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Nucleophilic cyclopropanation of [60]fullerene by the addition–elimination mechanism

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Information on the synthesis of monofunctionalized methanofullerenes C₆₀ obtained by the addition–elimination mechanism is generalized. The main reagents for cyclopropanation, mechanisms and optimal conditions for the processes, and the prospects for practical application of the products are considered.

Introduction

The discovery of fullerenes was recognized as one of the most amazing breakthrough scientific events of the 20th century that was awarded the Nobel Prize in Chemistry in 1996.

Fullerenes are attributed both to inorganic materials as new allotropic modifications of carbon and to organic compounds, since they manifest many properties of unsaturated hydrocarbons in chemical reactions. The chemistry of derivatives of this compound has become one of the most productive and significant areas of organic chemistry (both in theoretical and practical aspects). It is sufficient to say that several thousand publications on the chemistry of fullerene appeared over the past five years, and these studies are becoming more and more practical. For example, the use of fullerene derivatives in medicine seems to be a very promising approach. Some compounds based on C₆₀ are used in the photodynamic therapy of malignant tumors, others proved to be quite effective bacteriostatic and fungicidal agents (effective against the influenza virus, inhibit HIV-1 protease), and still others are antioxidants preventing neurodegenerative processes that lead, in particular, to Parkinson's disease.

The use of fullerene as an acceptor unit with poly-conjugated polymers in solar batteries is also an important approach. This field of organic photovoltaics is actively developing in research institutes and commercial structures in Russia and abroad. One should hope that in the coming years, fullerene compounds will become classical materials for organic electronics.

A primary role is currently given to the development of new effective approaches to organic modifications of fullerenes that would provide high yields of target products and facile incorporation of required functional groups. As

an electron-deficient polyene, C₆₀ is prone to radical addition, nucleophilic addition and cycloaddition reactions, while a decrease in the fullerene skeleton strain is the driving force of fullerene reactivity. It appears that various [2 + *n*]-cycloaddition processes are particularly promising in the functionalization of the fullerene sphere. As a rule, processes with *n* = 1, 2, 3 or 4 occur. The [2 + 1] variant, which is most common for synthetic organic chemists, is attractive from all points of view. Reactions of [2 + 1] cycloaddition result in compounds in which the fullerene cage is annulated with three-membered carbo- and heterocyclic moieties, *i.e.*, they give methanofullerenes, fullerenoaziridines or fullerenooxiranes. The reactions indicated above can occur by various mechanisms including, for example, the addition of carbenes, nitrenes, stabilized carbanions, *etc.*

The vast majority of researchers who develop various methods for the functionalization of the fullerene spheroid prefer [2 + 1]-cycloaddition processes and, above all, the Bingel reaction. It is reasonable, since this process is the most efficient way to synthesize methanofullerenes.

Ample information on fullerene chemistry has been accumulated to date. It is partially covered in reviews^{1–14} and monographs.^{15–18} Now that the useful properties of C₆₀ derivatives have been clearly determined, it is time for their real practical use and creation of effective optical and electrophysical instruments as well as essential pharmaceuticals.

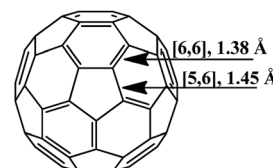


Fig. 1 The C₆₀ fullerene molecule.

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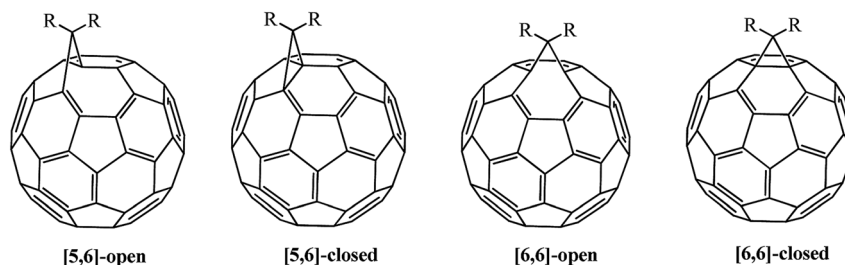
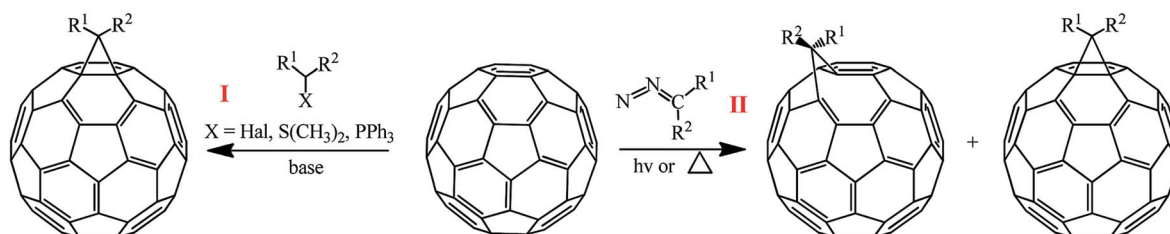


Fig. 2 The four theoretically possible isomeric methanofullerenes C_{60} .

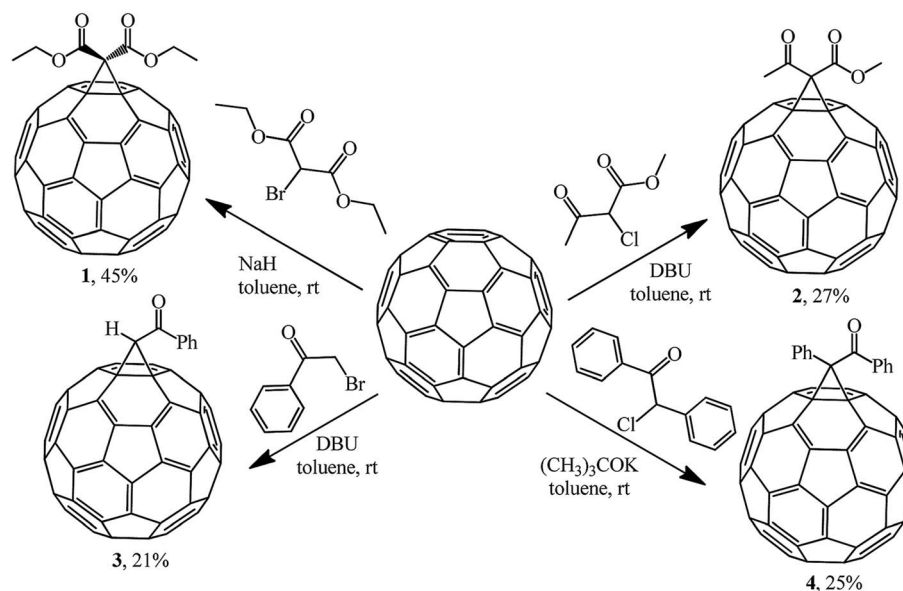


Scheme 1

This review, in which we touch upon the primary functionalization of the C_{60} core for purposes of selective synthesis of monofunctionalized carbon-chain products, includes the main achievements in the field of cycloaddition to [60]fullerene for the past 20 years, including principally important studies performed before that.

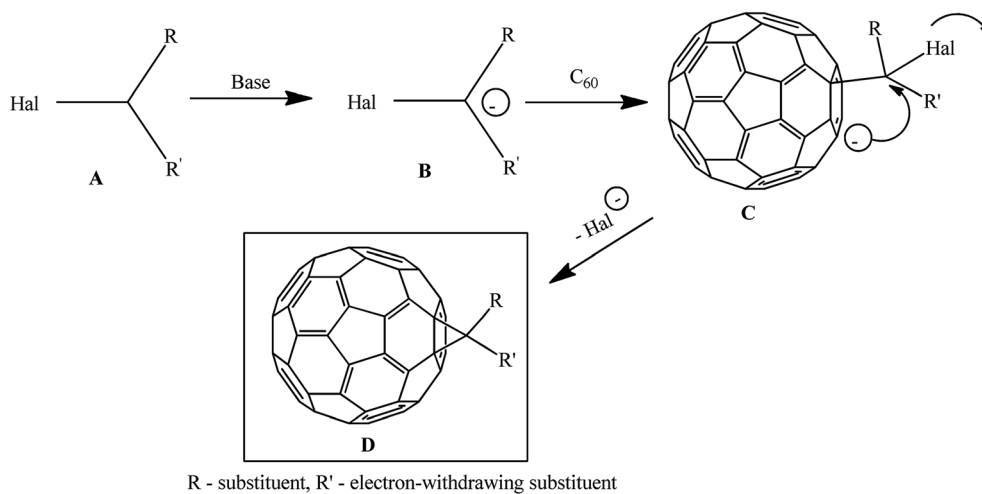
Results and discussion

The molecule of fullerene C_{60} is a closed hollow sphere composed of sp^2 -hybridized carbon atoms interconnected into three-dimensional frames. Twelve five-membered and 20 six-membered rings isolated from each other can be distinguished in it. All the carbon atoms are equivalent, and the molecule geometry implies that two types of bonds exist:

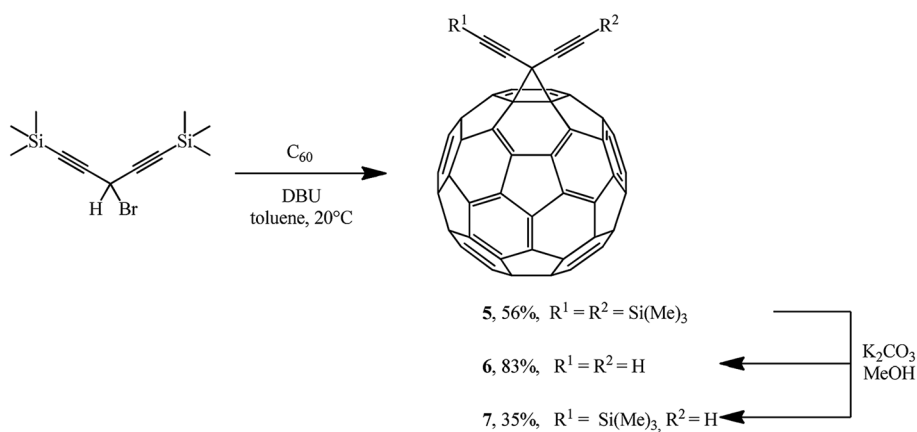


Scheme 2





Scheme 3



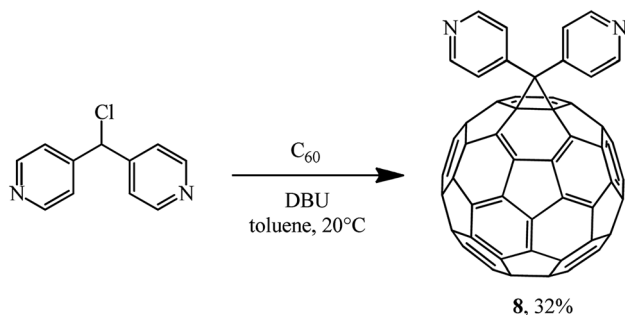
Scheme 4

[6,6] bonds located on the borders of two hexagons and [5,6] bonds located on the borders of hexagons and pentagons (Fig. 1). According to experimental and calculated data, the [6,6] bonds (1.38 Å long) in the C_{60} frame are shorter than

the [5,6] bonds (1.45 Å). Therefore, the former are considered as double bonds, while the latter, as single ones.¹⁹

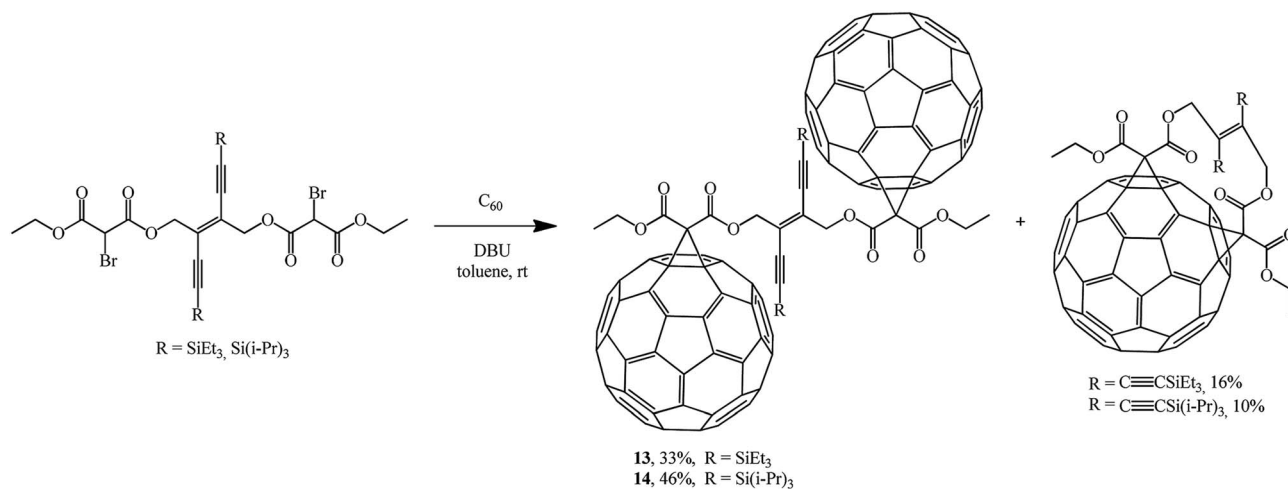
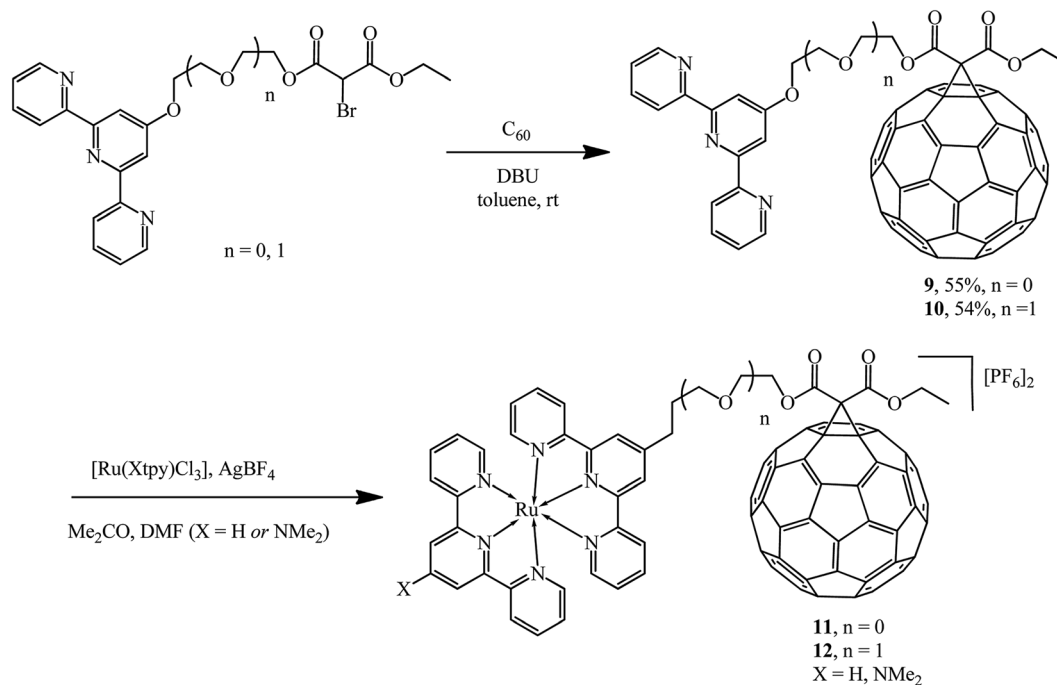
The spherical molecule of fullerene is highly strained, since the usually planar aromatic six-membered (benzene) rings must be twisted to build a sphere. As a result, the thermodynamic stability of C_{60} is lower than that of graphite.

The C_{60} molecule is highly symmetric (a truncated icosahedron) and contains a considerable number of double bonds. However, these bonds are not similar to those in benzene: the rings in the latter are planar, whereas the cells that compose the fullerene cage are three-dimensional and their double bonds are localized to a considerable extent. Strictly speaking, there is no π -electron system in the polyhedral molecule since this molecule is non-planar and its surface is close to a sphere. Therefore, the assignment of fullerenes to aromatic compounds is clearly incorrect. If one has to emphasize the formation of a single p-electronic



Scheme 5

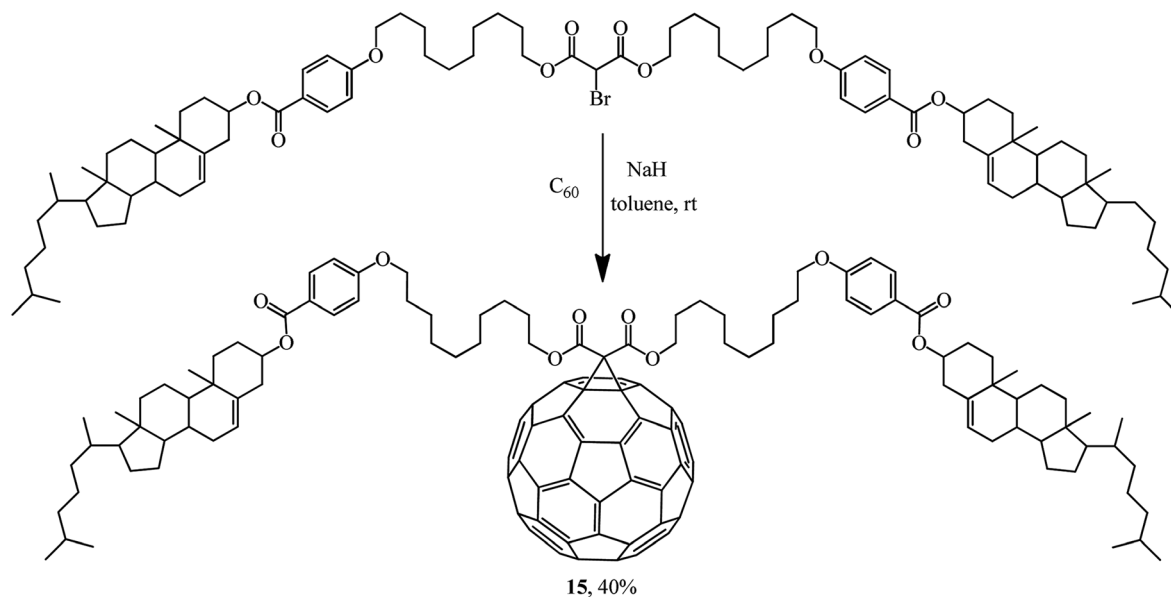




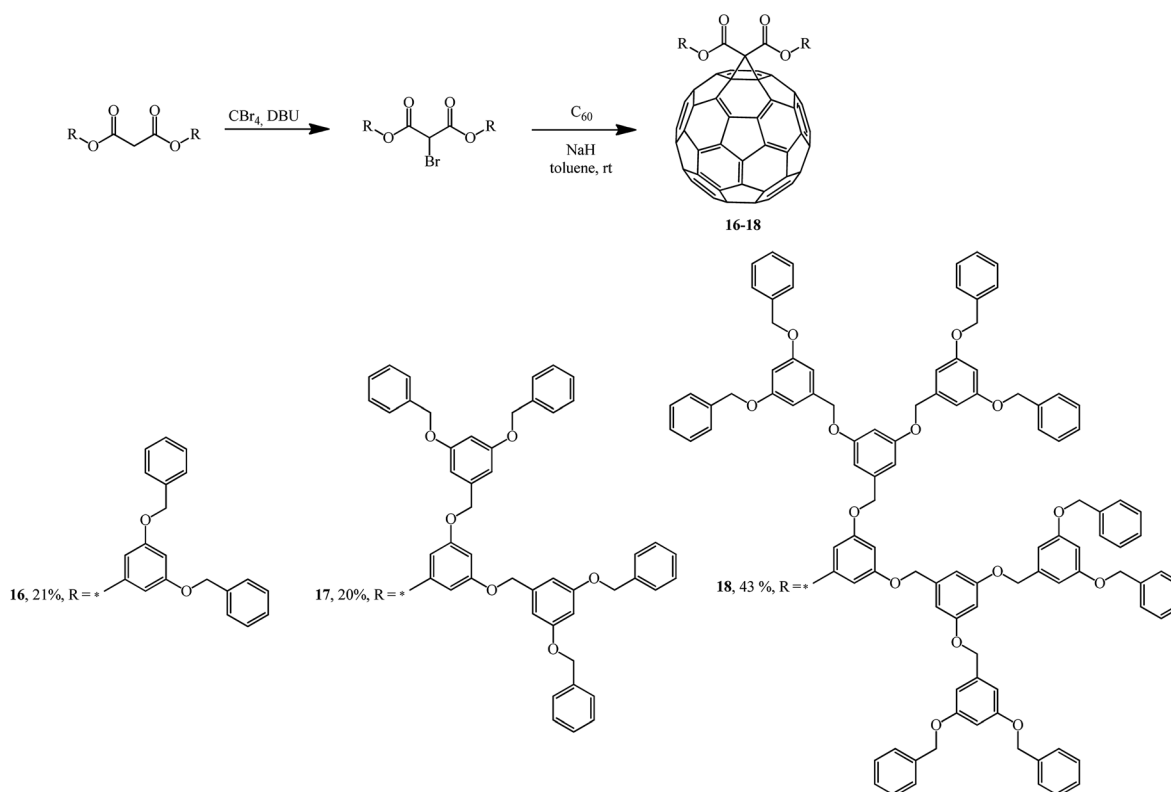
delocalized system leading to a certain energy gain, it is better to use the term “pseudo-aromaticity”. Comparison of the lengths of the bonds (double and single ones) in C_{60} indicates that some conjugation between single and double bonds in fullerene still exists. However, it is more similar to the conjugation of bonds in buta-1,3-diene than in totally aromatic benzene. It is this non-aromaticity that determines the chemical properties of fullerenes, which mainly involve opening of double bonds in the frame on treatment with various reagents.

The driving force behind the reactivity of fullerene involves the reduction of strain in its frame.¹⁶ Four isomers can theoretically exist in monofunctionalized fullerenes: [5,6]-open, [5,6]-closed, [6,6]-open and [6,6]-closed ones; only [5,6]-open and [6,6]-closed isomers are experimentally observed (Fig. 2). As interpreted in ref. 14 and 20, this fact is not due to the nature of substituents, but is explained by the conservation of energetically favorable energy levels in the isomers indicated above. Calculations showed that [6,6]-isomers of methanofullerenes have a closed transannular bond (π -homoaromatic structure) and [5,6]-isomers have an





Scheme 8



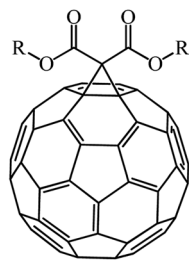
Scheme 9

open transannular bond (σ -homoaromatic structure), and the former are thermodynamically much more stable. In most cases, the [5,6]-open adducts formed initially can be converted into thermodynamically more stable [6,6]-closed isomers.

Of the numerous methods for functionalization of the fullerene core developed over the past 20 years, we will focus on the [2 + 1]-monocycloaddition processes as the most significant ones.

The methods for synthesizing methanofullerenes can be divided into two categories (Scheme 1): (I) nucleophilic cyclopropanation with stabilized carbanions that occur by the





- 19**, R = CH₂CH₃ **26**, R = (CH₂)₉CH=CH₂
20, R = (CH₂)₃CH₃ **27**, R = (CH₂)₅CH=CH(CH₂)₁₉CH₃
21, R = (CH₂)₅CH₃ **28**, R = (CH₂)₄CH=CH(CH₂)₇CH₃
22, R = (CH₂)₇CH₃ **29**, R = (CH₂)₄CH=CHCH₂CH=CH(CH₂)₄CH₃
23, R = (CH₂)₈CH₃ **30**, R = (CH₂)₅C≡C(CH₂)₁₀CH₃
24, R = (CH₂)₉CH₃ **31**, R = (CH₂)₈C≡C(CH₂)₇CH₃
25, R = (CH₂)₁₇CH₃ **32**, R = (CH₂)₁₂C≡C(CH₂)₇CH₃

Fig. 3 Dialkyl 1,2-[6,6]-methano-[60]-fullerene dicarboxylate derivatives 19–32.

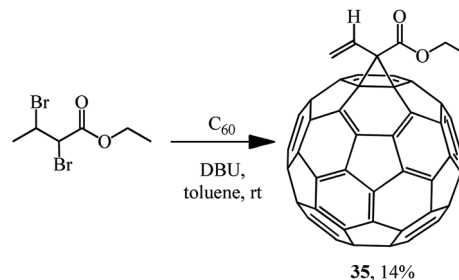
addition–elimination mechanism (Bingel reaction); (II) thermal addition of diazo compounds followed by thermolysis or photolysis of the pyrazoline intermediates and N₂ extrusion.

1. Synthesis of methanofullerenes based on halide-activated substrates according to Bingel

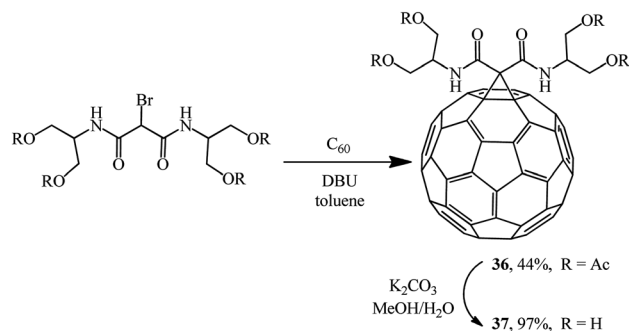
The most efficient way to synthesize methanofullerenes is by C₆₀ cyclopropanation with stabilized halo-carbanions. In the classical version, the process occurs upon treatment of C₆₀ with 2-bromomalonate in the presence of a base.

The nucleophilic cyclopropylation of fullerene was first reported in 1993 by Bingel in an original work describing the reaction of C₆₀ with 2-diethyl bromomalonate, methyl 2-chloroacetoacetate, ω-bromoacetophenone and desyl chloride in the presence of various bases, namely, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), NaH, and potassium *tert*-butylate at room temperature under the conditions and with the yields shown in Scheme 2.²¹

In all the cases, the reaction products were isolated by column chromatography on silica gel from the residues obtained after acidification of the reaction mixture (2 N H₂SO₄), drying and evaporation of the organic phases. Compounds 1–4 were obtained as crystalline dark brown powders, which is characteristic of the majority of mono-functionalized methanofullerenes C₆₀.

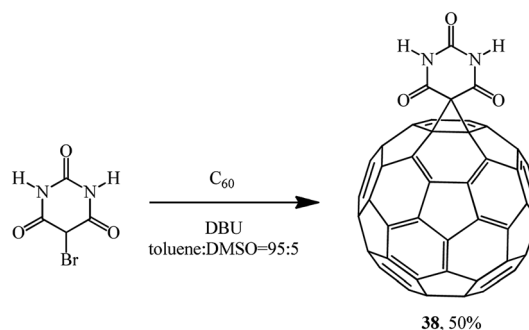


Scheme 11

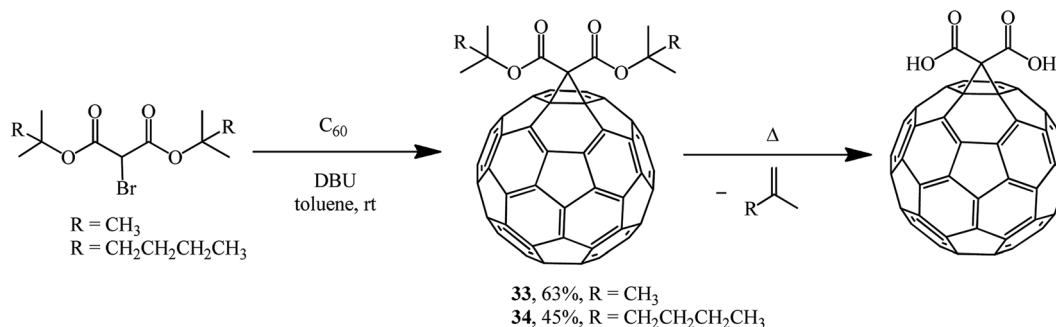


Scheme 12

The suggested reaction mechanism involves the initial deprotonation of halo derivative **A** by a base with generation of reactive nucleophile **B**, which attacks an electron-

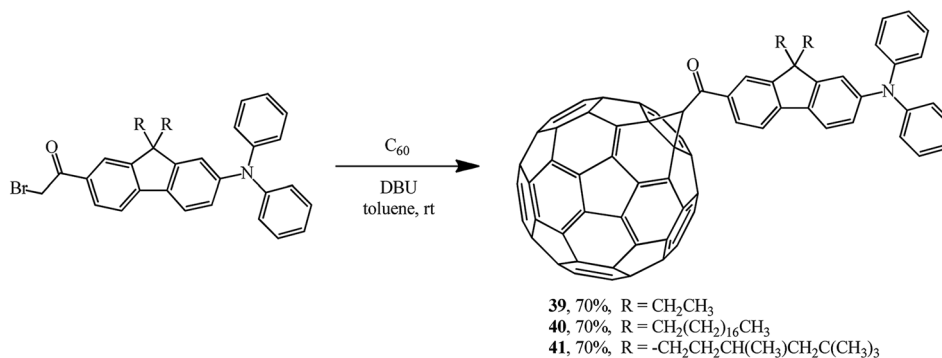


Scheme 13

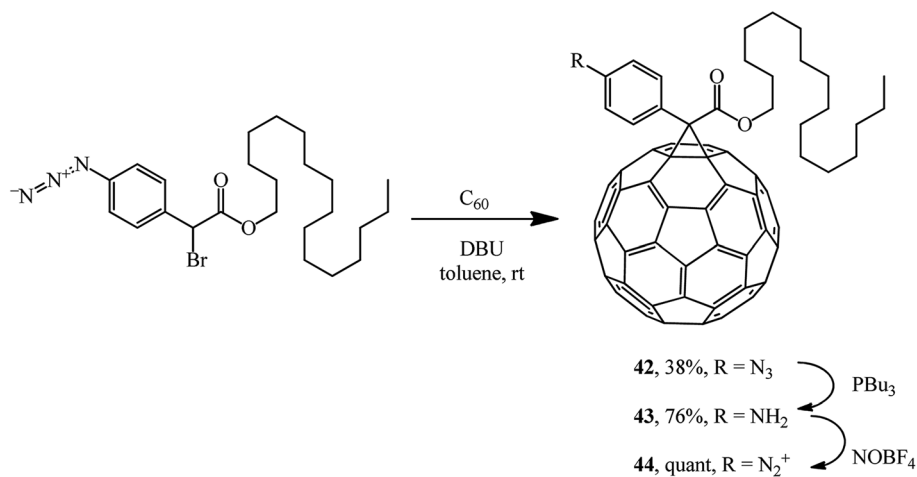


Scheme 10





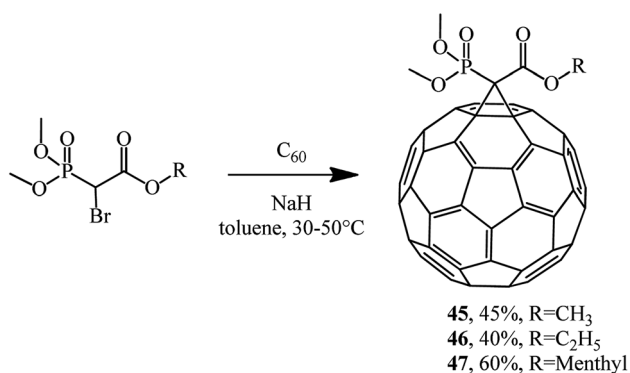
Scheme 14



Scheme 15

deficient double bond in fullerene C₆₀. The resulting carbanion C undergoes intramolecular S_N2 substitution of the halogen atom to give methano-derivative **D** (Scheme 3).¹⁶

The key agents for C₆₀ cyclopropanation under the “classical” Bingel reaction conditions include substrates with an activated halomethine function capable of forming stabilized carbanions, while the readily leaving halide group (mainly Cl⁻) ensures the intramolecular cyclization.



Scheme 16

The Bingel's approach was successfully expanded by F. Diederich who used 3-bromo-1,5-bis(trimethylsilyl)pent-1,4-diyne²² to give adduct **5** in the presence of DBU. Protodesilylation of **5** with potassium carbonate in tetrahydrofuran (THF)/MeOH results in the related hydrocarbon **6**. Controlled desilylation of **5** makes it possible to obtain monosubstituted diynofullerene **7** in 35% yield. The latter compound is interesting due to the prospects of its application in syntheses of hybrid structures (Scheme 4).^{23–25}

Later, the same scientists²⁶ used dipyrldylchloromethane that was obtained in two stages from 4-pyridinecarboxaldehyde (Scheme 5) and was capable of generating a stabilized carbanion under the Bingel reaction conditions in order to synthesize an adduct of monoaddition to fullerene **8**.

The versatility of the method was demonstrated by synthesizing a new series of ligands incorporating conjugated 2,2';6',2''-terpyridine (tpy) moieties.^{27–29} The latter were converted to **9** and **10** using the Bingel reaction and further converted to diads and triads with ruthenium **11** and **12**, where the pendant fullerene acted as an electron acceptor (Scheme 6).

In continuation of studies on fullerene functionalization, the reaction of bis(2-bromomalonate) with two equivalents of C₆₀



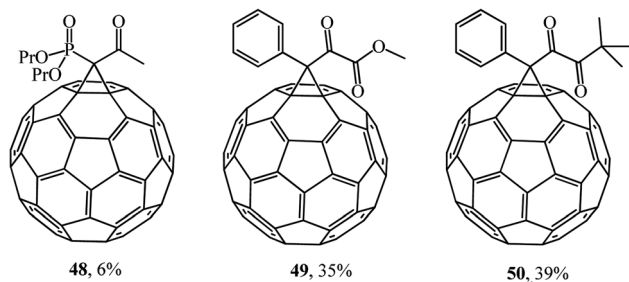
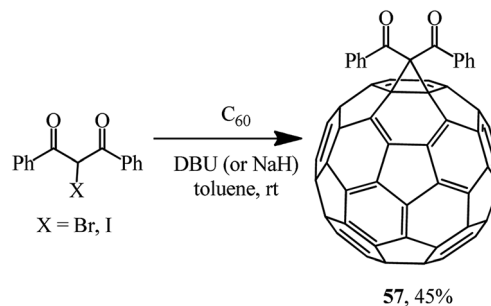
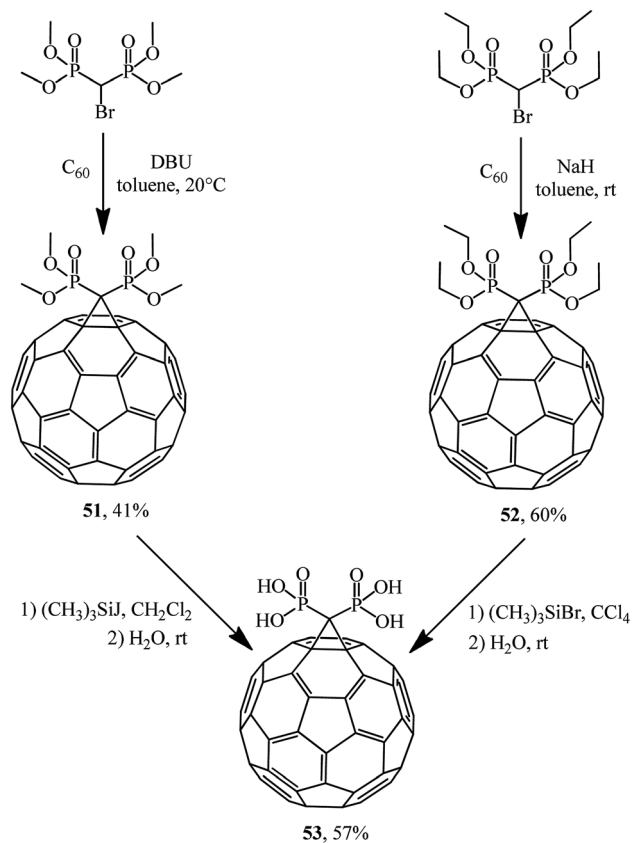


Fig. 4 Methanofullerenes 48–50.



Scheme 18



Scheme 17

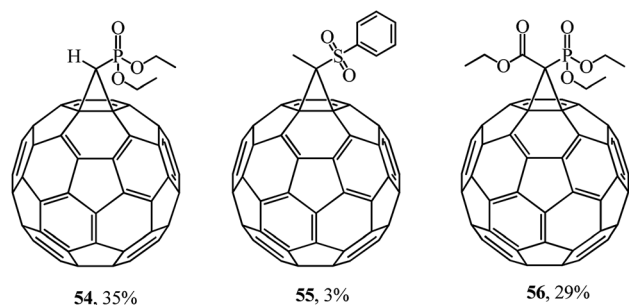
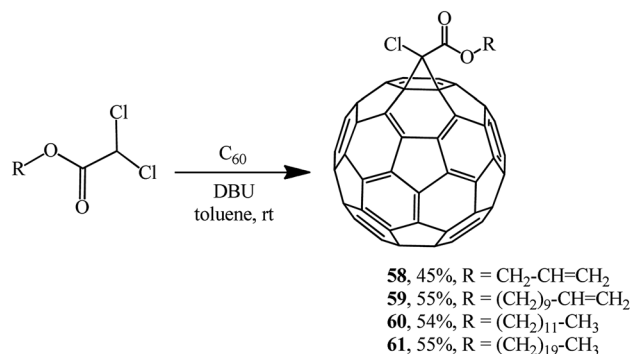


Fig. 5 Methanofullerenes 54–56.



Scheme 19

was performed to give bis-adducts **13**, **14** and the corresponding minor 1 : 1 adducts (Scheme 7).³⁰

Rather an interesting publication³¹ reported a synthesis of methanofullerene **15** whose frame includes two cholesterol residues. Its liquid-crystal and thermal properties were studied (Scheme 8).

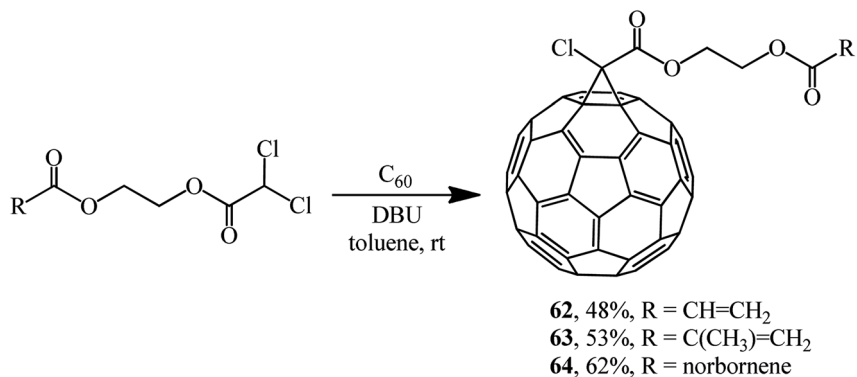
Addition of the resulting dendrons based on 3,5-substituted benzyl esters to C₆₀ gave fullerene-containing dendrimers as monoadducts **16–18**.³² The cyclopropanating agents were synthesized by bromination of the corresponding bis(3,5-dibenzoyloxybenzyl)propanedionate with the CBr₄-DBU system (Scheme 9).

Article³³ describes a synthesis of a number of mono-functionalized dialkyl 1,2-[6,6]-methano-[60]-fullerene dicarboxylate derivatives whose structures contain substituents with various chain lengths, namely, saturated and unsaturated hydrocarbon groups (compounds **19–32**). Reactions of fullerene C₆₀ with dialkyl bromomalonates in the presence of sodium hydride give the target products in 35–69% yields (Fig. 3).

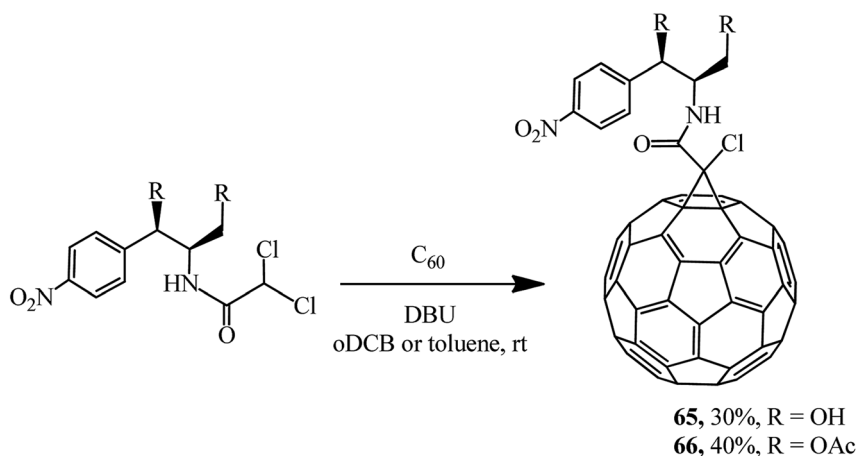
A study of the physical characteristics of the presented dialkyl 1,2-[6,6]-methano-[60]-fullerene dicarboxylates showed that compounds **20**, **21** and **23** were dark brown solids with very high melting points. Dioctyl and longer-chain saturated and unsaturated dialkyl 1,2-[6,6]-methano-[60]-fullerene dicarboxylates **22** and **24–32** are viscous liquids that do not crystallize from organic solvents.

