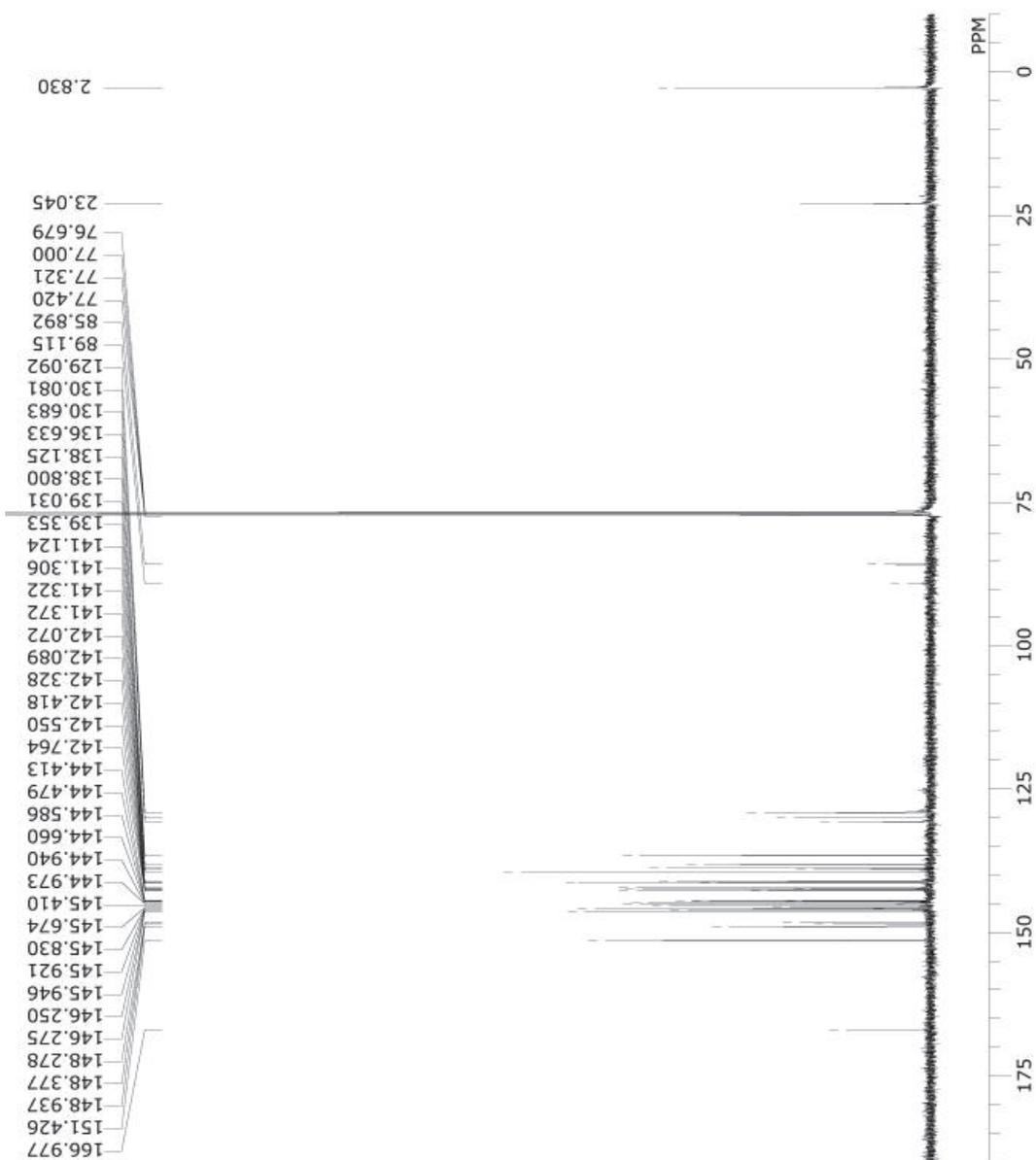
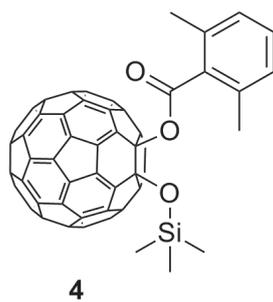


Figure 3-41. ^{13}C NMR spectrum of **4** in $\text{CS}_2\text{-CDCl}_3$

Cyclic Voltammograms

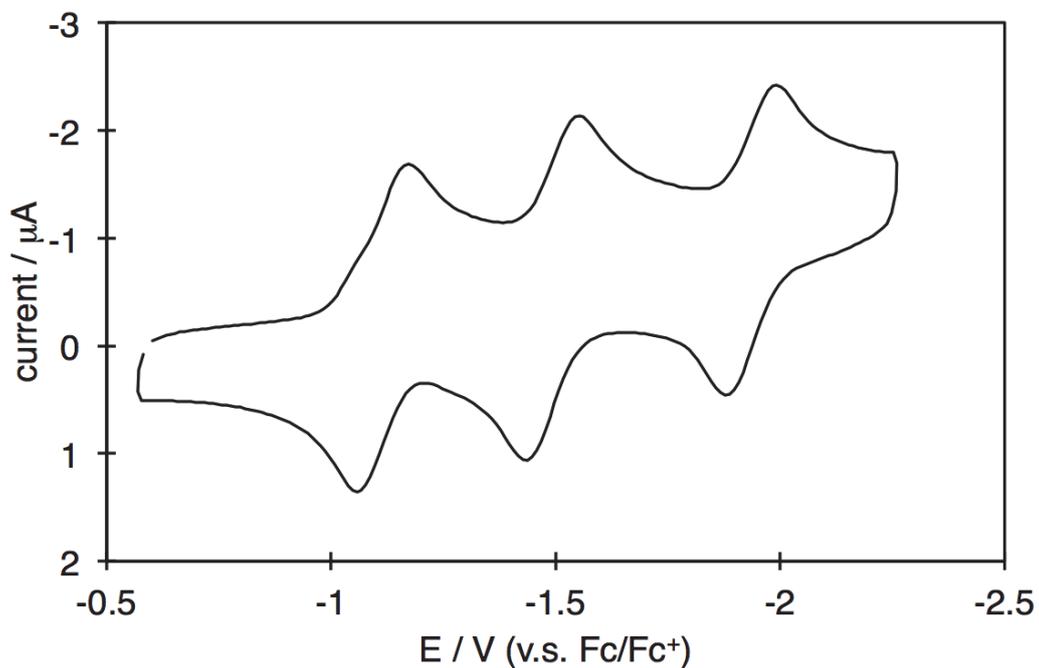


Figure 3-42. Cyclic voltammogram of **3** in 1,2-Cl₂C₆H₄ solution containing Bu₄N⁺PF₆⁻ (50 mM) as a supporting electrolyte at 25 °C

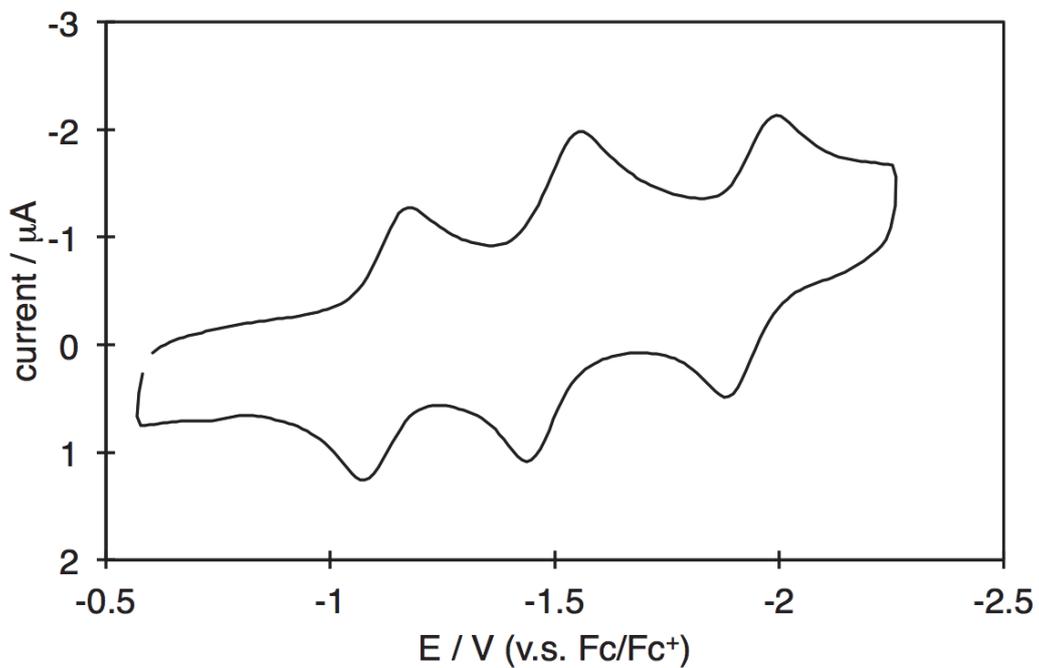


Figure 3-43. Cyclic voltammogram of **4** in 1,2-Cl₂C₆H₄ solution containing Bu₄N⁺PF₆⁻ (50 mM) as a supporting electrolyte at 25 °C