The Bingel approach is significantly expanded if bis-*tert*-butyl- and bis(2-methylhexan-2-yl)2-bromomalonates are

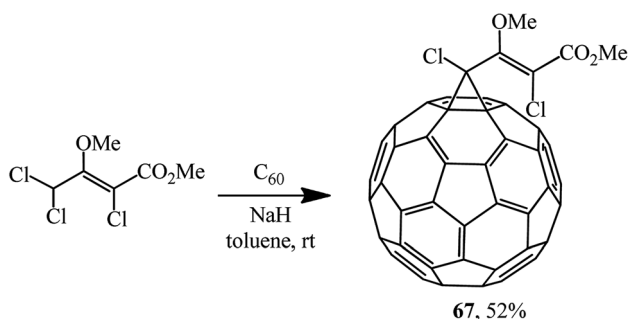




Scheme 20



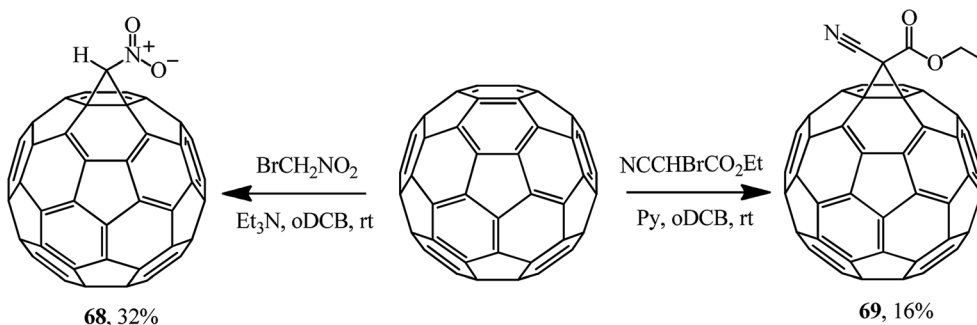
Scheme 21



Scheme 22

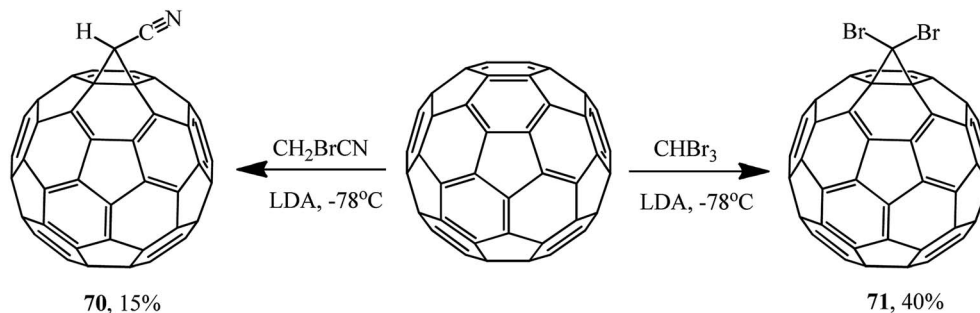
used as halogen-activated substrates for synthesizing methanofullerenes to give **33** and **34**, which were converted to the corresponding C₆₀ diacids under specific conditions (Scheme 10).³⁴

The compounds **33** and **34** synthesized are thermo-cleavable fullerene materials and can be used as buffer layers for increasing the efficiency of inverted organic solar cells. In this case, the efficiency of inverted solar cells increases due to improved dissociation of excitons and electron transfer, along with a reduction in the series resistance.

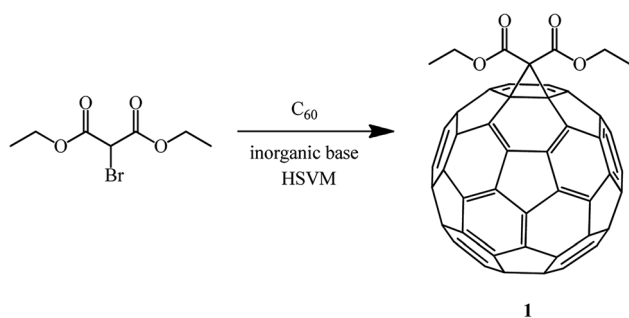


Scheme 23

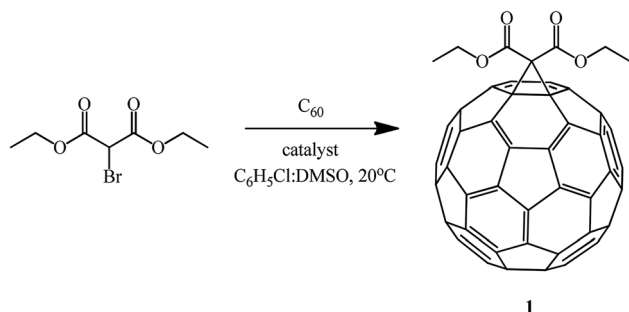




Scheme 24



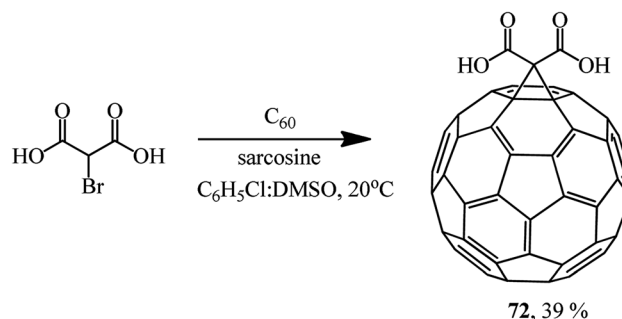
Scheme 25



Scheme 26

Table 2 Optimization of Bingel's synthesis in the presence of amino acids and dimethyl sulfoxide without a base

Entry	Catalyst	C ₆ H ₅ Cl : DMSO (v/v)	Yield of 1, %
1	—	2 : 1	0
2	<i>N</i> -Ethylglycine	2 : 1	37
3	Glycine	2 : 1	33
4	<i>N</i> -Benzylglycine	2 : 1	38
5	Sarcosine	2 : 1	42
6	Sarcosine	20 : 1	5
7	Sarcosine	20 : 3	8
8	Sarcosine	4 : 1	17
9	Sarcosine	5 : 2	39
10	Sarcosine	5 : 3	41
11	Sarcosine	4 : 3	38



Scheme 27

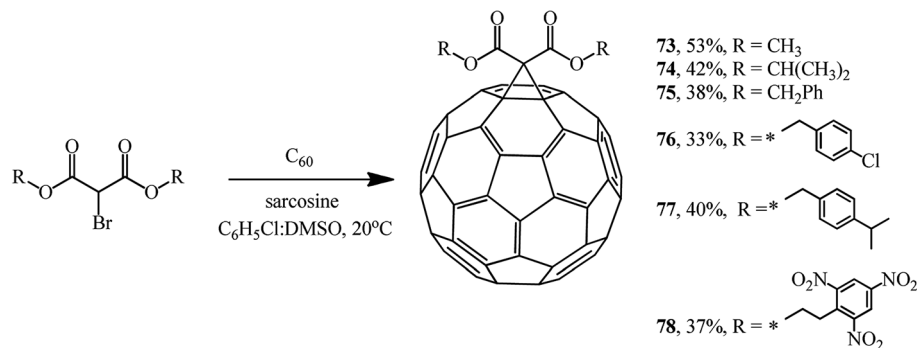
Table 1 Results of Bingel's synthesis with inorganic bases under HSVM conditions in the absence of solvents

Entry	Base	Yield of 1, %
1	NaOAc	59
2	Na ₂ CO ₃	51
3	NaHCO ₃	48
4	Ca(OH) ₂	45
5	Na ₂ B ₄ O ₇ × 10H ₂ O	44
6	K ₂ CO ₃	29
7	NaOH	11
8	KOH	17
9	Alkaline Al ₂ O ₃	10

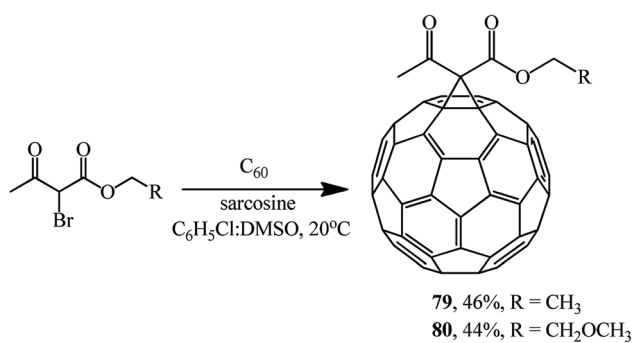
The principal possibility of using α,β -dibromo derivatives of acid esters in the Bingel reaction was demonstrated by synthesizing methanofullerene 35 (Scheme 11).³⁵

In a search for highly water-soluble fullerene derivatives, condensation of equimolar amounts of a bromomalondiamide derivative and C₆₀ gave adduct 36,³⁶ hydrolysis of which resulted in methanofullerene 37 (Scheme 12). However, neither tetraacetate 36 nor even tetraol 37 showed any noticeable water solubility. Therefore, the reaction of C₆₀ with a large excess of the aforementioned





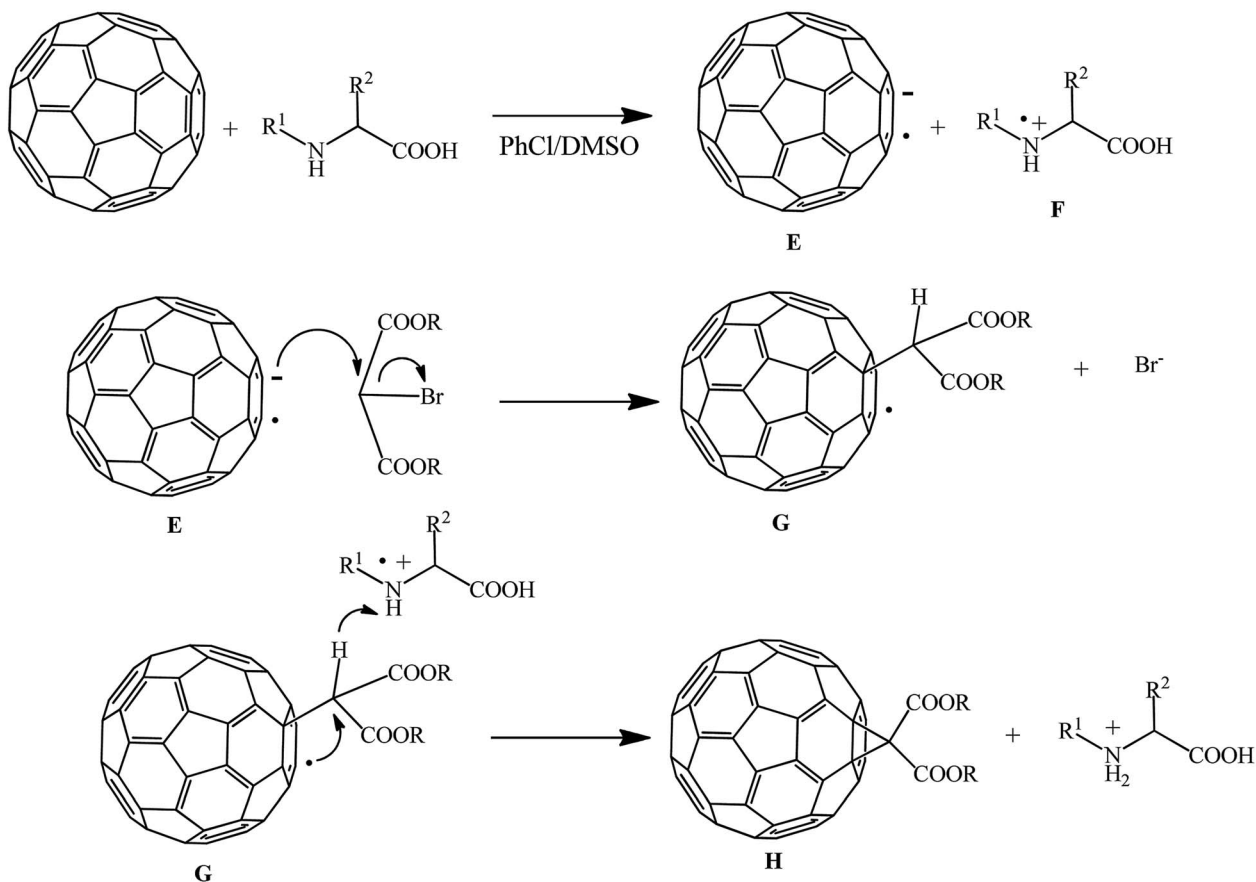
Scheme 28



Scheme 29

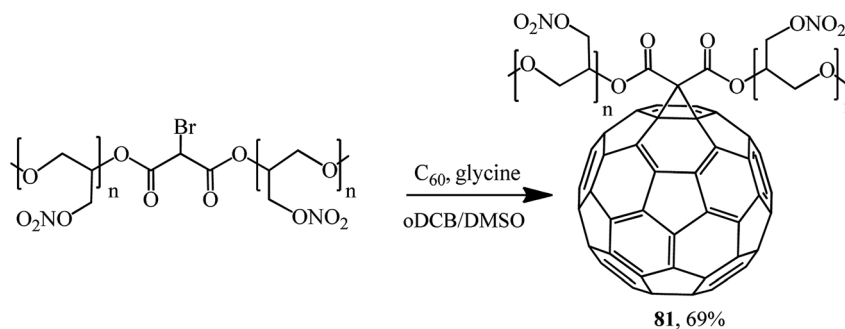
bromomalonodiamide (>10 equiv.) was carried out to give a mixture of 4–6 substituted cyclopropanation products, which was then hydrolyzed under similar conditions. The solubility of the resulting mixture of methanofullerenes **37** ($n = 4-6$) in water was found to be 240 mg mL^{-1} which, as noted in ref. 36, appears to be a good result for fullerene derivatives.

The reaction of 5-bromobarbituric acid with C₆₀ in toluene : dimethylsulfoxide (DMSO) solution (95 : 5, v/v) gave monocyclopropanation adduct **38** as a brown powder (Scheme 13). This synthesis is the first example of intermolecular photodimerization of a C₆₀ derivative in

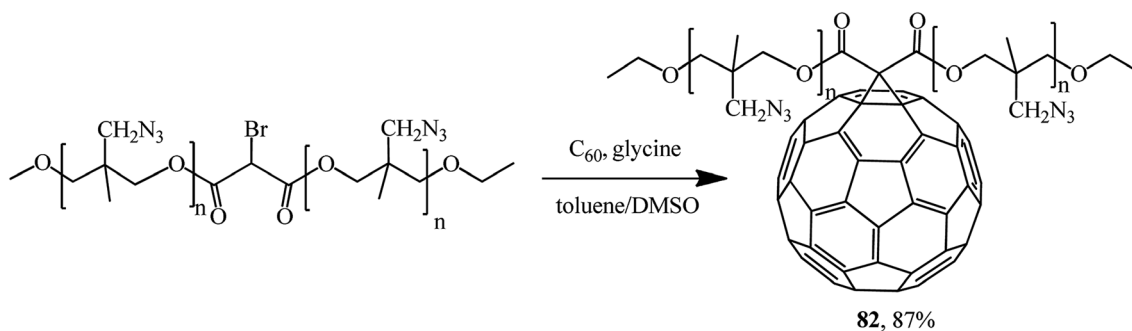


Scheme 30

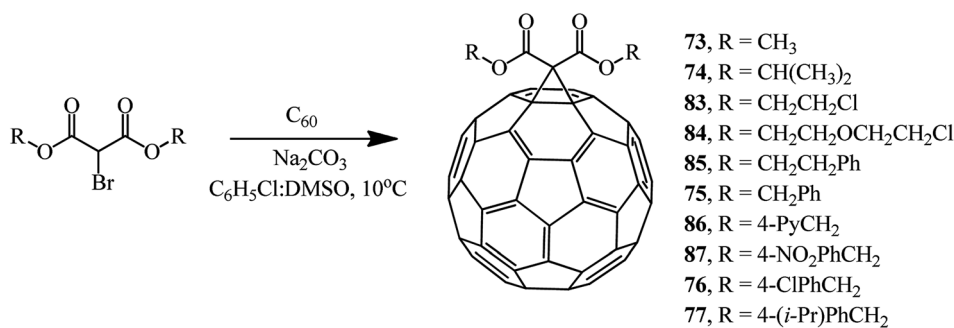




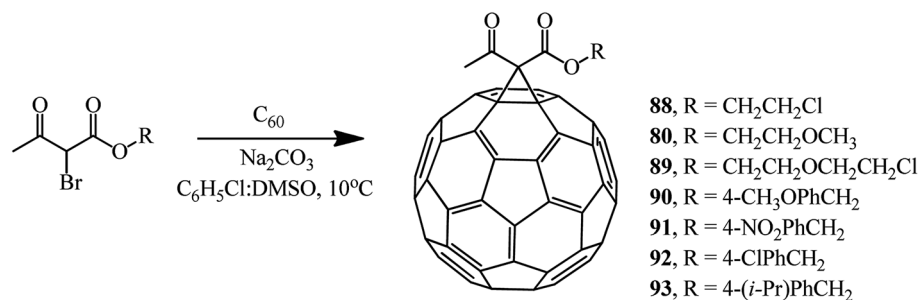
Scheme 31



Scheme 32

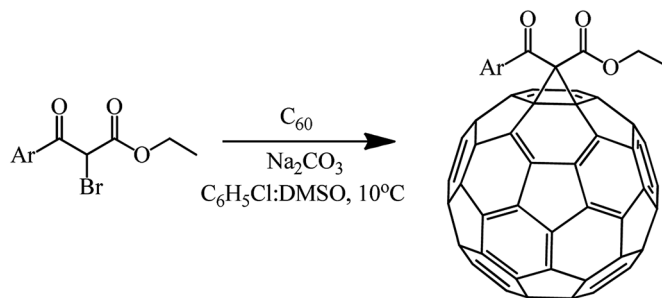


Scheme 33

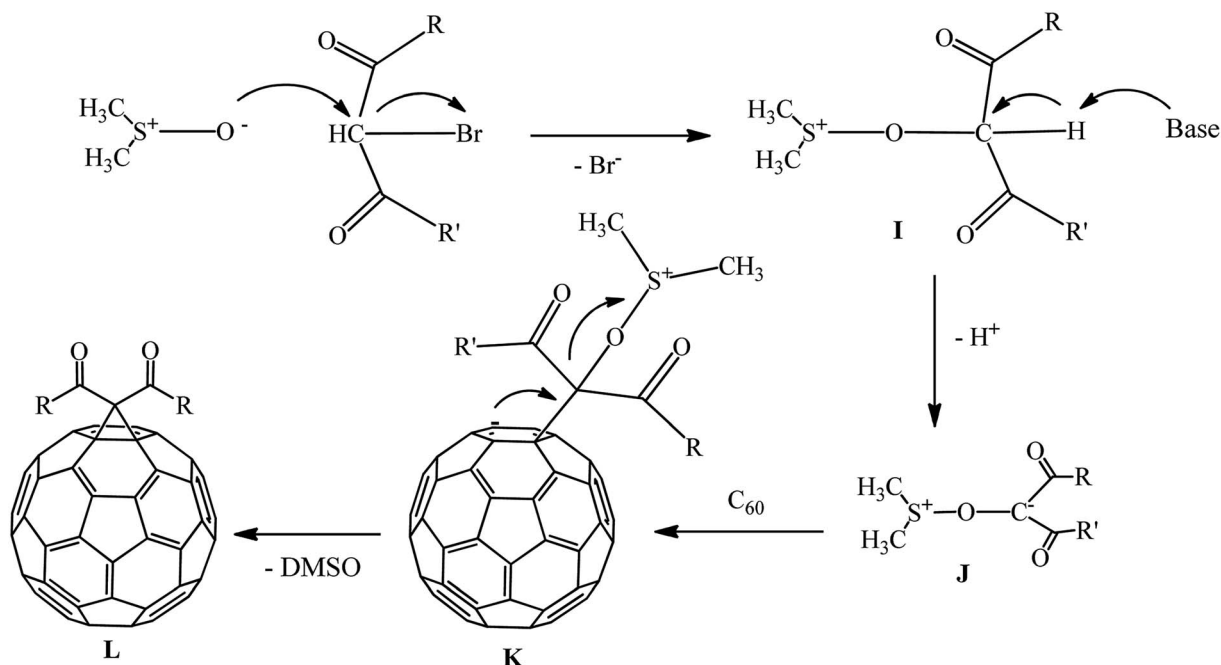


Scheme 34

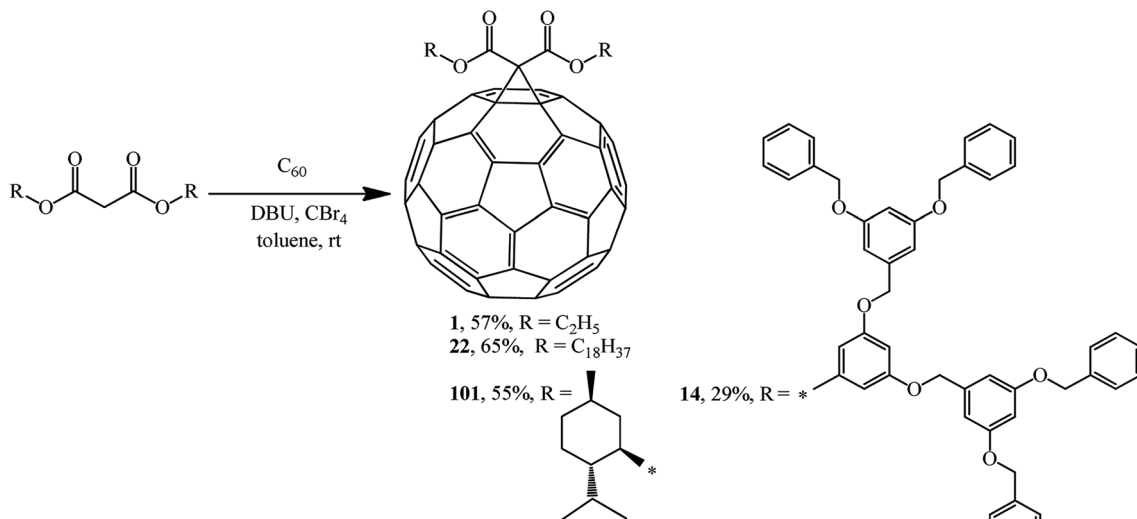




Scheme 35



Scheme 36



Scheme 37



Table 3 Ester substituents in the cyclopropane ring of methanofullerenes in the Bingel–Hirsch reaction

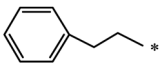
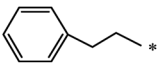
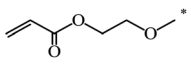
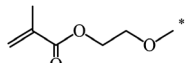
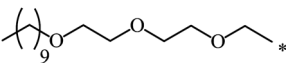
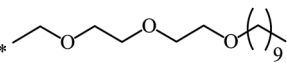
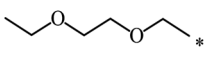
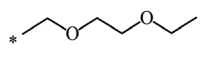
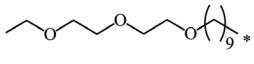
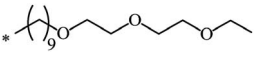
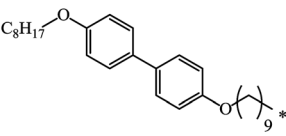
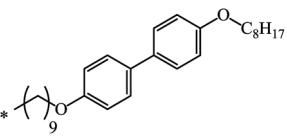
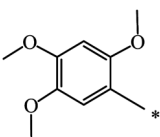
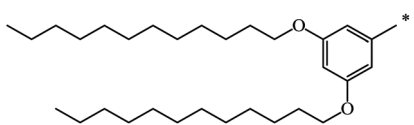
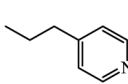
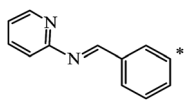
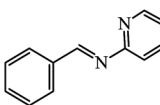




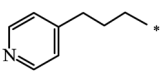
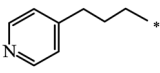
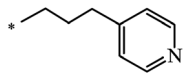
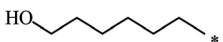
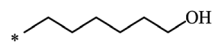
Entry	R ¹	R ²	Yield, %	Reference
73	CH ₃	CH ₃	28	62
17	C ₄ H ₉	C ₄ H ₉	35	
19	C ₈ H ₁₇	C ₈ H ₁₇	32	
102	(CH ₂) ₂ OCH ₃	(CH ₂) ₂ OCH ₃	21	
85			37	
103	(CH ₂) ₁₁ -CH ₃	CH ₃	59	49
104	(CH ₂) ₁₉ -CH ₃	CH ₃	50	
105	(CH ₂) ₂ -O-CH ₃	C ₂ H ₅	nr ^a	63
106	CH ₂ -CH=CH ₂	CH ₂ -CH=CH ₂	32	64
107	(CH ₂) ₉ -CH=CH ₂	CH ₃	50	51
108		CH ₃	59	
109		CH ₃	46	
110			48	65
111			nr	66
112			nr	66
113			51	67
114		CH ₃	51	68
115			47	69
116			33	70
117			23	71
118			21	
119		CH ₃	50	72
120			40	
121			50	



Table 3 (Contd.)

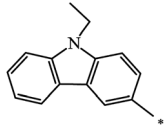
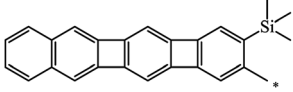
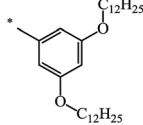
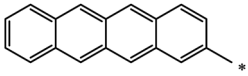
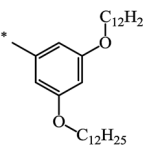
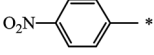
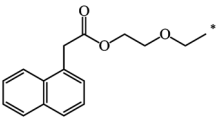
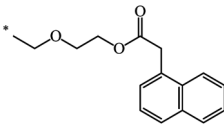
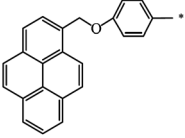
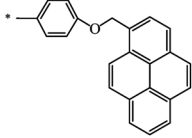
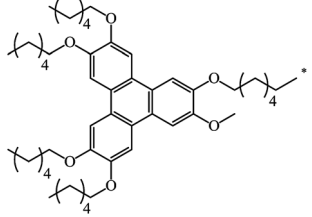
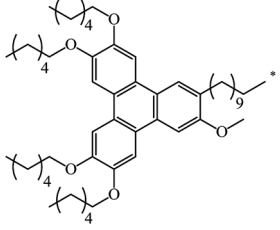
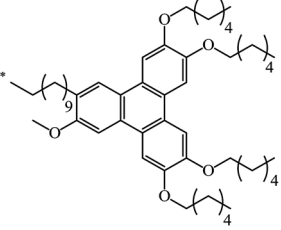
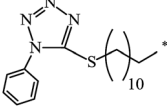
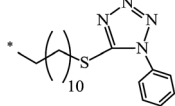
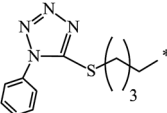
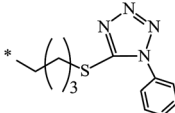
Entry	R ¹	R ²	Yield, %	Reference
122		C ₂ H ₅	22	73
123			52	74
124			27	75
125		CH ₃	16	76
126			39	
127			48	77
128		C ₂ H ₅	62	78
129			62	
130			38	79
131			nr	80



Table 3 (Contd.)

Entry	R ¹	R ²	Yield, %	Reference
132				
133				
134				
135		C ₂ H ₅	14	81
136		C ₂ H ₅	21	
137			45	82
138	(CH ₂) ₃ -Br	C ₁₈ H ₃₇	70	83
139	(CH ₂) ₁₂ -N ₃	C ₁₈ H ₃₇	11	

^a nr – the yield is not provided.

homogeneous solution that was made possible by the formation of supramolecular assemblies in which the fullerenes are maintained in close proximity.³⁷

Cyclopropanation of C₆₀ also smoothly occurs with α -bromoketones. It was used to incorporate a diphenylamino-fluorene chromophore group into fullerene structure. Using this scheme, new acceptor–keto–donor assembly diads **39**,³⁸ **40**,³⁹ **41** (ref. 40) were obtained in yields of about 70% (Scheme 14). Molecules of this kind are characterized by an increase in the relative intensity of the fluorescent zone. This is explained by direct covalent bonding of diphenylamino-fluorene moieties with the fullerene frame, which facilitates efficient intramolecular processes of electron or energy transfer.

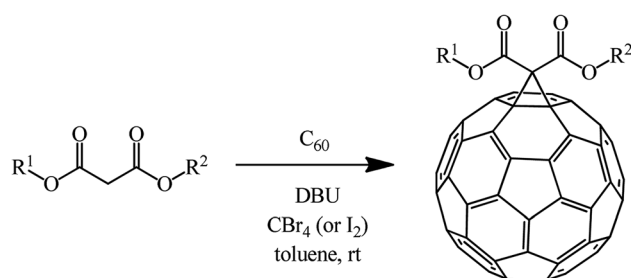
Methanofullerene **42** containing a phenylazide group was used for grafting C₆₀ to a nanotube *via* aniline derivative **43** and diazonium salt **44** (Scheme 15).⁴¹

Phosphonate reagents with a reactive methylene group that underwent monobromination were found to be very reactive agents for C₆₀ cyclopropanation. For example, the reaction of dimethoxybromomethylphosphonate alkyl esters with fullerene gave P-modified methanofullerenes **45–47** (Scheme 16).⁴²

Using the methodology developed, the same researchers⁴³ expanded this series by synthesizing (NaH,

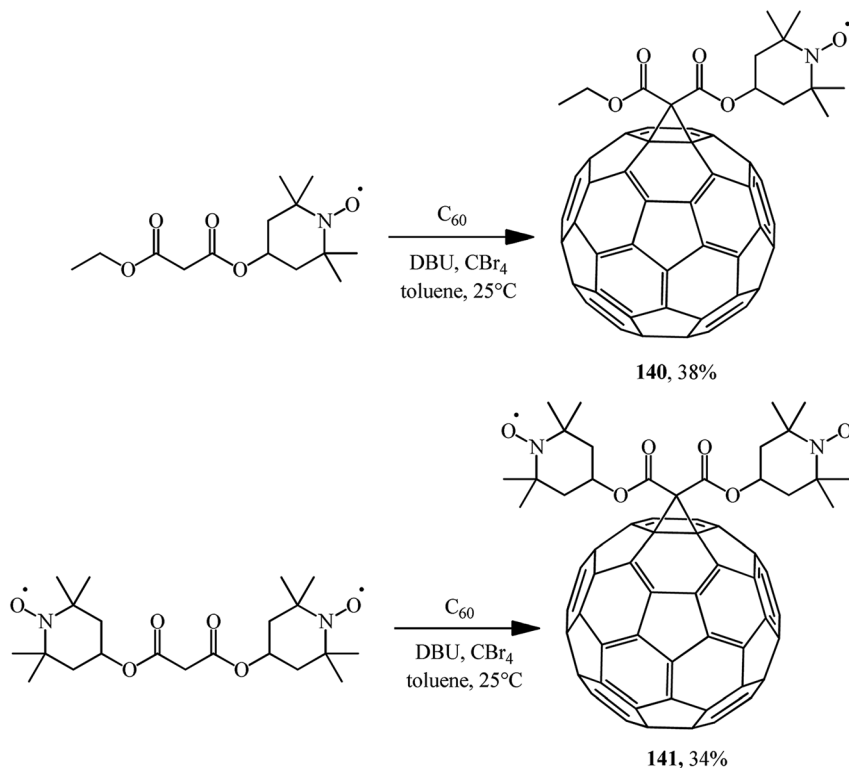
THF) phosphorylated methanofullerene **48**, phenyl-containing α -ketoester **49** and diketones **50** (Fig. 4). According to the authors, the latter compounds are interesting objects for studying their biological activity and may be useful in the search for new functional materials.

Bis-methanophosphonates were also used in C₆₀ cyclopropanation to give adducts **51** (ref. 44) and **52**,⁴⁵ which were treated with iodo- and bromotrimethylsilanes to give acid **53** *via* labile trimethylsilyl ethers easily hydrolyzable on stirring in an organic-aqueous medium (Scheme 17). Acid **53** is unstable in organic solvents and poorly soluble in water.



Scheme 38





Scheme 39

The multidisciplinary studies by F. Diederich⁴⁶ also dealt with various methanofullerenes incorporating phosphonate or sulfone groups. In the syntheses of **54–56**, the corresponding cyclopropanating agent reacted with C_{60} in oDCB (Fig. 5).

By varying the conditions of the reaction of C_{60} with 2-bromo- or 2-iodo-1,3-diphenylpropane-1,3-dione in the presence of various bases (Scheme 18), the optimal conditions for the process giving the highest possible yield of methanofullerene **57** (45%) were determined.⁴⁷ It was found that a bromohaloketone : DBU ratio of 1.0 : 2.4 had to be strictly maintained.

The approach by M. Miftakhov implemented in a number of publications^{48,49} that involved the use of dichloroacetic acid derivatives with an activated dichloromethine function capable of forming stabilized carbanions as a new cyclopropanating agent proved to be fruitful. The methine proton in dichloroacetic acid derivatives is strongly activated, therefore a carbanion is readily generated from it, while the readily leaving group (Cl^-) ensures the intramolecular cyclization. Examples of aliphatic derivatives of dichloroacetic acid are presented in Scheme 19.

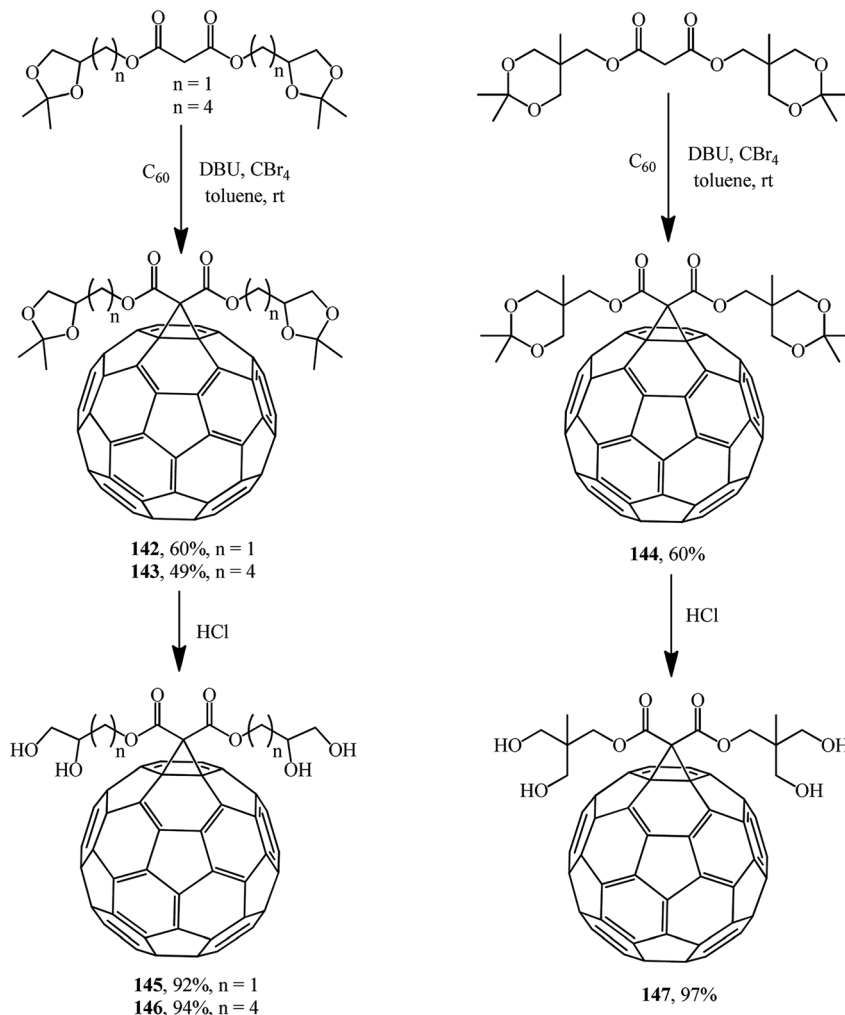
Using dichloroacetic acid derivatives and the Bingel methodology at the key stages, facile syntheses of fullerene-containing monomers of (meth)acrylic **62** and **63** and norbornene types **64** have been developed, aimed at their subsequent conversion into high-molecular compounds for application in solar cells (Scheme 20).^{50,51}

Keeping in mind that the broad-spectrum antibiotic laevomycetin contains the CHCl_2 dichloromethine function that is reactive in the Bingel reaction, a group of researchers⁵² attempted to obtain its conjugate with fullerene as a continuation of these studies. In an experimental test, laevomycetin reacted with C_{60} in oDCB solution to give monoadduct **65**. In a similar way, the cyclopropanation of fullerene with laevomycetin diacetate in toluene solution to give methanofullerene **66** (Scheme 21) was also successfully implemented.

Unlike dichloroacetic acid esters that were previously used for C_{60} cyclopropanation, methyl (2*Z*)-2,4,4-trichloro-3-methoxybut-2-enoate obtained in two stages from hexachlorobutadiene contains no activating α -carboxy function. Nevertheless, it was assumed⁵³ that due to the concerted action of donor (MeO) and acceptor (CO_2Me , Cl) substituents in the substrate, the level of CH-acidity is sufficient for quite successful implementation of the Bingel reaction under standard conditions. As one can see from structure **67**, the donor and acceptor parts in the target product are effectively cross-conjugated (Scheme 22).

The literature sources covering the Bingel reaction offer a variety of bases used in the syntheses of methanofullerenes. Examples of the use of alternative activating bases are also provided, for example, the use of triethylamine in a synthesis of nitromethanofullerene **68** from bromonitromethane and pyridine in a synthesis of ethyl





Scheme 40

cyanocarboxymethanofullerene **69** from ethyl bromocyanacetate (Scheme 23). According to ref. 54, the methanofullerenes with acceptor substituents (NO_2 , CO_2Et) they isolated are promising in the design of photoconversion devices.

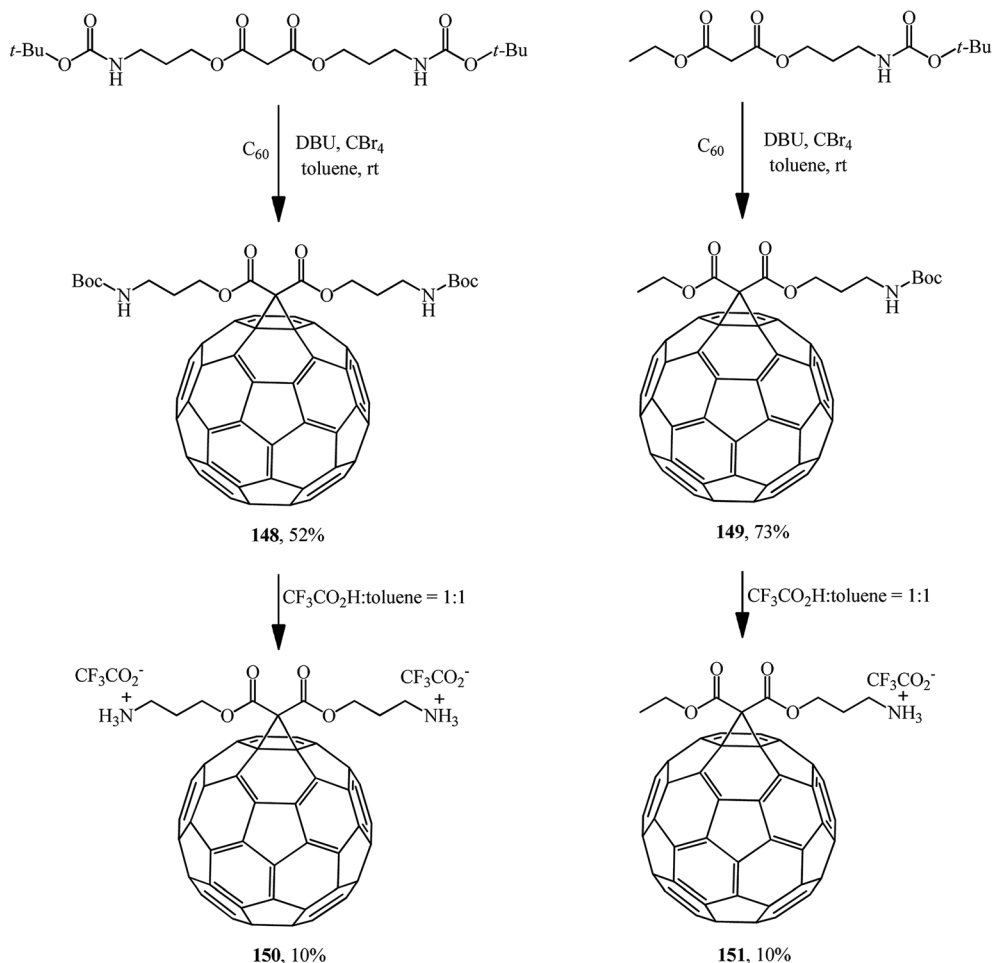
The reactions of fullerene with bromoacetonitrile and tribromomethane also resulted in 1'-cyano- **70** and 1',1'-dibromo-1,2-methano[60]fullerenes **71**, respectively. Since the reaction in the presence of sodium hydride failed, a stronger base, namely lithium diisopropylamide (LDA), had to be used (Scheme 24).⁵⁵

In order to increase the product yield and simultaneously simplify the process, the reaction of C_{60} with diethyl bromomalonate under high-speed vibration milling (HSVM) conditions in the absence of solvents was studied.⁵⁶ As a result, the opinion was formulated that under these conditions methanofullerenes can be obtained in good or even excellent yields in the presence of inorganic bases (Scheme 25).