Data of Single Crystal X-ray Structural Analyses

Table 3-3. Crystal and refinement data for **2a**

Empirical formula	C ₆₉ H ₁₀ O ₃ · 0.5CS ₂
Formula weight	924.89
Temperature	93(2) K
Radiation	MoK α ($\lambda = 0.71073$ Å)
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁
Unit cell dimensions	<i>a</i> = 10.2075(13) Å
	<i>b</i> = 30.954(4) Å
	<i>c</i> = 11.9650(16) Å
	$\alpha = 90^\circ$
	$\beta = 107.043(2)^\circ$
	$\gamma = 90^\circ$
V (Å ³)	3614.5(8)
Z	4
Density ρ calc (g·cm ⁻³)	1.700
Absorption coefficient (mm ⁻¹)	0.159
F(000)	1864
Crystal dimensions (mm ³)	0.13 · 0.04 · 0.03
range for data collection	$2.09 \leq \theta \leq 25.03^\circ$
Index ranges	$-12 \leq h \leq 12$
	$-36 \leq k \leq 36$
	$-14 \leq l \leq 14$
Reflections collected / unique	34969 / 12745 ($R_{\text{int}} = 0.0476$)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12745 / 1846 / 1381
Goodness-of-fit on F^2	1.015
Final <i>R</i> indices [$I > 2\sigma(I)$] ^{a, b)}	$R1 = 0.1163$, $wR2 = 0.2896$
<i>R</i> indices (all data) ^{a, b)}	$R1 = 0.1370$, $wR2 = 0.3091$
Largest diff. peak and hole (e·Å ⁻³)	1.475 / -1.018

^{a)} $\Sigma(|F_o| - |F_c|) / \Sigma|F_o|$

^{b)} $wR2 = [\Sigma\omega(|F_o|^2 - |F_c|^2)^2 / \Sigma(\omega F_o^4)]^{1/2}$

Table 3-4. Crystal and refinement data for **3**

Empirical formula	C ₇₆ H ₁₄ O ₄ ·CS ₂
Formula weight	1067.00
Temperature	123(2) K
Radiation	CuK α ($\lambda = 1.54187$ Å)
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	$a = 9.8980(3)$ Å
	$b = 15.7352(4)$ Å
	$c = 27.3241(7)$ Å
	$\alpha = 90^\circ$
	$\beta = 98.3298(17)^\circ$
	$\gamma = 90^\circ$
V (Å ³)	4210.8(2)
Z	4
Density ρ calc (g·cm ⁻³)	1.683
Absorption coefficient (mm ⁻¹)	1.718
F(000)	2160
Crystal dimensions (mm ³)	1.50 · 0.50 · 0.20
range for data collection	$3.25 \leq \theta \leq 66.99^\circ$
Index ranges	$-115 \leq h \leq 11$
	$-185 \leq k \leq 18$
	$-325 \leq l \leq 32$
Reflections collected / unique	46184 / 7491 ($R_{\text{int}} = 0.1189$)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7491 / 0 / 751
Goodness-of-fit on F^2	1.276
Final R indices [$I > 2\sigma(I)$] ^{a), b)}	$R1 = 0.0984$, $wR2 = 0.2266$
R indices (all data) ^{a), b)}	$R1 = 0.1457$, $wR2 = 0.2686$
Largest diff. peak and hole (e·Å ⁻³)	0.665 / -0.534

^{a)} $\Sigma(|F_o| - |F_c|) / \Sigma|F_o|$

^{b)} $wR2 = [\Sigma\omega(|F_o|^2 - |F_c|^2)^2 / \Sigma(\omega F_o^4)]^{1/2}$

Table 3-5. Crystal and refinement data for **4**

Empirical formula	C ₇₂ H ₁₈ O ₃ Si
Formula weight	958.95
Temperature	123(2) K
Radiation	CuK α ($\lambda = 1.54187$ Å)
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	$a = 16.0566(5)$ Å
	$b = 14.0283(6)$ Å
	$c = 18.1004(6)$ Å
	$\alpha = 90^\circ$
	$\beta = 104.9930(11)^\circ$
	$\gamma = 90^\circ$
V (Å ³)	3938.26(14)
Z	4
Density ρ calc (g·cm ⁻³)	1.617
Absorption coefficient (mm ⁻¹)	1.053
F(000)	1952
Crystal dimensions (mm ³)	0.30 · 0.30 · 0.30
range for data collection	$4.04 \leq \theta \leq 67.00^\circ$
Index ranges	$-19 \leq h \leq 19$
	$-16 \leq k \leq 16$
	$-21 \leq l \leq 21$
Reflections collected / unique	43509 / 7026 ($R_{\text{int}} = 0.0926$)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7026 / 0 / 691
Goodness-of-fit on F^2	1.106
Final R indices [$I > 2\sigma(I)$] ^{a, b)}	$R1 = 0.0786$, $wR2 = 0.1860$
R indices (all data) ^{a, b)}	$R1 = 0.1131$, $wR2 = 0.2172$
Largest diff. peak and hole (e·Å ⁻³)	0.461 / -0.523

^{a)} $\Sigma(|F_o| - |F_c|) / \Sigma|F_o|$

^{b)} $wR2 = [\Sigma\omega(|F_o|^2 - |F_c|^2)^2 / \Sigma(\omega F_o^4)]^{1/2}$

References and Notes

† The contents of this chapter have already been published in the following paper. Hashiguchi, M.; Obata, N.; Maruyama, M.; Yeo, K. S.; Ueno, T.; Ikebe, T.; Takahashi, I.; Matsuo, Y. *Org. Lett.* **2012**, *14*, 3276–3279.

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Appendix

OPV Performance

Compounds **3** and **4** were both examined for suitability in organic photovoltaic (OPV) application, via the fabrication of bulk heterojunction solar cells with poly(3-hexylthiophene) (P3HT) or poly(4,8-bis-octoxybenzo(1,2-b:4,5-b)dithiophene-2,6-diyl-alt-(dodecyl-thieno(3,4-b)thiophene-2-carboxylate)-2,6-diyl) (PBDTTT)²⁷ as the donor material in the active layer. I summarized the device performances in Table 3. The current density-voltage (J - V) characteristics under AM 1.5G simulated solar illumination at an intensity of 100 mW/cm² and corresponding external quantum efficiency (EQE) spectrum are shown in Figure 4. Device 1 showed impressive performance with an open-circuit voltage (V_{OC}) of 0.74 V, a short-circuit current density (J_{SC}) of 5.4 mA/cm², and a fill factor (FF) of 0.34. The power conversion efficiency (PCE) obtained was 1.3%. The low-lying LUMO (-3.55eV) and HOMO (-5.12eV) levels of the low band gap polymer, PBDTTT, are compatible with the low-lying LUMO levels of compounds **3** and **4**. This results in a more efficient exciton dissociation process between donor and acceptor material, giving higher V_{OC} as compared to when using P3HT. In addition, PBDTTT absorbs in the near-IR region of the solar spectrum, and this contributes to the higher J_{SC} seen in devices 1 and 2. Due to the recent push towards using low band gap polymers as electron-donating material in OPVs, electron-accepting material with low-lying LUMO levels, such as compounds **3** and **4**, are expected to play a strategic role in future enhancement of OPV performance.

In addition, inverted OPVs, the more stable counterpart of normal-type OPVs, were fabricated with the use of compounds **3** and **4**. The attempt to test the compatibility of such low-LUMO electron acceptors with the inverted design was met with unexpected results. The V_{OC} and FF of inverted P3HT-based device **5** were both higher than that of normal-type P3HT-based device **3**. However, the PCE was comparatively lower (0.29%), due to a lower J_{SC} . The respectable V_{OC} and FF values obtained for the inverted devices indicated that there is immense potential for the use of low LUMO acceptors such as compounds **3** and **4** in inverted-type OPVs as well.

Table 3-6. OPV device performance for compounds **3** and **4**

Device	type	Compound	Donor	V_{OC} (V)	J_{SC} (mA/cm ²)	FF	PCE (%)
1 ^a	normal	4	PBDTTT	0.74	5.4	0.34	1.3
2 ^a	normal	3	PBDTTT	0.69	5.0	0.32	1.1
3 ^b	normal	4	P3HT	0.46	2.2	0.39	0.40
4 ^b	normal	3	P3HT	0.46	2.1	0.29	0.28
5 ^c	inverted	4	P3HT	0.51	1.25	0.46	0.29
6 ^c	inverted	3	P3HT	0.46	0.94	0.47	0.20

^a Device configuration for normal-structured OPV devices: glass/ITO/PEDOT:PSS/PBDTTT:fullerene (88 nm)/Ca (20 nm)/Al (80 nm). PBDTTT and each fullerene derivative in mixture (1:1 wt ratio) were dissolved in 1,2-dichlorobenzene (total conc. was 2.0wt%) and spin-coated.

^b Device configuration, glass/ITO/PEDOT:PSS/P3HT:fullerene (80 nm)/LiF (0.15nm)/Al (80 nm). P3HT and each fullerene derivative in mixture (1:1 wt ratio) were dissolved in chlorobenzene (total conc. was 2.0wt%) and spin-coated. After fabrication, post-annealing was conducted at 150 °C for 10 min.

^c Device configuration for inverted-structured OPV devices: glass/ITO/TiO_x (40 nm)/P3HT:fullerene (130 nm)/PEDOT:PSS (40 nm)/Au (90 nm). P3HT and each fullerene derivative in mixture (5:3 wt ratio) were dissolved in chlorobenzene (total conc. was 3.2 wt%) and spin-coated. After fabrication, post-annealing was conducted at 150 °C for 5 min, followed by 70 °C for 30 min.

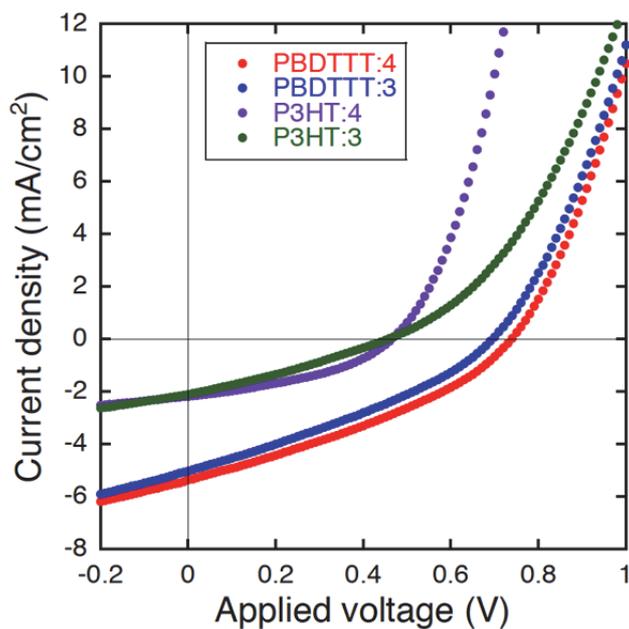
OPV Fabrication

A 145-nm-thick, patterned indium-tin oxide (ITO) coated glass with a sheet resistance of 8 Ω/square was used as the substrate. A conductive material, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, Clevios P VP AI4083 purchased from Heraeus), was spin-coated on the glass/ITO substrate to obtain a 30-nm-thick film. For the donor materials used in the devices, poly(4,8-bis-octoxybenzo(1,2-b:4,5-b)dithiophene-2,6-diyl-alt-(dodecyl-thieno(3,4-b)thiophene-2-carboxylate)-2,6-diyl) (PBDTTT) and poly(3-hexylthiophene) (P3HT) were purchased from commercial suppliers. For fabrication of PBDTTT-based devices, PBDTTT:acceptors in a 1:1 mixture (wt ratio) was dissolved in 1,2-dichlorobenzene (total conc. was 2.0wt%) and spin-coated. Calcium (Ca, 20 nm) and aluminum electrode (Al, 80 nm) were deposited in vacuum (3×10^{-4} Pa) on top of the active layer. For fabrication of P3HT-based devices, P3HT:acceptors in a 1:1 mixture (wt ratio) was dissolved in chlorobenzene to obtain each solution (total concentration, 2.0 wt%) and spin-coated. Lithium fluoride (LiF, 0.15 nm) and Al electrode (80 nm) were deposited in vacuum (3×10^{-4} Pa) on top of the active layer. After that, the devices were heated at 150 °C for 10 min. All

devices were encapsulated in a glove box in a nitrogen atmosphere. The photocurrent of the fabricated OPV devices was investigated with a sweeping voltage using a source measurement unit controlled by a computer under simulated solar light using an AM1.5G light source with a 100 mW/cm² intensity. Incident light intensity was calibrated to 1 sun (100 mW/cm²) with a standard Si photodiode. The current density vs voltage (*J-V*) characteristics were measured for an area of 0.04 cm². The external quantum efficiency (EQE) was measured under a constant power generated by monochromatized photons using a xenon lamp and a halogen lamp.

For inverted-type devices, the ITO electrode was first etched with Zn powder and 0.1M HCl. Cleaning via sonication in pure water was then carried out, which was followed by UV-ozone treatment. A TiO_x layer was deposited on the ITO substrate via the chemical bath deposition method as described by Takahashi et al.^{28,29} Active layer solutions of donor polymers and acceptor fullerenes in monochlorobenzene were stirred at 50 °C overnight. These were spin coated on the respective substrates at 3000 rpm for 1 min, and left to stand in air for 30 min. Then, a PEDOT:PSS solution was also spin-coated on top of the active layer at 5000 rpm for 1 min. All spin-coating procedures were conducted in a glove box with a relative humidity of less than 10%. A Au metal electrode was vacuum deposited on the PEDOT:PSS layer. Masking during this procedure gives an effective cell area of 1.0 cm². The devices were heated on a hotplate at 150 °C for 5 min, followed by 70 °C for 30 min. Finally, photocurrent-voltage (*J-V*) measurements were conducted with a solar simulator on the unencapsulated devices in an ambient atmosphere. Similarly, incident light intensity was calibrated to 1 sun (100 mW/cm²) with a standard Si photodiode.

(a)



(b)

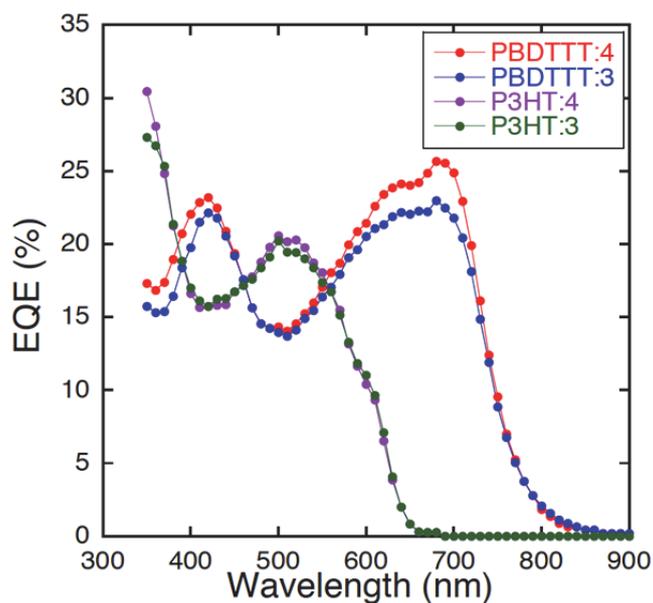


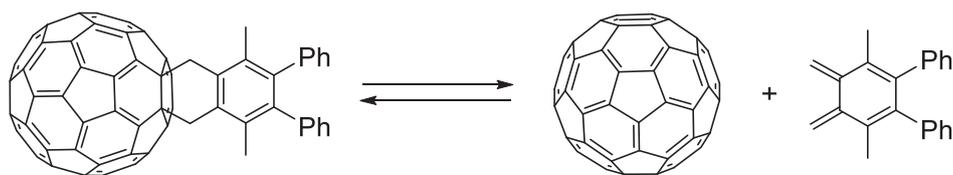
Figure 3-44. OPV performance for the PBDTTT-based (device 1 and 2) and P3HT-based (device 3 and 4) devices with compounds 3 and 4. (a) J - V curves obtained under AM1.5G illumination (100 mW/cm², 1 sun). (b) External quantum efficiency (EQE) as function of wavelength of the OPV device.

4. FeCl₃-Mediated Retro-Reactions of Fullerene Derivatives to C₆₀[†]

4.1 Introduction

A retro-reaction is a backward reaction that converts the products of the corresponding forward reaction into starting materials¹. In some cases, retro-reactions are used effectively. For instance, a soluble tetrabenzoporphyrin precursor (1,4:8,11:15,18:22,25-tetraethano-29*H*,31*H*-tetrabenzob[*b,g,l,q*]porphyrin) undergoes a retro-Diels–Alder reaction upon heating to give a semiconducting tetrabenzoporphyrin that is used in organic photovoltaic devices². Retro-reactions of fullerene derivatives have been known since 1993. Many types of fullerene derivatives take part in retro-reactions under various conditions to afford parent fullerenes. For example, Diels–Alder adducts of fullerenes with anthracene or pentacene are converted under heating to the parent fullerenes via the retro-Diels–Alder reaction³ as shown in Scheme 4-1. Some methanofullerenes prepared by the Bingel reaction release their organic addends to give fullerenes through electrochemical reactions⁴, chemical reduction⁵, and reductive ring opening reactions⁶. Some pyrrolidinofullerenes, which are obtained by the Prato reaction, give parent fullerenes by electrochemical reduction⁷, chemical reactions with dipolarophiles⁸, and so on⁹. In addition, isoxazolino[3,4:1,2]fullerenes¹⁰ and 2-pyrazolino[3,4:1,2]fullerenes¹¹ have known to undergo retro-reaction in the presence Cu(II) oxidant.