It has been found that some weak inorganic bases are very effective in Bingel's mechanochemical reactions of C_{60} under high-speed vibration milling conditions without a solvent. A comparative analysis and study of bases revealed the fact that the presence of sodium acetate in the system provides the maximum yield of the mono-adduct, whereas a significant amount of bis-adducts is formed in the presence of potassium carbonate (Table 1).

Recently, a method for fullerene cyclopropanation by bromo-substituted substrates with a reactive methylene function in the presence of amino acids and dimethyl sulfoxide and without a base was suggested. This method was claimed to be efficient.⁵⁷ Sarcosine, glycine, *N*-ethylglycine, and *N*-benzylglycine were used as the catalytic additives. As shown by experimental data for the reaction with diethyl bromomalonate, the yield of products varies from 5 to 42% and depends on the presence of a particular amino acid, stoichiometric ratio of reagents, and nature of solvents (C_6H_5Cl :DMSO) (Table 2). The process is completed in 1–2 hours at 20 °C (Scheme 26).





Scheme 41

This method allows the cyclopropanation of fullerene to be performed at room temperature with bromomalonates and bromoacetoacetates that are sensitive to bases. This approach proved to be convenient for involving bromomalonate in the cyclopropanation of C_{60} to give methanofullerene **72**, which is impossible to synthesize under "classical" Bingel reaction conditions (Scheme 27).

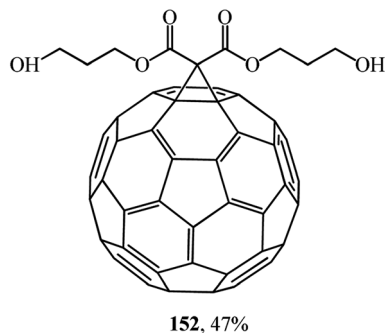
Using sarcosine as a catalyst, monofunctionalized methanofullerenes **73–78** (Scheme 28) and **79** and **80** (Scheme 29) were isolated in a similar way.⁵⁷

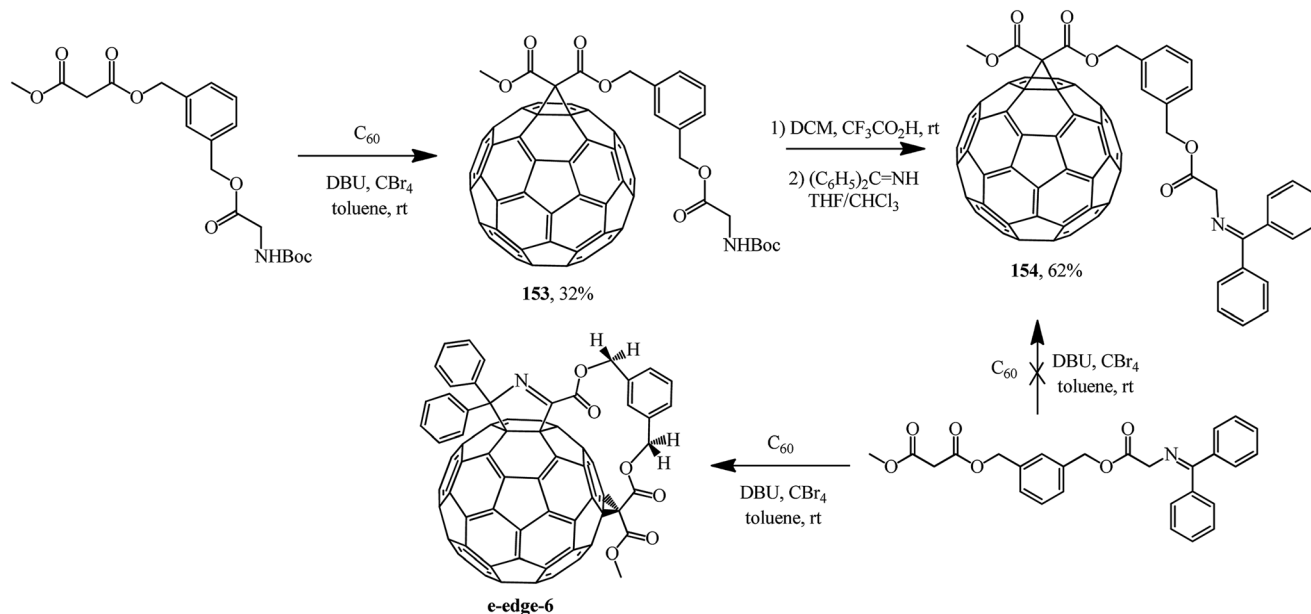
The assumed process mechanism is presented in Scheme 30. The fullerene anion radical **E** and amino acid radical cation **F** are formed in the presence of dimethylsulfoxide due to electron transfer from the amino acid to C_{60} . Subsequently, radical anion **E** attacks the methylene group of bromomalonate to give radical **G** with elimination of a bromide ion. At the final stage of cyclization with participation of the amino acid radical ion, methanofullerene **H** is formed.

The new energy-enriched derivative **81** was synthesized by a modified Bingel's reaction of C_{60} with bromomalonic acid poly (glycidyl nitrate) ester (Scheme 31).⁵⁸

A promising fullerene-containing polymer **82** based on bromomalonic acid poly (3-azidomethyl-3-methyl oxetane) ester was also obtained by a modified Bingel's reaction (Scheme 32).⁵⁹

The compounds with a reactive methylene group used in the Bingel reaction can include not only bromomalonates but also α -bromo- β -ketoesters, 2-bromo-1,3-diketones, and

Fig. 6 Di(carboxypropan-3-ol)methanofullerene **152**.



other bromo-substituted reactive substrates. By changing the process technique to some extent and using the DMSO/ Na_2CO_3 system,⁶⁰ we isolated methanofullerenes in good yields even at 10 °C. In fact, cyclopropanation of C_{60} with various bromomalonate esters in the presence of DMSO/ Na_2CO_3 (with a 20-fold excess of ether and a 40-fold excess of Na_2CO_3) in a binary $\text{C}_6\text{H}_5\text{Cl}/\text{DMSO}$ solvent mixture showed the presence of methanofullerenes **73–77** and **83–87** in 29–68% yields even in 5 min after the start of the reaction (Scheme 33).

Various brominated β -ketoesters and aromatic ethyl bromoformyl acetates react with fullerene C_{60} under identical conditions to give monocyclopropanation adducts **88–93** (34–63%) and **94–100** (43–66%) (Schemes 34 and 35).

The mechanism of cyclopropanation in the presence of the DMSO/ Na_2CO_3 catalytic system was studied. It is assumed that nucleophilic attack of the dimsil anion on the bromine-containing center of the substrate to give dimethylsulfoxonium intermediate **I** occurs. At the next stage, **I** loses a proton in the weakly alkaline environment to give intermediate **J**. The latter reacts with the fullerene to form an intermediate charged complex **K**, followed by its intramolecular cyclization with elimination of DMSO and formation of methanofullerene **L** (Scheme 36).

Cyclopropanation in the presence of DMSO/ Na_2CO_3 is valuable precisely because it allows one to functionalize not only C_{60} fullerene but also the C_{70} molecule, as well as single-walled carbon nanotubes and, which is particularly valuable, also graphene.

The nearly comprehensive Bingel method presented above makes it possible to synthesize methanofullerenes predominantly from bromo-substituted substrates with diverse structures containing a reactive methylene function.

2 The Bingel–Hirsch technique in the synthesis of methanofullerenes

In the previous chapter, Bingel's approach was noted as an almost comprehensive method for synthesizing methanofullerenes mainly based on bromo-substituted substrates. After the method was improved by his colleague, A. Hirsch, it was named the Bingel–Hirsch method.

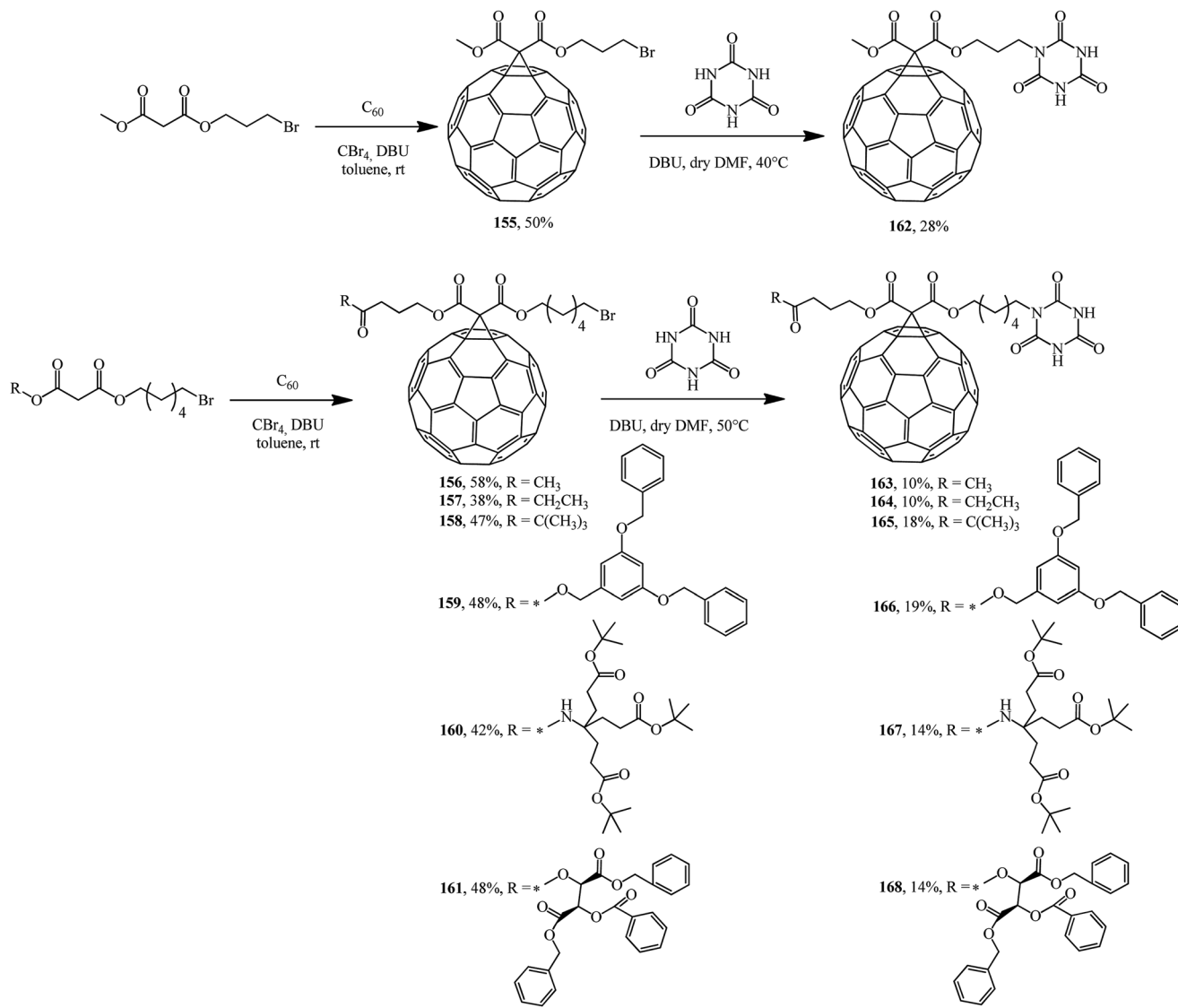
Using four different malonates containing chiral and sterically hindered dendritic side chains as examples, X. Camps and A. Hirsch⁶¹ developed a method for synthesizing methanofullerenes in a “one-pot” reaction involving tetrabromoethane and DBU. The monoadducts were synthesized by direct treatment of C_{60} with malonates in the presence of CBr_4 and DBU in a molar ratio of 1 : 1.5 : 1.5 : 3, respectively. The cyclopropanation of fullerene under these conditions occurred smoothly even at room temperature to give the corresponding mono adducts **1**, **14**, **22** and **101**. Their yields were found to be comparable to, or even higher than those in the case of the process with bromomalonates (Scheme 37).

The Bingel–Hirsch approach was further extended to include malonates with various substituents listed in Table 3 (Scheme 38).

Using the Bingel–Hirsch technique, methanofullerenes **140** and **141** were obtained using malonates with nitroxide-containing radicals (Scheme 39).⁶⁴ It has been found for the first time that these compounds combined with the known anticancer drug cyclophosphamide show high antitumor activity against P-388 leukemia.

The same researchers isolated and characterized mono-functionalized methanofullerenes differing in the number of acetonide groups, for example, compounds **142–144**.⁶⁵

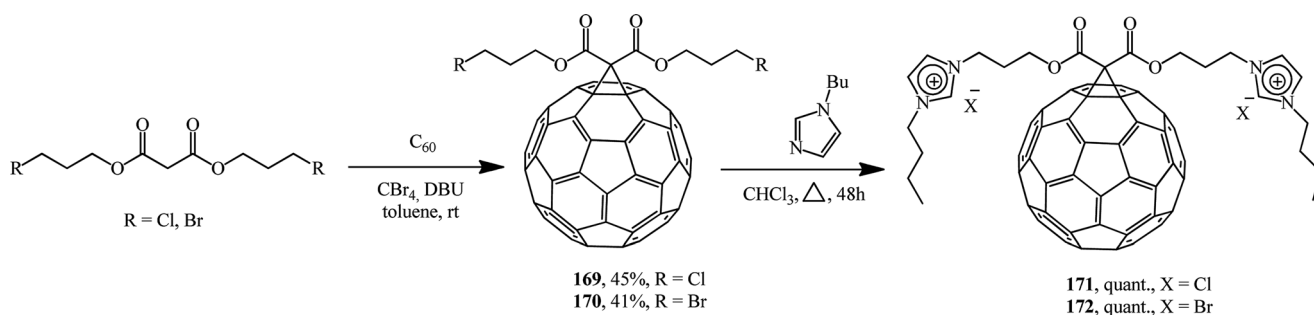




Scheme 43

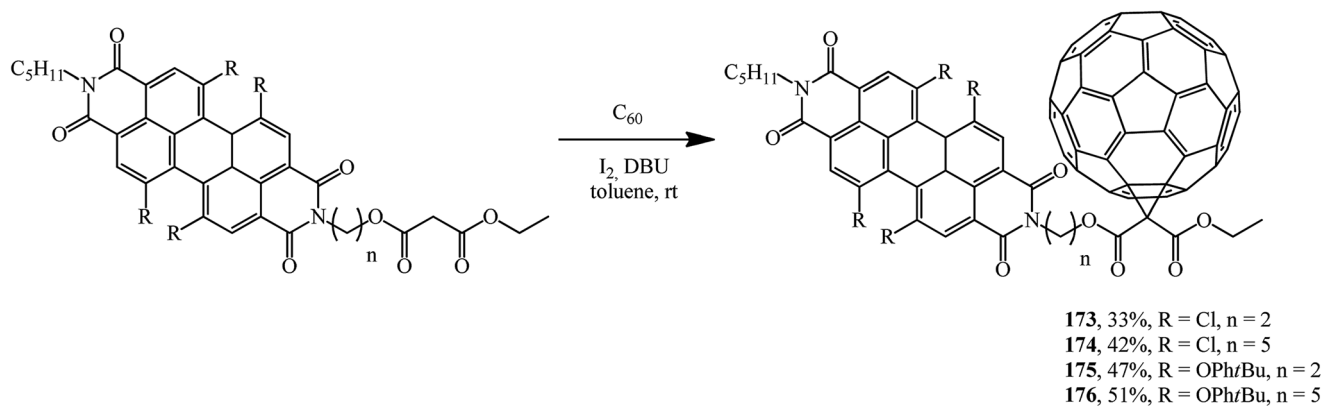
Removal of acetonide protection results in new chromatographically pure water-soluble polyol methanofullerenes **145–147** in nearly quantitative yields (Scheme 40).

Mono- and diamino-functionalized methanofullerenes **148** and **149** were obtained by the Bingel–Hirsch reaction using N-protected malonic derivatives synthesized by the

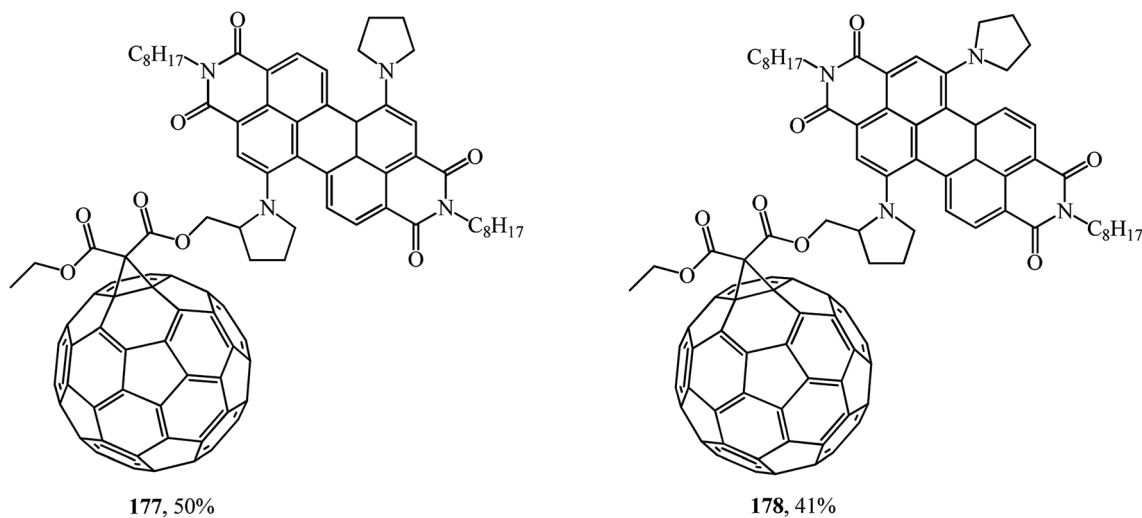


Scheme 44



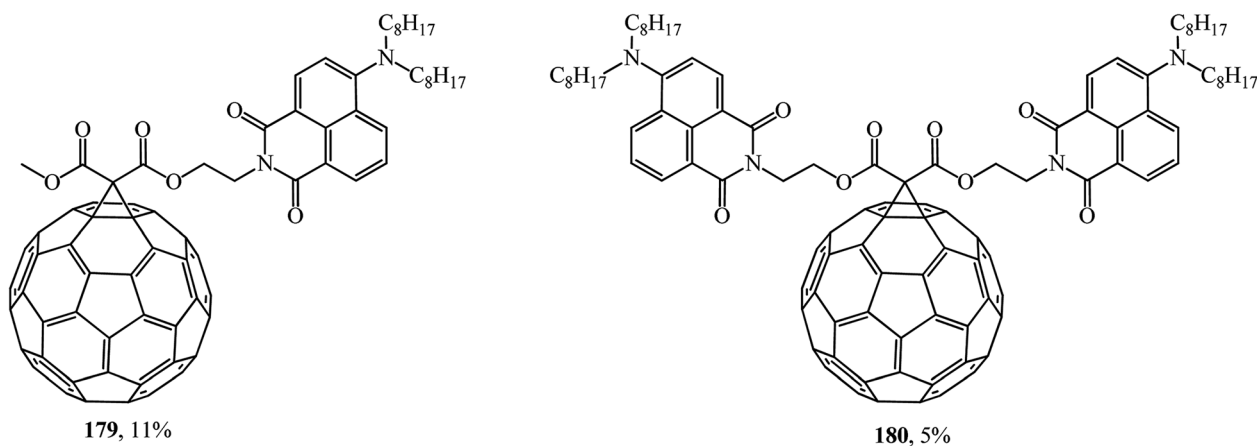


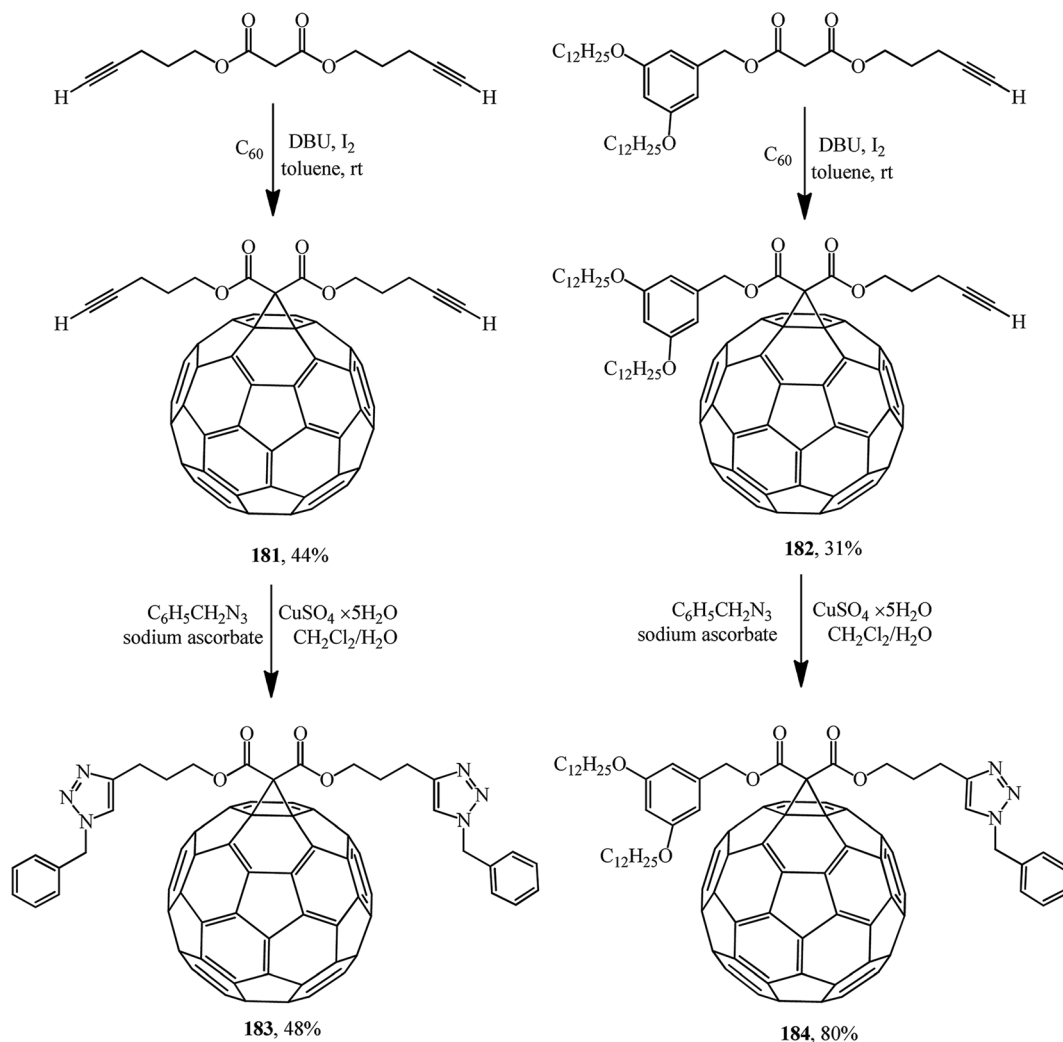
Scheme 45

Fig. 7 Fullerene–perylenediimide diads **177** and **178**.

reaction of *tert*-butyl *N*-(3-hydroxypropyl)carbamate with malonyl chloride in the presence of pyridine (Scheme 41).⁸⁶ Removal of *tert*-Boc-protected amine groups was performed

using trifluoroacetic acid; the methanoaminofullerenes **150** and **151** that were isolated exhibited good solubility in water.

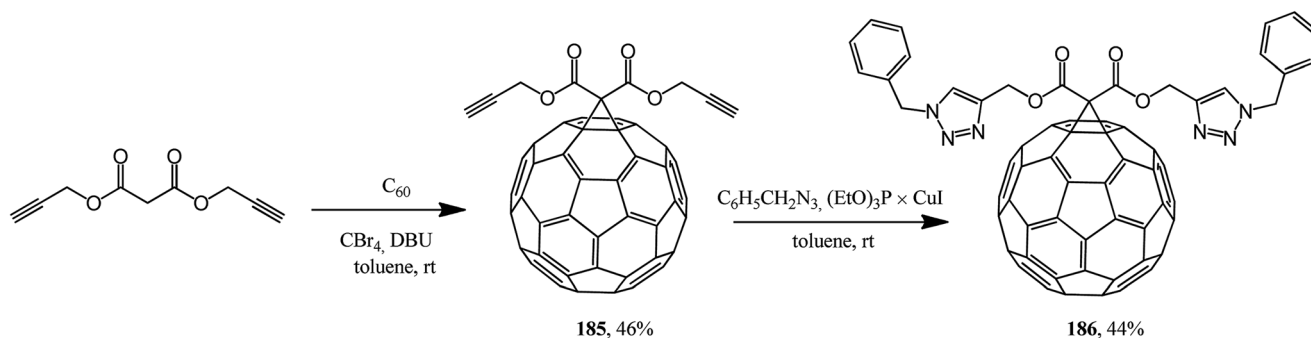
Fig. 8 Fullerene–naphthalimide diads **179** and **180**.

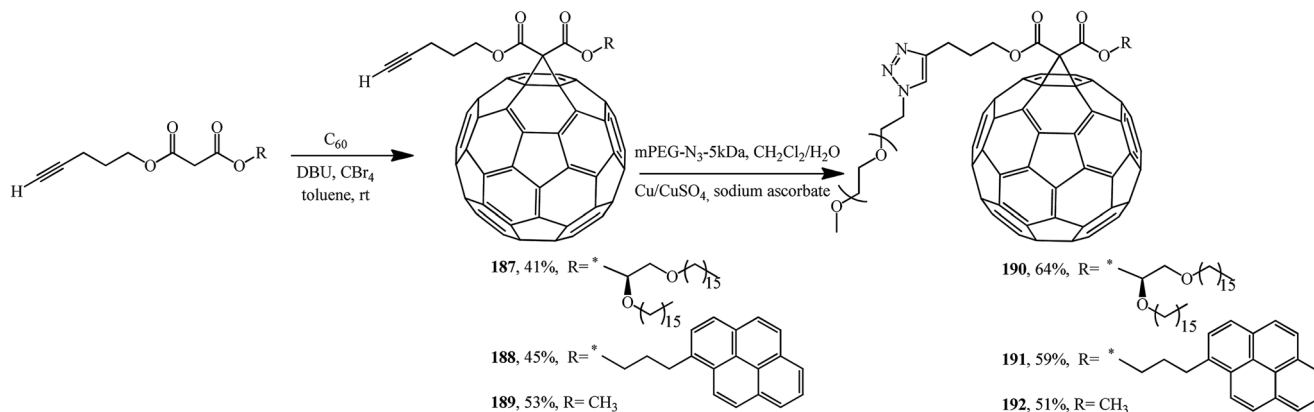


Studies on the synthesis of methanofullerenes with practical purposes, primarily for medical purposes, attract considerable attention. For instance, monoadducts **150** and diamine adducts **151** (ref. 86) as well as adduct **152** (ref. 87) (Fig. 6) selectively inactivate neuronal isoforms of nitric

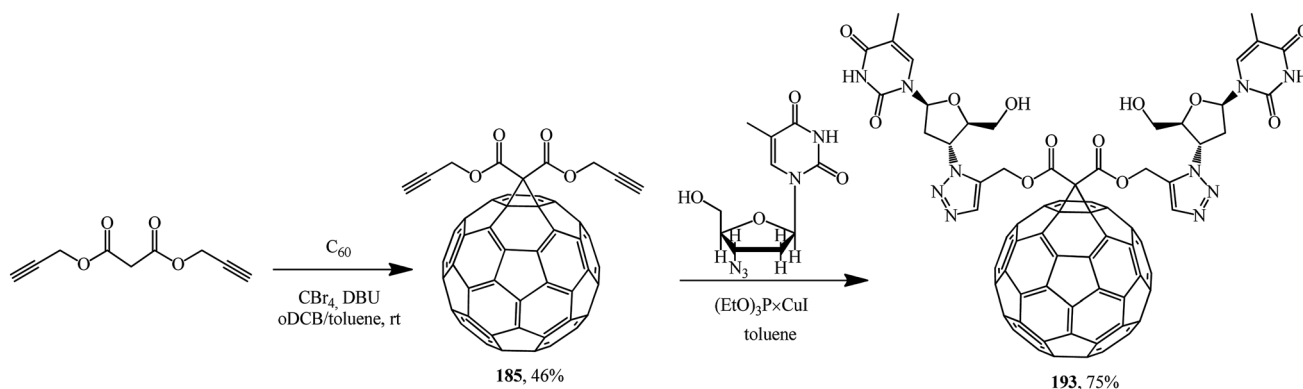
oxide synthase by splitting reactive oxygen intermediates from NO and formation of citrulline in the presence of arginine.

Treatment of spacer-bound derivative of 1,3-bis-(hydroxymethylbenzene)diester with methyl malonate and Boc-ester of





Scheme 48

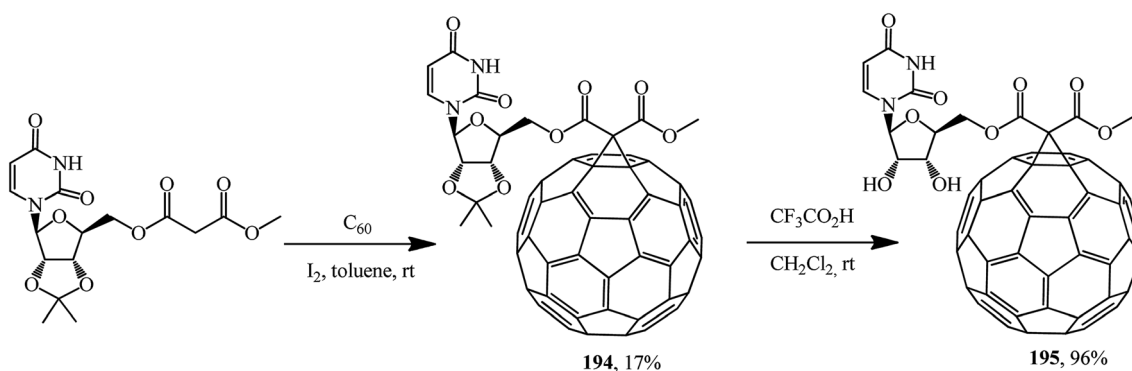


Scheme 49

glycine with fullerene C₆₀ gave the expected adduct **153**.⁸⁸ Based on the latter, removal of the *tert*-butyloxycarbonyl protecting group (Boc) with 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyran (DCM) and treatment with benzophenone imine gave block **154** containing an *N*-(diphenylmethylene)glycine moiety (Scheme 42). Under Bingel-

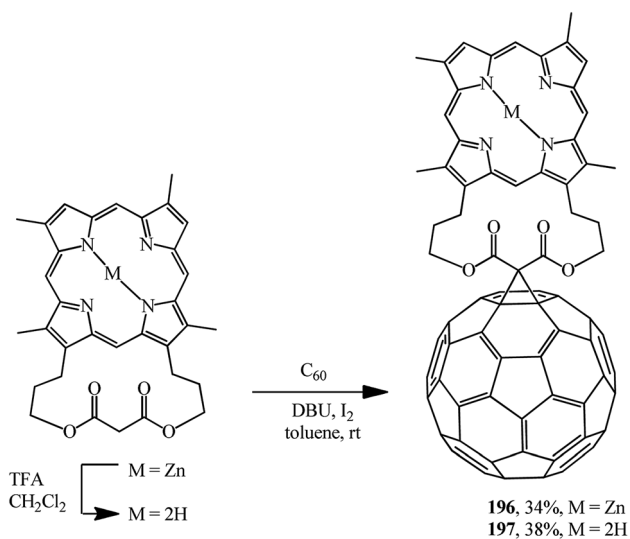
Hirsch conditions, this moiety can act as a cyclopropanating “element”, as shown by the example of a regioselective synthesis of *ansa*-type **e-edge-6** with participation of an acyclic compound with a simpler structure.

Due to the availability of malonates with very diverse structures, the Bingel–Hirsch reaction is widely used for the



Scheme 50





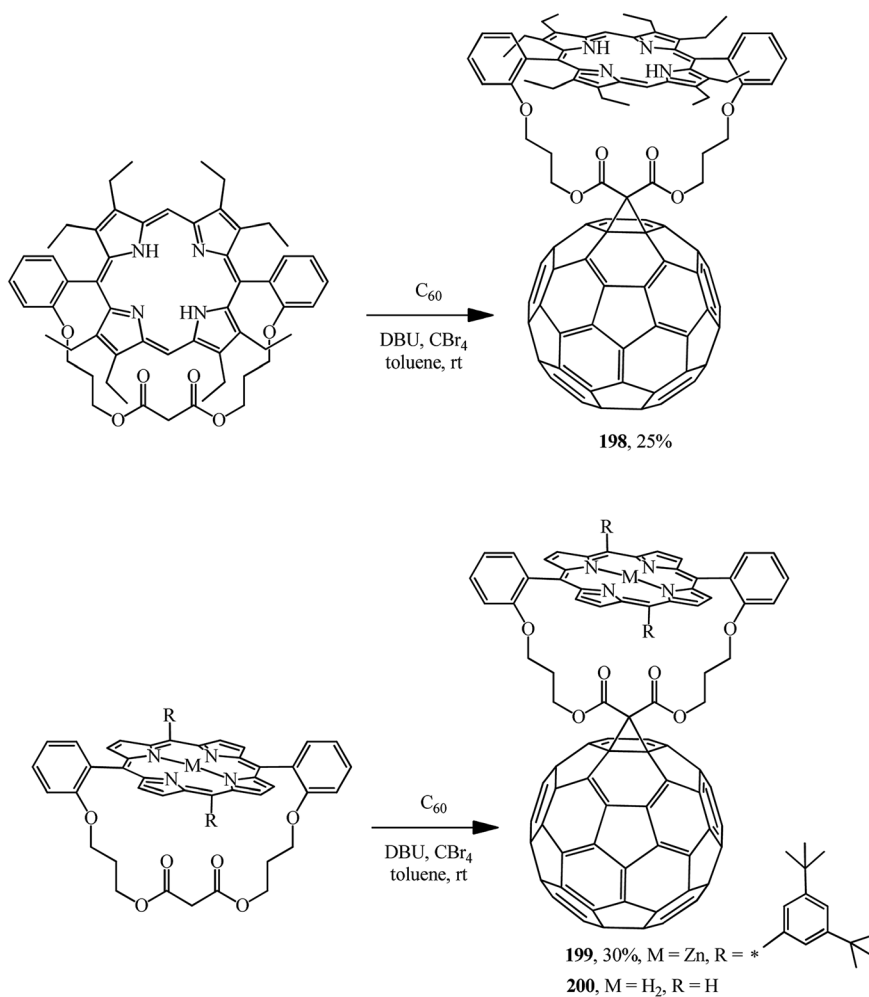
Scheme 51

functionalization of the fullerene sphere in targeted syntheses of new compounds with useful properties.

In fact, a series of terminal bromoalkyl fullerene adducts **155–161** were synthesized. Treatment of these adducts with cyanuric acid gave substitution products **162–168** (Scheme 43).⁸⁹

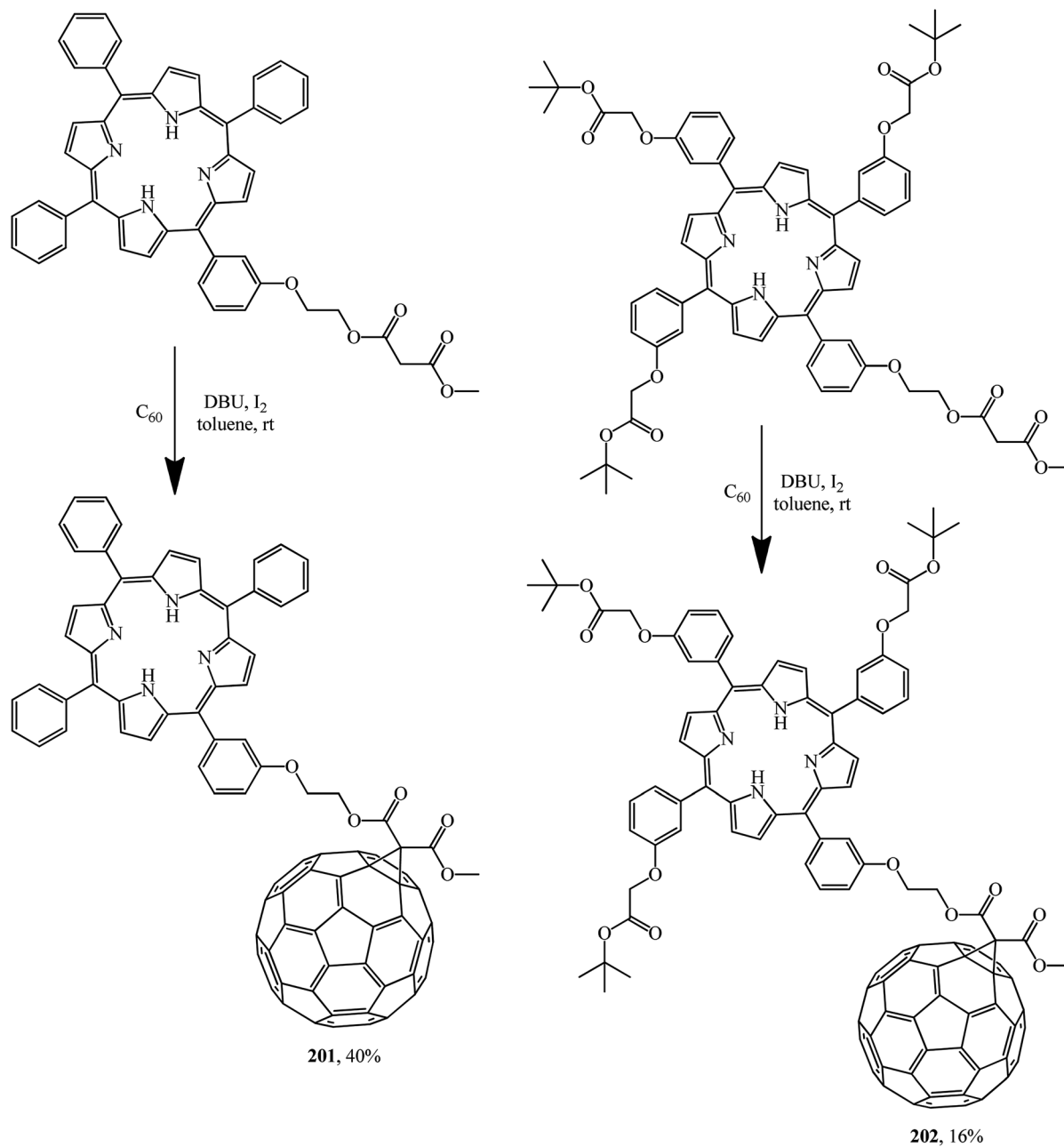
The adducts that were isolated were used in self-assembly and in studies of the photophysical properties of supramolecular donor-acceptor fullerene-porphyrin nano-hybrids bound by a hydrogen bond based on a Hamilton receptor.⁹⁰

Methanofullerenes can also be obtained using halogenated malonic esters **169** and **170**.⁹¹ Reactions of the compounds obtained with 1-butylimidazole convert the former into a series of “fullerene-ionic liquid” hybrids **171** and **172** (Scheme 44). Combinations of C₆₀ and ionic liquids give rise to new unique properties of the conjugates such as solubility in water, which was higher than 800 mg mL; moreover, the hybrids were employed for the



Scheme 52





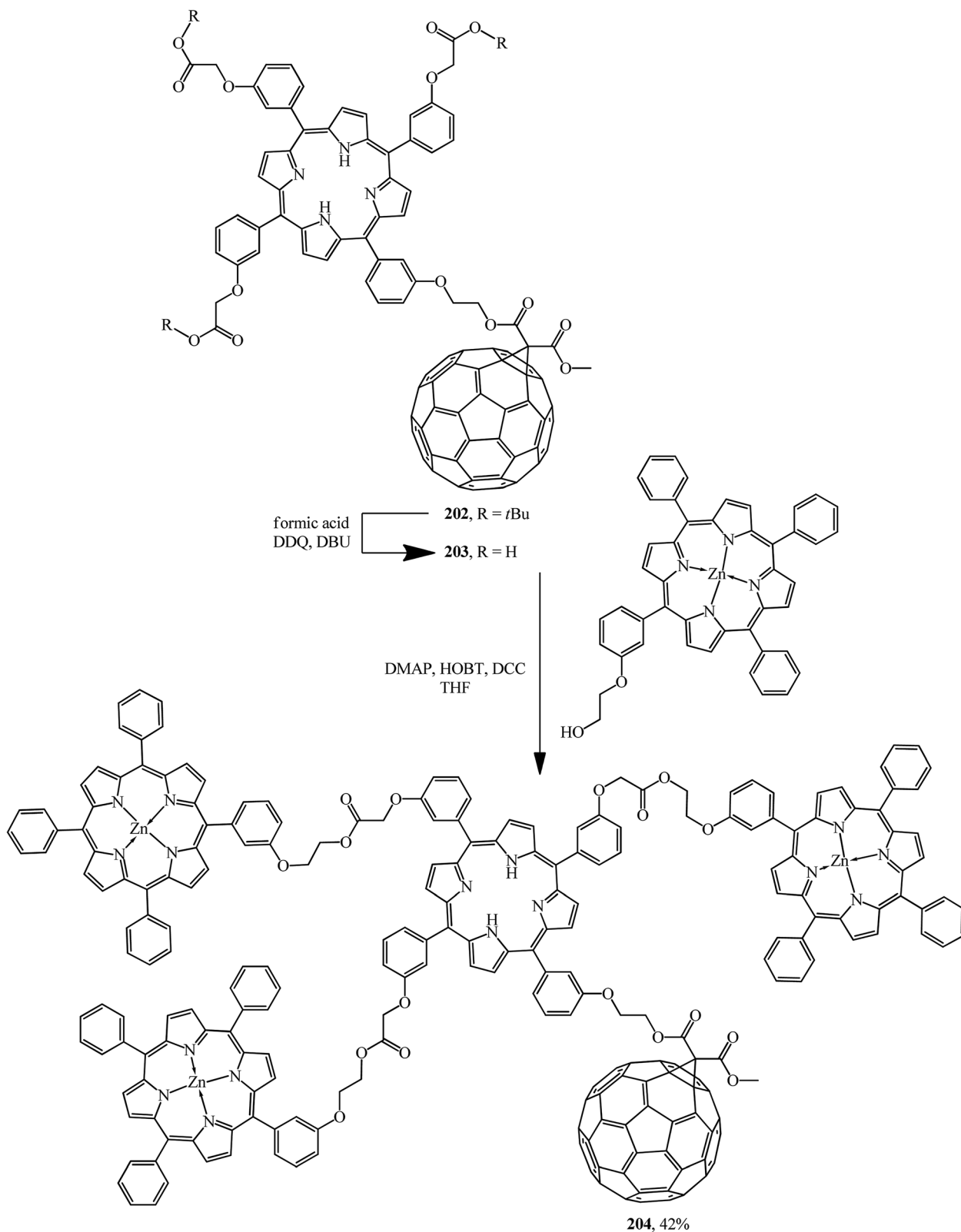
Scheme 53

immobilization of palladium nanoparticles through ion exchange followed by reduction with sodium borohydride.