Scheme 4-1. retro-Diels–Alder reaction

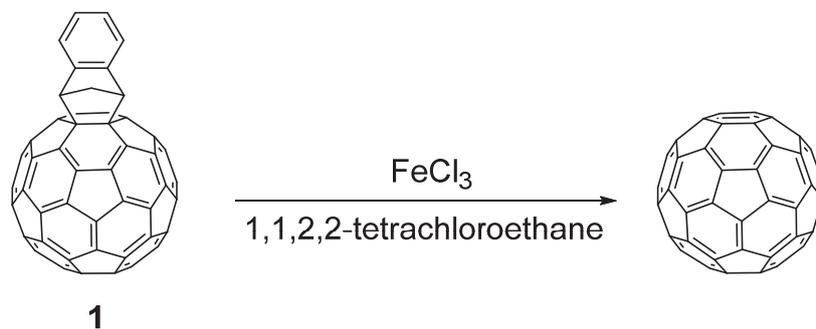


From the results of experiments of FeCl₃-mediated reaction of fullerenes as mentioned in Chapter 2 and 3, I came up with the idea that retro-reaction of C₆₀ derivatives can take place using FeCl₃. In this chapter, I found that iron(III) chloride, FeCl₃, mediates retro-reactions of various fullerene derivatives. I investigated the FeCl₃-mediated retro-reactions of indene–C₆₀ monoadduct (ICMA)¹² and phenyl-C₆₁-butyric acid methyl ester (PCBM)¹³, which are commonly used electron-accepting materials for photovoltaic applications. The developed reaction employs inexpensive FeCl₃, proceeds under mild conditions (at room temperature), and is easy to perform. In addition, the retro-reaction has a substrate selectivity and can suggest various application. These favorable features will make this new reaction practical, and open up new opportunities in fullerene-based

materials science.

4.2 Retro-Reaction of Diels–Alder Adduct of [60]Fullerene

At First, I selected an indene adduct, ICMA (**1**, Table 4-1) in order to investigate the FeCl₃-mediated retro-reaction. ICMA is a Diels–Alder adduct of isoindene, derived from thermal isomerization of indene at high temperature (ca. 245 °C). Because isoindene is a less favorable (higher energy) form in comparison with indene, a thermally induced retro-Diels–Alder reaction generating isoindene hardly occurs. ICMA is thus stable, and does not participate in the retro-reaction even upon heating at 150 °C (Table 4-1, entry 1). In contrast, in the presence of FeCl₃, ICMA was converted into parent C₆₀ at 25 °C.

Table 4-1. Reaction conditions and yields for the retro-reaction of ICMA (**1**)

entry	equiv. of FeCl ₃	Temperature (°C)	reaction time (h)	conversion of 1 (%) ^a	HPLC area ratio (%) ^a	yield of C ₆₀ (%) ^b
1	0	150	5	— ^c	— ^c	— ^c
2	2	25	5	4.5	1.1	— ^d
3	5	25	5	44	38	11
4	10	25	2	78	55	25
5	10	25	5	98	89	28
6	10	80	0.5	98	96	34
7	20	25	0.5	87	86	30
8	20	25	1	98	95	37
9	20	80	0.5	99	94	32
10	50	25	1	97	90	32

^a Conversion of C₆₀ and selectivity of product were determined by HPLC analysis. ^b Isolated yield. ^c No reaction. ^d Unrecoverable.

A typical reaction procedure for the FeCl₃-mediated retro-reaction of ICMA is given as follows: Treatment of ICMA (500 mg, 0.60 mol) with FeCl₃ (1.94 g, 12.0 mol) in 1,1,2,2-tetrachloroethane (10 mL) at 25 °C for 1 h gives a reaction mixture, which are passed through a short column of silica gel with toluene as eluent. Concentration of the collected solution and precipitation by addition of 2-propanol yields black crystals of C₆₀ (isolated yield: 37%; Table 4-1, entry 8). Separation with silica gel chromatography was not necessary because the retro-reaction was highly selective for soluble material (i.e., high HPLC area ratio). Only a short path of silica gel was needed to remove excess iron contents.

As in the case of FeCl₃-mediated reactions of C₆₀ (as noted in Chapter 2 and Chapter 3), I used a fairly uncommon solvent, 1,1,2,2-tetrachloroethane. Aromatic organic solvents such as toluene and *o*-dichlorobenzene, which are often used in fullerene chemistry, were not suitable for this retro-reaction. Those solvents led to a side reaction, namely, Lewis acidic FeCl₃-mediated hydroarylation of C₆₀¹⁴. This in turn led to a lower yield of C₆₀. As an alternative solvent for this retro-reaction, 1,1,2,2-tetrachloroethane was chosen because it does not have an aromatic component and can dissolve fullerene and fullerene derivatives.

Using this solvent, the retro-reaction proceeded more smoothly when larger amount of FeCl₃ was used (Table 4-1, entries 2–4). A longer reaction time (entry 5) and a higher reaction temperature (entry 6) gave slightly better results in reactions using 10 equiv. of FeCl₃. The best result was obtained in the reaction using 20 equiv. of FeCl₃, a reaction temperature of 25 °C, and a reaction time of 1 h (entry 8), whereas a shorter reaction time (entry 7) and a higher reaction temperature (entry 9) did not give better results. The use of 50 equiv. of FeCl₃ gave lower isolated yield (entry 10).

The isolated yield was low in comparison with the high conversion in the retro-reaction as observed by HPLC; this was attributed to the formation of unidentified insoluble products. The HPLC area ratio is related to the soluble fraction of the products. I presume that the insoluble products are fullerene oligomers¹⁵.

I attempted the retro-reaction using other Lewis acids (AlCl₃, BF₃·Et₂O, RuCl₃, FeCl₂, NiCl₂, CoCl₂, and ZnCl₂), as well as *p*-toluenesulfonic acid, in place of FeCl₃, but similar reactivity was not observed. Only AlCl₃ showed weak reactivity, giving conversion of less than 10%, and thus the reaction with AlCl₃ is not practical.

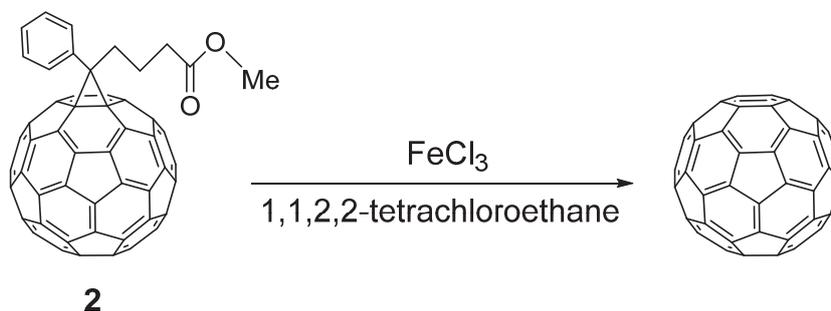
I considered the reason why FeCl₃ mediated the retro-reaction of ICMA. I have previously studied

FeCl₃-mediated reactions for fullerene functionalization¹⁶ and found that FeCl₃ oxidizes fullerene to give fullerene radical cation (as mentioned in Chapter 2 and Chapter 3). This oxidation involves formation of a C₆₀-Cl bond via redox conversion of Fe^{III}Cl₃ to Fe^{II}Cl₂, whereupon chloride is extracted to give C₆₀^{•+} and FeCl₄⁻. I speculate that ICMA participates in a similar FeCl₃-mediated oxidation, giving radical cation of ICMA, which undergoes C-C bond cleavage between C₆₀ and indene. This reaction probably involves other complex reaction paths, and the whole reaction mechanism remains unclear.

4.3 Retro-Reaction of PCBM

Next I investigated the FeCl₃-mediated retro-reaction of other typical fullerene derivatives. PCBM (**2**) is a standard electron-accepting material for organic solar cells. In the presence of FeCl₃, retro-reaction of PCBM was found to proceed at 25 °C (Table 4-2). With the use of 20 equiv. of FeCl₃ at 25 °C for 1 h, the conversion reached 100% (Table 4-2, entries 1–5). Under these conditions, however, the HPLC area ratio was only 40%. This implies many side reactions occurred in this reaction system. I consider that FeCl₃ reacts with the ester group of PCBM, thus causing the formation of complex side products. The isolated yield of C₆₀ was 14%.