Fullerene conjugates are of considerable interest for practical applications. For example, in order to improve the energy transfer from the dye as a photoactive antenna to the fullerene part in photovoltaic systems, a group of fullerene-perylene diimide diads **173–176** was obtained from the corresponding *N*-malonyl perylene diimides and characterized (Scheme 45). Their electrochemical and photophysical properties were studied.^{92–94}

It was demonstrated using steady-state and time-resolved spectroscopy that quantitative photoinduced energy transfer occurs from the perylene diimide moiety, which acts as a light-harvesting antenna, to the C_{60} unit playing the role of an energy acceptor.⁹⁴ At the authors' suggestion, the fullerene was intentionally attached at the bay region of the perylene diimide to achieve close proximity of the two chromophores and to ensure efficient photoinduced electron transfer⁹⁵ (Fig. 7).

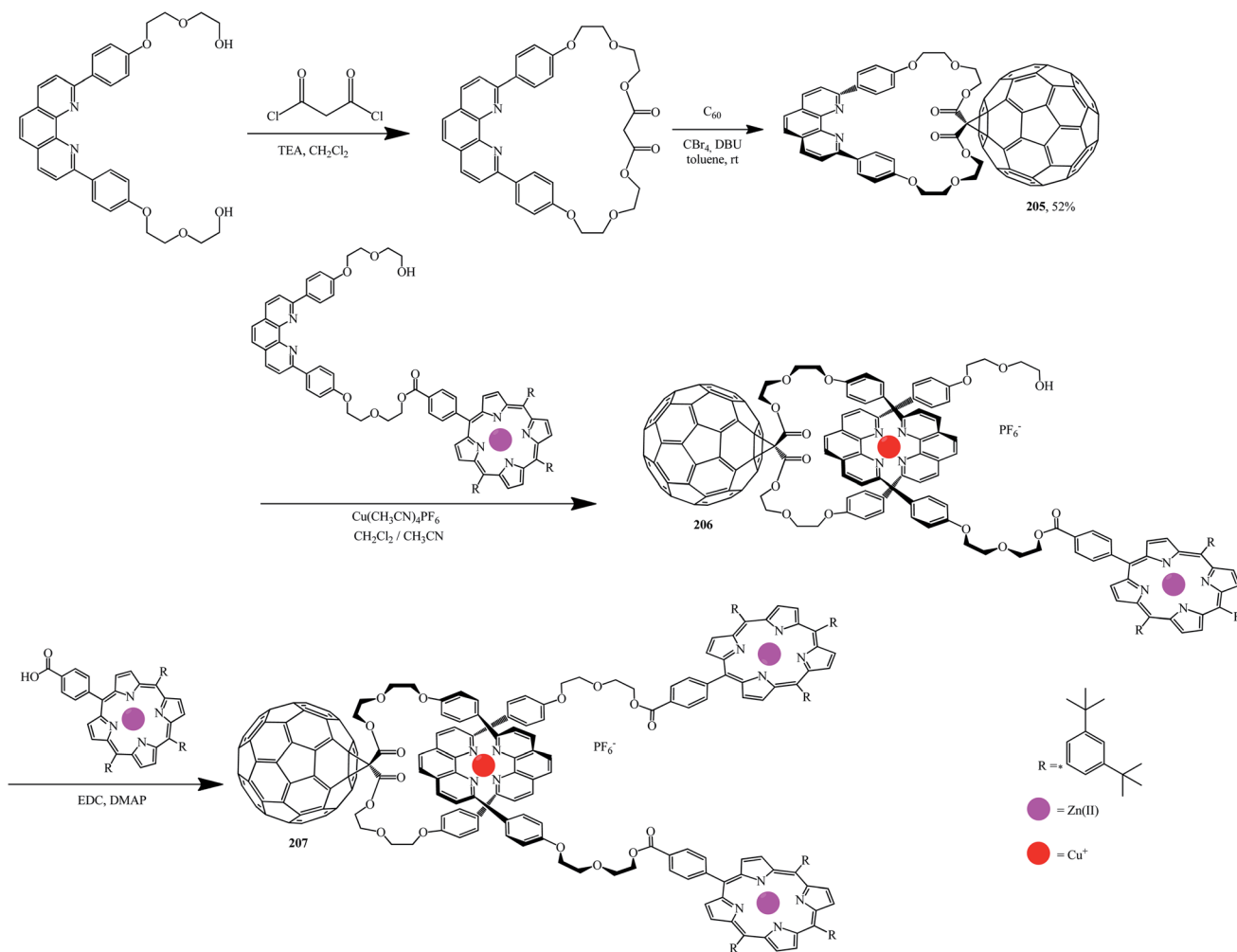




Scheme 54

Fullerene C_{60} diads can also be formed with 4-amino-1,8-naphthalimide chromophores (Fig. 8). A study of the fluorescent properties of the monoadducts obtained identified the role of

naphthalimide chromophore with charge transfer as a light absorbing antenna and an excited fullerene sensitizer. According to ref. 96, conjugates **179** and **180** are of great practical importance.



Scheme 55

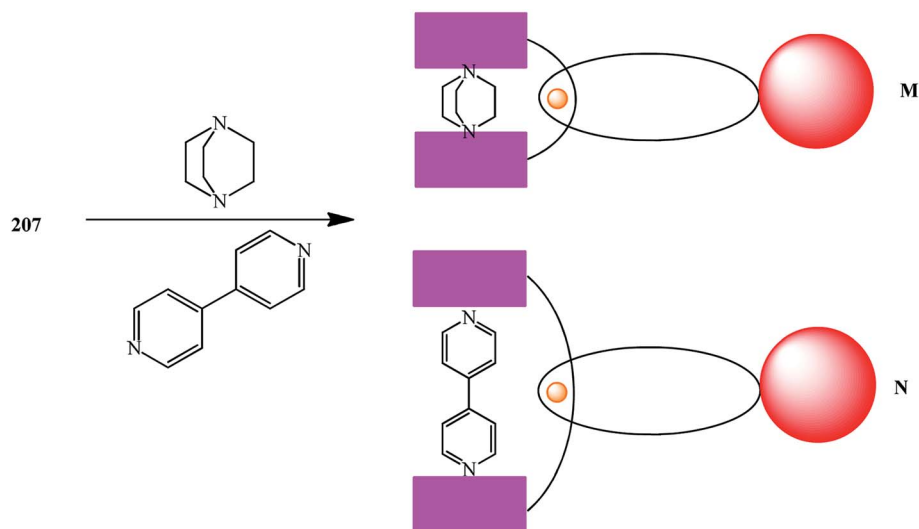
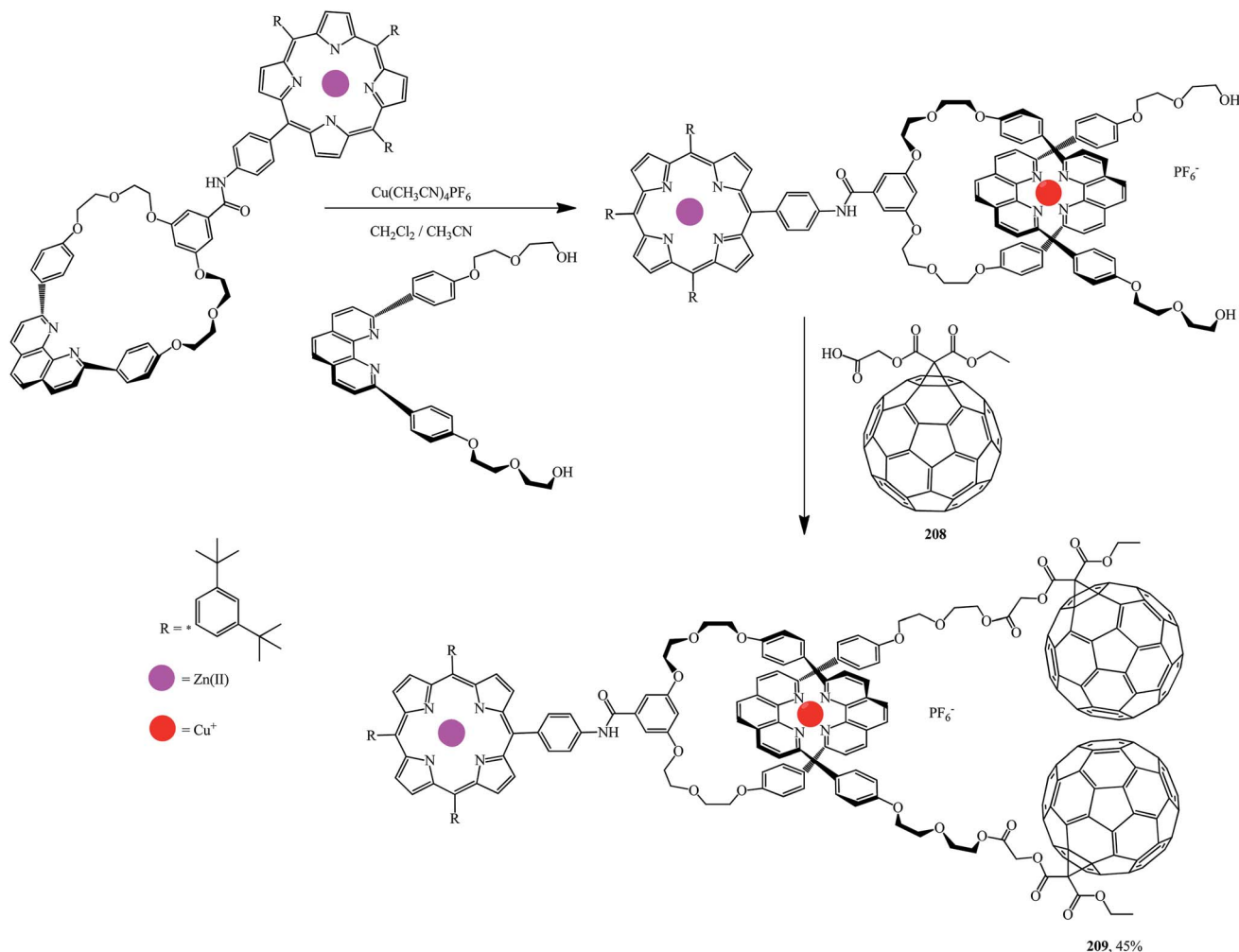


Fig. 9 Formation of 1 : 1 sandwich complexes.

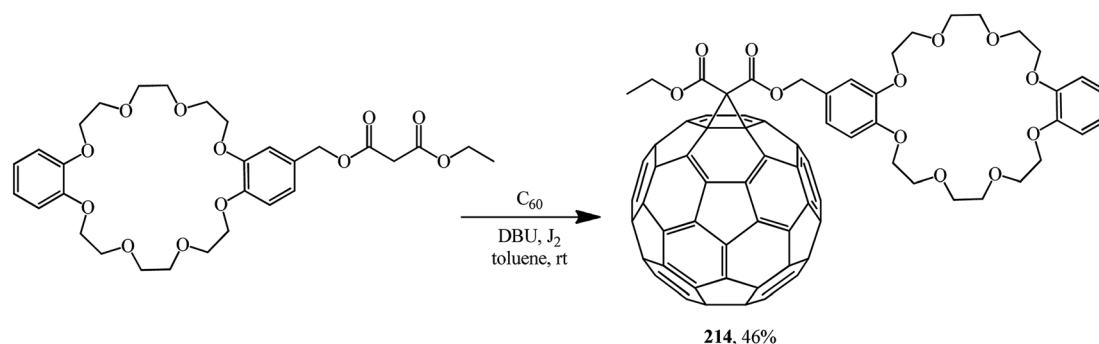


Scheme 56

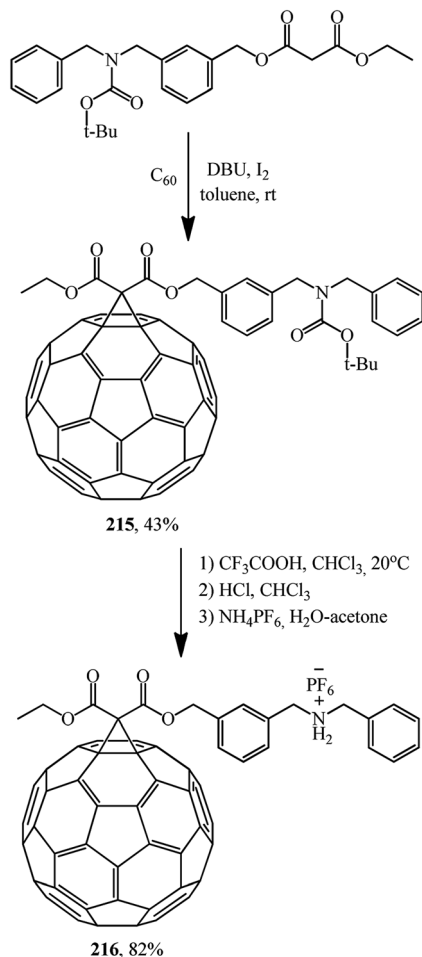
Fullerene-containing derivatives carrying alkyne functional groups are attractive in terms of various transformations. A considerable number of studies deal with the synthesis of fullerene-containing malonates with terminal acetylene bonds which then easily react with azides by the

“click-chemistry” mechanism to give the corresponding triazole derivatives.

One of the variants was implemented in ref. ⁹⁷ where, for example, compounds **181** or **182** were synthesized and used as building blocks under copper-mediated Huisgen 1,3-



Scheme 57



Scheme 58

dipolar cycloaddition conditions to afford 1,2,3-triazole derivatives **183** or **184**, respectively (Scheme 46).

This approach was implemented in ref. 98 where the originally isolated symmetric 61-bis(propargyloxycarbonyl) methano[60]fullerene **185** was converted according to Huisgen into adduct **186** (Scheme 47).

Using malonates containing a terminal-acetylenic bond, the corresponding fullerene-containing adducts **187–189** were synthesized (Scheme 48).⁹⁹ Treatment of the latter with excess methoxypoly(ethylene glycol)azide in the presence of copper shavings and copper(II) sulfate gave triazoles **190–192** in the yields indicated in Scheme 48.

A methanofullerene containing triazole and deoxythymidine moieties that is promising in terms of biological activity was described in ref. 100 For this purpose, diacetylenic precursor **185** was synthesized, which in the presence of catalytic amounts of $(\text{EtO})_3\text{P} \times \text{CuI}$ reacted with azidodeoxythymidine to give the desired compound **193** (Scheme 49).

Based on methyl uridinemalonate synthesized, cyclopropanation first gave a fullerene conjugate with uridine

194, deblocking of which gave its analogue **195** in an almost quantitative yield (Scheme 50).¹⁰¹

Using the Bingel–Hirsch reaction, the class of methanofullerenes was expanded with adducts containing porphyrin radicals. Numerous publications dealing with the synthesis of porphyrin–fullerene diads already exist, where the subject of the mutual effect of the C_{60} sphere and porphyrin moiety is also covered. The keen interest in these extremely important aromatic heterocyclic systems underlying natural compounds, such as hemoglobin, chlorophyll and vitamin B_{12} , is quite understandable. This is particularly true for combinations with fullerene where extraordinary results may be expected.

For example, in ref. 102 and 103 the original [3,7,12,17-tetramethyl-2,18-(propanoxypropanoxypropano)-21*H*,23*H*-porphine-29,31-dionato-(2-)]-zinc was demetallated with trifluoroacetic acid and these compounds were converted into the corresponding “porphyrin–fullerene” diads **196** and **197** under Bingel–Hirsch reaction conditions (Scheme 51).

Porphyrin–fullerene diads **196** and **197** bound with a bislactone show promising photophysical properties in photosynthesis simulation.

Using a similar route, covalent-bound porphyrin–fullerene diads with “parachute” topology **198**,¹⁰⁴ **199** and **200** (ref. 105) were obtained (Scheme 52).

In all cases, luminescence quenching was observed upon formation of porphyrin–fullerene diads, which is characteristic of the original porphyrin derivatives.

A detailed electrochemical and photophysical study revealed that the porphyrin–fullerene diads **201** and **202** synthesized allow storing a nearly 1.7 eV radical ion pair state with a lifetime of one nanosecond. In this context, the flexible linkage, powering a through space charge transfer, prevents, however, stabilization of the radical ion pair state beyond nanoseconds (Scheme 53).⁸²

Light harvesting, unidirectional energy transfer, charge transfer, and charge-shift reactions are attainable due to dendritic architectures bound to C_{60} , which gives rise to the successful mimicry of the primary events in photosynthesis. Therefore, as a continuation of studies,¹⁰⁶ compound **202** synthesized was quantitatively converted by hydration of its ester moiety to the corresponding triacid **203**. Addition of excess porphyrin to the latter in the presence of 4-dimethylaminopyridine (DMAP), 1-hydroxybenzotriazole hydrate (HOBT) and *N,N'*-dicyclohexylcarbodiimide (DCC) in THF gave dendritic porphyrin–fullerene conjugate **204** (Scheme 54).

The interest in incorporation of donor porphyrin moieties into the C_{60} molecule is due to the search for covalent-bound diads as models of natural electron transfer centers and as potential photochemical molecular devices. Two methods are used to achieve favorable steric conditions favoring the electronic transfers in these diads. The first one involves separating the donor and fullerene moieties by flexible bonds, while the second one involves “face-to-face” aligning the porphyrin plane directly to the C_{60} sphere. Upon photoexcitation, long-lived states with separated



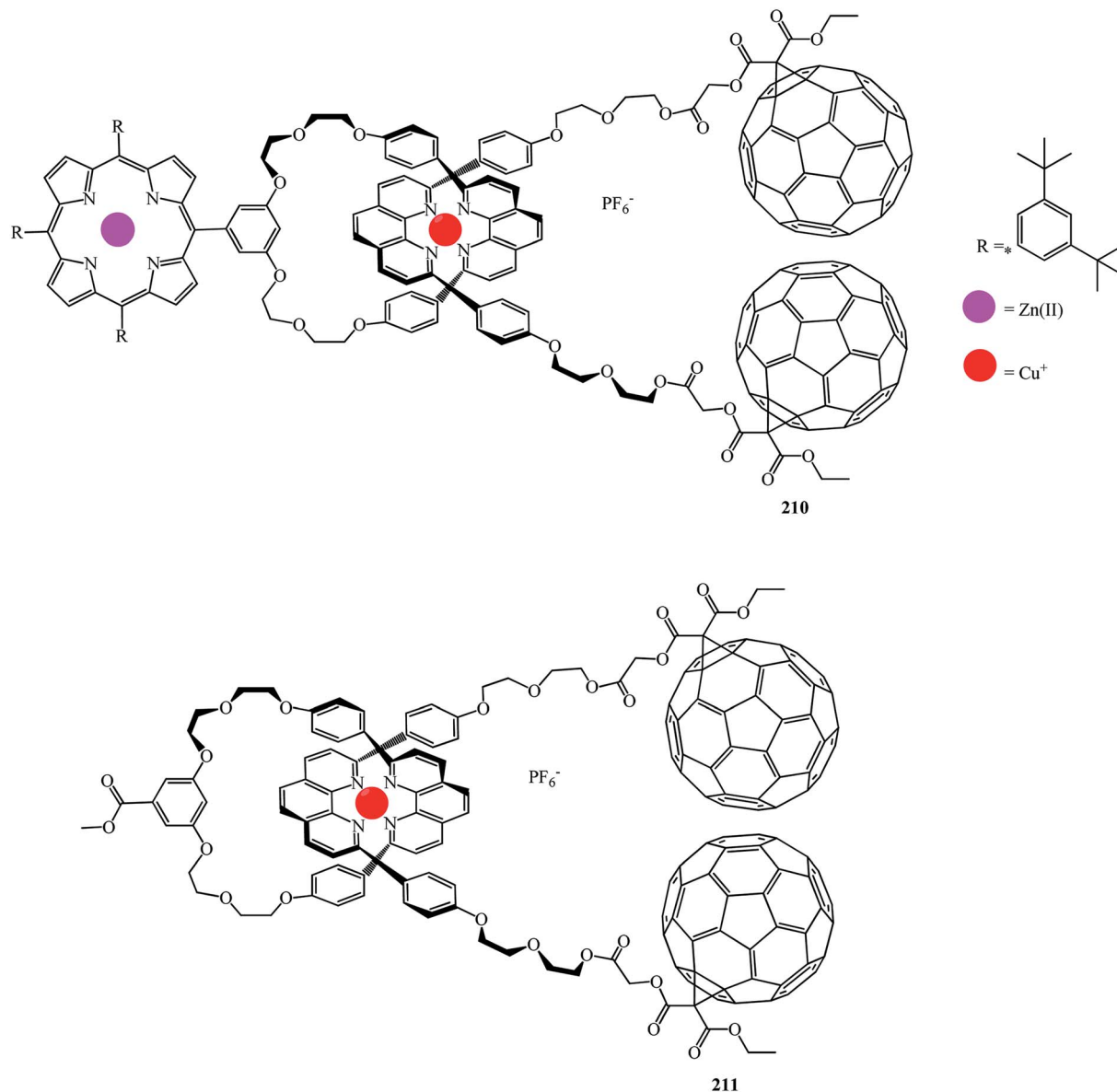


Fig. 10 Fullerene–porphyrin rotaxanes 210 and 211.

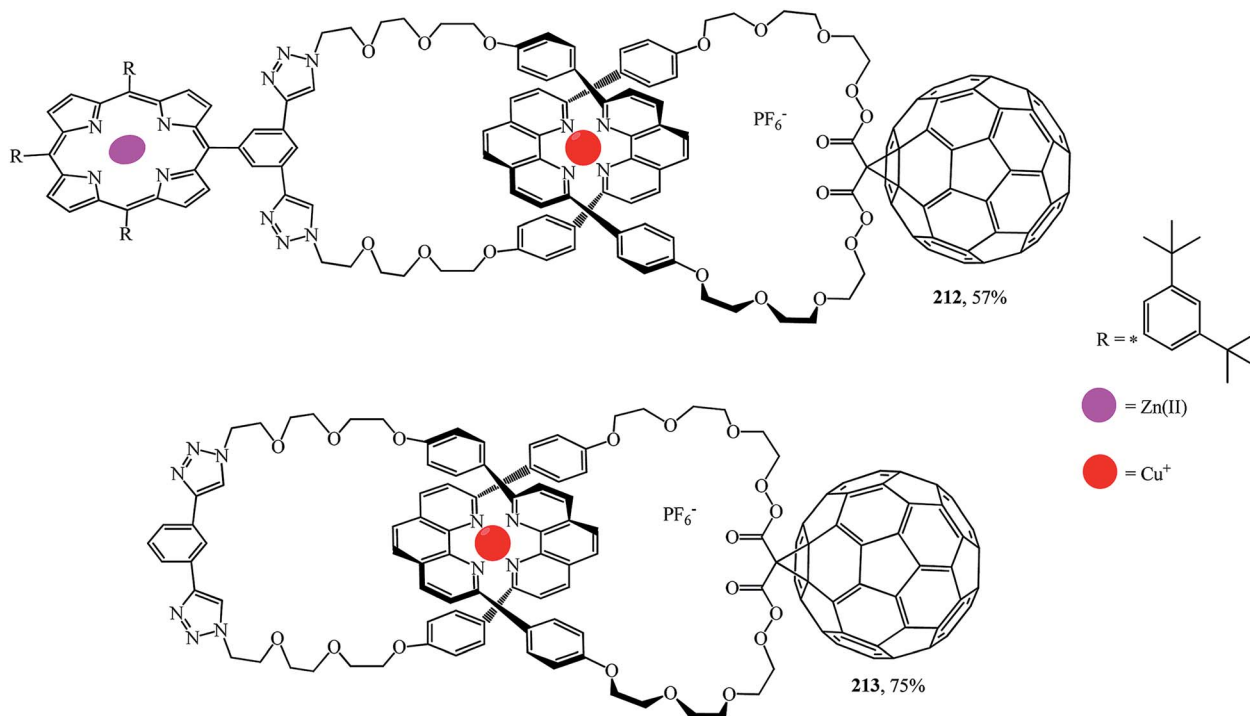
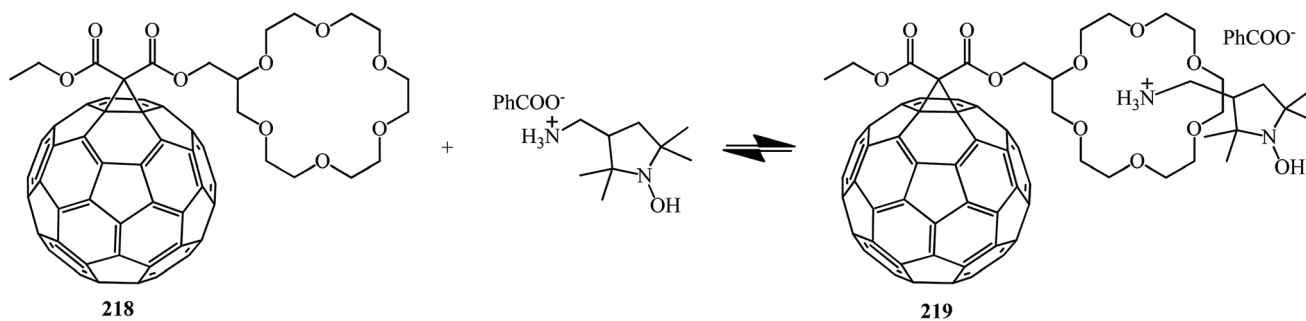
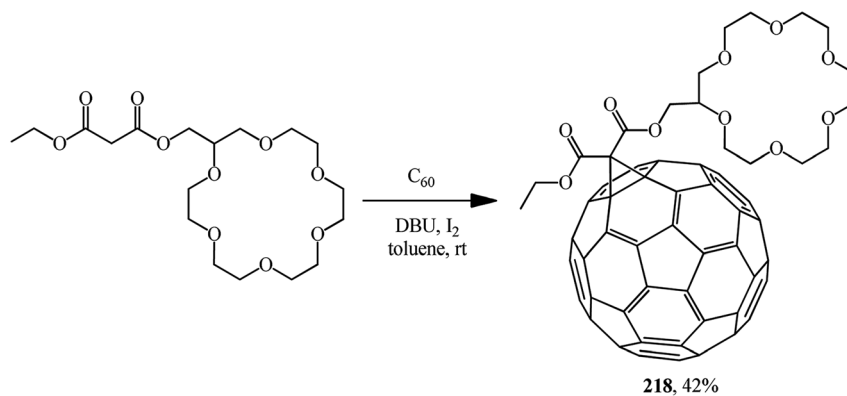
charges are formed in this type of covalent-bound diads. In fact, arranging four bulky chromophore porphyrin groups at C₆₀ periphery enhances the light collection function and the light conversion of the resulting hybrid **204**. The authors showed that the latter can demonstrate two main functions of photosynthesis: light assembly and charge transfer; as a result, this approach results in highly efficient solar energy conversion.

Methanofullerenocarboxylates are also considered as candidates in the creation of rotaxanes, non-covalent bound self-organizing Sauvage-type systems that are promising for creating photochemical molecular devices. In these systems, electro- and photoactive components are incorporated into the linear part of the system or are as if threaded on the latter. Electron or energy transfers occur in these

systems upon external impact. The presence of charged moieties in the molecules does not change the electrophilicity of rotaxane spheres in comparison with that of the non-functionalized methanofullerene.

Using standard techniques, macrocycles were developed onto which fullerene was then grafted. For example, fullerene-based compound **205** was obtained from a macrocyclic precursor by the Bingel–Hirsch reaction. Complexation of **205** with a molecule containing the second phenanthroline group with zinc porphyrin on one end is then performed in the presence of Cu(I) in order to isolate tetrahedral complex **206**. Addition of a porphyrin carboxylic acid to the other end of complex **206** gives the target rotaxane **207** (Scheme 55).^{107,108}



Fig. 11 Porphyrin-C₆₀-[2]catenanes 212 and 213.

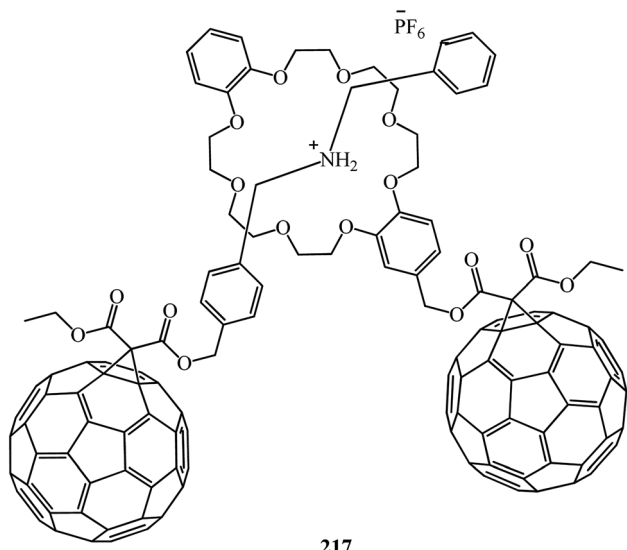
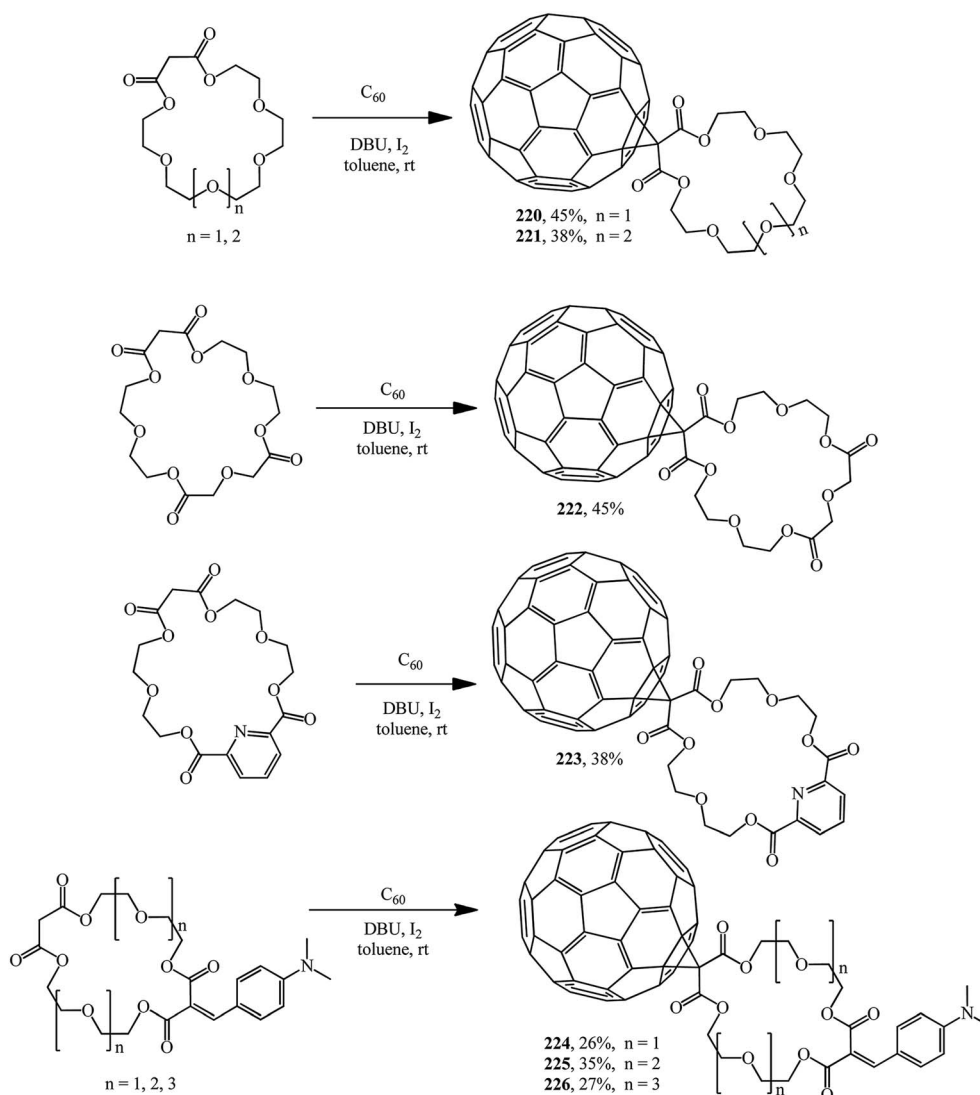


Fig. 12 Supramolecular C_{60} dimer **217**.

Titration of porphyrin–fullerene rotaxanes with 1,4-diazabicyclo-[2.2.2]octane (DABCO) or 4,4'-bipyridine led to photo- and redoxactive catenanic architectures **M** and **N**, which upon photoexcitation undergo a sequence of short-range energy and electron transfer events to give a long-lived charge-separated radical-pair state (Fig. 9).¹⁰⁸

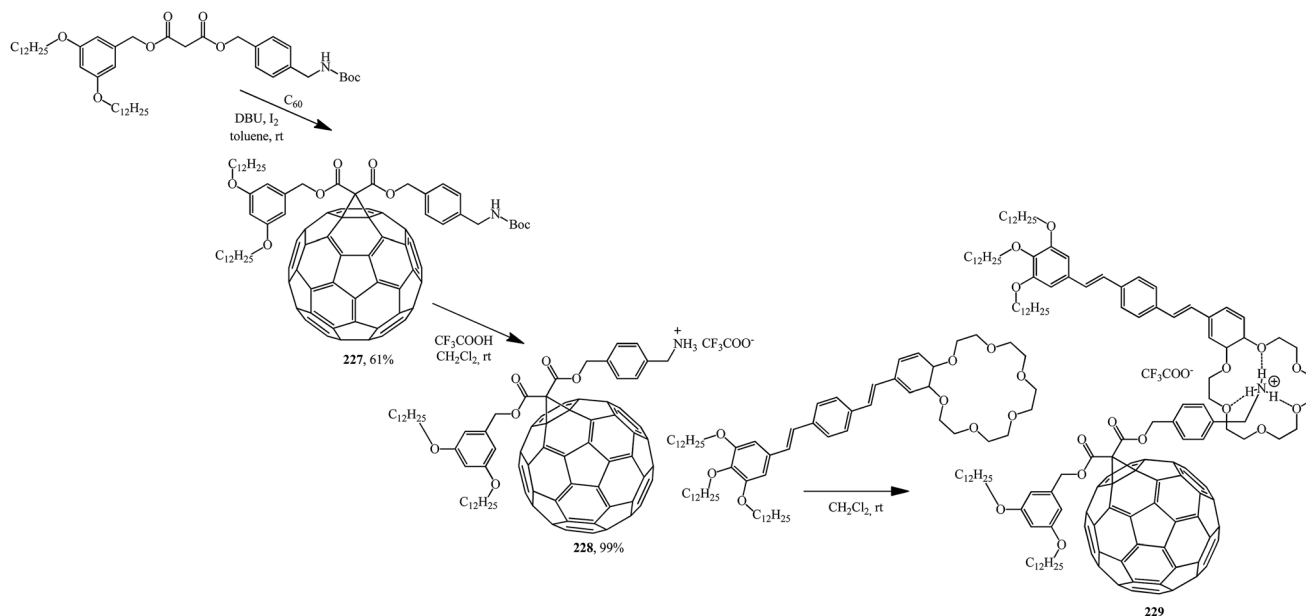
Using the methodology reported in ref. 108 and 109 a series of porphyrinorotaxanes included in the structure and containing fullerene stoppers¹⁰⁹ were synthesized by a convergent route. First, a macrocyclic structure with a 1,10-phenanthroline moiety attached to the porphyrin part was formed. This process was accompanied by the formation of a tetrahedral Cu(I) complex with a linear phenanthroline group and hydroxyls at both ends (Scheme 56). At the final stage, esterification of this diol with fullerene-carboxylic acid **208** at room temperature gave rotaxane **209**.

Fullerene–porphyrin rotaxanes **210** and **211** were synthesized in a similar way (Fig. 10).



Scheme 61





Scheme 62

A synthesis of the first [2]catenanes with porphyrin and fullerene subunits **212** and **213**, which combined the advantages of both “click-chemistry” and Sauvage’s methods, was performed in yields that are very good for Bingel’s reaction (Fig. 11).¹¹⁰ This new electron donor-acceptor catenane family was extensively studied by spectroscopic, computational, electrochemical and photo-physical methods.

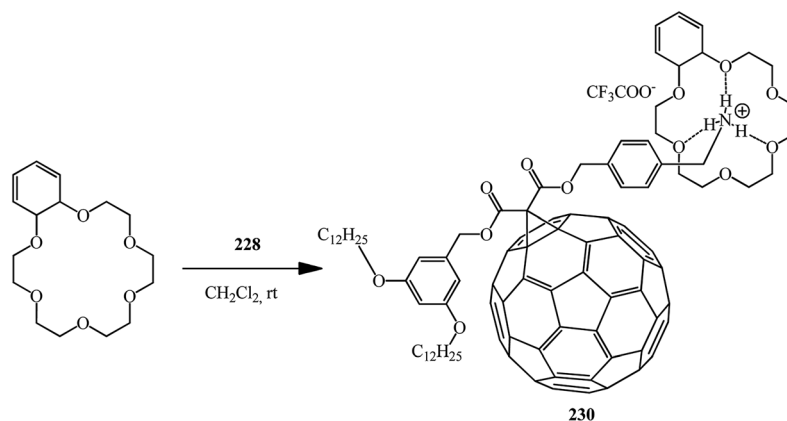
Thus, the use of C_{60} as an electron acceptor in catenanes simultaneously ensures the transfer of electrons over long distances and reduces the rate of reverse electron transfer. It has been shown¹¹⁰ that supramolecular methods can be used to create high-complexity 3D nanostructures containing electron donors and acceptors that generate long-lived charged separated states upon photoexcitation. The use of

these materials in light energy conversion systems, in photovoltaic devices in particular, will be the subject of intense fundamental studies in the near future.

Fullerene–crown ether conjugates have been the subject of several investigations in view of possible supramolecular modulation of the electronic properties of fullerenes.^{111–115}

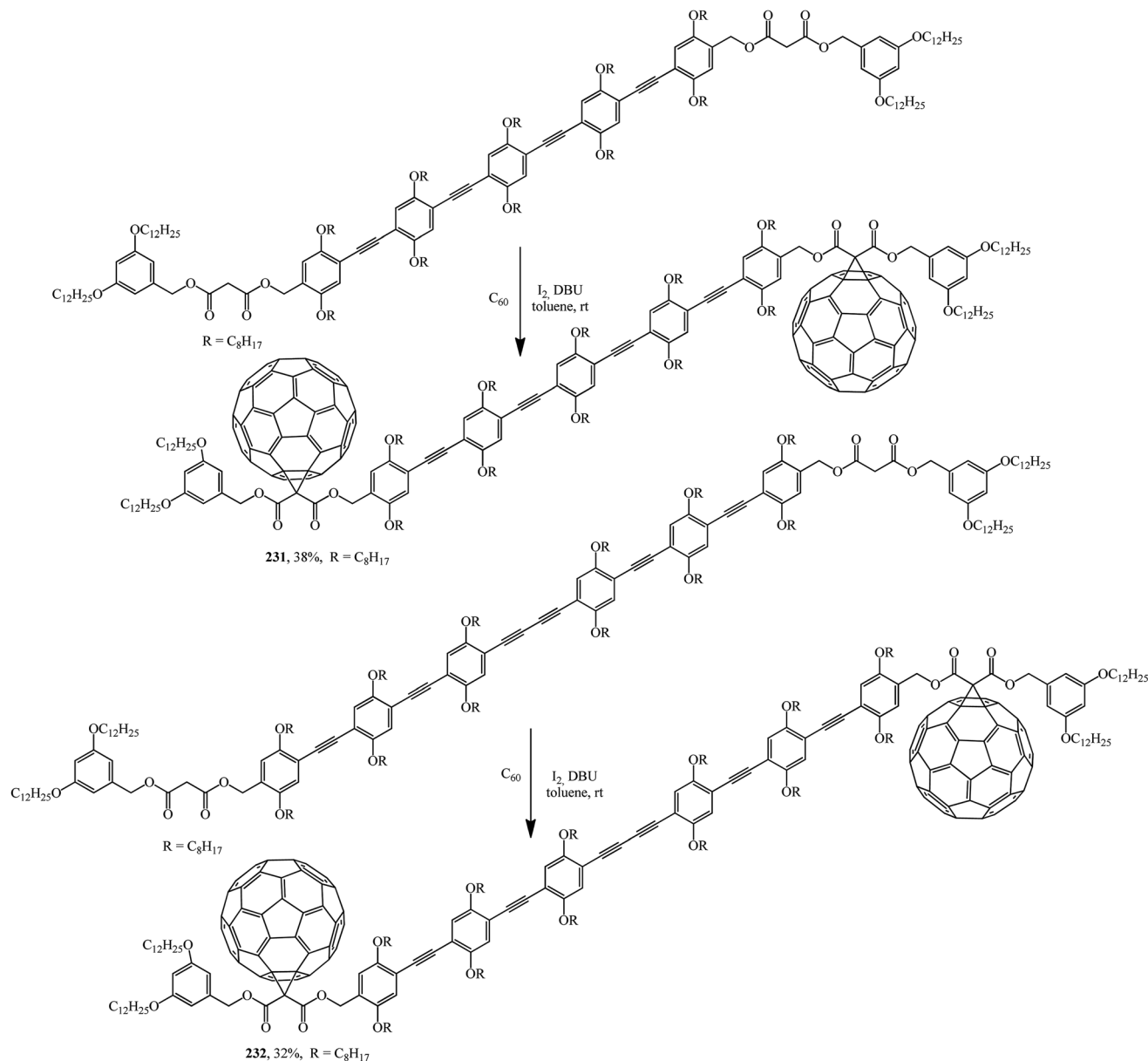
One of the first references to monofunctionalized fullerene–crown ether conjugates obtained by the Bingel–Hirsch method can be found in ref. 116. This paper reported a synthesis of a C_{60} adduct with dibenzo-24-crown-8 macrocyclic polyether (DB24C8) **214** (Scheme 57).

In addition, article¹¹⁶ reports a synthesis, *via* intermediate **215**, of an adduct of dibenzylammonium salt **216** covalently bound to carbon allotrope C_{60} (Scheme 58).



Scheme 63





Scheme 64

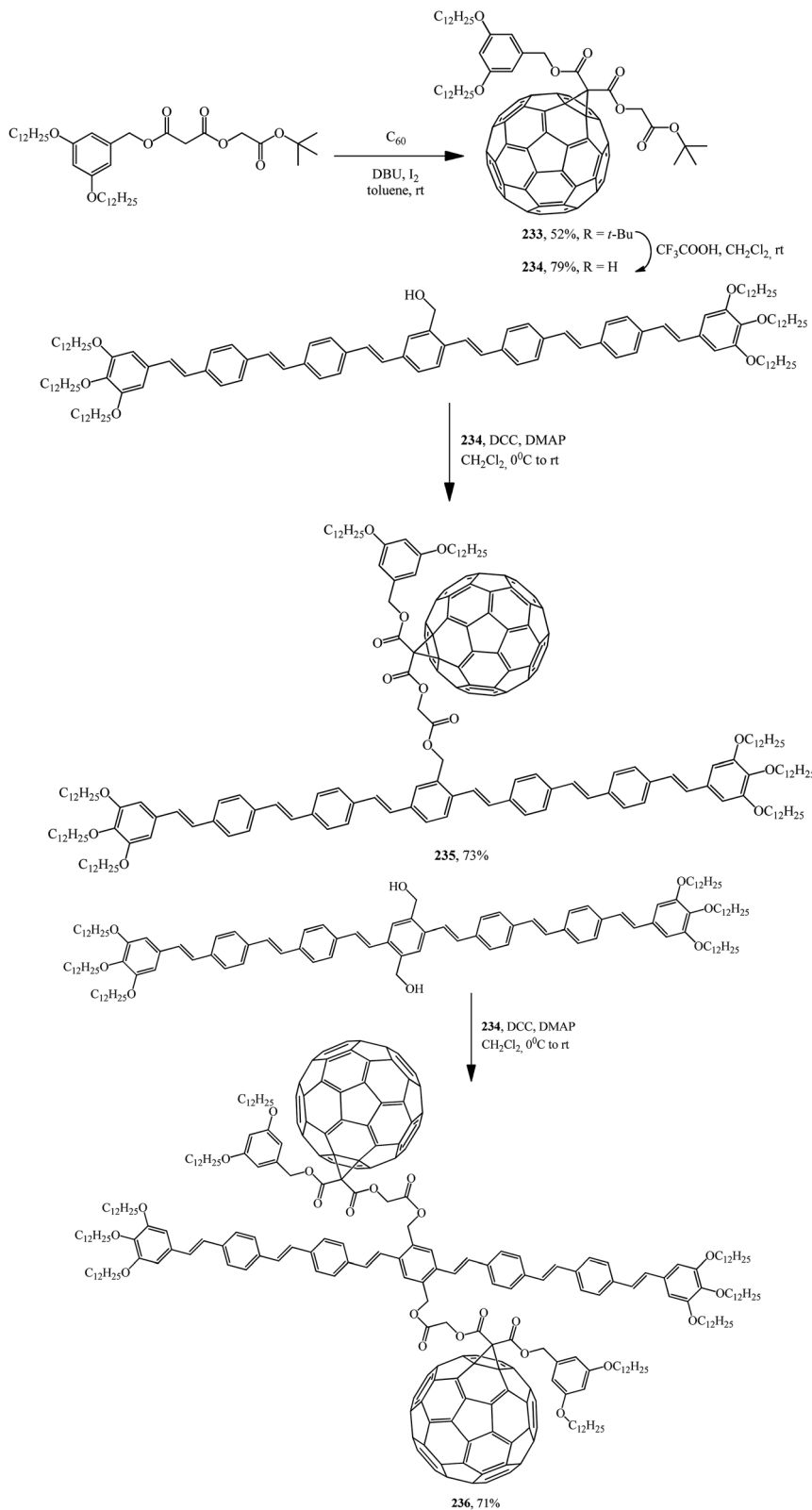
Conjugate **214** forms a stable, pseudorotaxane-like 1 : 1 complex with dibenzylammonium hexafluorophosphate. Equally, the C₆₀ dibenzylammonium conjugate **216** threads through the cavity of DB24C8 to form a 1 : 1 complex with a pseudorotaxane-like geometry. Furthermore, the C₆₀-DB24C8 adduct **214** and the C₆₀ dibenzylammonium conjugate **215** interact with each other by hydrogen bonding and ion-dipole interactions to form the first supramolecular C₆₀ dimer **217** (Fig. 12). In all the three cases, the dibenzylammonium component is threaded through the cavity of the crown ether macrocycle.

A time resolved EPR spectrum of a radical-triplet pair (RTP) in the quartet excited state was recorded by irradiating a solution of a fullerene-crown ether conjugate **218**

(Scheme 59) and an ammonium aminoxyl radical with visible laser light. This is the first direct observation of an RTP in liquid solution for a stable host-guest complex between a macrocyclic ligand bearing a triplet precursor and an aminoxyl ammonium cation.

E. Sartori *et al.*¹¹⁷ performed a comparative analysis of the complexing properties of several methanofullerenes incorporating a macrocyclic crown ether bound to C₆₀. Studies of the complexing properties of the methanofullerenes with respect to ammonium ions with various degrees of substitution made it possible to identify the particularly high complexing ability toward mono-substituted ammonium ions. The first observation of a RTP is reported which occurs upon photoexcitation of a host-



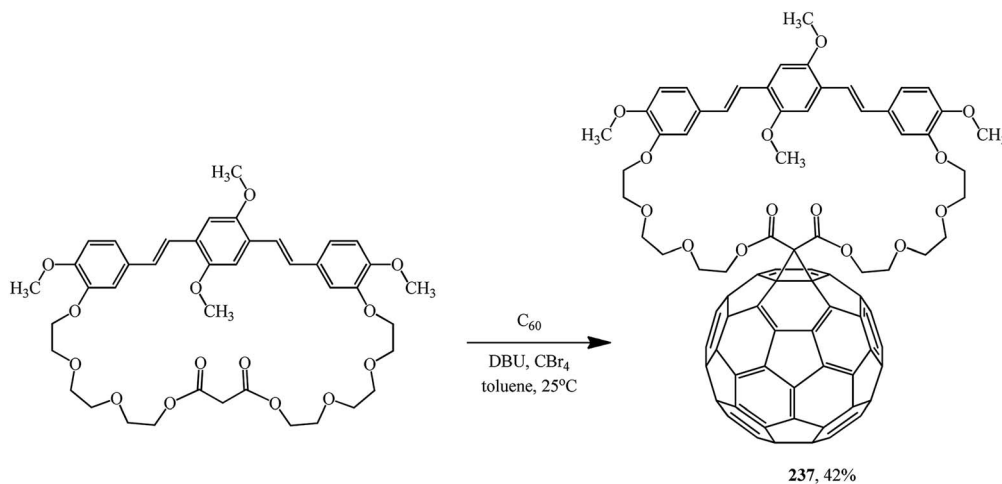


Scheme 65

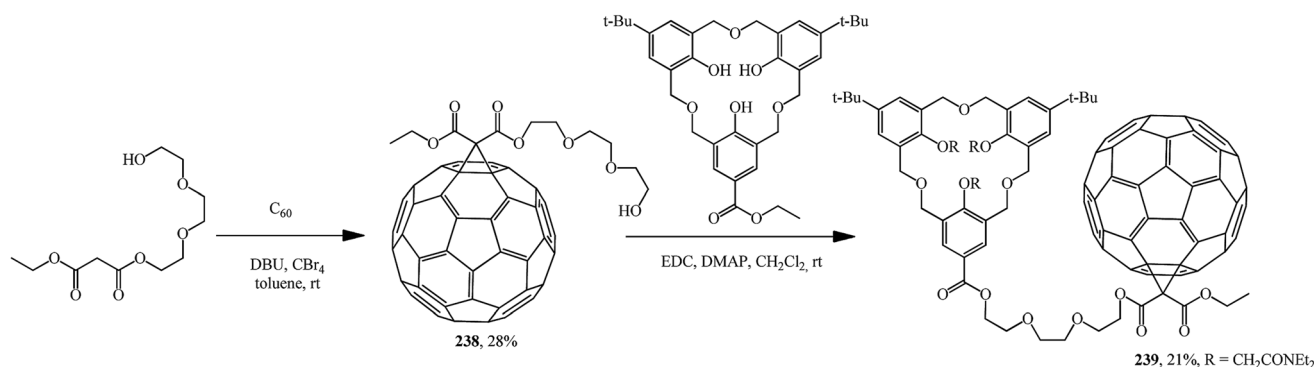
guest complex between [60]fullerene-crown ether conjugate **218** and the benzoate ammonium salt of 3-aminomethyl-[2,2,5,5-tetramethylpyrrolidin-1-oxyl] with

formation of non-covalent **219**. The electrochemical behavior of the compounds obtained and the results of their analysis by ESR method were considered (Scheme 60).





Scheme 66



Scheme 67

Methanofullerenes in which the malonate part is a linker between C₆₀ and the macrocyclic crown ether were reported by Pasini. Based on malonate type crown ethers, C₆₀ conjugates with symmetric polyether groups **220–223** (ref. 118) and **224–226** (ref. 119) were synthesized using iodine as the halogenating agent (Scheme 61).

Based on the readily available adduct **227**, a synthesis of derivative **228** with an ammonium subunit capable of forming a supramolecular complex with oligo(*p*-phenylenevinylene) (OPV) similarly to the well-known π -binding in ammonium-crown ether **229** was developed. Preliminary luminescence studies show that an intramolecular photo-induced process appears in this new supramolecular assembly C₆₀-OPV (Scheme 62).¹²⁰

Using the same principle and methanofullerene **228** with an ammonium subunit derivative synthesized by authors,¹²⁰ the formation of supramolecular complex **230** with dibenzo-24-crown-6 was proved¹²¹ (Scheme 63).

Publications of this kind open a path for creating stable non-covalent supramolecular assemblies with combined crown ether and fullerene units that are not available in

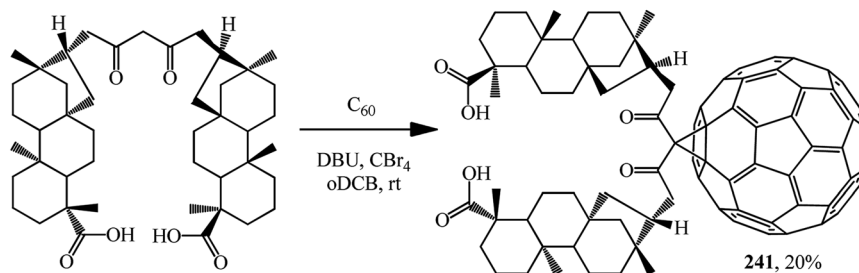
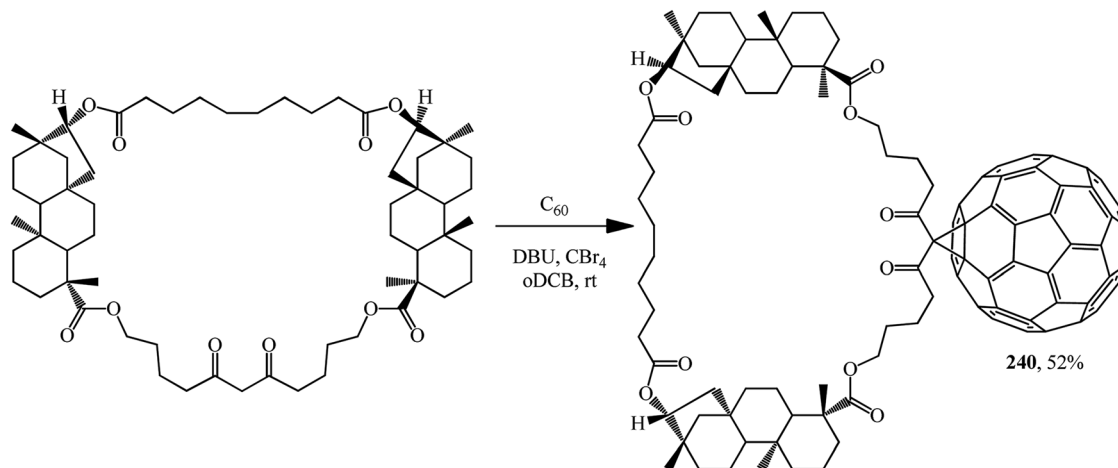
literature. Using successfully chosen molecular components, new supramolecular architectures with various photoinduced intercomponent processes can be constructed.

Examples of cycloaddition to buckminsterfullerene C₆₀ where high-molecular objects are involved rather than low-molecular ones are of appreciable interest.

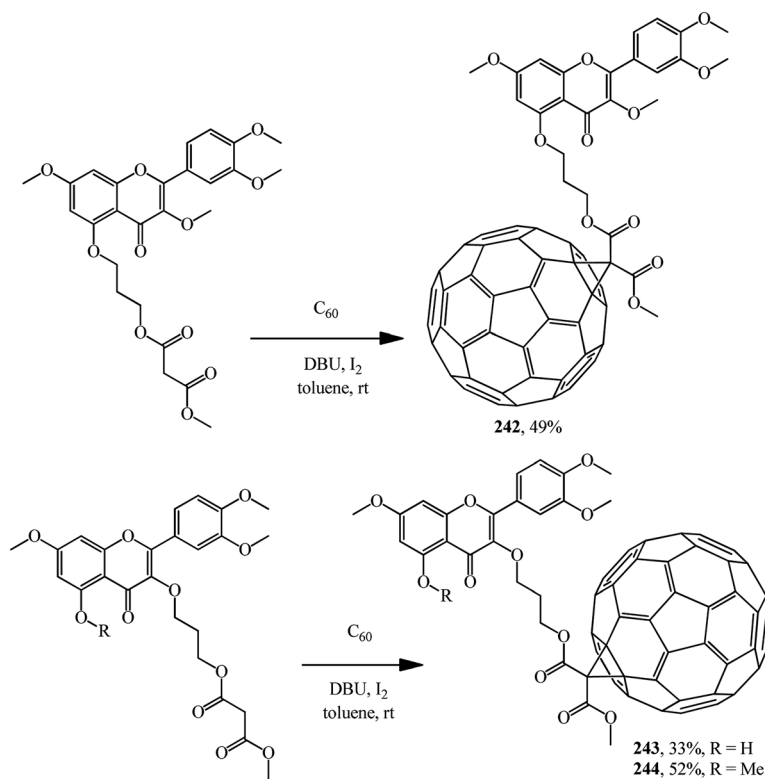
For instance, oligomers are used as starting materials in the Bingel-Hirsch reaction: disymmetrically substituted oligo(phenyleneethynediyl) (OPE) derivatives were prepared from 2,5-bis(octyloxy)-4-[(triisopropylsilyl)ethynyl]benzaldehyde by an iterative approach.¹²² The starting dimalonic esters in disymmetrically substituted OPE derivatives undergo cyclopropanation to give the corresponding C₆₀-OPE conjugates **231** and **232** (Scheme 64).

Derivatives **231** and **232**, the structure of which includes a long conjugation chain, were tested as active materials in photovoltaic devices. The performance of devices prepared from these products shows that the efficiency of devices can be significantly improved by increasing the donor ability of the OPE moiety.





Scheme 68



Scheme 69



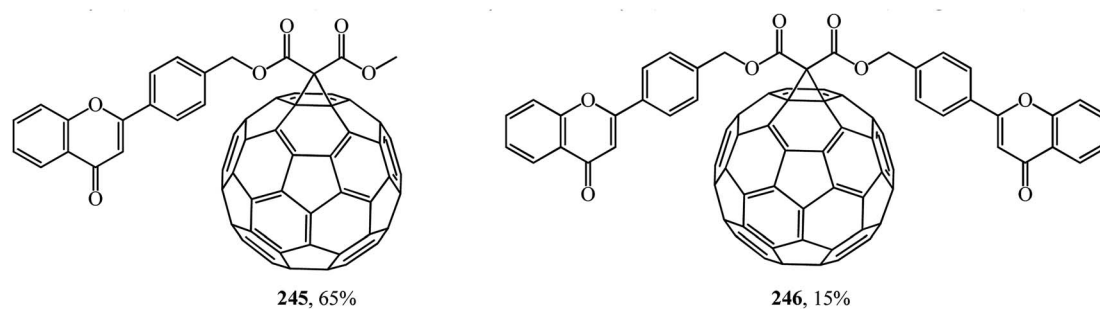


Fig. 13 Fullerene–flavonoid conjugates 245–246.

Later, the same group of scientists isolated acid **234** itself from fullerene carboxylic acid *tert*-butyl ether derivative **233**. The reaction of **234** with oligophenylenevinylene heptamers containing one or two hydroxy groups gave C₆₀–OPV conjugates incorporating one **235** (ref. 123) or two **236** (ref. 124) fullerene subunits (Scheme 65).

The electrochemical properties of the resulting C₆₀–OPV derivatives were studied by cyclic voltammetry. While the first reduction of both C₆₀–OPV conjugates is centered on the C₆₀ unit, the oxidation is centered on the OPV rod. Photophysical studies revealed that intramolecular photo-induced processes of energy and electron transfer from the OPV central unit to the attached fullerene moieties appeared. The charge separation process shows a significant dependence on the solvent nature.

A symmetrical fullerene–bis(styryl)benzene diad **237** was synthesized in practice-oriented studies into single-component organic solar cells. In this case, the oxyethylene macrocyclic spacer attached to bis(styryl)benzene served as the cyclopropanating agent (Scheme 66).¹²⁵

The overall power conversion efficiency calculated for solar cells made of the bis(styryl)benzene–fullerene diad was as low as 0.022%, which was the highest value reported at the time, under high-level irradiation conditions, for solar cells based on diads in which a fullerene is tethered to a phenylenevinylene structure.

The separately prepared hydroxy-containing fullerene block **238** was fused by the carbodiimide method with the homooxalix[3]arene moiety to give compound **239**, which exhibits interesting selfcomplexation–decomplexation properties in response to the solvent polarity (Scheme 67).¹²⁶

A macrocycle having two isosteviol moieties and malonate fragment was synthesized and its ability to inhibit the growth of *Mycobacterium tuberculosis* H37Rv *in vitro* at a minimum concentration of 1 mg × cm⁻³ was demonstrated. The macrocycle and the acyclic analogue add fullerene C₆₀ at the activated methylene group to furnish the corresponding methanofullerene conjugates **240** and **241** (Scheme 68).¹²⁷

A number of methanofullerenes containing natural flavonoids were synthesized by A. C. Tome's team.¹²⁸ Starting from quercetin, a natural flavonol with high

antioxidant activity, three novel fullerene–flavone derivatives **242**–**244** were synthesized (Scheme 69).

Similarly, fullerene–flavonoid derivatives **245**, **246** were subsequently obtained from methyl(4'-flavonylmethyl)- and bis(4'-flavonylmethyl)malonates (Fig. 13).¹²⁹

The scope of fullerene–flavonoid conjugates **247**–**249** bearing one or two 3,5-di-*tert*-butyl-4-hydroxyphenyl groups was successfully expanded in ref. 130 using chalcone, flavone and flavanone as the starting materials (Scheme 70).

Coumarins are attractive synthetic objects due to their high quantum yields of radiation and photostability. Moreover, coumarin derivatives are often used as signal elements in sensors and in complex photophysical systems. Therefore, studies aimed at the synthesis of new covalent-bound fullerene–coumarin diads **250**, **251** (ref. 131) and **252**, **253**,¹³² as well as studies of their photophysical properties (Fig. 14) are quite timely.

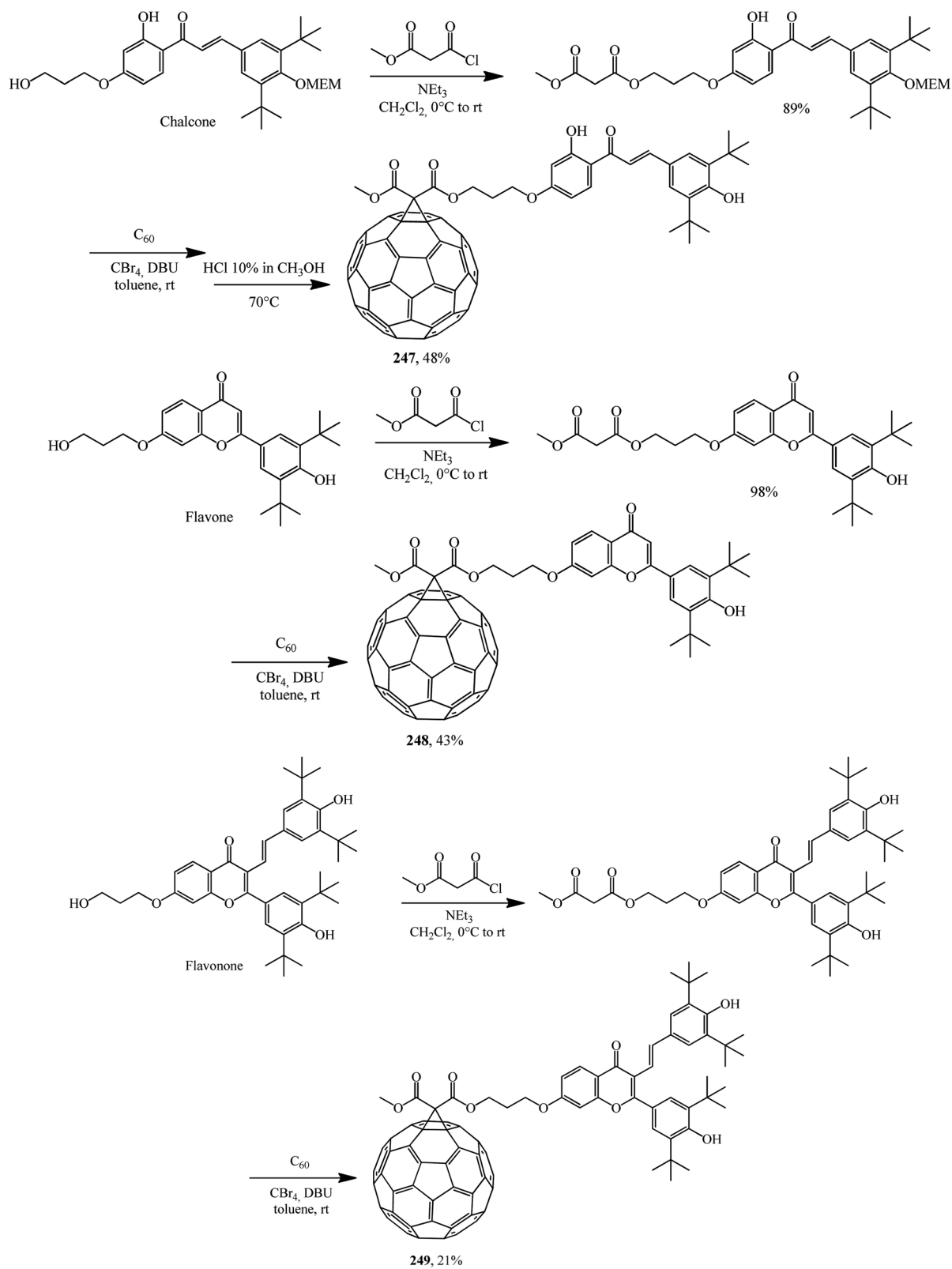
Fluorescence quenching of the coumarin fluorophore in the diads results from efficient dipole–dipole resonance energy transfer from the coumarin moiety to the fullerene moiety.

The malonate derivative of coumarin that was synthesized, which contains a benzothiazole chromophore block as a continuation of the π-conjugated system of the coumarin skeleton, undergoes a Bingel–Hirsch reaction to give fullerene–coumarin diad **254** (Scheme 71).¹³³

The electron interactions between the two components of diad **254** were studied by UV/Vis spectroscopy, fluorescence emission and electrochemical measurements. Studies clearly show the existence of electronic interactions between C₆₀ and modified coumarin in the ground state; efficient electron-transfer quenching of the singlet excited state of the coumarin moiety by the appended fullerene sphere was also observed. As a result of intramolecular transfer of electrons from coumarin to C₆₀, quenching of the characteristic radiation of coumarin in diad **254** occurs, as demonstrated in photoluminescence experiments performed in non-polar and polar solvents.

A considerable number of studies deal with dendrons functionalized with fullerene. This direction is headed by J.-F. Nierengarten. Fullerene-functionalized dendrons, where C₆₀ serves as the branching core or fullerene is located in





Scheme 70

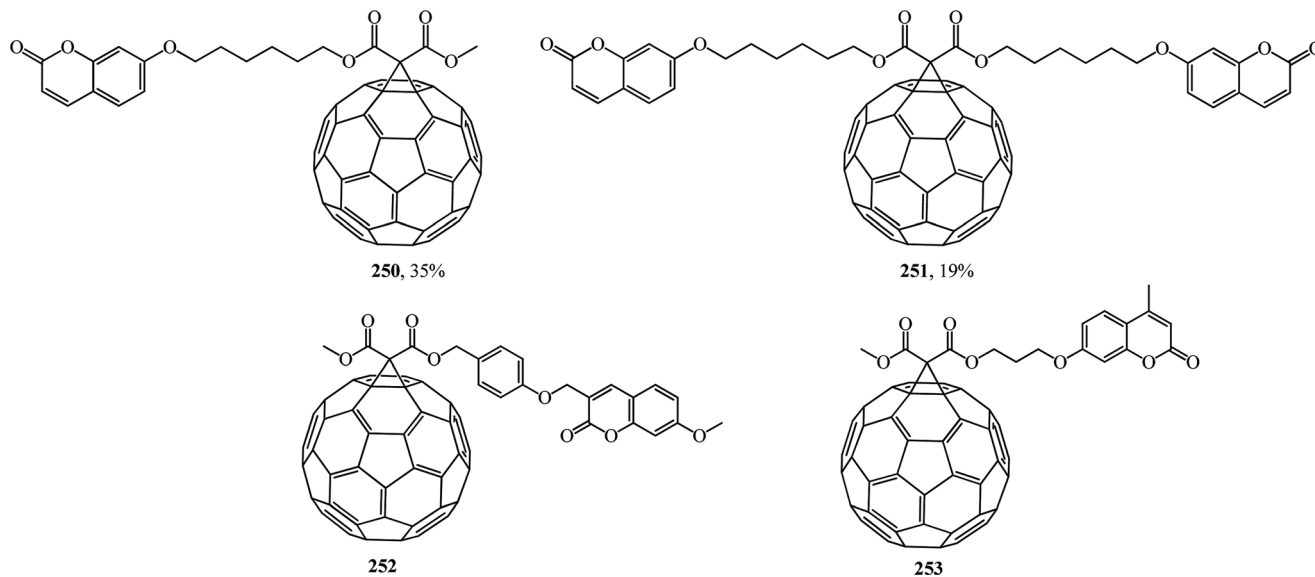
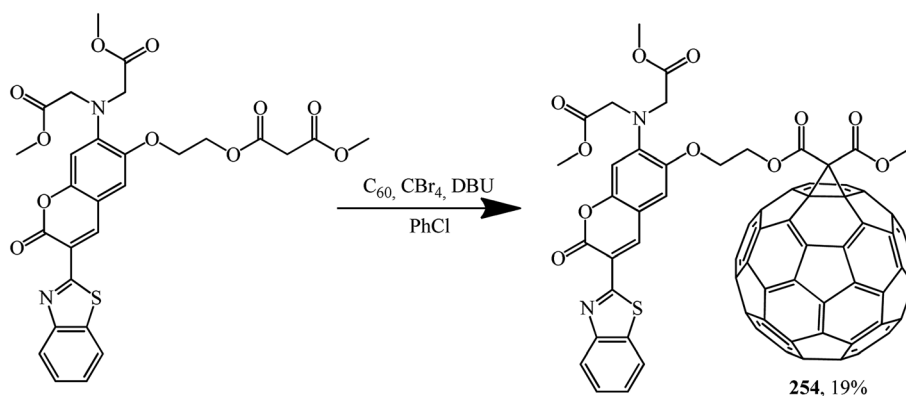


Fig. 14 Fullerene–coumarin diads 250–253.



Scheme 71

each branching unit, became the subject of their studies. 1,3,5-Substituted benzenes are convenient building blocks in the creation of such dendrimeric structures.

Bearing in mind that the solubility of C_{60} in polar solvents, in water in particular, is extremely low, derivatives of methanofullerenes that are free from this drawback are particularly promising as the possible range of product applications expands significantly. For example, a group of scientists¹³⁴ reported a hitherto unknown amphiphilic methanofullerene derivative **256** obtained *via* its intermediate *tert*-butyl adduct **255**. Owing to the high solubility of **256** in polar solvents widely used in sol–gel treatment, it was successfully included into a sol–gel (Scheme 72).

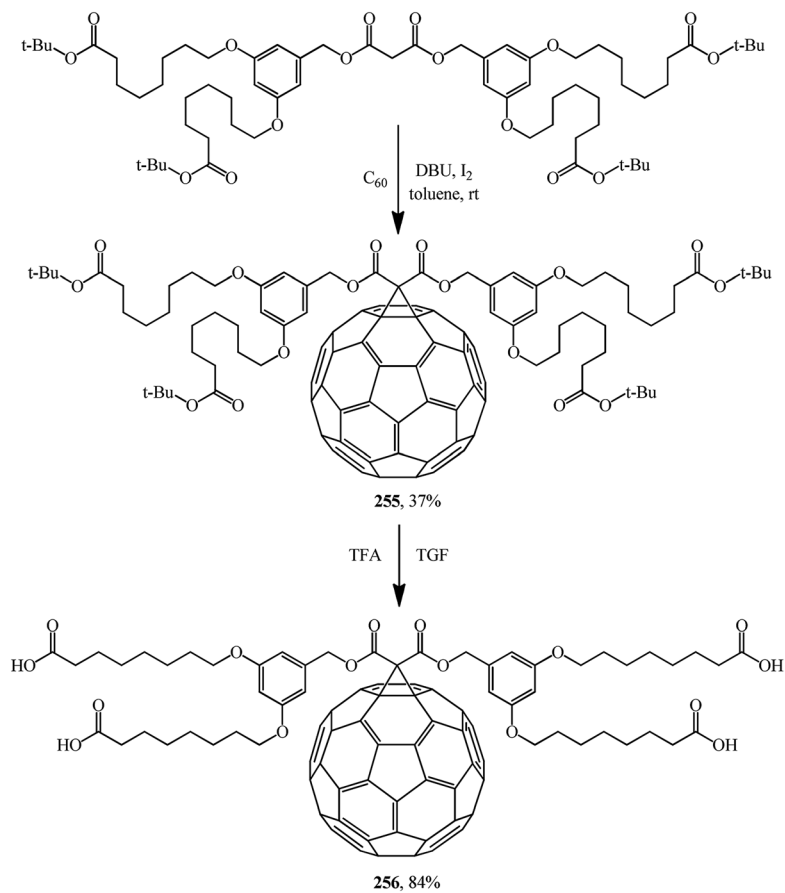
Similarly to the synthesis *via* methanofullerene–dicarboxylic acid mono-ester **258** reported in (Scheme 73),¹³⁵ a related derivative **261** was obtained (Scheme 74)¹³⁶ The authors¹³⁵ also showed that the reaction of compound **258**

with a catalytic amount of DMAP in CH_2Cl_2 at room temperature afforded **259** in a good yield (72%). In this case, the unstable carbanion resulting from the decarboxylation reaction is immediately quenched by the more acidic DMAP- H^+ resulting from the reaction of DMAP with the carboxylic acid function of **258**; therefore, the conversion of **258** into **259** occurs smoothly under these conditions.

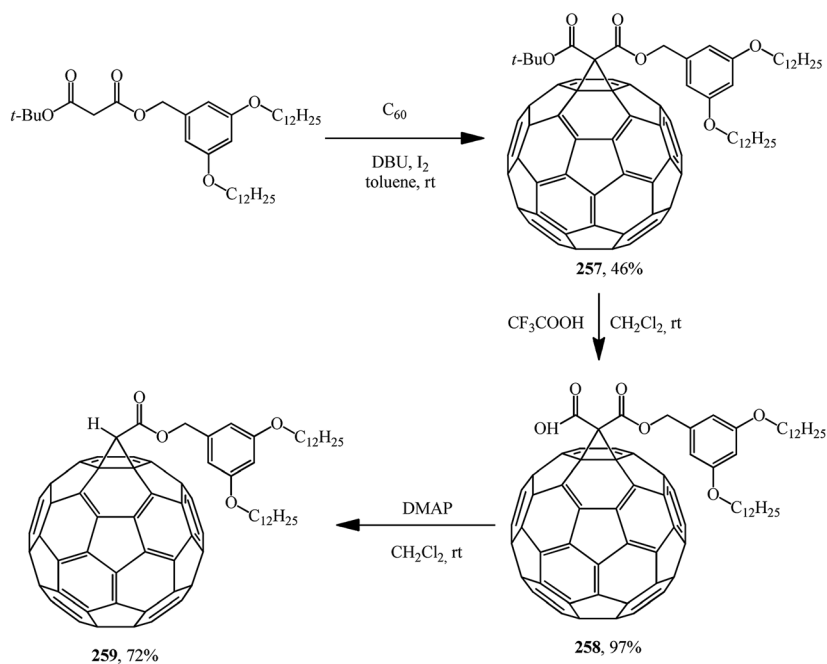
Further, fullerene-functionalized dendrons (**265**, **267**) containing a C_{60} sphere at each branching unit were prepared by a convergent approach using successive DCC-mediated esterification followed by elimination of a *tert*-butyl ester moiety under acidic conditions (Scheme 74).

It was found in a study on the electrochemical properties of methanofullerenes that their cyclic voltammograms differed only a little from those of the C_{60} molecule.^{137–139} It was concluded on this basis that methanofullerenes maintain the unique electrochemical properties of the original



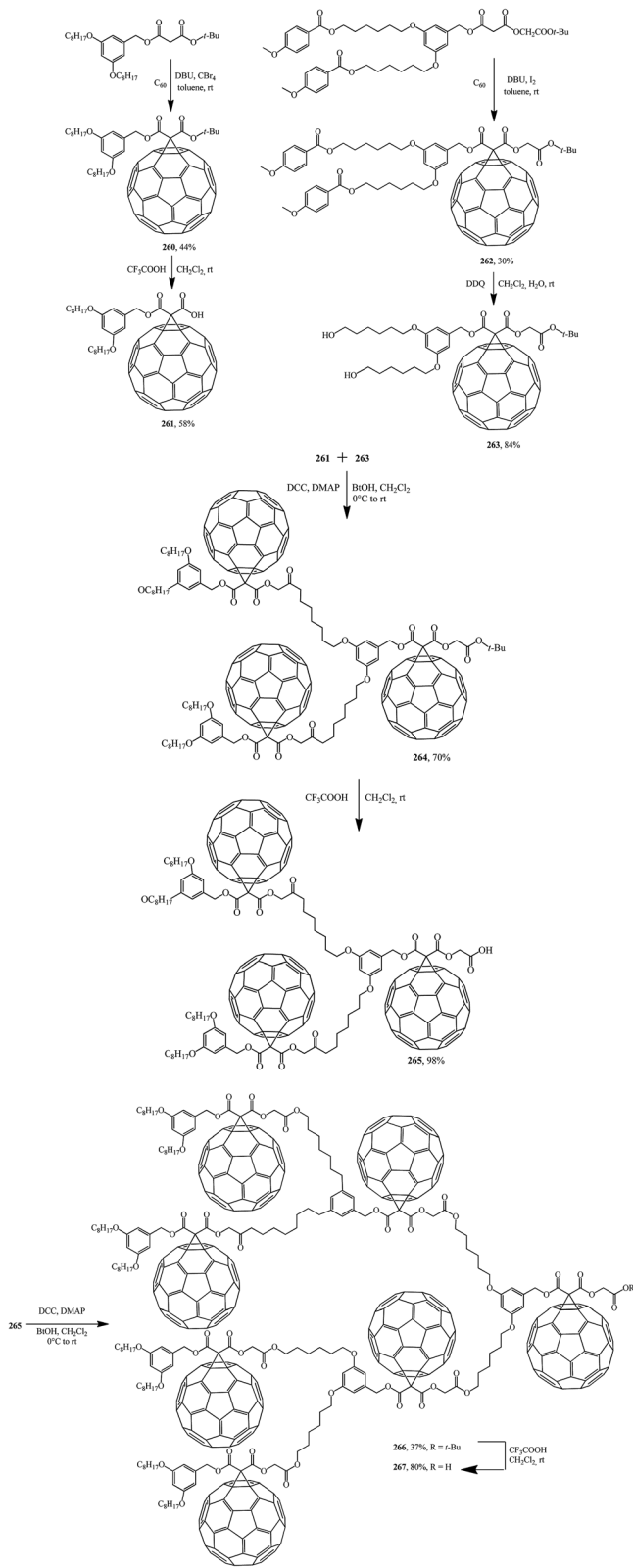


Scheme 72



Scheme 73





C_{60} . This conclusion prompted the creation of covalently bound donor-acceptor diads based on fullerenes by attaching donor fragments to the C_{60} frame. The

significance of this direction is determined by the fact that, as compared to planar acceptors, the fullerene moieties in such diads provide a low value of reorganization energy in photocatalytic processes. As a result of this advantage, covalent-bound fullerene-containing diads became irreplaceable models for studying the key points of photosynthesis and for creating photovoltaic cells and optoelectronic materials. Taking the above into consideration, there is a need for fundamental studies on the development of fullerene-containing dendrimer structures. Studies on the synthesis of dendrimer structures with one fullerene-containing center were carried out under the direction of R. Deschenaux and were reported in ref. 140. Addition reactions of mesomorphic malonate-based dendrimers (up to the fourth generation) to C_{60} gave liquid-crystal symmetrical fullerene derivatives **268–273** (Fig. 15) and non-symmetrical ones **274, 275** (Fig. 16). The supramolecular organization of fullerene-based molecular units was studied by X-ray diffraction. Two structural modes were identified. The supramolecular organization of low generation dendrimers is determined by steric factors. For high generation dendrimers, the mesogenic groups impose a microphase organization.