Table 4-2. Reaction conditions and yields for the retro-reaction of PCBM (**2**)



entry	equiv. of FeCl ₃	Temperature (°C)	reaction time (h)	conversion of 2 (%) ^a	HPLC area ratio (%) ^a	yield of C ₆₀ (%) ^b
1	2	25	12	21	2.7	— ^c
2	5	25	12	45	5.3	— ^c
3	10	25	1	48	4.8	— ^c
4	10	25	12	85	30	5.6
5	20	25	1	100	40	14
6	20	25	3	100	43	10
7	50	25	1	100	62	6

^a Conversion of C₆₀ and selectivity of product were determined by HPLC analysis. ^b Isolated yield.

^c Unrecoverable.

Lastly, I examined this retro-reaction using methanofullerene **3** (3'*H*-cyclopropa[1,9][5,6]fullerene- C_{60} -*I*-3',3'-dicarboxylic acid, 3',3'-bis(1,1-dimethylethyl) ester) and pyrrolidinofullerene **4** (2'*H*-[5,6]Fullereno- C_{60} -*I*-[1,9-*c*]pyrrole) (Figure 4-1). However, the retro-reaction did not proceed at all. The recovery of both compounds was nearly 100%. Regarding compound **3**, I believe the electron-withdrawing ester group prevents oxidation of the fullerene part, in turn preventing the reaction. The stability of compound **4** is explained by delocalization the positive charge formed on the nitrogen atom.

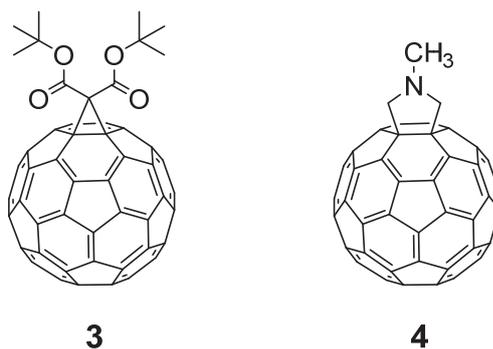


Figure 4-1. Methanofullerene **3** and pyrrolidinofullerene **4**

4.4 Conclusion

I reported that FeCl₃-mediated retro-reactions of fullerene derivatives to give C₆₀. ICMA and PCBM underwent the retro-reaction in the presence of 20 equiv. of FeCl₃ at 25 °C for 1 h and were converted to C₆₀. In contrast, Bingel-product **3** and Prato-product **4** did not react under reaction conditions. The advantages of this reaction are the use of inexpensive FeCl₃, mild reaction conditions, and simple operations.

Potential applications of FeCl₃-mediated retro-reaction are considered below. (i) This reaction could be utilized in a protection–deprotection procedure for regioselective synthesis of fullerene derivatives. For instance, the indene group would mask a particular fullerene double bond, and could be removed after subsequent polyfunctionalization¹⁷. (ii) Considering the substrate selectivity observed in this work, this reaction could aid in the separation and purification of mixtures of fullerene derivatives. By adding FeCl₃, undesired products would be converted to C₆₀, which could be easily removed because of its solubility and polarity are very different from those of fullerene derivatives. (iii) Surface reforming of thin films is an interesting potential application. Application of FeCl₃ onto thin films of fullerene derivatives would form C₆₀ on the film surface. This would then lower solubility, similar to the conversion of a soluble tetrabenzoporphyrin precursor into insoluble tetrabenzoporphyrin².

Experimental Section

Methods and Materials

All reactions were carried out under nitrogen atmosphere. Analytical gradient reversed-phase HPLC was performed on an Agilent 1200 series instrument equipped with an ODS column (YMC-Pack ODS-AM, 5 micron, 4.6 x 150 mm). All runs used linear gradients of methanol (solvent A) and toluene (solvent B). The gradient ran from 25% B up to 55% B over 25 min. Flow rate was 1.0 mL/min and routine UV detection was performed at 290 nm.

Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Wako Pure Chemical Industries, or other commercial suppliers and used after appropriate purification. Fullerene Derivatives were purchased from Frontier Carbon Co. or Sigma-Aldrich Co. Iron(III) chloride was purchased from Wako Pure Chemical Industries and used as received.

Retro-reaction of ICMA (1)

To a mixture of **1** (500 mg, 0.60 mol) and iron(III) chloride (1.94 g, 12.0 mol) was added 1,1,2,2-tetrachloroethane (10 mL) at room temperature. After stirring for 1 h, an adequate amount of water was added to quench the reaction. The resulting solution was passed through a pad of silica gel (eluent: toluene) and the volatiles were removed with rotary evaporator. The product was crystallized by adding 2-propanol as a poor solvent, and the resulting precipitate was collected by filtration and dried under reduced pressure (100°C, 1 mmHg) to give C₆₀ (158 mg, 37% isolated yield, analytically pure) as black crystals.

Retro-reaction of PCBM (2)

To a mixture of **2** (450 mg, 0.49 mol) and iron(III) chloride (1.78 g, 11.0 mol) was added 1,1,2,2-tetrachloroethane (9 mL) at room temperature. After stirring for 1 h, an adequate amount of water was added to quench the reaction. The resulting solution was passed through a pad of silica gel (eluent: toluene) and the volatiles were removed with rotary evaporator. The crude product was purified by silica gel chromatography (eluent: toluene/hexane = 1/1) to give C₆₀ (50 mg, 14% isolated yield, analytically pure) as black crystals.

References and Notes

[†] The contents of this chapter have already been published in the following paper. Hashiguchi, M.; Ueno, T.; Matsuo, Y. *Fullerenes, Nanotubes and Carbon Nanostructures* **2014**, *in press*. [DOI:10.1080/1536383X.2012.742429]

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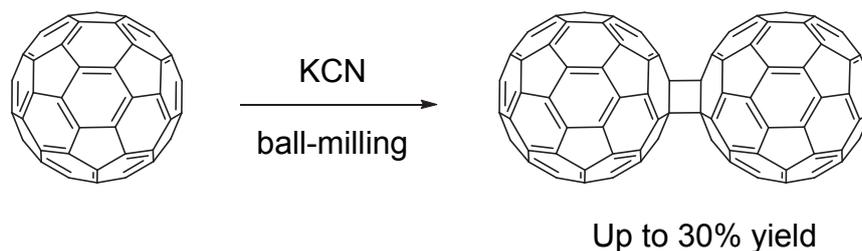
5. Solution-Phase Synthesis of Dumbbell-Shaped C₁₂₀ by FeCl₃-Mediated Dimerization of C₆₀[†]

5.1 Introduction

Fullerene chemists and carbon cluster scientists have devoted much attention to fullerene dimers such as C₁₂₀ and C₁₂₀O, because of their unique structures that are thought to be intermediates in fullerene polymerization.¹ Among them, special attention has been paid to buckminsterfullerene dimer, C₁₂₀, which is composed of only carbon atoms.^{1,2} C₁₂₀ was first synthesized by Komatsu and co-workers in 1997.^{2a-c} The structure of C₁₂₀ has been determined by single-crystal X-ray crystallography, which revealed a dumbbell shape with two single bonds connecting the two C₆₀ units. C₁₂₀ has been used to investigate photoinduced electron transfer,³ ultrafast energy relaxation dynamics,⁴ adsorption on a gold surface,^{5a-c} application as a supramolecular oscillator,⁶ and chemical modifications for functionalizing the dimer.^{2c,7}

The first reported C₁₂₀ synthesis used high-speed vibration milling (Scheme 5-1).^{2a-c} This solid-phase synthesis is advantageous from the viewpoint of green chemistry, because organic solvent is not necessary. On the other hand, a solution-phase synthesis of the dimer C₁₂₀ has yet to be reported. Solution-phase synthesis offers certain advantages: the synthesis can be conducted by using common laboratory glassware and controlled by managing solution concentration and temperature, which are features applicable to industrial production.

Scheme 5-1. Solid-phase synthesis of C₁₂₀



From the results of investigations of FeCl₃-mediated reaction of fullerenes as mentioned in Chapter 2-4, I consider that FeCl₃ play an important role as an oxidant in this reactions. Therefore, I anticipate that FeCl₃-mediated dimerization of fullerene take place in solution via fullerene radical cation.

In this chapter, I investigate FeCl₃-mediated solution-phase synthesis of dumbbell-shaped C₁₂₀, where dimerization of C₆₀ proceeds in the presence of inexpensive FeCl₃.

5.2 Synthesis of Dumbbell-shaped C₁₂₀

Treatment of C₆₀ with 20 equiv. of FeCl₃ in 1,1,2,2-tetrachloroethane for 3 h at 150 °C afforded C₁₂₀ in 21% isolated yield (Scheme 5-1). A typical reaction procedure for the FeCl₃-mediated synthesis of C₁₂₀ is as follows. To a solution of C₆₀ (500 mg, 0.69 mmol) in 1,1,2,2-tetrachloroethane (10 mL) at 25 °C, FeCl₃ (2.25 g, 14 mmol) was added. After stirring at 150 °C for 3 h, a sufficient amount of water was added to quench the reaction. Formation of C₁₂₀ was verified by HPLC (Figure 5-1). The product was extracted with *o*-dichlorobenzene (200 mL). The organic layer was washed with distilled water, and the solvent was evaporated. The product was purified by preparative HPLC separation (COSMOSIL 5PBB column; eluent: *o*-dichlorobenzene) to obtain the C₁₂₀ (106 mg, 21% isolated yield, analytically pure) as black crystals.

Scheme 5-2. FeCl₃-mediated synthesis of C₁₂₀ in solution

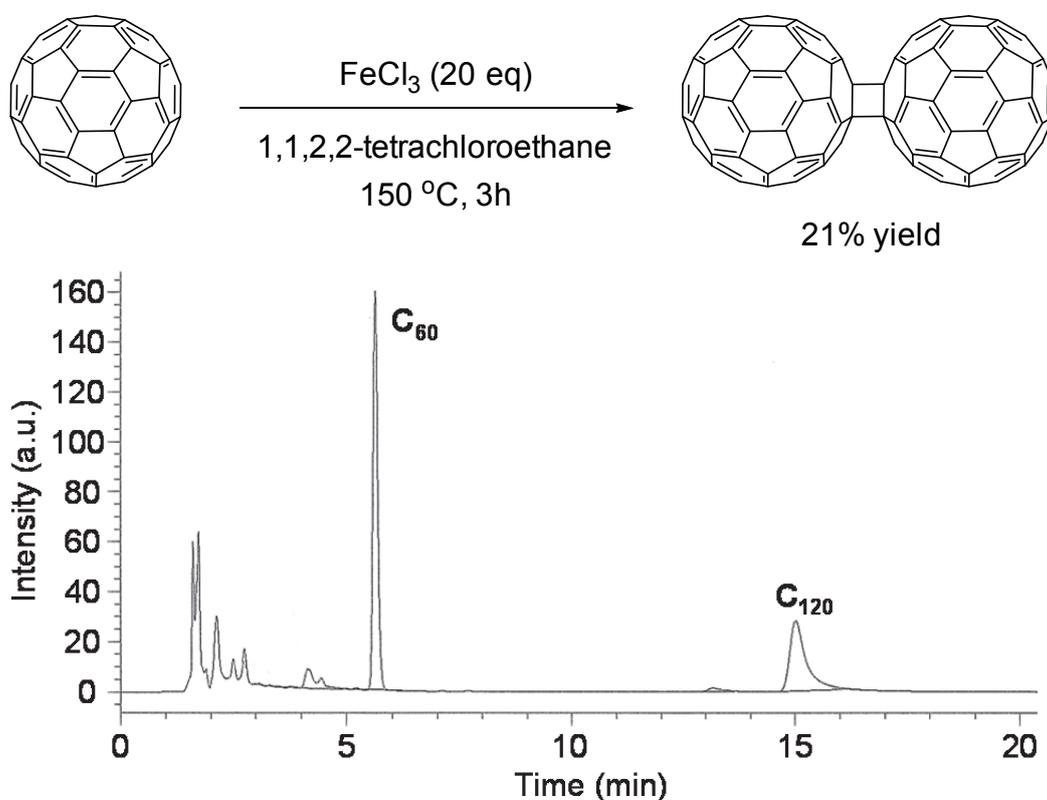


Figure 5-1. HPLC chart for the synthesis of C₁₂₀ using FeCl₃

C_{120} was characterized by spectroscopic methods as well as X-ray crystallography. Electrospray ionization (ESI) mass spectrometry data showed a parent peak for C_{120} . Compared with the reported IR spectrum of C_{60} ,⁸ the IR spectrum of C_{120} contained many more peaks and agreed with the reported data.^{2b} No signal was observed in the 1H NMR spectrum. The ^{13}C NMR spectrum exhibited 16 signals due to the sp^2 fullerene carbon atoms with one signal for the sp^3 carbon atoms, indicating that the dimer has D_{2h} symmetry. Our NMR data are the same as the authentic data reported by Komatsu et al.^{2a} Finally I confirmed the molecular structure by X-ray diffraction analysis (Figure 5-2) using single crystals grown from a two-layer system using 1,2-dichlorobenzene (good solvent) and toluene (poor solvent). A triclinic $P-1$ crystal contains one C_{120} and four toluene molecules in its unit cell. This crystal's formula is analogous to the reported one, $C_{120} \cdot (o\text{-dichlorobenzene})_4$.

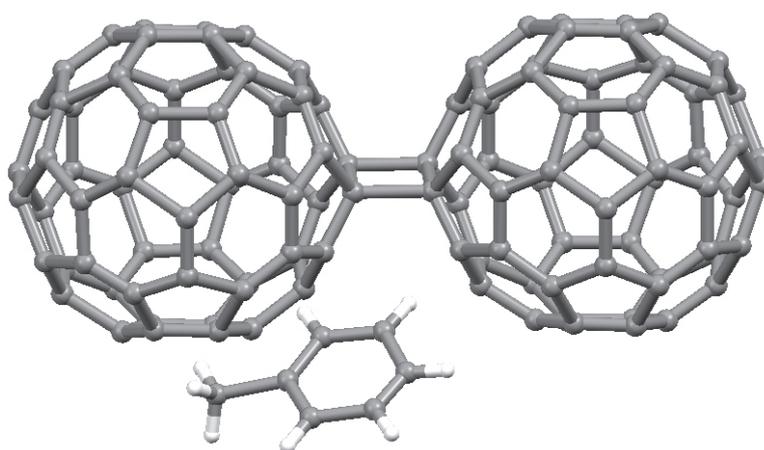
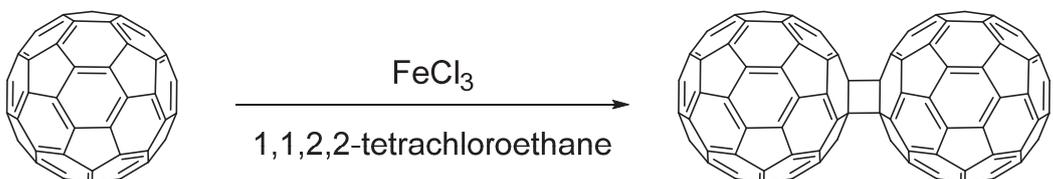


Figure 5-2. Crystal structure of $C_{120} \cdot (\text{toluene})_4$. Three of the toluene molecules in the unit cell are omitted for clarity.

5.3 Reaction Conditions

The results of reaction condition optimization are shown in Table 1, which lists conversion of C_{60} , HPLC area ratio of C_{120} , and isolated yield of C_{120} for various conditions (amount of $FeCl_3$, reaction temperature, and reaction time). I chose 1,1,2,2-tetrachloroethane as the solvent because it lacks an aromatic component and dissolves C_{60} . Aromatic organic solvents such as toluene and *o*-dichlorobenzene, often used in the synthesis of fullerene derivatives, are unsuitable for this reaction. The use of aromatic solvents causes a side reaction, hydroarylation,⁹ which is mediated by the Lewis acidic $FeCl_3$.

Table 5-1. Reaction conditions and yields for the synthesis of C₁₂₀.


entry	equiv. of FeCl ₃	temperature (°C)	reaction time (h)	Conversion of C ₆₀ (%) ^a	HPLC area ratio of C ₁₂₀ (%) ^a	isolated yield of C ₁₂₀ (%) ^b
1	10	25	6	25	— ^c	— ^c
2	10	40	7	42	— ^c	— ^c
3	10	80	7	44	— ^c	— ^c
4	10	120	3	41	8.7	— ^d
5	10	150	1	20	19	— ^d
6	10	150	3	39	33	15
7	10	150	8	55	23	10
8	20	150	1	21	1.7	— ^d
9	20	150	3	68	29	21
10	20	150	9	85	23	13
11	5	150	3	34	30	11

^a Conversion of C₆₀ and HPLC area ratio of C₁₂₀ determined by HPLC analysis. ^b Isolated yield. ^c No reaction. ^d Unrecoverable.

The use of 10–20 equiv. of FeCl₃ to C₆₀ was necessary to carry out this reaction effectively. I have previously reported FeCl₃-mediated polyarylation of fullerene,¹⁰ synthesis of fullerenyl esters,¹¹ and retro-reactions of fullerene derivatives to C₆₀.¹² In all three previous cases, the use of 10–20 equiv. of

FeCl₃ was also necessary. I consider all these FeCl₃-mediated reactions involving a common key intermediate, namely, fullerene radical cation, which is generated in the presence of 10–20 equiv. of FeCl₃.