Structures containing both the C_{60} core and moieties that provide liquid crystal properties should not be ignored. In these cases, not only are existing properties improved but also new ones often appear. The synthesis of methanofullerene **276**, the first C_{60} -functionalised liquid crystal dendrimer possessing a chiral mesophase (Scheme 75),¹⁴¹ can serve as an example.

In continuation of studies on this subject, B. Dardel *et al.*¹⁴² isolated various symmetrical **277** and non-symmetrical **278** fullerene-containing liquid crystal dendrimers (Fig. 17). They were characterized by the method based on the electro-optical Kerr effect, by determination of the permanent dipole moment, which is sensitive to the molecular polar ordering and anisotropy of polarizability, and by hydrodynamic methods in solution.

The effect of covalent-bound fullerene on the polarity, electro-optical, and viscometric properties of fullerene derivatives was identified and analyzed. It was concluded that fullerene produces a change in the original ordering in dendrite molecules, which mainly resulted in a correction of the shape asymmetry of these molecules as a whole.

Using convergent and modular synthetic methodology, symmetrical **279, 280** (Fig. 18), and non-symmetrical **281–283** (Fig. 19) methanofullerodendrimers were obtained.¹⁴³ The rather low yield of the target product (14–28%) is explained by participation of mesomorphic malonate derivatives with substituents that create spatial hindrance in this process. The liquid-crystal properties of malonates and fullerodendrimers were studied by polarized optical microscopy, differential scanning calorimetry, and X-ray diffraction.

The design, synthesis and liquid-crystal properties of hybrid compound **284** built of rod-like OPV and disc-like poly(benzyl ether) units were reported (Fig. 20).¹⁴⁴



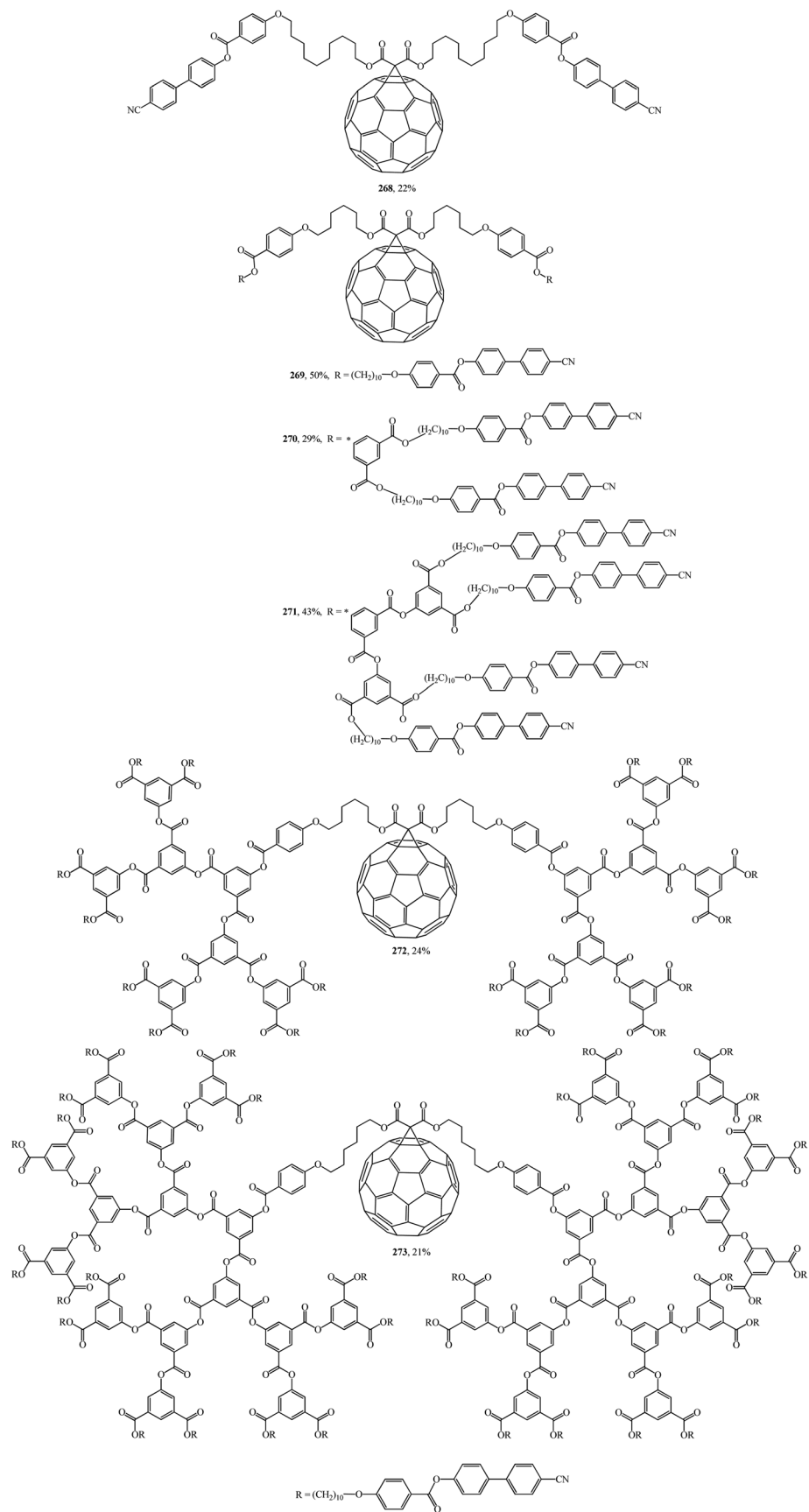


Fig. 15 Symmetrical fullerene-containing mesomorphic dendrimers 268–273.



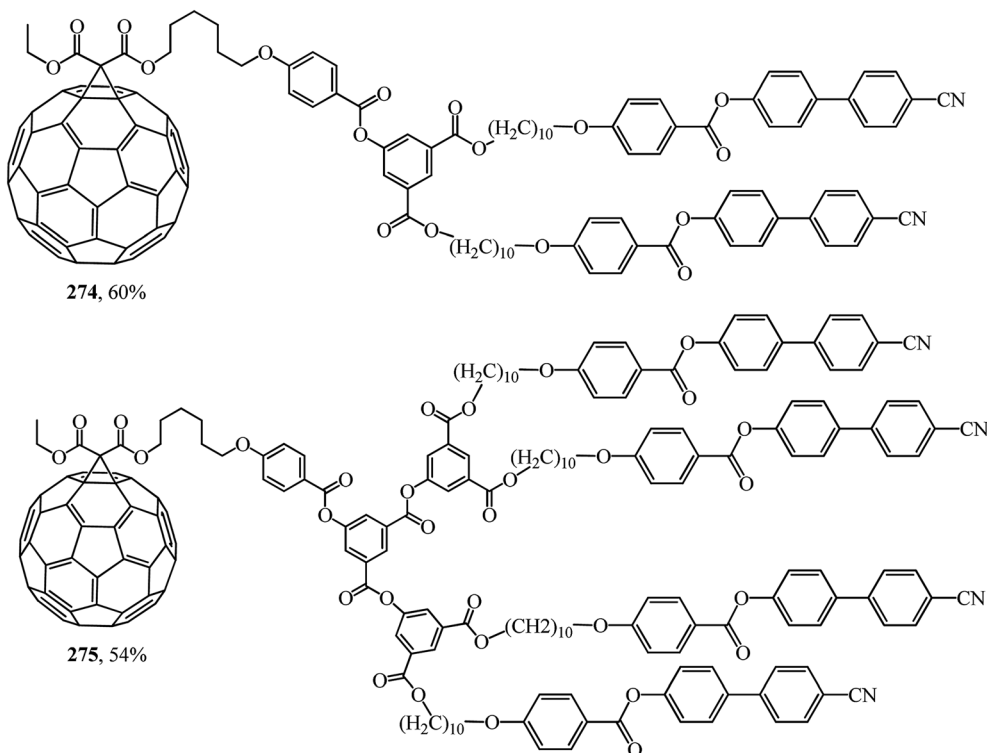


Fig. 16 Non-symmetrical fullerene-containing mesomorphic dendrimers 274 and 275.

An unusual way to obtain bis[60]fullerodendrimers was chosen by Deschenaux *et al.*¹⁴⁵ The synthetic modular approach developed in that study allowed new substances to be isolated by assembling type I methanofullerenes **285**, **286** containing a terminal olefin, and type II methanofullerenes **287**, **288** containing an α,β -unsaturated carbonyl olefin (Fig. 21). Both mono[60]fullerodendrimers and their fullerene-free analogues were synthesized in this study.

First- and second-generation poly(aryl ester) dendrons carrying cyanobiphenyl mesogens were used as liquid-crystalline promoters. First-generation mono- **289**, **290** and bis-[60]fullerodendrimers **291** were obtained from mono-[60]fullerene derivatives **285** and **287** (Scheme 77) under olefin cross metathesis reaction conditions aided by the very efficient second-generation Grubbs catalyst according to general Scheme 76.

The second generation of bis-[60]fullerodendrimer **292** based on mono-[60]fullerenes **286**, **288** containing a terminal double bond was also implemented by the proven technique and is shown in Scheme 78.

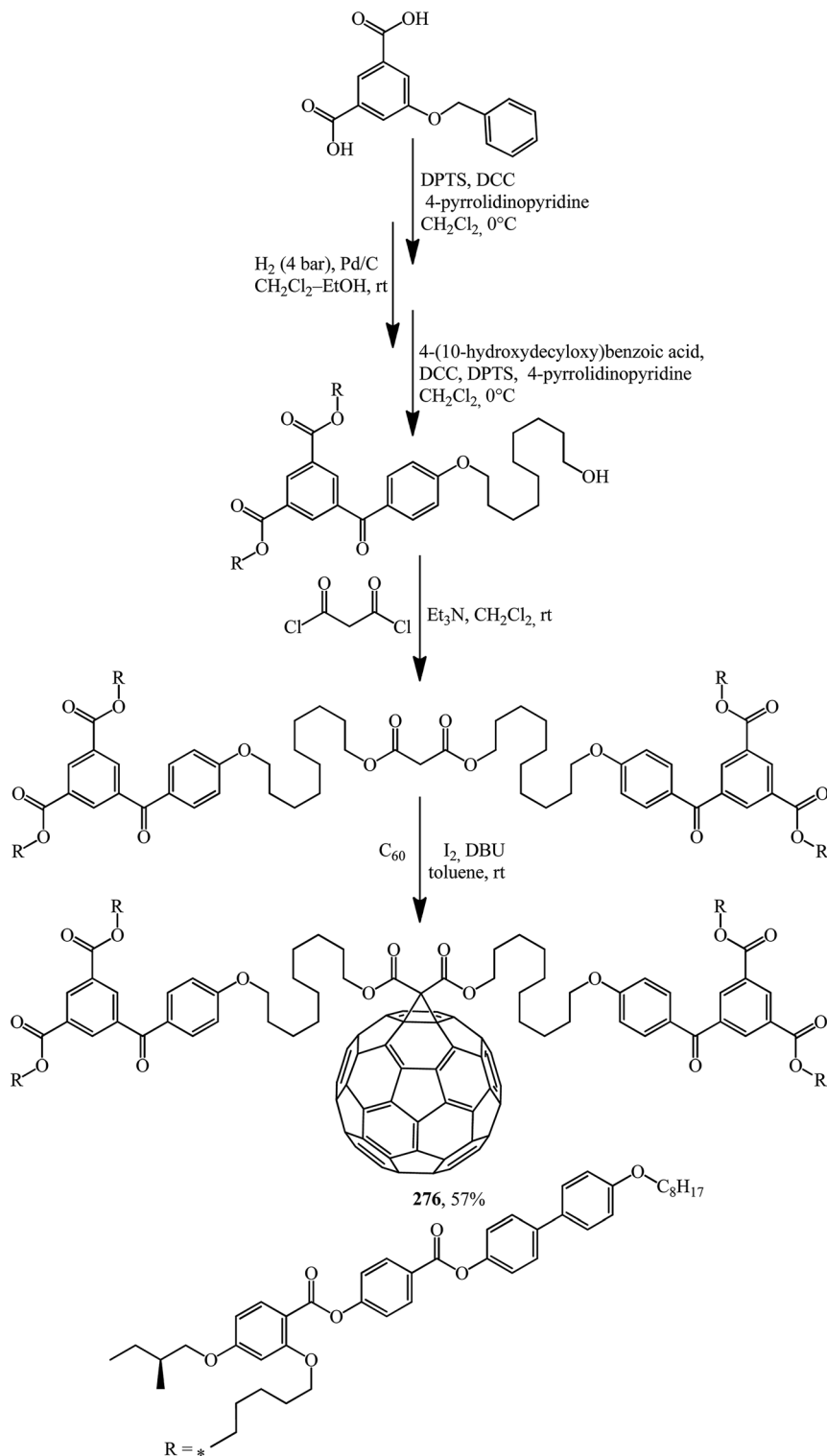
The liquid-crystal properties were studied by polarized optical microscopy, differential scanning calorimetry, and small-angle X-ray scattering. Nematic, smectic, and multi-segregated lamellar phases were observed in agreement with the nature and structure of dendrimers.¹⁴⁵ Owing to its versatility and tolerance towards many functional groups, olefin cross-metathesis proved to be the reaction of choice

for the elaboration of molecular materials with complex architectures.

Excellent candidates for organizing fullerenes into supra-molecular ordered structures were reported in ref. 146 Moreover, a new class of nondendritic hybrid C_{60} -containing bended molecules corresponds to liquid crystals. In this case, the goal is achieved using two approaches: in the first one, a fullerene is incorporated by the Bingel–Hirsch method into the center of a bended malonate to give **293** (Scheme 79). In the second one, two alcohol groups are grafted onto a fullerene-containing malonate with simplified structure **294** in the presence of 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS)/DCC and a similar product **295** is isolated (Scheme 80).

A fruitful idea exists to use malonates with a combination of various functions in the Bingel–Hirsch process, which is a path for generating target products with planned characteristics. In fact, grafting of a ferrocene-containing liquid-crystal malonate derivative (1-[10-{4-[(cholest-5-en-3 β -yloxy) carbonyl]phenoxy}-decyloxy carbonyl]-1'-[4-(hydroxyphenoxy) carbonyl]ferrocene) to C_{60} led to a mixed fullerene–ferrocene adduct **296** that was found to contain smectic phase A (Scheme 81).¹⁴⁷ Cholesterol can be used as a liquid-crystal promoter. X-ray diffraction experiments and volumetric measurements indicated that **296** is organized in double layered structures. The corresponding supramolecular organization within the mesomorphic lamellar phase is characterized by a microsegregation of the different units (ferrocene, fullerene, and cholesterol) in distinct sublayers.





Scheme 75

In such a smectic A phase, C_{60} imposes the arrangement of the other molecular moieties.

Previously we noted the extremely low solubility of C_{60} and the high need for water-soluble compounds based on it

to study its biological properties. It appears that one of the approaches to solve this problem may involve synthesizing dendrimers with hydrophilic substituents at the fullerene frame.



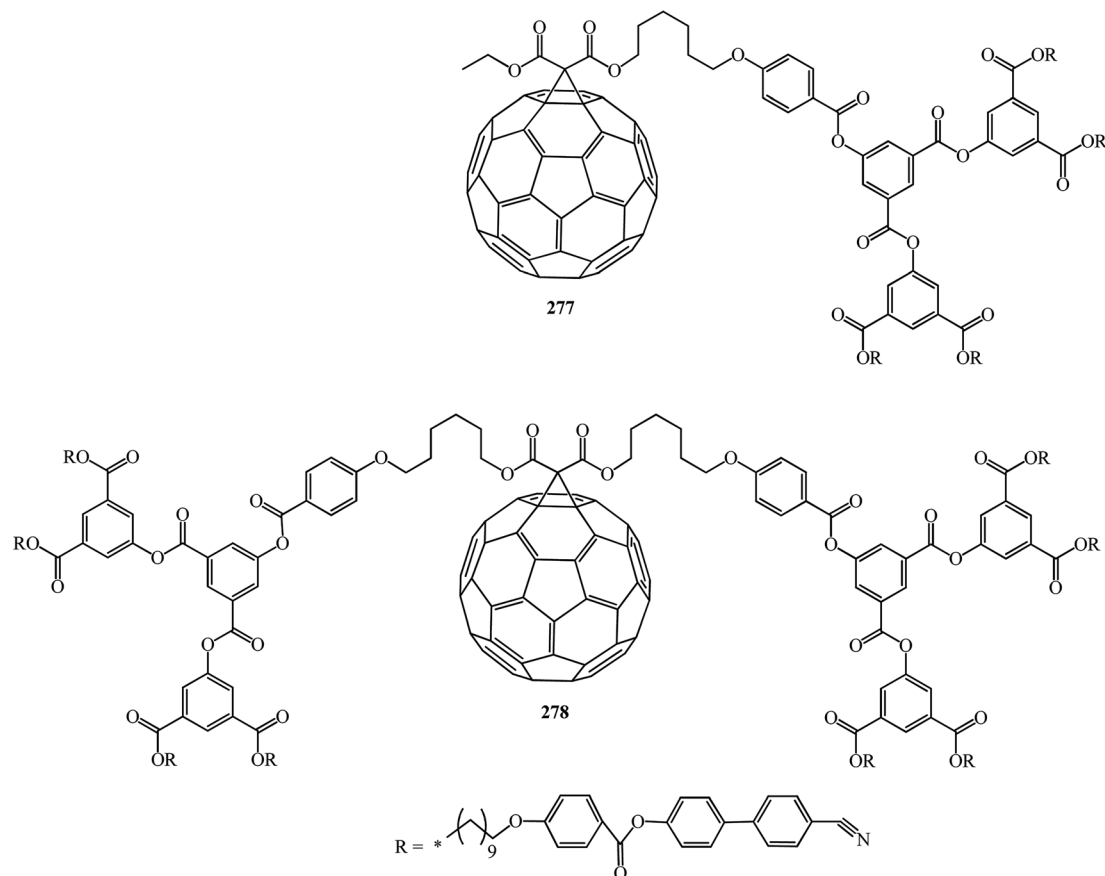


Fig. 17 Fullerene-containing liquid crystalline dendrimers 277 and 278.

The authors¹⁴⁸ describe an ingenious enantioselective synthesis of a large series of optically active dendri-adducts of fullerenes, whose chirality is solely due to their architecture.

2-(*tert*-Butoxy)-2-oxoethyl ethyl propanedioate was used as the starting malonate. It was converted to adduct **297** under Bingel–Hirsch reaction conditions. Treatment of the latter with $\text{TsOH} \times \text{H}_2\text{O}$ resulted in 2-(*tert*-butoxy)-2-oxoethyl ethyl-1,2-methano[60]fullerene-61,61-dicarboxylate **298** (Scheme 82).³⁰

Methanofullerene **298** thus obtained was used as the base adduct in the coupling of first-, second- and third-generation dendrons, which led to the expected dendrite fullerene derivatives of the first **299**, second **300** and third **301** generations, respectively, that are characterized by fairly good solubility in water (Scheme 83).¹⁴⁸

Various drugs are currently actively developed on the basis of methanofullerenes. In particular, there is much hope to find an anti-AIDS drug. HIV-1 protease, the protein responsible for virus penetration into blood cells, has a spherical cavity with a diameter of 10 Å whose shape remains unchanged upon all mutations. This size almost coincides with the diameter of the C_{60} molecule. Methanofullerenes were found to inhibit the HIV-1 protease. Apparently taking this information into account, the team

headed by Professor Hirsch performed the nucleophilic cyclopropanation of C_{60} with a second-generation bis(polyamide)-malonate dendrimer in the presence of CBr_4 and DBU to give methanofullerene **302** (Scheme 84).¹⁴⁹ Removal of the terminal *tert*-butyl groups provides dendro [60]fullerene **303** with 18 carboxylic groups at the periphery. Methanofullerene **303** showed antiviral properties in biological tests. This is explained by the fact that the fullerene frame is close in size to the active center of the HIV-1 protease enzyme. As a result, some methanofullerenes can penetrate into the hydrophobic cavity of the enzyme and inhibit it.

The same team performed a synthesis of non-symmetrical fullerene-containing dendrite diads terminated by a metallo-tetraphenylporphyrin ($\text{M} = \text{ZnII}$, CoII , CoIII) on one end and by Newkome-type amide dendrons on the other end.¹⁵⁰ Cyclopropanation of C_{60} with second-generation dendrons zinc(II)-porphyrin and cobalt(II/III)-porphyrin gives fullerene monoadducts **304** and **305** that represent a new type of dendritic diads (Scheme 85).

The formation of Co in oxidation states +II and +III was achieved by treatment with $\text{Na}_2\text{S}_2\text{O}_4$ or with O_2 in the presence of CN^- and SCN^- ions, respectively, to give



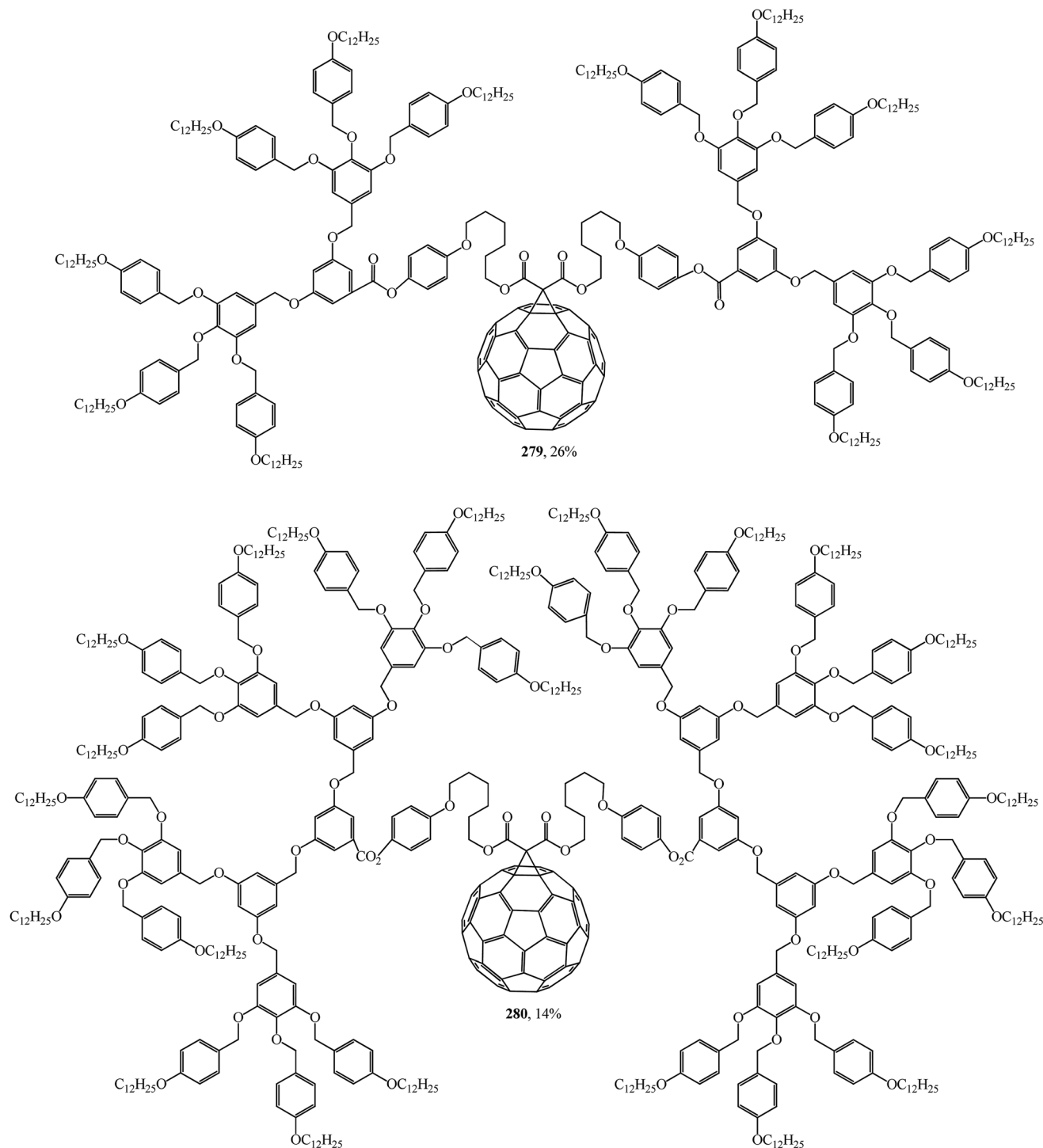


Fig. 18 Symmetrical fullerene-containing liquid crystal dendrimers 279 and 280.

a paramagnetic complex cobalt(II)-porphyrin-dendrimer-fullerene **306** and diamagnetic axially coordinated complexes cobalt(III)-porphyrin-dendrimer-fullerene **307** and **308**. Deprotection of the *tert*-butyl groups terminating the dendritic branch of diads **304** and **305** generates the corresponding water-soluble micellar systems zinc(II)-

porphyrin-[60]fullerene **309** and cobalt(II/III)-porphyrin-[60]fullerene **310** in quantitative yields. Due to their amphiphilic character, aggregates are formed in water.

The idea to create polyamide malonic dendrofullerenes, which correlates with the studies of the Hirsch team, is provided in ref. 151 A synthesis of water-soluble fullerene



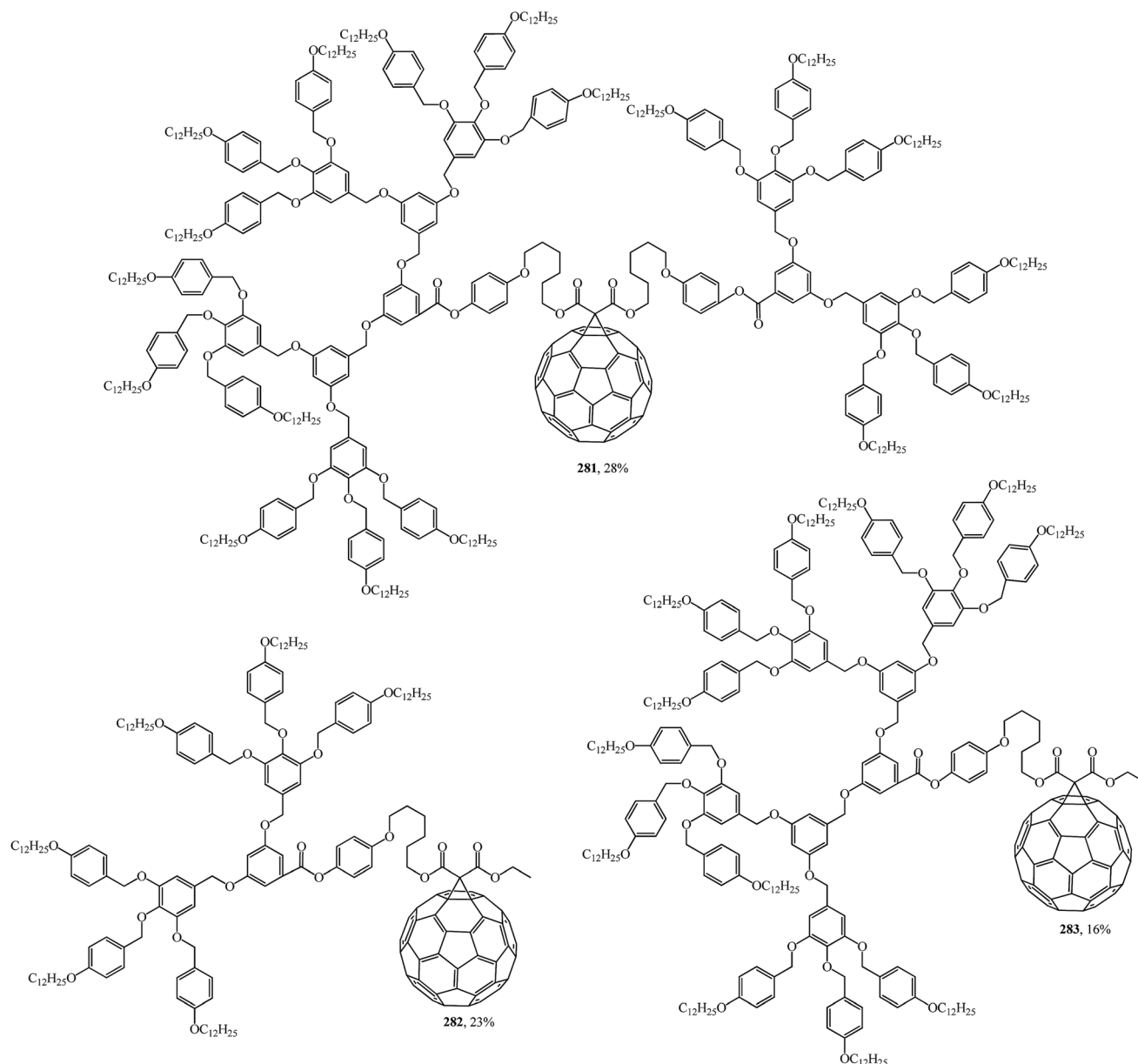


Fig. 19 Non-symmetrical fullerene-containing liquid crystal dendrimers 281–283.

derivatives bearing a poly(amidoamine) dendron with peripheral carboxylic groups on one side and an alkyne moiety on the other side was also reported.

Fullerodendrimers with *tert*-butyl ester groups at the periphery (311, 313) were first prepared by treating C_{60} with unsymmetrical malonates under Bingel–Hirsch reaction conditions (Schemes 86 and 87). The *tert*-butyl esters were then cleaved using formic acid to give the corresponding first- and second-generation carboxyfullerene derivatives (312, 314) (Schemes 86 and 87). Second-generation fullerodendrimer 314 with eight carboxylic groups at the periphery is easily soluble in water, whereas first-generation compound 312 with its four carboxylic groups can only be

solubilized in a basic medium. These compounds self-assemble into micelle-like aggregates probably composed of a C_{60} cluster surrounded by a poly(amidoamine) shell.

The alkyne moiety was then used as a chemical anchor to immobilize in water fullerodendrimers on the surface of azido-coated polymer nanoparticles by means of the copper(I)-catalyzed azide and alkyne cycloaddition reaction. At room temperature, this reaction competes with azido cycloaddition onto the fullerene core. Given the high density of anchoring azide groups on the nanoparticle surface and the size of the fullerodendrimers, the unreacted azides are still reactive and are available for subsequent



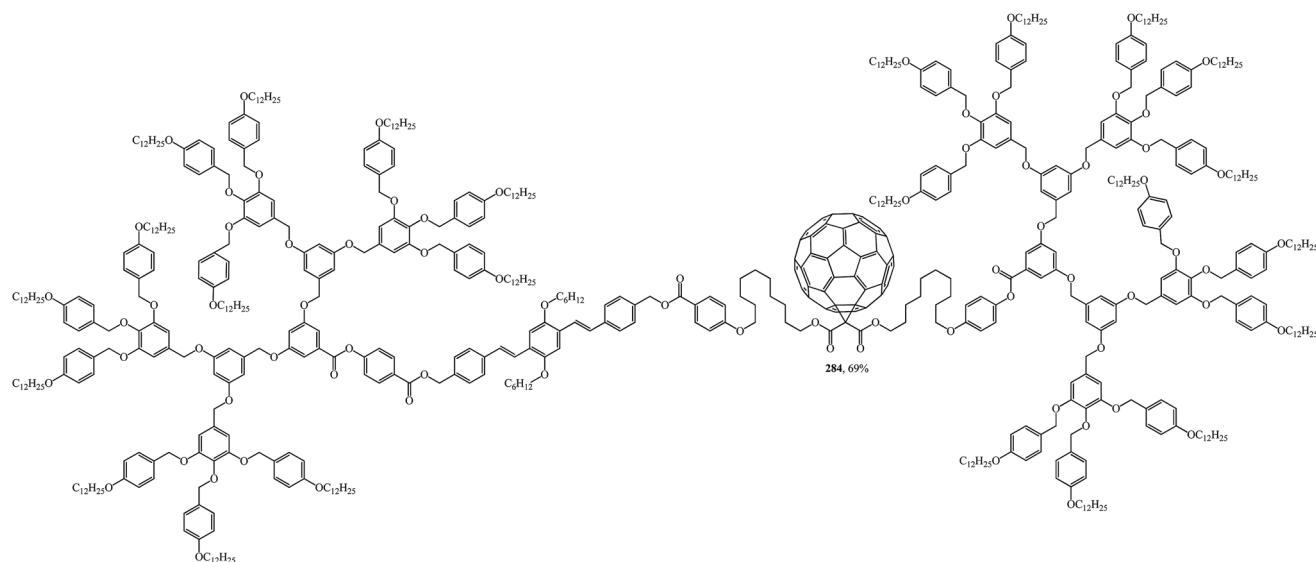


Fig. 20 Fullerene-containing liquid crystal dendrimer 284.

functional arrangements. This strategy paves the way for the design of functional fullerene-rich nanomaterials that could be of interest in the field of materials science.

A wide range of electroactive donor-acceptor systems based on C_{60} , in particular, for light-induced charge separation in artificial photosynthetic systems and photovoltaic devices, was suggested by authors.¹⁵² They synthesized

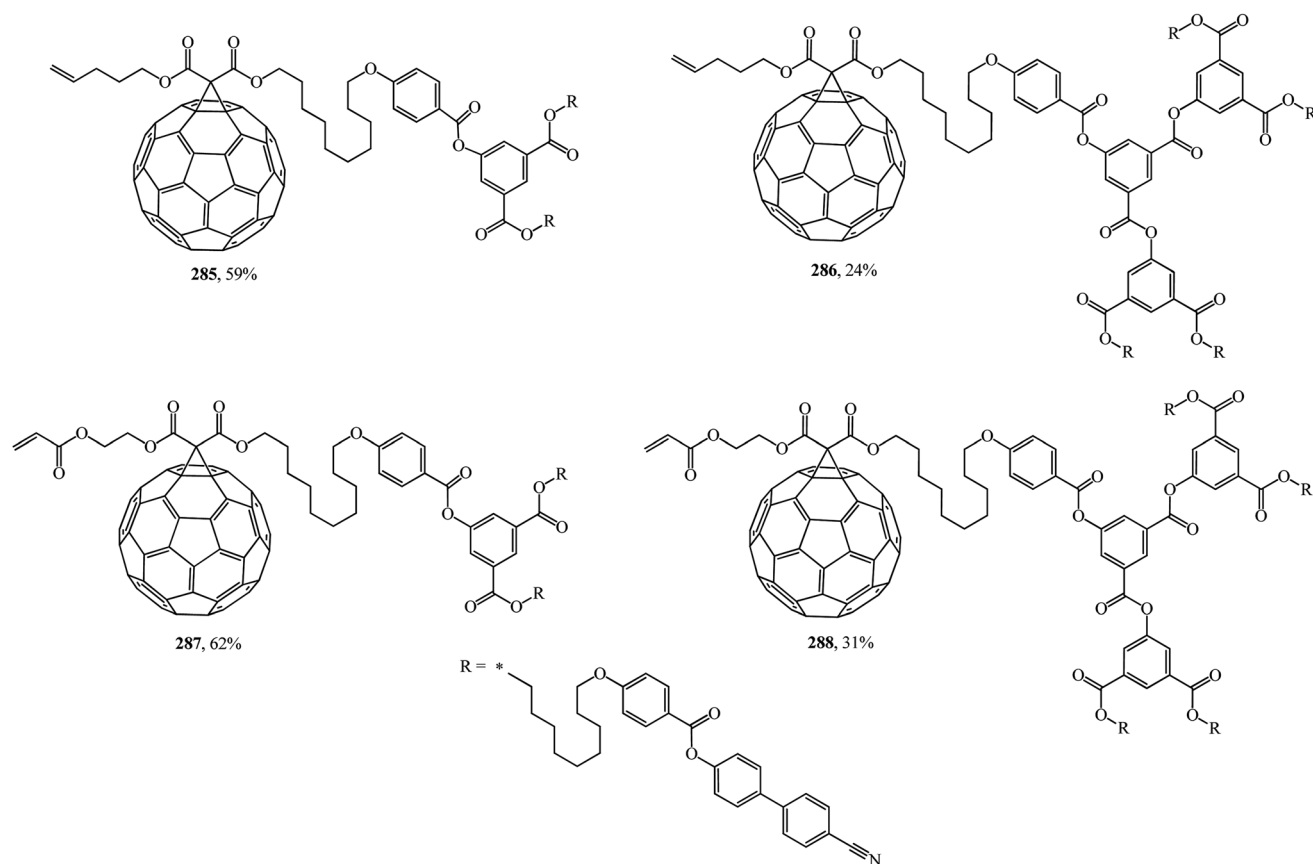
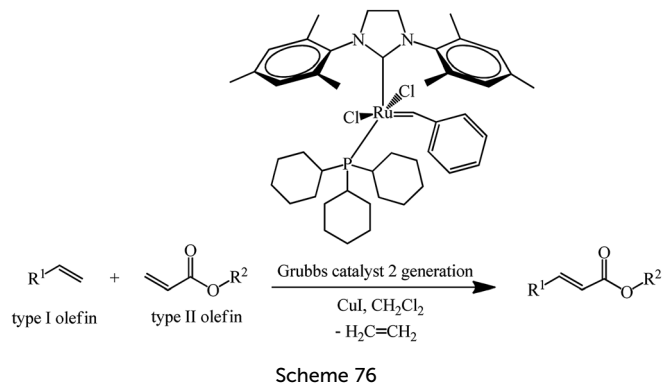


Fig. 21 Fullerene-containing dendrimers 285–288.





novel C_{60}/π -extended tetrathiafulvalene diads **315–320** (Fig. 22) and triads **321–327** (Fig. 23).

The oxidative properties of the new compounds were determined by cyclic voltammetry at room temperature. Semi-empirical (PM3) theoretical calculations were carried out to better understand the geometric and electron properties of the systems obtained. Additionally, photophysical measurements (fluorescence and transient absorption spectra) were carried out.

In ref. 153, the synthetic methodology, liquid crystal properties, supramolecular organization and electrochemical behavior of mesomorphic C_{60} -tetrathiafulvalene derivative **328**, which is the first liquid crystal representative of this family, are reported (Fig. 24).

The following standalone studies were performed. Publication¹⁵⁴ describes a synthesis of methanofullerene **329**, which on treatment with pyridinium chlorochromate (PCC) gives compound **330** (fullerene grafting to a related aldehyde failed, probably due to side reactions with the carbonyl function under basic conditions), which reacts with *S*-methyl dithiocarbamate to give **331** (Scheme 88).

Fullerene-based Schiff bases are prepared and used to stabilise the $[ReO]^{3+}$ core. To this end, the authors conducted ligand exchange reactions of $[NBu_4][ReOCl_4]$ with bidentate SN Schiff bases to produce mixed-ligand C_{60}/Re complexes for radiopharmaceutical purposes.

Based on 8-(acetylthio)octyl ethyl malonate, 61-ethyloxycarbonyl-61-[8-(acetylthio)octyl-1-oxycarbonyl]-1,2-methano[60]fullerene **332** was synthesized. The latter was converted to a hexakis adduct by adding a malonate containing the 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) moiety (Scheme 89). The catalytic composite C_{60} -TEMPO₁₀@Au allowed for the oxidation of various primary and secondary alcohols under mild conditions to the corresponding aldehyde and ketone analogues with efficiencies as high as 79–98%, thus giving values typical of homogeneous catalysis, while retaining at the same time all the advantages of heterogeneous catalysis, *e.g.*, easy separation by filtration from the reaction mixture.¹⁵⁵

Using asymmetric phosphorus-containing malonates in fullerene cyclopropanation, two series of new phosphine

derivatives based on C_{60} protected by borane **334**, **335** were synthesized and characterized (Scheme 90).¹⁵⁶

Deprotection of the phosphine–borane complexes was performed using tertiary amines such as DABCO in dry toluene at 50–60 °C under argon atmosphere (Scheme 91). Preliminary complexation experiments with rhodium were performed using chloro(1,5-cyclooctadiene)rhodium(i) dimer, whereas complexation with rhenium was carried out using bis(perthiobenzoato)(dithiobenzoato)rhenium(III) **336**.