I performed further reaction condition optimization. Below 80 °C, C₆₀ was consumed, and no C₁₂₀ was observed by HPLC (Table 5-1, entries 1–3). At 120 °C, I observed formation of C₁₂₀ with an area ratio of 8.7% in the HPLC analysis (entry 4). The reaction at 150 °C for 3–9 h produced C₁₂₀ more effectively (entries 5–11). In particular, the reaction using 10 equiv. of FeCl₃ for 3 h at 150 °C afforded the highest HPLC area ratio of 33%. Under this set of conditions, however, the isolated yield was only 15% because low conversion of C₆₀ made purification of C₁₂₀ difficult due to peak broadening in the HPLC separation. The maximum isolated yield of 21% was achieved when the reaction was conducted with 20 equiv. of FeCl₃ for 3 h at 150 °C (entry 9). I consider this is a respectable isolated yield, because the first report by Komatsu and co-workers described 18% isolated yield for the solid-state synthesis of C₁₂₀. In addition, the quantity (106 mg) of C₁₂₀ obtained in this experiment is workable. Reaction times longer than 5 h gave lower isolated yield (entries 7, 10). I consider that C₁₂₀ partially dissociate to C₆₀ by long hours of heating at 150 °C or higher temperature.^{2a, 2b, 13}

The limited isolated yield of C₁₂₀ is basically the result of its very low solubility, which causes work-up difficulties as well as isolation and purification problems. An observed side product was C₁₂₀O,¹⁴ which was characterized by ESI mass spectrometry and ¹³C-NMR. I attribute this side product to a small amount of dissolved oxygen, which reacts with the radical cation intermediate. Furthermore, I surmise formation of higher molecular weight components such as trimer and tetramer, which may lower the isolated yield from reactions run for longer times. This possibility is consistent with our finding that, in longer reactions, conversion of C₆₀ was higher but the yield of C₁₂₀ was lower; the maximum isolated yield achieved at a reaction time of 3 h. The formation of trimer and higher molecular weight components has also been observed in solid-phase synthesis.^{2c} Selective and high yielding synthesis of the dimer is a challenge left for future investigation.

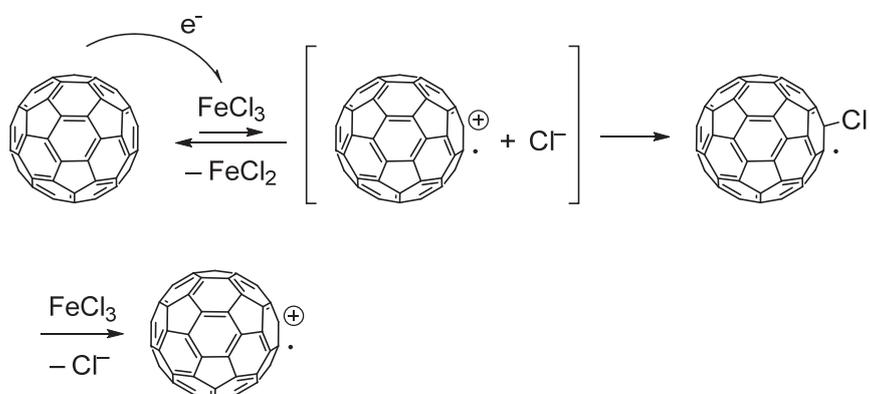
I attempted the reaction using other Lewis acids and iron complexes (AlCl₃, BF₃·Et₂O, RuCl₃, FeCl₂, NiCl₂, CoCl₂, and ZnCl₂) in place of FeCl₃, but similar reactivity was not observed. I attributed this specific reactivity of FeCl₃ for the dimerization of C₆₀ to both the Lewis acidity and oxidizing power of FeCl₃.

5.4 Proposed Reaction Mechanisms

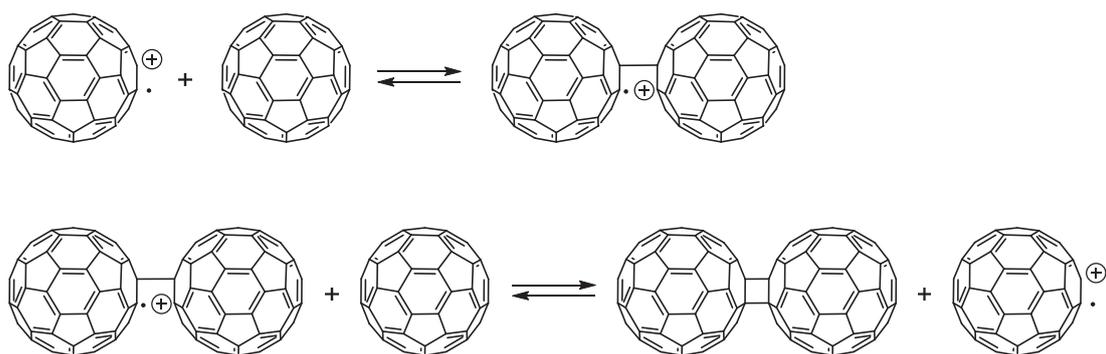
Next, I propose a reaction mechanism for this FeCl₃-mediated dimerization reaction of C₆₀. As noted in Chapter 2 and Chapter 3, I have developed various FeCl₃-mediated reactions and proposed that FeCl₃ can oxidize C₆₀ to generate a fullerene radical cation.¹⁰⁻¹² Similarly, Fukuzumi et al. have reported that Fe³⁺-exchanged zeolite generates a fullerene radical cation.¹⁵ In line with the previous findings, I hypothesize that FeCl₃ mediates formation of fullerene radical cation in this fullerene dimerization reaction. First, electron transfer occurs from C₆₀ to FeCl₃, generating C₆₀^{•+} and FeCl₂ as well as Cl⁻ (Scheme 5-2a). Although electron transfer from C₆₀ to FeCl₃ may appear electrochemically unfavorable, some perturbation such as coordination of chloride to C₆₀ can change its frontier orbital energy level. Then, C₆₀^{•+} can form a bond with Cl⁻, to generate ClC₆₀[•], which can react with FeCl₃ to regenerate the key intermediate C₆₀^{•+} and FeCl₄ (Scheme 5-2a). This abstraction of chloride can take place because of the Lewis acidity of FeCl₃. Afterward, C₆₀^{•+} forms a covalent bond with unreacted C₆₀ to give an intermediate C₆₀[•]-C₆₀⁺, which abstracts an electron from C₆₀ to produce the stable dumbbell-shaped dimer C₁₂₀ (Scheme 5-2b). I suggest that the reactive species C₆₀[•]-C₆₀⁺ reacts with dissolved oxygen to form the side product C₁₂₀O.

Scheme 5-3. Proposed reaction mechanism via fullerene radical cation

(a) Generation of fullerene radical cation



(b) Synthesis of dumbbell-shaped C₁₂₀



5.5 Remarks on Our Approach through Fullerene Cation

The reported high-speed vibration milling technique for the solid-phase synthesis^{2a-c} had generally employed fullerene anion that was generated by using KCN. The solution-phase fullerene functionalization also employs anionic species of fullerene in general,¹⁶ because fullerene anions are usually stabilized in the solution. In addition, fullerene radical anions are known to be stable because of high electron affinity of fullerene. Fullerene radical anion can undergo dimerization to give $[C_{60}-C_{60}]^{2-}$.¹⁷ But this dimerization is in equilibrium. Monomeric fullerene radical anion is largely major in this equilibrium. More importantly, fullerene radical anion does not react with C_{60} itself.¹⁷

Our approach is based on cationic mechanism. Our finding is that fullerene radical cation can have reactivity against C_{60} in solution phase with the present reaction condition to give the dumbbell-shaped dimer C_{120} . This understanding is supported by our previous investigations on $FeCl_3$ -mediated fullerene functionalization through the fullerene radical cation¹⁰⁻¹² and ESR-observation of the fullerene radical cation in Fe^{3+} -exchanged zeolite.¹⁵

5.6 Conclusion

I reported the solution-phase synthesis of dumbbell-shaped C_{120} through $FeCl_3$ -mediated dimerization of C_{60} . The reaction in 1,1,2,2-tetrachloroethane for 3 h at 150 °C gave the product in respectable isolated yield of 21%. I hypothesized that the reaction proceeds via a fullerene radical cation intermediate generated from C_{60} and oxidative $FeCl_3$. The successful use of $FeCl_3$ in this method is of particular interest because iron-mediated transformations avoid the use of expensive and toxic transition metals. These findings will provide opportunities for further investigation to obtain polymeric structures of fullerenes in the solution phase as well as to expand applied research on C_{120} .

Experimental Section

Methods and Materials

All reactions were carried out under nitrogen atmosphere. Analytical high-performance liquid chromatography (HPLC) was performed on a Buckyprep column (Nacalai Tesque Inc., 4.6 x 250 mm) using toluene as eluent (flow rate: 1.0 mL/min, detected at 290 nm). Preparative HPLC was performed on a 5PBB column (Nacalai Tesque Inc., 20 mm x 250 mm) using ODCB as eluent (flow rate: 8 mL/min, detected at 290 nm with an UV spectrometer, Shimadzu SPD-6AV). NMR spectra were reported in part per million from C₆D₄Cl₂. Mass spectra were measured with ESI-mass spectrometer (Negative mode) equipped on an ODS column.

Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Wako Pure Chemical Industries, or other commercial suppliers and used after appropriate purification. [60]Fullerene was purchased from Frontier Carbon Co. Iron(III) chloride was purchased from Wako Pure Chemical Industries and used as received.

Synthesis of dumbbell-shaped C₁₂₀

To a solution of C₆₀ (500 mg, 0.69 mmol) in 1,1,2,2-tetrachloroethane (10 mL) at 25 °C, FeCl₃ (2.25 g, 14 mmol) was added. After stirring at 150 °C for 3 h, a sufficient amount of water was added to quench the reaction. The product was extracted with *o*-dichlorobenzene (200 mL). The organic layer was washed with distilled water, and solvent was evaporated. Purification of the product was performed by preparative HPLC separation (COSMOSIL 5PBB column; eluent: *o*-dichlorobenzene) to obtain the C₁₂₀ (106 mg, 21% isolated yield, analytically pure) as black crystals.

¹H NMR (400 MHz, 1,2-Cl₂C₆D₄): no signal; ¹³C NMR (100 MHz, 1,2-Cl₂C₆D₄): δ 76.19, 138.78, 140.46, 141.73, 141.76, 142.33, 142.49, 142.73, 144.14, 144.77, 144.87, 144.94, 145.42, 145.85, 146.91, 151.19; React IR (ATR): 523.6 (s), 544.7 (w), 550.3 (w), 560.3 (w), 573.8 (w), 611.2 (w), 707.6 (w), 745.4 (w), 763.6 (w), 768.6 (w), 795.6 (w), 806.1 (w), 830.2 (w), 848.6 (w), 960.5 (w), 1032.8 (w), 1100.3 (w), 1185.1 (w), 1424.7 (w), 1456.0 (w), 1462.7 (w) cm⁻¹; ESI-MS (-): *m/z* calcd for C₁₂₀ (M⁻): 1441.2; found, 1441.9.

References and Notes

† The contents of this chapter have already been published in the following paper. Hashiguchi, M.; Inada, H.; Matsuo, Y. *Carbon* **2013**, *61*, 418–422.

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6. Conclusion

The drawback to industrialization of fullerene is the production costs. Although the present price of [60]fullerene is still expensive, in an extreme instance, it is possible to significantly reduce variable cost (i.e., materials cost) by mass production and mass distribution. A fixed cost (i.e., employment cost, equipment cost) accounts for a substantial percentage of production cost in common chemical products. Fullerene industry is no exception, the more it scales up, the more the rate of the fixed cost to in the production costs increases. It is important that I make production process as simple as possible in order to reduce fixed costs. To achieve the aim, I focused attention on the availability of FeCl₃, and investigated FeCl₃-mediated reactions of [60]fullerene and fullerene derivatives.

At first, I developed a facile synthetic method of polyarylated fullerenes and fullereryl esters using inexpensive iron(III) chloride (FeCl₃). These methods require only versatile reagents (i.e., C₆H₅X, RCOOH, and H₂O) and simple handling such as stirring at room temperature. Hence, these methods are suitable for industrial manufacture. In addition, this methodology enables the synthesis of fullerene electron-acceptors that have low LUMO levels. The LUMO levels of the diester and siloxyl derivatives were found to be similar to that of [60]fullerene. These low-LUMO acceptors gives the opportunity to employ a wider range of donor materials, especially those with low LUMO levels such as low band gap polymers.

Next, I reported that FeCl₃-mediated retro-reactions of fullerene derivatives to give C₆₀. Indene-C₆₀ monoadduct (ICMA) and phenyl-C₆₁-butyric acid methyl ester (PCBM) undergo retro-reactions in the presence of FeCl₃ at 25 °C for 1 h, affording their parent C₆₀. Substrate selectivity was found; the retro-reaction for methanofullerene (Bingel-reaction product) and pyrrolidinofullerene (Prato-reaction product) did not proceed at all to afford 100% recovery. The use of inexpensive FeCl₃, mild reaction conditions, simple operations, substrate selectivity are advantageous and suggest several potential applications.

At last, I investigated a solution-phase synthesis of dumbbell-shaped C₁₂₀ via FeCl₃-mediated dimerization of C₆₀. In the presence of FeCl₃, C₆₀ in 1,1,2,2-tetrachloroethane reacted at 150 °C to produce a dumbbell-shaped dimer C₁₂₀. I propose a reaction mechanism that includes FeCl₃-mediated generation of an intermediate C₆₀ radical cation, which reacts with C₆₀ to form the dimer. The respectable chemical yield (21%) and quantity (106 mg) of the product will open new possibilities for investigating solution-phase polymerization of fullerenes as well as for conducting applied research on C₁₂₀.

I developed FeCl₃-mediated synthesis of C₆₀ derivatives and retro-reaction of C₆₀ derivatives. As the result, I am assured of the diversity of FeCl₃ in fullerene chemistry. I established some breakthrough synthetic methods using only inexpensive and ubiquitous chemicals without unconventional apparatus. In addition, as noted in introduction of the thesis, iron reagents are environmentally-friendly materials. I am firmly convinced that my research lead the growth and development of fullerene science.

List of Publications

FeCl₃-Mediated Reactions of Fullerene

1) Facile Fullerene Modification: FeCl₃-mediated Quantitative Conversion of C₆₀ to Polyarylated Fullerenes Containing Pentaaryl(chloro)[60]fullerenes

Masahiko Hashiguchi, Kazuhiro Watanabe, Yutaka Matsuo

Org. Biomol. Chem. **2011**, *9*, 6417–6421.

2) FeCl₃-Mediated Synthesis of Fullerenyl Esters as Low-LUMO Acceptors for Organic Photovoltaic Devices

Masahiko Hashiguchi, Naoki Obata, Masashi Maruyama, Kee Sheng Yeo, Takao Ueno, Tomohiko Ikebe, Isao Takahashi, Yutaka Matsuo

Org. Lett., **2012**, *14*, 3276–3279.

3) Solution-Phase Synthesis of Dumbbell-Shaped C₁₂₀ by FeCl₃-Mediated Dimerization of C₆₀

Masahiko Hashiguchi, Hiroshi Inada, Yutaka Matsuo

Carbon **2013**, *61*, 418–422.

4) FeCl₃-mediated Retro-reactions of Fullerene Derivatives to C₆₀

Masahiko Hashiguchi, Takao Ueno, Yutaka Matsuo

Fullerenes, Nanotubes and Carbon Nanostructures **2014**, *in press*.

[DOI:10.1080/1536383X.2012.742429]

Other Publications

5) Kilogram-scale [60]fullerene separation from a fullerene mixture:

Selective complexation of fullerenes with 1,8-diazabicyclo[5.4.0]undec-7-ene(DBU)

Koichi Nagata, Eiji Dejima, Yasuharu Kikuchi, Masahiko Hashiguchi

Chem. Lett. **2005**, *34*, 178–179.

6) Efficient and Scalable Method for [60]Fullerene Separation from a Fullerene Mixture: Selective Complexation of Fullerenes with DBU in the Presence of Water

Koichi Nagata, Eiji Dejima, Yasuharu Kikuchi, Masahiko Hashiguchi

Org. Process Res. Dev. **2005**, *9*, 660–662.

- 7) Organic photovoltaics based on solution-processed benzoporphyrin
Yasuharu Sato, Takaaki Niinomi, Masahiko Hashiguchi, Yutaka Matsuo, Eiichi Nakamura
Proc. SPIE Opt. Photon. **2007**, 6656.
- 8) Regioselective Synthesis of 1,4-Di(organo)[60]fullerenes through DMF-assisted Monoaddition of Silylmethyl Grignard Reagents and Subsequent Alkylation Reaction
Yutaka Matsuo, Akihiko Iwashita, Yoko Abe, Chang-Zhi Li, Keiko Matsuo, Masahiko Hashiguchi, Eiichi Nakamura
J. Am. Chem. Soc., **2008**, *130*, 15429–15436.
- 9) Synthesis, Electrochemical and Photophysical Properties, and Electroluminescent Performance of the Octa- and Deca(aryl)[60]fullerene Derivatives
Yutaka Matsuo, Yoshiharu Sato, Masahiko Hashiguchi, Keiko Matsuo, Eiichi Nakamura
Adv. Funct. Mater. **2009**, *19*, 2224–2229.
- 10) Penta(organo)[60]fullerenes as Acceptors for Organic Photovoltaic Cells
Takaaki Niinomi, Yutaka Matsuo, Masahiko Hashiguchi, Yoshiharu Sato, Eiichi Nakamura
J. Mater. Chem. **2009**, *19*, 5804–5811.
- 11) [60]Fullerene Purification; Reduction of Impurity C₆₀O via Trialkyl Phosphine
Masahiko Hashiguchi, Koichi Nagata, Katsutomo Tanaka, Yutaka Matsuo
Org. Process Res. Dev. **2012**, *16*, 643–646.

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