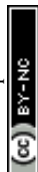
The presence of fullerene covalent-bound to the polymer chain results in a completely new type of macromolecules whose repeating structure contains carbon nanoparticles with sizes comparable to the correlation distances in high-molecular compounds. As a result, fullerene-containing polymers acquire unique physical properties that are significantly different from the polymers containing no C_{60} .^{157–159} Incorporation of fullerene into polymer chains in the role of photo- and electroactive blocks (a subject of intense competing research in recent years) should afford new materials with outstanding structural, electrochemical and photophysical properties. It is the high content of C_{60} in macromolecules that explains the appearance of extraordinary physical properties in such polymers, which can be achieved upon conversion of a fullerene-containing low-molecular compound into a high-molecular one. It should be noted that, despite the existing variety of methods for fullerene incorporation into polymer chains, the most effective way to obtain macromolecules with the highest possible C_{60} content involves the polymerization of a fullerene-containing monomer.

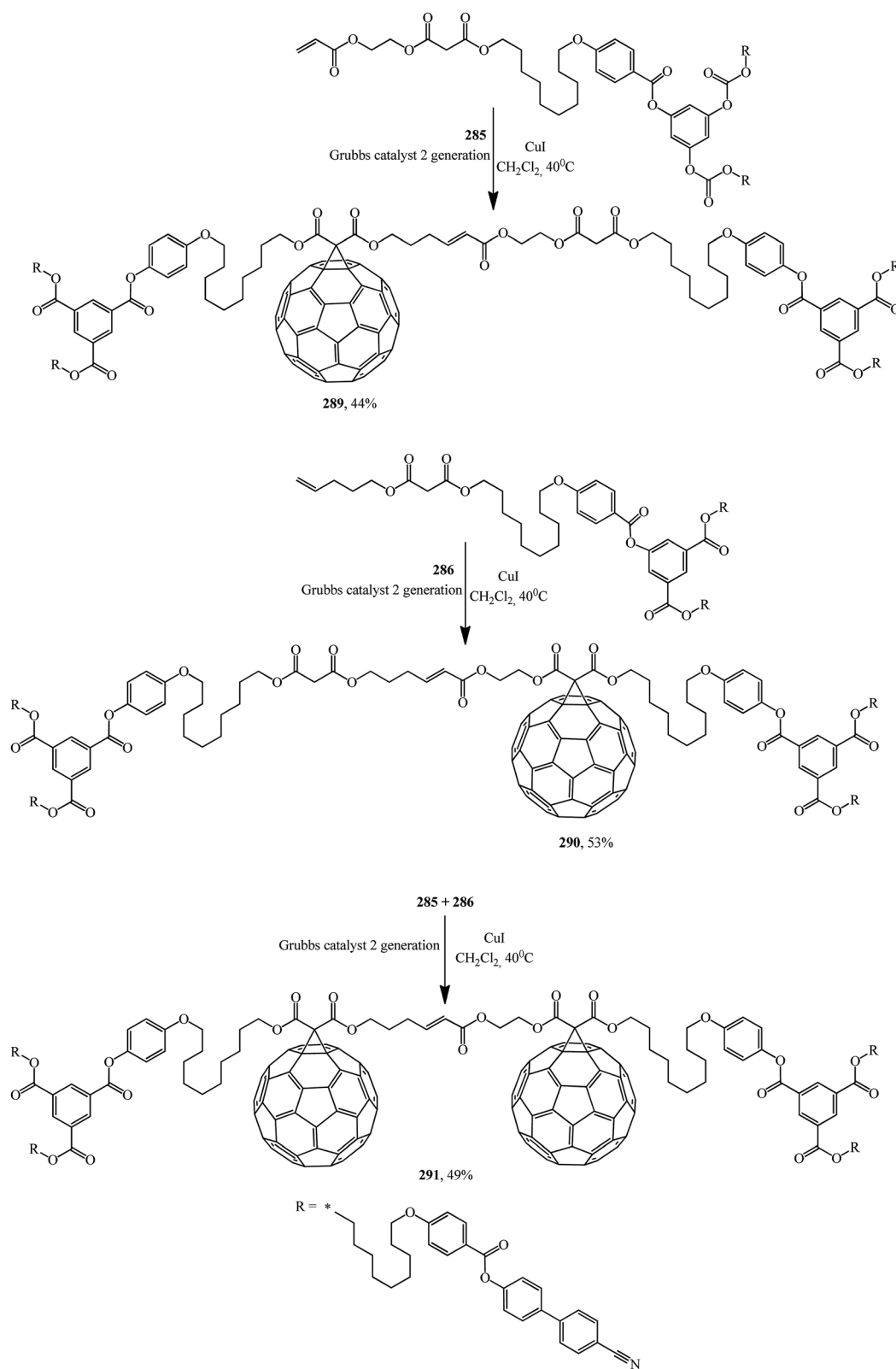
Scientific literature presents examples of synthesizing low-molecular functionalized C_{60} methano derivatives. As a rule, these are compounds containing functional groups intended for involvement in polymer analogous reactions and polycondensation processes.

A prepolymer pre-synthesized from polyethylene glycol methyl ether and malonyl chloride was treated with C_{60} under Bingel–Hirsch conditions in order to obtain fullerene-containing high-molecular compound **337** (Scheme 92).¹⁶⁰

The low yield of the product can be easily explained by steric hindrance. As a rule, this kind of polymer analogous reactions produce polymers containing various units, where not each repeating unit of the macromolecule contains the C_{60} “framing group”. As a result, the regular structure of the polymer is lost and hence the performance characteristics of the target product are affected.

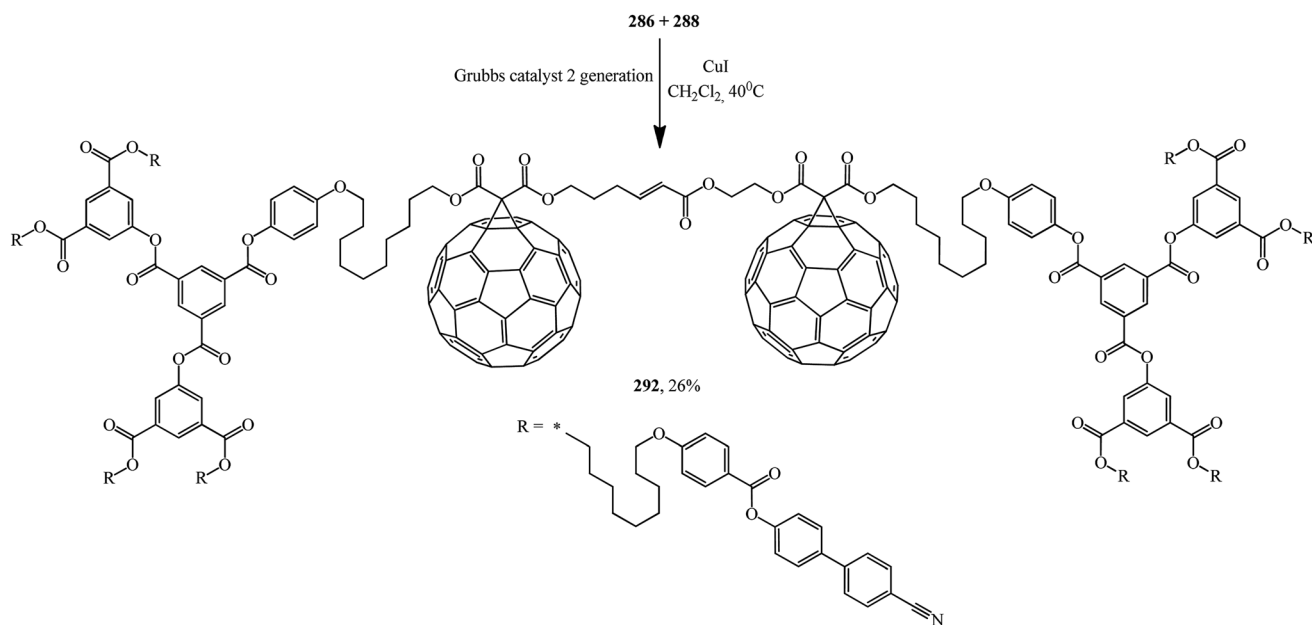
Some samples from the series of fullerenes covalent-functionalized with polyethylene glycol were included as additives to $CH_3NH_3PbI_3$ ($\sim 10^{-5}$ mol mol⁻¹) to the most common organic–inorganic perovskite used in perovskite solar cells. A photovoltaic study performed using these materials shows the following beneficial effects: reduced hysteresis and high moisture resistance, owing to which solar cells retain up to 97% of their initial power conversion efficiency. The observed effect is most likely due to the hygroscopicity of polyethylene glycol macromolecular



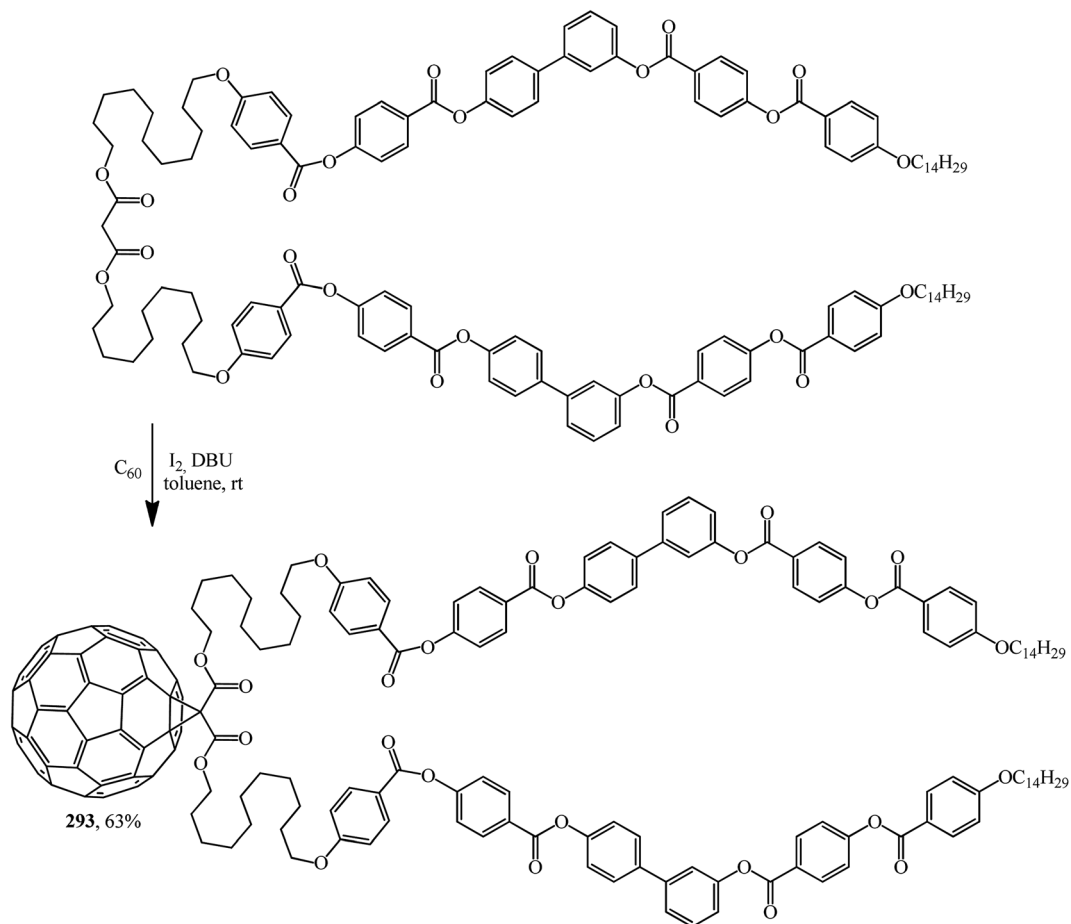


Scheme 77



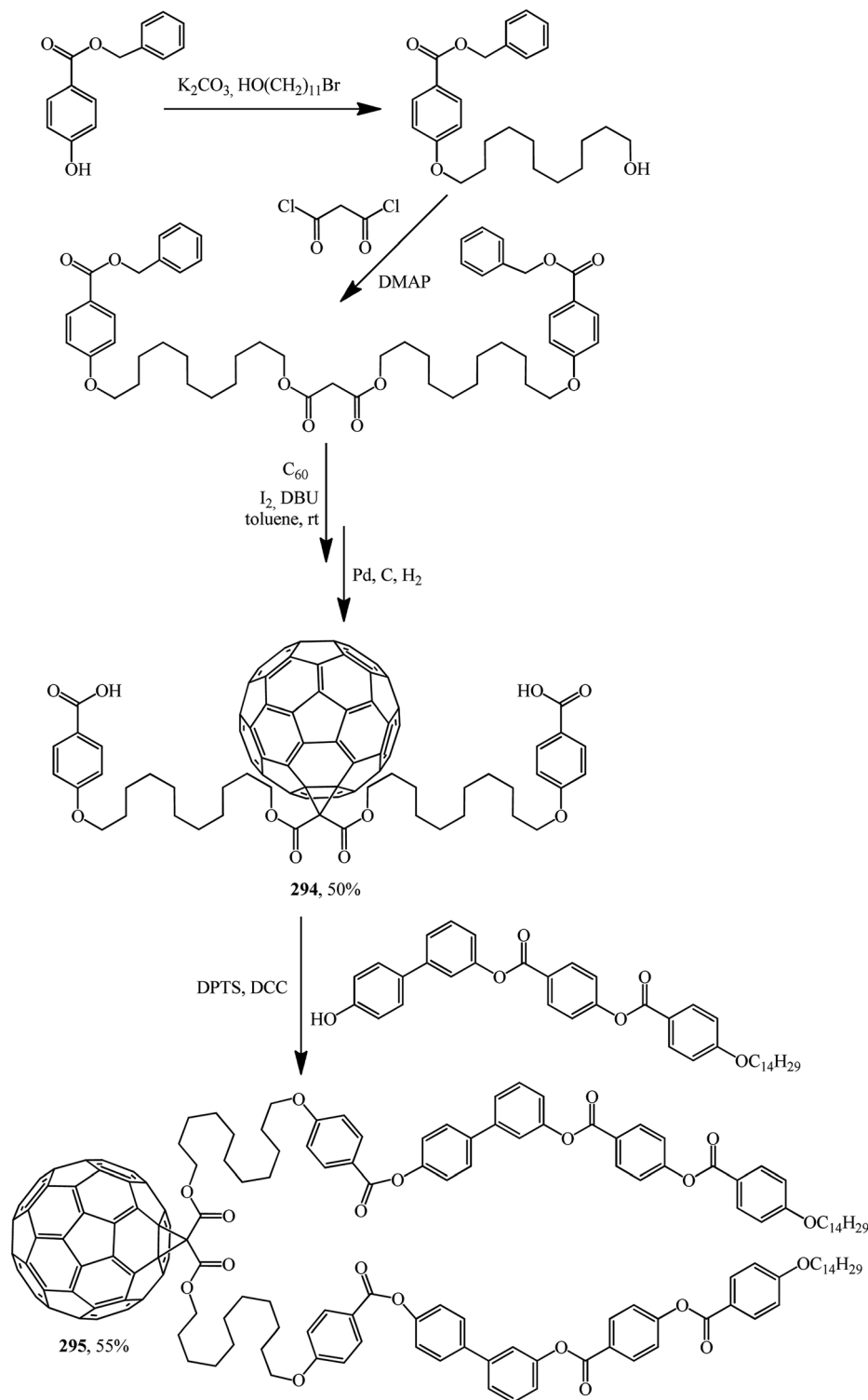


Scheme 78



Scheme 79





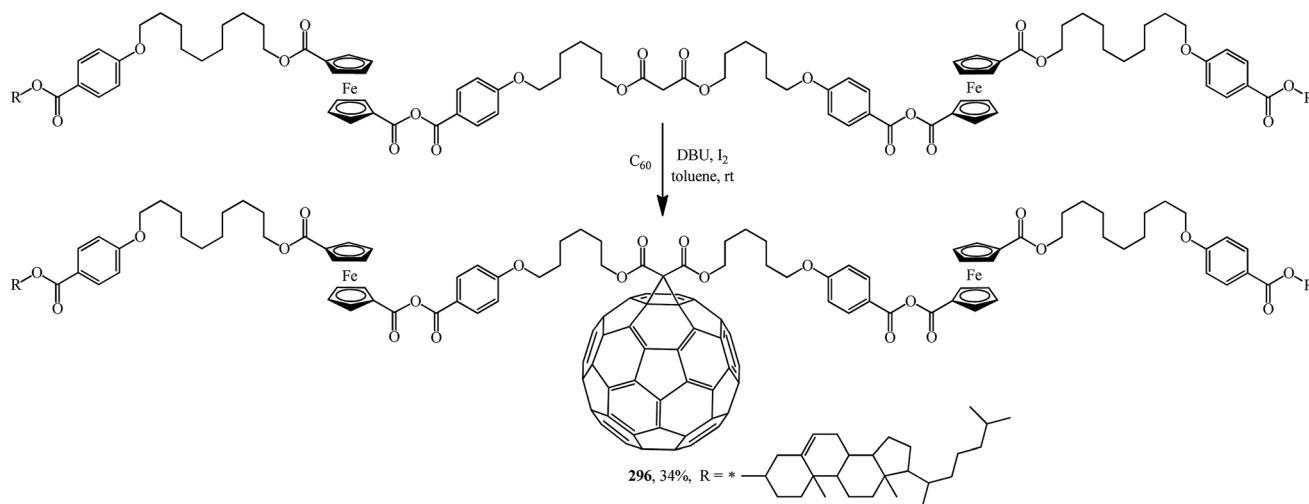
Scheme 80

chains, which helps water to be retained, thereby preventing perovskite degradation.

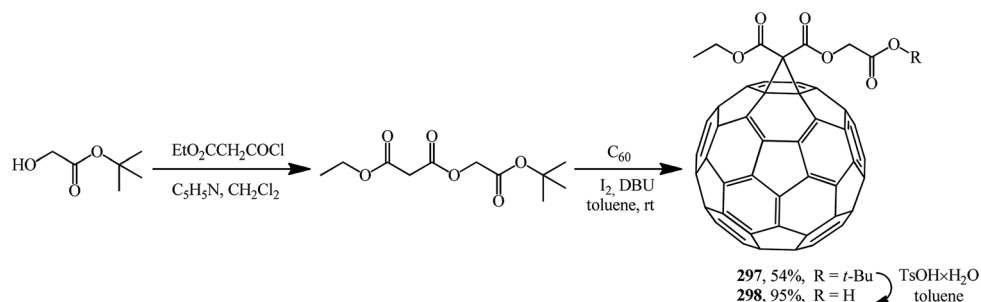
Yet another example of polymer analogous cycloaddition is reported in ref. 83. It is suggested to bind the fullerene frame located in the side chain to the main chain through

a 1,2,3-triazole derivative. Preliminarily, radical polymerization is used to obtain a block copolymer of styrene and propargyloxy styrene with a malonate group in the side chain, namely, 3-azidopropyl octadecylmalonate. The latter is then used in cycloaddition to C_{60} (Bingel–Hirsch) to give





Scheme 81



Scheme 82

fullerene-containing functionalized copolymer **338** with good solubility in common organic solvents and a number-average molecular mass of $71\,000\text{ g mol}^{-1}$ (Scheme 93).

A multistep synthetic procedure for preparing novel C_{60} -anchored two-armed poly(*tert*-butyl acrylate) was developed. For this purpose, two-armed poly(*tert*-butyl acrylate) bearing a malonate ester core with well-controlled molecular weight (number-average molecular mass: $14\,700\text{ g mol}^{-1}$) was synthesized by atom transfer radical polymerization. An effective Bingel reaction between C_{60} and the well-defined polymer was then carried out to yield C_{60} -anchored polymer **339** (Scheme 94). A related dibromo-functionalized methanofullerene **340** was also synthesized.¹⁶¹

Scientific literature contains very interesting examples of substrates that can be used as cyclopropanating agents as alternatives to malonic acid derivatives. For example, information is available that spiromethanofullerenes containing a reactive free formyl **341** and diacetyl **342** groups were synthesized by the Bingel–Hirsch process (Scheme 95).¹⁶²

Meldrum's acid derivatives are also original cyclopropanating agents. Under Bingel–Hirsch reaction conditions, they gave a number of methano derivatives **343–353** in moderate yields (Scheme 96).¹⁶³

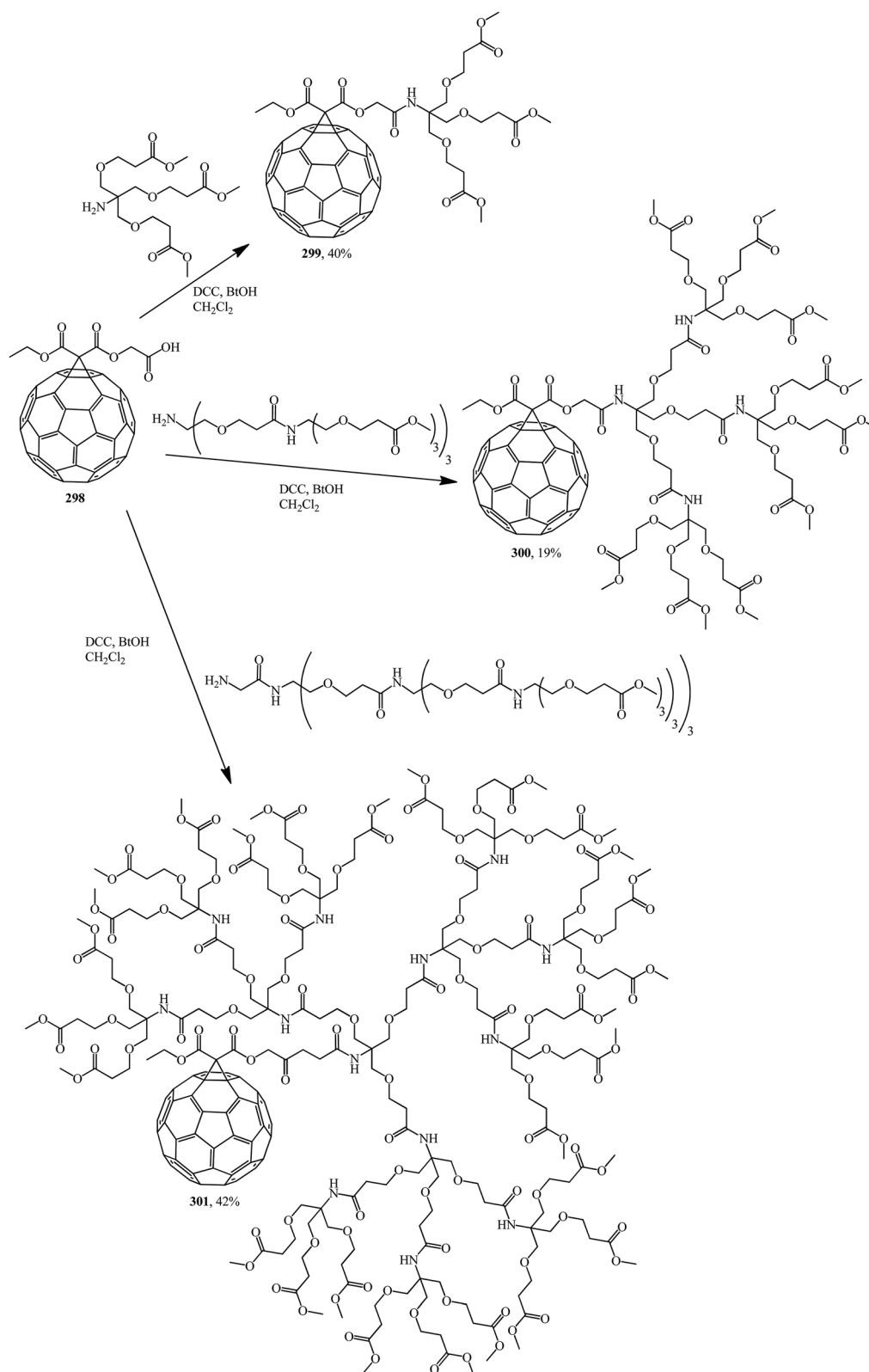
According to the authors, the carbene intermediate mechanism is most acceptable for this reaction (Scheme 97).

Meldrum's acid **O** reacts with I_2 under basic reaction conditions in the presence of DBU to give α -iodine-substituted product **P**, which eliminated HI to give carbene intermediate **Q**. Then it added to C_{60} to form the mono-addition product **Q** or a double addition product, depending on the concentration of carbene intermediate **R** in the reaction system.

N-(Diphenylmethylene)glycinate esters were suggested as non-traditional cyclopropanating agents. Under Bingel–Hirsch reaction conditions, they were converted to methanofullerene iminoesters **354**, **355**,¹⁶⁴ **356**, **357** (ref. 165) (Scheme 98).

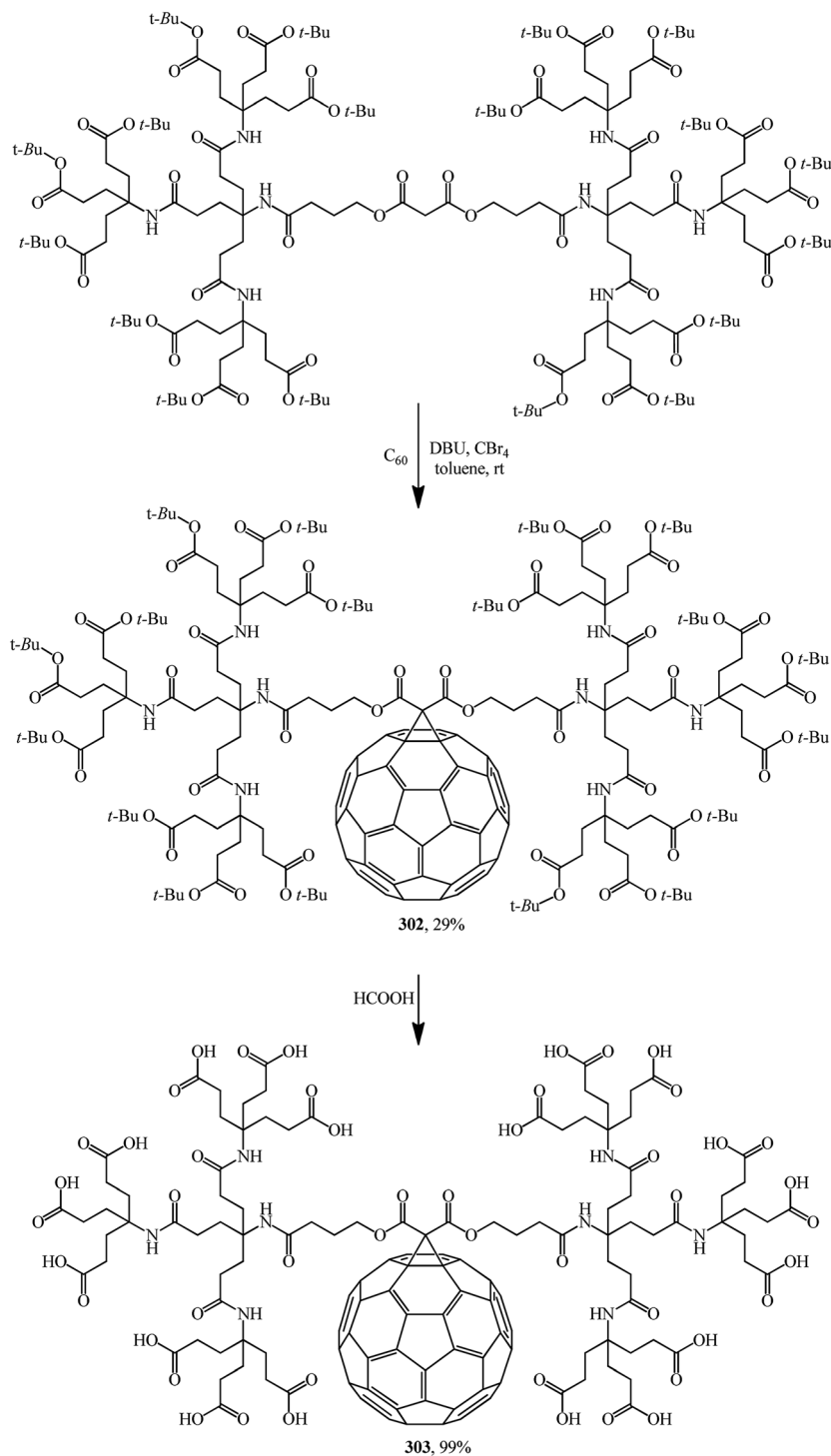
Based on a number of thiophene-containing ketones and C_{60} in the Bingel–Hirsch process, mono-ketone modified methanofullerene derivatives **358–361** were synthesized (Scheme 99).¹⁶⁶





Scheme 83





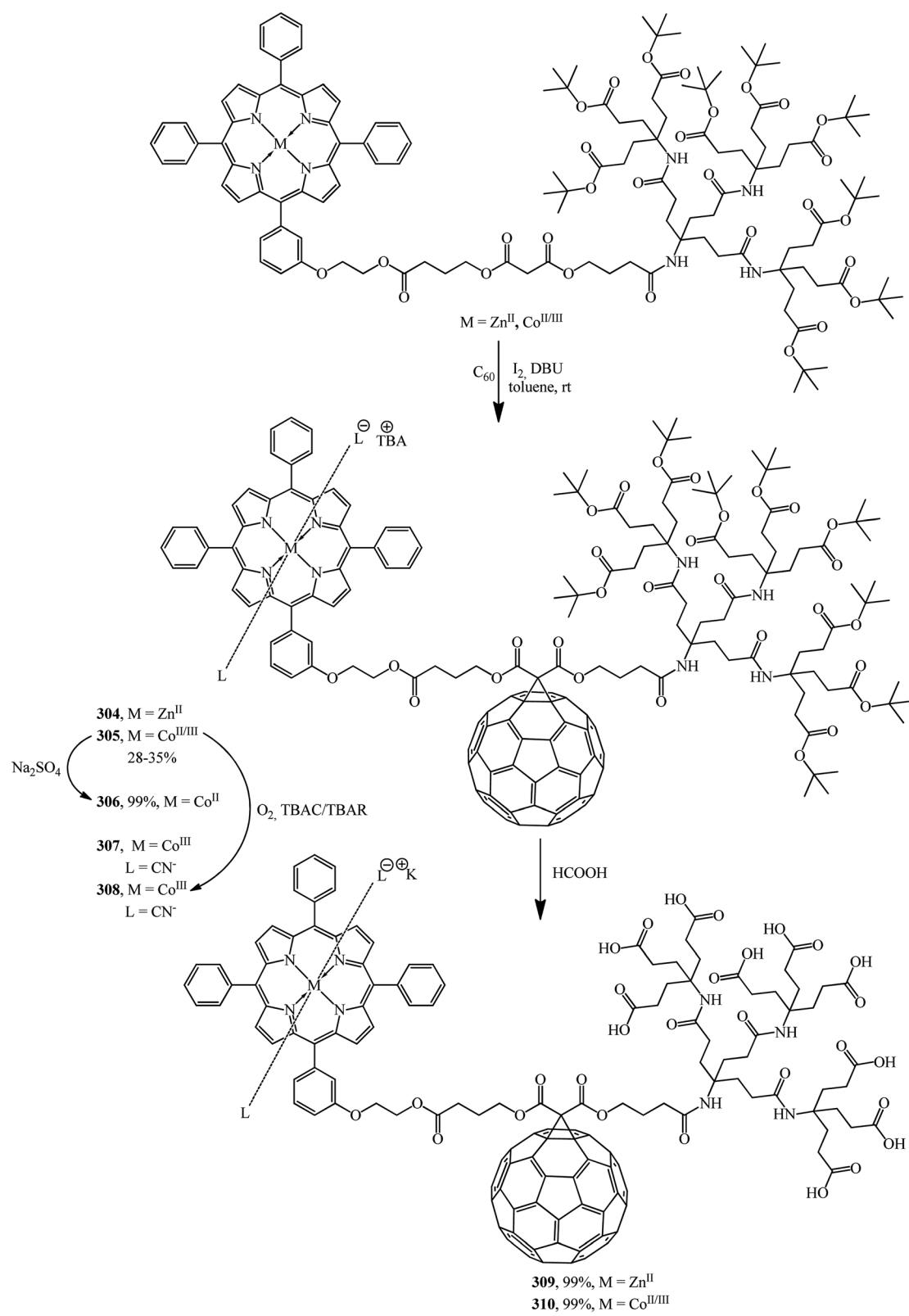
Scheme 84

The authors note that compound **361** is the best one in this series. It shows the highest efficiency of 1.27% under pristine conditions. Methanofullerene **361** has the highest solubility and the lowest unoccupied molecular orbital level among newly synthesized derivatives in this paper and it can be affect to modify the donor–acceptor bulk-heterojunction and improve electron attraction ability from P3HT donor.

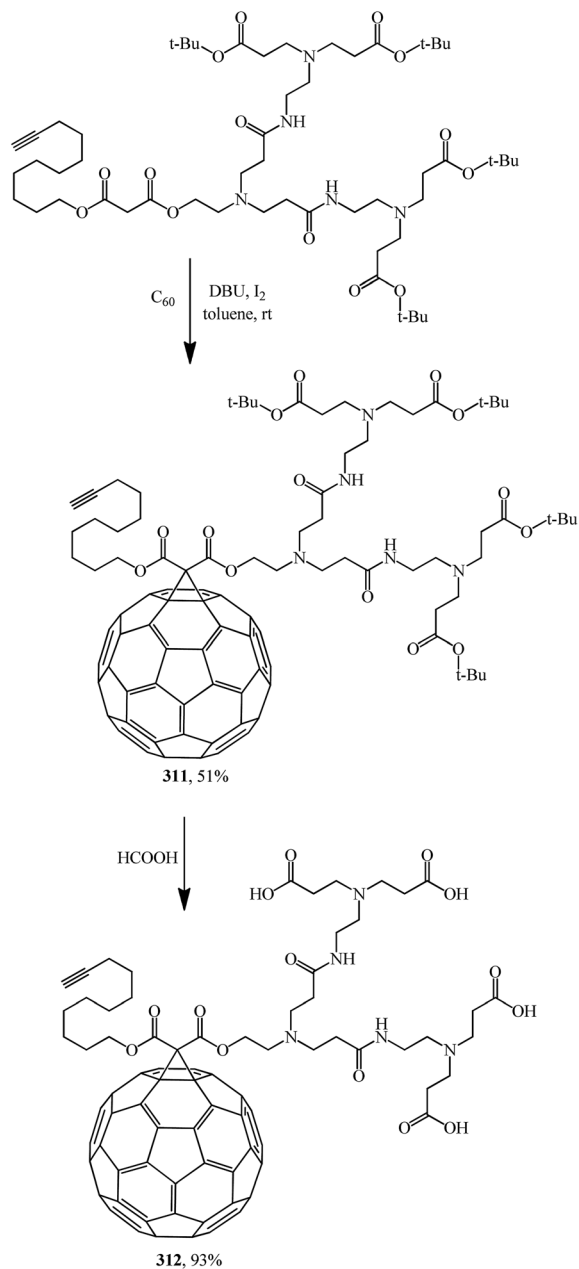
3. Other methods for the synthesis of methanofullerenes by the addition–elimination mechanism

Methanofullerenes can be obtained in low yields (15–25%) by reactions of phosphorous ylides with C_{60} . The first derivatives of [6,6]-closed methanofullerenes **362–368** obtained by this scheme were described in ref. 167 in 1994 (Scheme 100).





Scheme 85

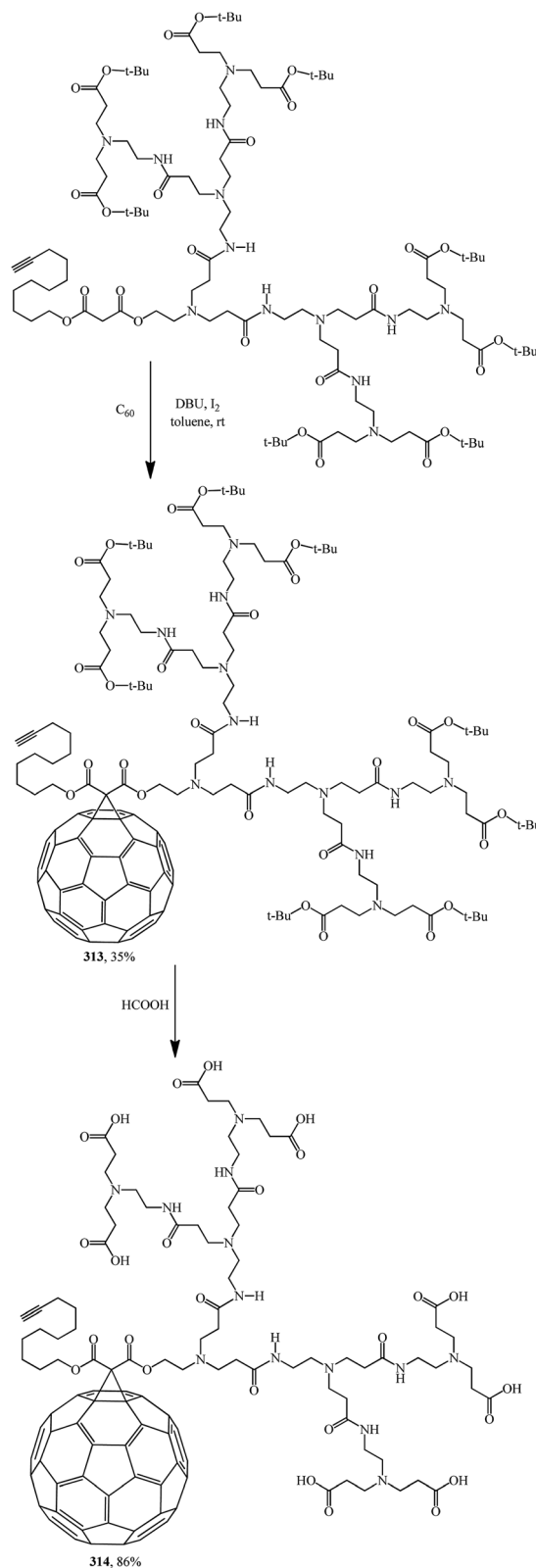


Scheme 86

Wilson *et al.*¹⁶⁸ used sulfonium ylides instead of phosphorus ylides. In this case, [6,6]-methanofullerenes were obtained from stabilized sulfonium ylides **369–374**, which in turn were obtained by treatment of sulfonium salts with a base (NaH or NaOH). It was noted that the reaction rates depended on the ylide nucleophilicity, while the yield of the target product reached 58% (Scheme 101).

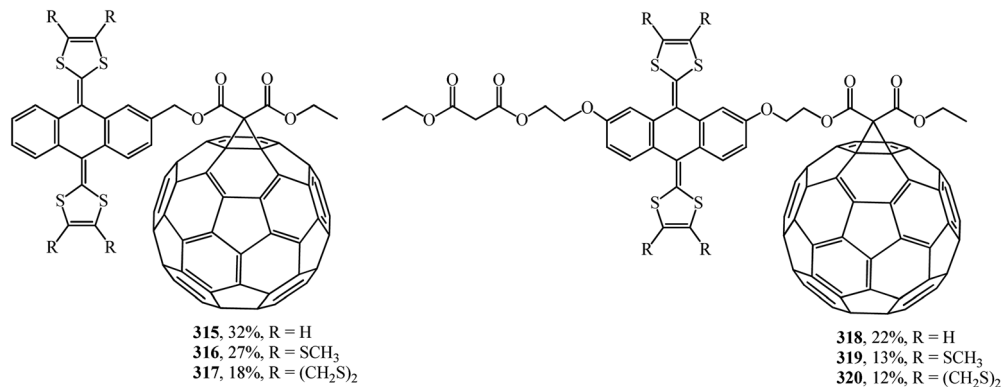
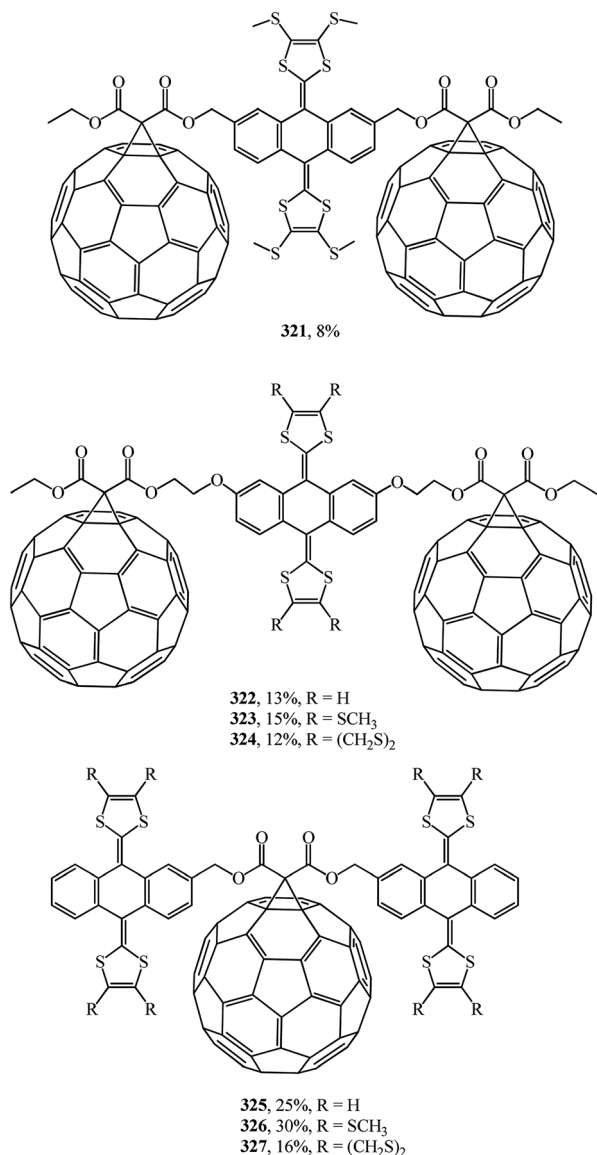
Examples of the participation of sulfur ylides in the synthesis of methanofullerenes are given in ref. 169 The reaction of fullerene with dimethylsulfonium α -formylalkylide gave novel 2,2-[60]fulleroalkanal **375** having a formyl group at the bridge-head carbon. This derivative **375** was readily converted into a variety of *N*-aryl-2,2-[60]

fulleroaldimines **376–380** by condensation with aromatic amines (Scheme 102). One of them showed efficient



Scheme 87



Fig. 22 C₆₀/π-extended tetrathiafulvalene diads 315–320.Fig. 23 C₆₀/π-extended tetrathiafulvalene triads 321–327.

quenching of the fullerene core fluorescence due to photo-induced intramolecular electron transfer.

A new fullerene reaction with silylated nucleophiles was described.¹⁷⁰ The cyclopropanation of C₆₀ with silylated nucleophiles, such as silyl ketene acetals, silyl ketene thioacetals, and silyl enol ethers derived from α-halo carbonyl compounds, smoothly occurred in the presence of KF/18-crown-6 to give the corresponding methanofullerene derivatives **381–389** in moderate to good yields (Scheme 103).

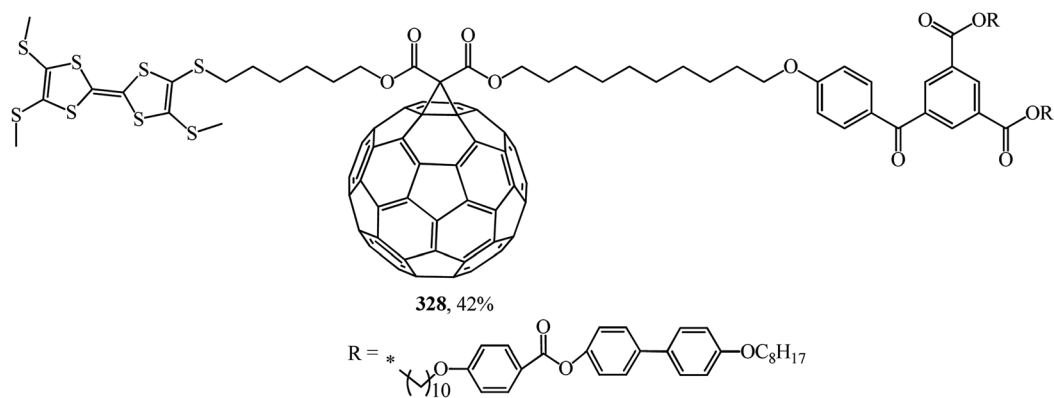
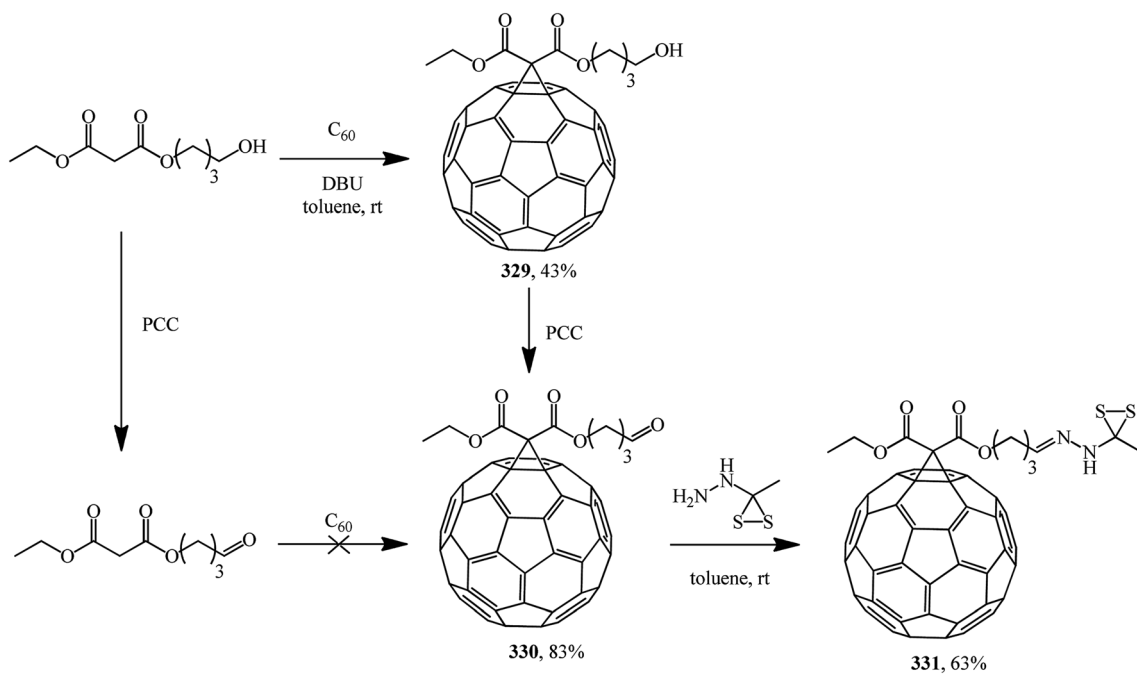
Further, the same team¹⁷¹ synthesized 2,2-[60]fullerenoalkanal **390–394** by a fluoride ion mediated reaction of fullerene with 2-bromo enol silyl ethers that were easily prepared by 2-bromination of the corresponding enol silyl ethers (Scheme 104). The reactivity differed significantly depending on the stability of the 2-bromo enol silyl ethers. High yields and selectivities were achieved in the reaction of 2-bromo enol trimethylsilyl ethers under mild conditions (KF/18-crown-6-ether). On the other hand, the reaction of stable 2-bromo enol *tert*-butyldimethylsilyl ethers required the use of more reactive tetrabutylammonium fluoride as a fluoride ion source.

This rearrangement method allows various substituents, including large bulky groups, to be incorporated in C₆₀. An additional advantage of the method is that the Bingel reaction is performed in an almost neutral medium. Reactions of C₆₀ with similar silylketene acetals under photochemical conditions and without F⁻ result in dihydrofullerene acetate rather than methanofullerenes.¹⁷²

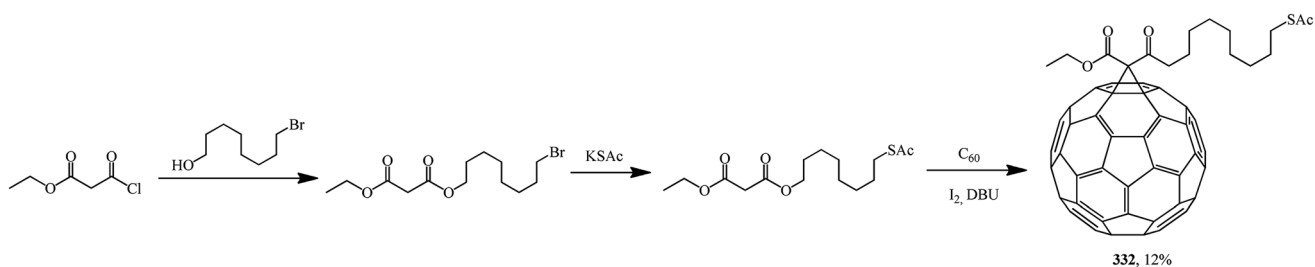
An original synthetic method was suggested: hard-to-access aminomethanofullerenes were synthesized by the reaction of carbon clusters with cyanoacrylates in the presence of ethylmagnesium bromide and Ti(Oi-Pr)₄ (catalyst).¹⁷³ Cyanoacrylates containing cyclic or symmetrical substituents are used to obtain primary methanofullerenes **359–398** (Scheme 105) and **399–402** (Fig. 25).

A possible process mechanism involves the following. In the first step, the reaction of Ti(Oi-Pr)₄ with EtMgBr affords dialkoxytitanacyclopropane **S**, which exists in equilibrium with the ethylene complex. The presence of fullerene in the reaction mixture causes a displacement of the ethylene molecule from complex **S** to give the



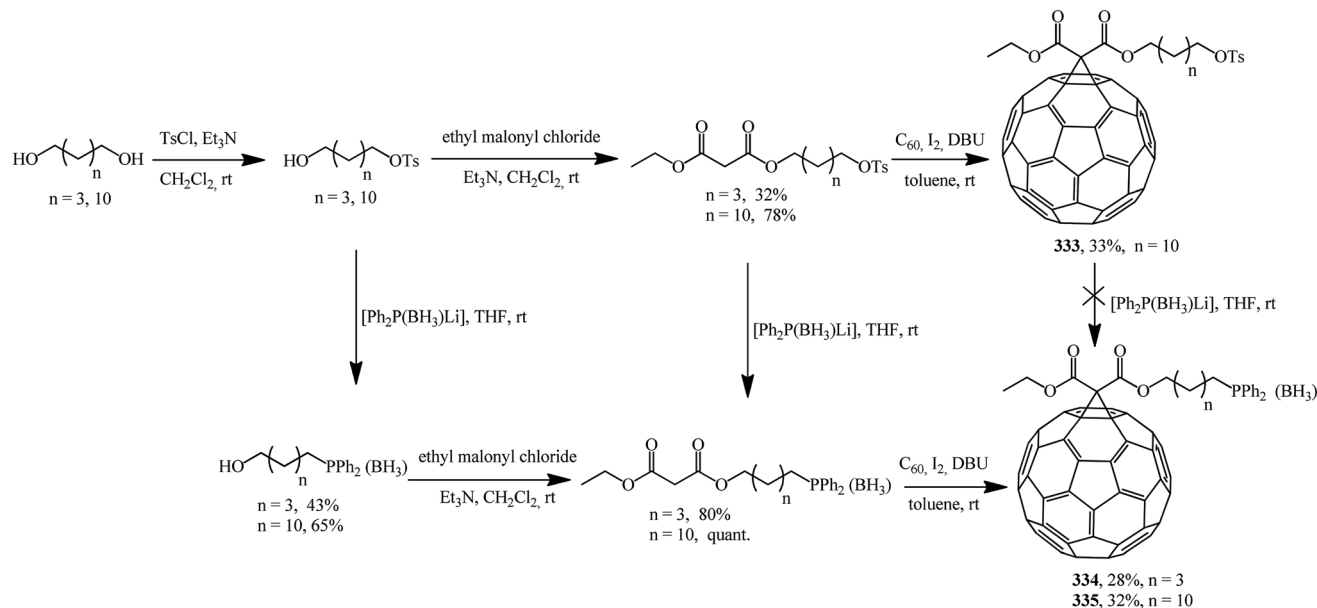
Fig. 24 C₆₀-tetrathiafulvalene **328**.

Scheme 88

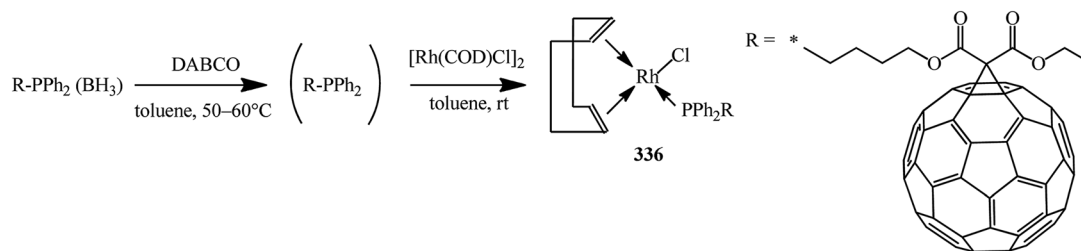


Scheme 89

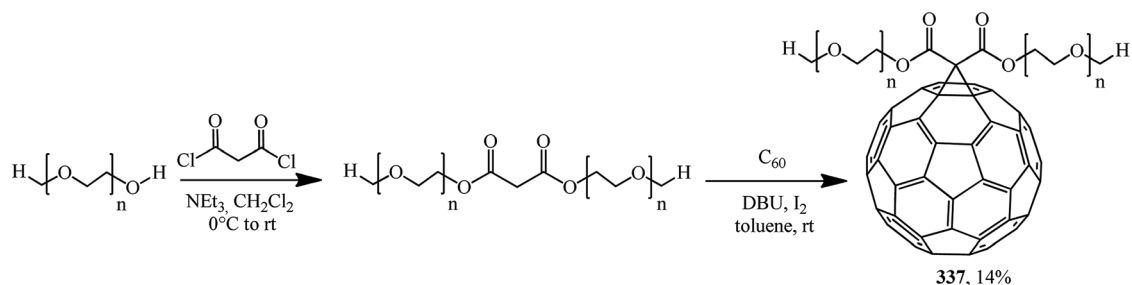




Scheme 90



Scheme 91



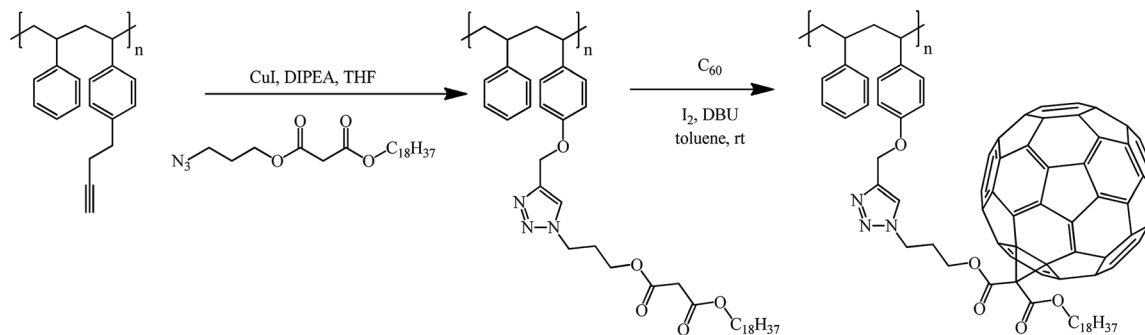
Scheme 92

key intermediate of this reaction, *i.e.*, fullerotitanacyclopropane **T**. The subsequent reaction of intermediate **T** with cyanoacrylate produces azatitanacyclic C_{60} adduct **U**, which reacts with EtMgBr to regenerate dialkoxytitanacyclopropane **S**, thus completing the catalytic cycle. Upon completion of the reaction, complex **U**

undergoes hydrolysis to give aminomethanofullerenes **V** (Scheme 106).

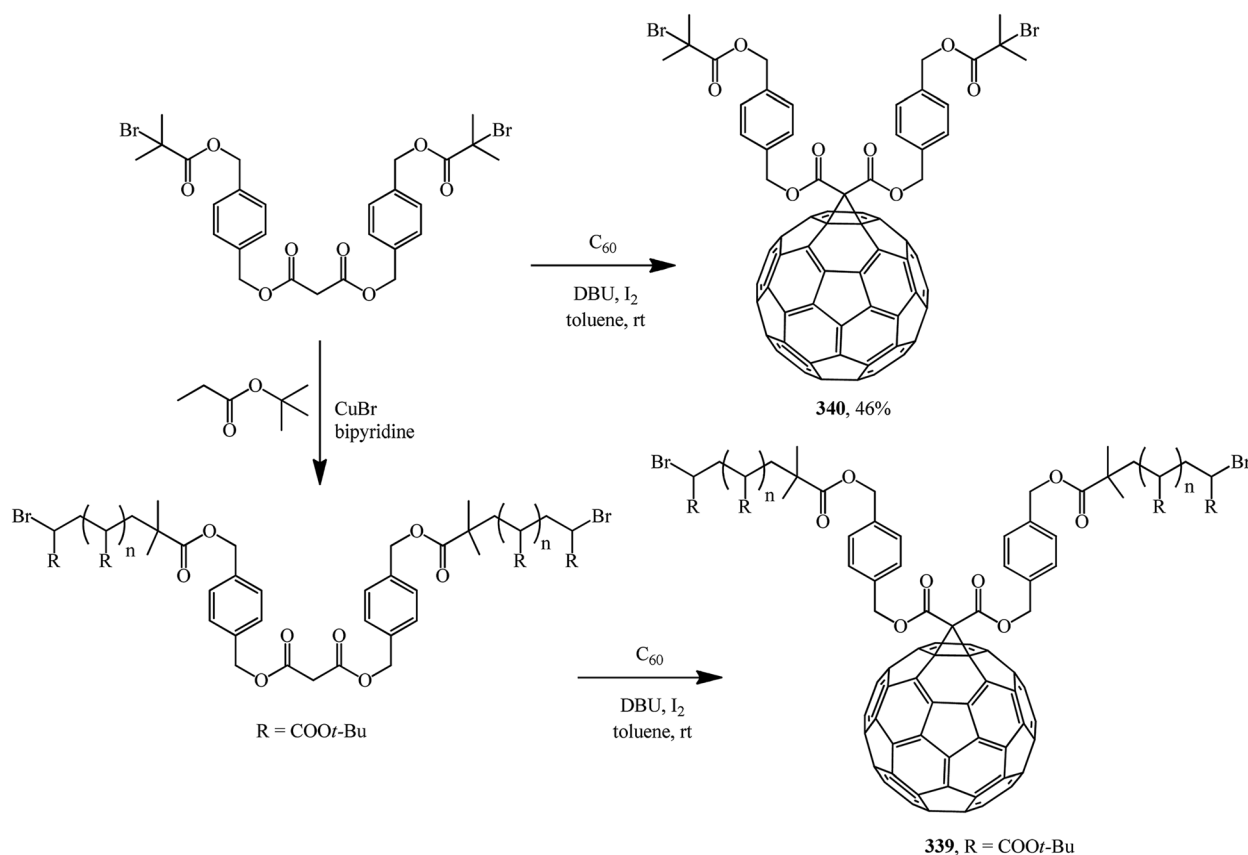
To synthesize secondary aminofullerenes within the described approach, isonitriles are used instead of cyanoacrylates to give *N*-substituted amino methanofullerenes **403–409** (Fig. 26).¹⁷⁴





338

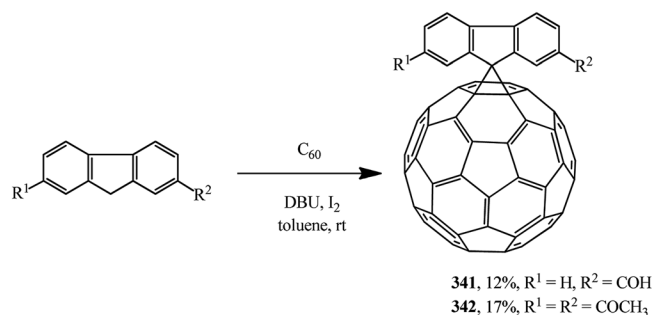
Scheme 93



339, R = COO-t-Bu

Scheme 94

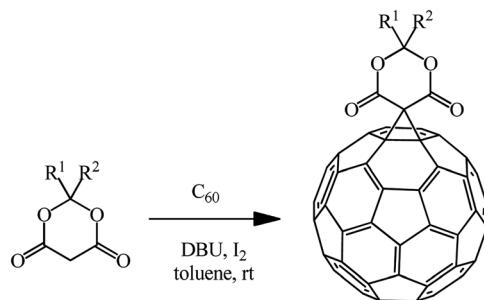
O. Sinyashin's team performed a series of studies by to synthesize methanofullerenes with involvement of phosphorus-containing compounds. Reactions of cyclic β -diketones (acenaphthenequinone, aceanthrenequinone, and *N*-alkylisatins) with hexaethyltriaminophosphine in the presence of fullerene C_{60} under mild conditions were studied. This process occurs *via* deoxygenation of a dicarbonyl compound by a P(III) derivative and is likely to involve the intermediate formation of β -keto-carbenes to give the corresponding spirobicycles **410–415** (ref. 175) and **416** (ref. 176) (Scheme 107). Studies on the electrochemical behavior of the



341, 12%, $R^1 = H, R^2 = COH$
342, 17%, $R^1 = R^2 = COCH_3$

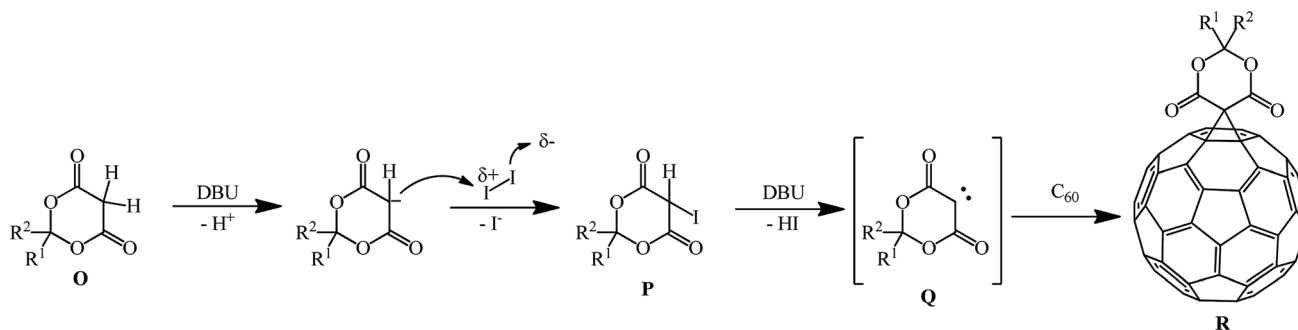
Scheme 95



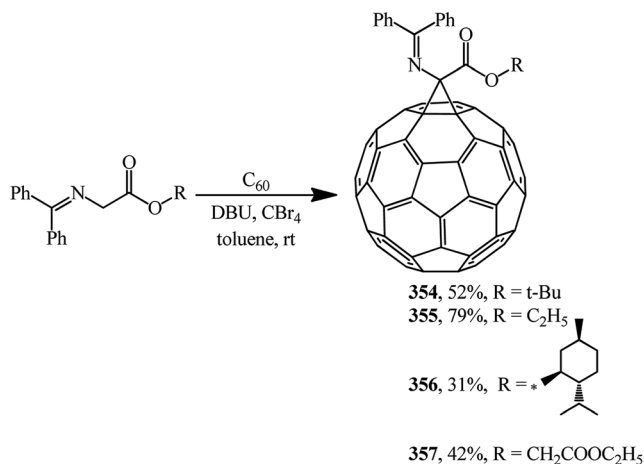


- 343**, 41%, $R^1 = R^2 = \text{CH}_3$
344, 41%, $R^1 = \text{CH}_3$, $R^2 = \text{C}_2\text{H}_5$
345, 40%, $R^1 = \text{CH}_3$, $R^2 = \text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_3$
346, 39%, $R^1 = \text{CH}_3$, $R^2 = n\text{-C}_6\text{H}_{13}$
347, 41%, $R^1 = R^2 = (\text{CH}_2)_4$
348, 39%, $R^1 = R^2 = (\text{CH}_2)_5$
349, 35%, $R^1 = \text{CH}_3$, $R^2 = \text{C}_6\text{H}_5$
350, 38%, $R^1 = \text{CH}_3$, $R^2 = 4\text{-CH}_3\text{-C}_6\text{H}_4$
351, 33%, $R^1 = \text{CH}_3$, $R^2 = 4\text{-NO}_2\text{-C}_6\text{H}_4$
352, 30%, $R^1 = R^2 = \text{C}_6\text{H}_5\text{CH}_2$
353, 28%, $R^1 = \text{CH}_3$, $R^2 = 4\text{-F-C}_6\text{H}_4$

Scheme 96



Scheme 97

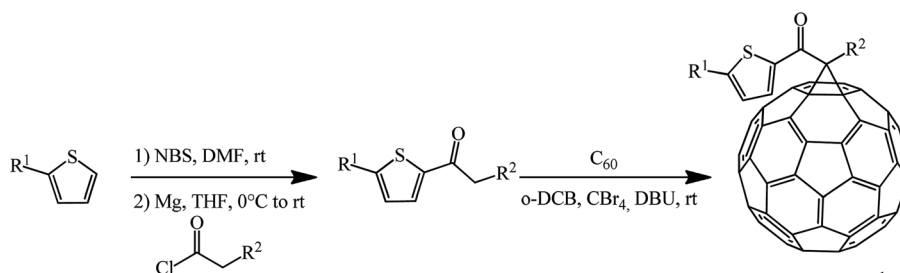


Scheme 98

methanofullerenes obtained made it possible to recommend them as acceptor components in organic solar cells.¹⁷⁷

Conclusions

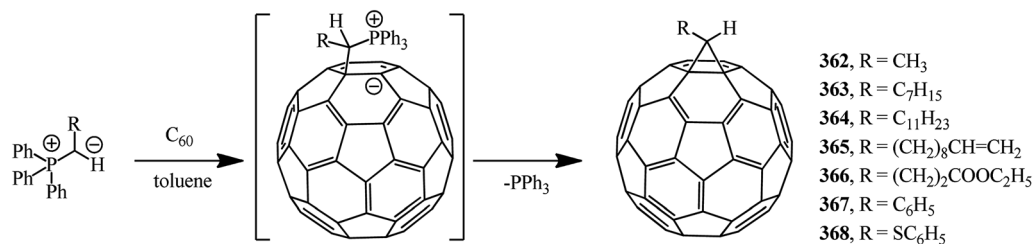
Thus, our analysis of literature sources dealing with the nucleophilic cyclopropanation of fullerene with stabilized carbanions by the addition-elimination nucleophilic cyclopropanation mechanism led to the following conclusions. The Bingel reaction is among the most efficient methods for synthesizing methanofullerenes. It is almost universal and allows one to synthesize C_{60} methano derivatives from halo-substituted substrates containing reactive methylene functions with various structures. The



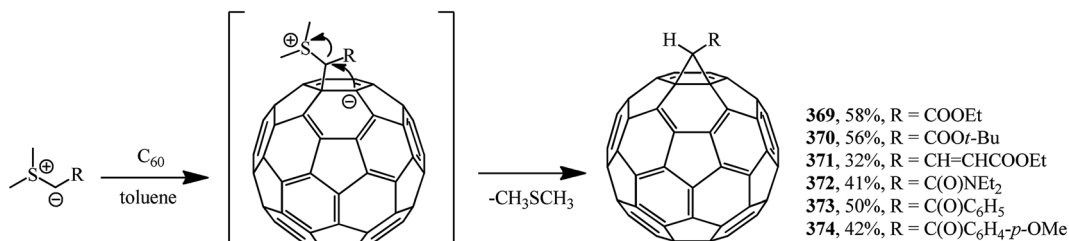
- 358**, 37%, $R^1 = \text{H}$, $R^2 = n\text{-hexyl}$
359, 35%, $R^1 = \text{thiophen-2-yl}$, $R^2 = n\text{-hexyl}$
360, 33%, $R^1 = n\text{-hexyl}$, $R^2 = n\text{-butyl}$
361, 39%, $R^1 = 2\text{-hexylthiophen-5-yl}$, $R^2 = n\text{-hexyl}$

Scheme 99

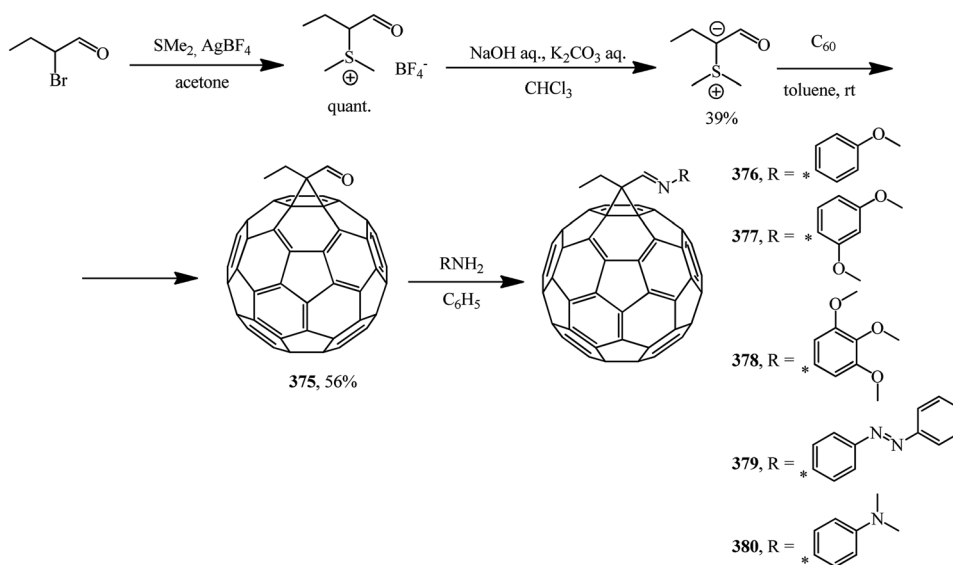




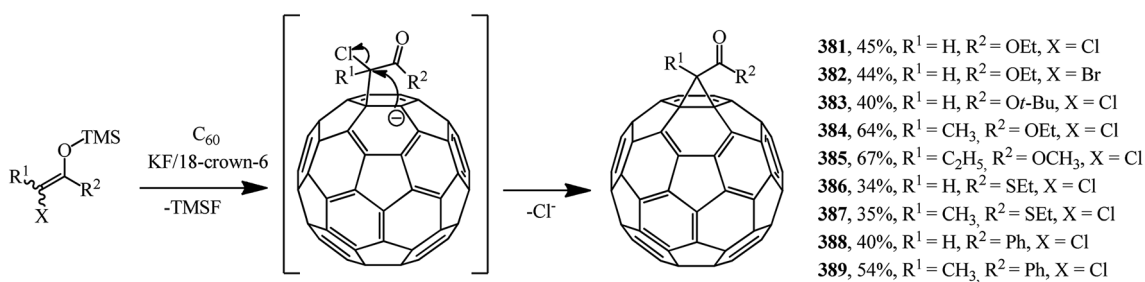
Scheme 100



Scheme 101

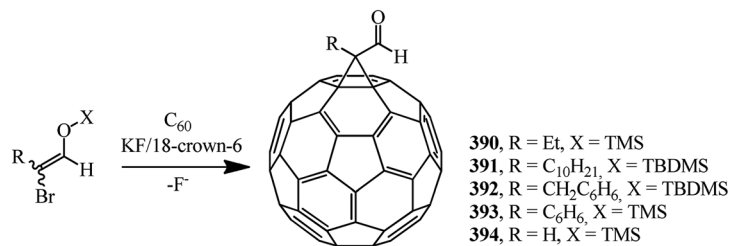


Scheme 102

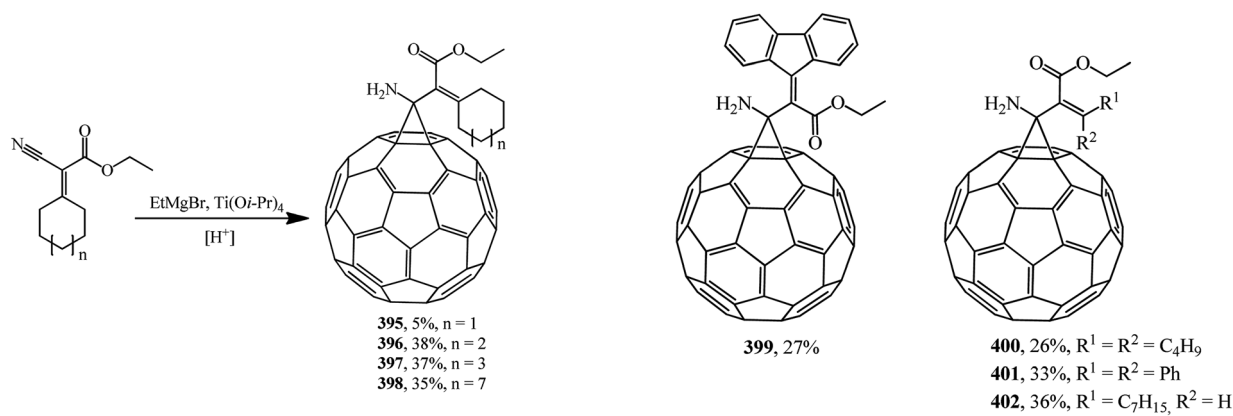


Scheme 103



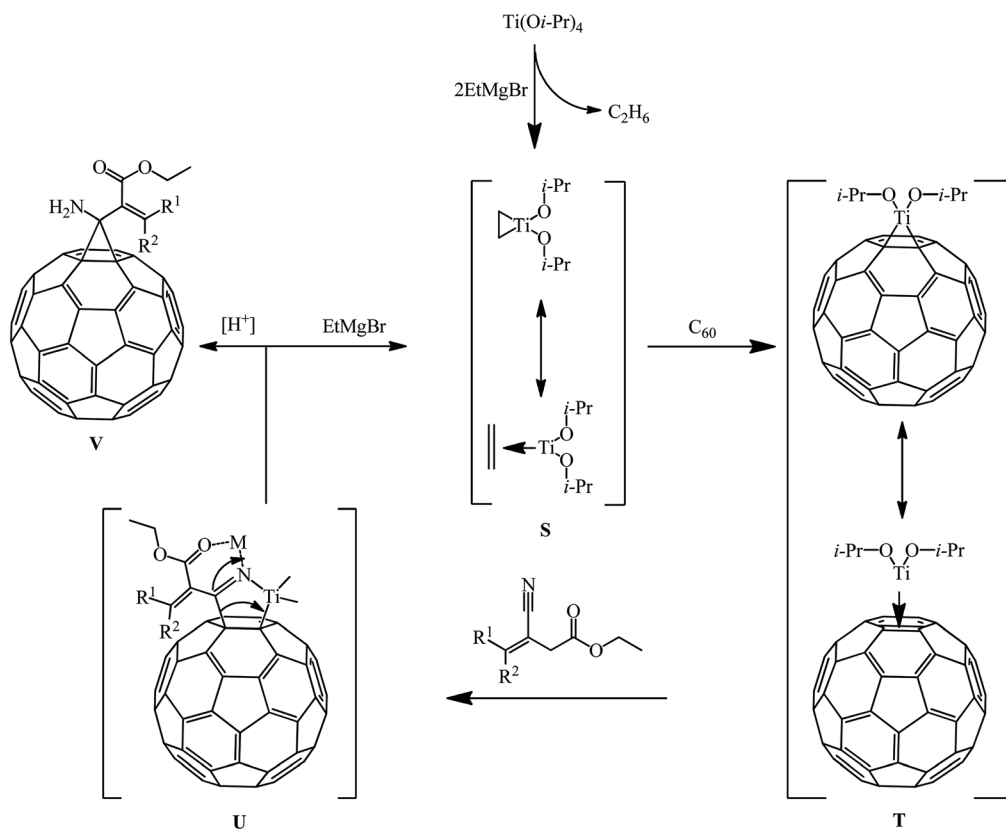


Scheme 104



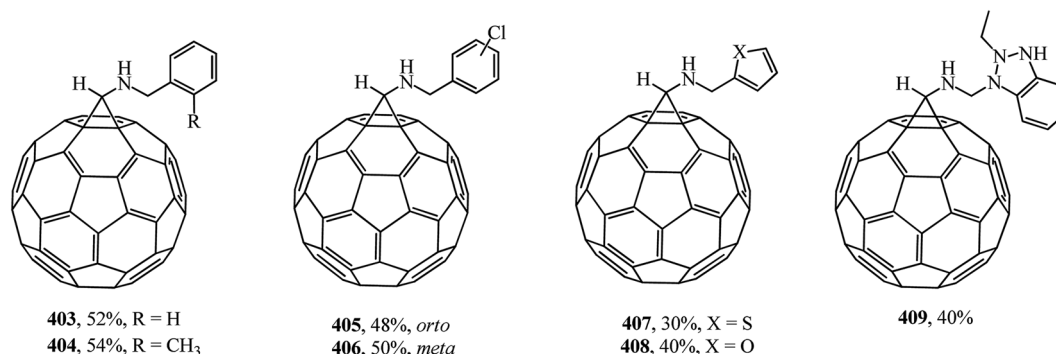
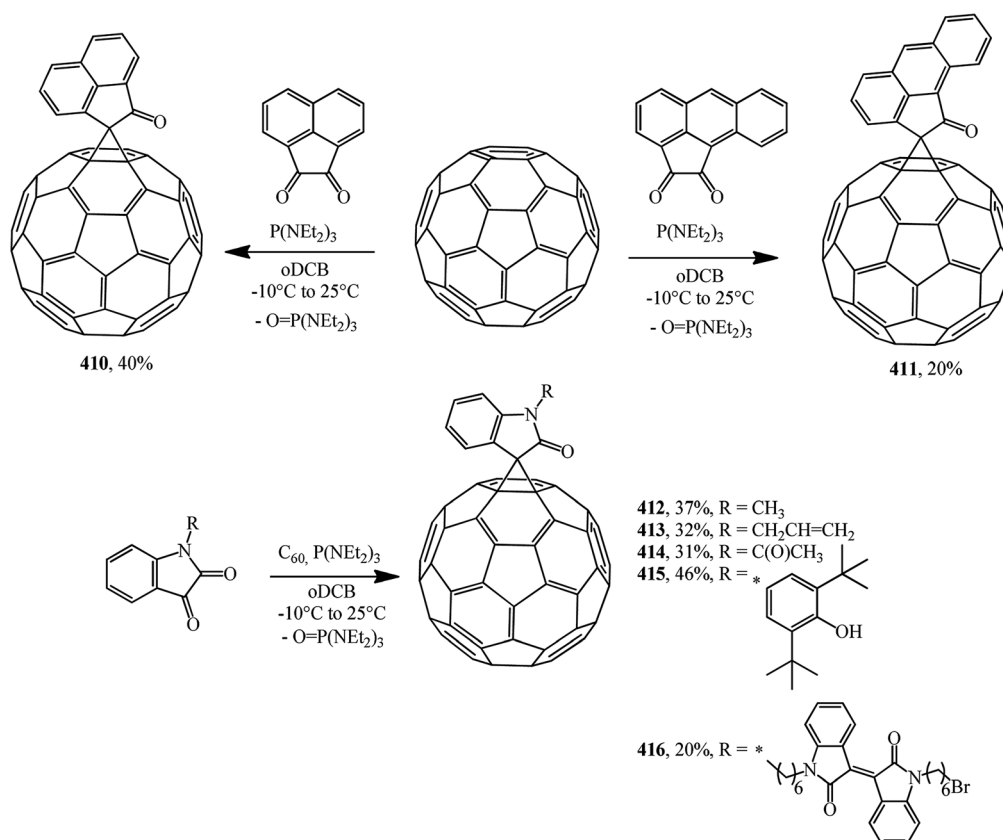
Scheme 105

Fig. 25 Aminomethanofullerenes 399–402.



Scheme 106



Fig. 26 Structures of *N*-substituted amino methanofullerenes 403–409.

Scheme 107

advantages of this method for fullerene functionalization include simple and mild reaction conditions that provide good yields of the target products. However, this technique assumes the presence of an additional stage, *i.e.*, preliminary halogenation of a cyclopropanating agent.

The Bingel approach modified by Hirsch allows one to obtain methanofullerenes by a “*one-pot*” reaction: a malonate substrate, CBr₄ (or I₂) and DBU as a base are used simultaneously. In this case, the synthesis of adducts is performed by

direct treatment of C₆₀ with malonates and their yields increase somewhat, as the authors note.

The synthesis of methanofullerenes can be performed using sulfur or phosphorus ylides, silyl derivatives, isonitriles, cyanoacrylates, cyclic β-diketones, *etc.* as alternative nucleophilic cyclopropanating agents. The base needs to be selected individually in such cases.

In all the above examples of fullerene C₆₀ functionalization, selective formation of [6,6]-bridging adducts occurs. That is why the nucleophilic cyclopropanation of fullerene that occurs by



the addition–elimination mechanism is currently used most widely by organic chemists in order to synthesize various methanofullerenes.

Conflicts of interest

Authors declare that they have no conflicts of interest.

Acknowledgements

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