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Fonctionnalisation Multiple d'Hexa-adduits du C_{60} par Chimie « Click »

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Abbreviation.

br	broad
calcd.	calculated
CuAAC	Copper Catalyzed Azide-Alkyne Cycloadditions
DBU	1,8-Diazobicyclo[5,4,0]undec-7ene
DCC	N,N'-dicyclohexylcarbodiimide
DIBAL-H	Diisobutylaluminium hydride
DMAP	4-Dimethylaminopyridine
DMF	N,N'-dimethylformamide
GPC	Gel permeation chromatography
HOMO	Highest occupied molecular orbital
HPLC	High performance liquid chromatography
IR	Infrared
IUPAC	International Union of Pure and Applied Chemistry
LUMO	Lowest unoccupied molecular orbital
MALDI-TOF	Matrix Assisted Laser Desorption/Ionisation - Time Of Flight
NMR	Nuclear magnetic resonance
PMB	Para-methoxybenzyl
redox	reduction/oxydation
sh	shoulder
TBAF	Tetrabutylamonium fluoride
TFA	Trifluoroacetic acid
THF	Tetrahydrofuran
TMS	Trimethylsilyl
UV/vis.	Ultraviolet/visible
ε	Molar attenuation coefficient

Résumé.

Le C_{60} a été découvert en 1985 par H.W. Kroto, R.F. Curl et R.E. Smalley,[1] ce qui leur a valu le prix Nobel de chimie en 1996. Le C_{60}, aussi appelé Buckminsterfullerène, est le plus stable et le plus abondant représentant de la famille des fullerènes. Après le graphite et le diamant, les fullerènes sont la troisième forme allotropique connue du carbone. Ils correspondent à des cages creuses de carbone formés de pentagones et d'hexagones fusionnés. La chimie du C_{60} et des autres fullerènes s'est beaucoup développée dès la première production en quantité macroscopique de ces composés par W. Krätschmer et D. Huffman en 1990.[2] Les propriétés remarquables du C_{60} et des autres fullerènes ont également attiré l'attention de la communauté scientifique. Contrairement au graphite et au diamant, les fullerènes sont solubles dans divers solvants organiques adaptés aux transformations chimiques. Le C_{60} possède d'intéressantes propriétés photophysiques, notamment la désexcitation quasi-quantitative des états excités singulet en état triplet par croissement inter-système. Les propriétés électrochimiques du C_{60} sont aussi remarquables. Le C_{60} peut être facilement réduit (jusqu'à 6 fois par 6 étapes monoélectroniques successives), mais est plus difficilement oxydable.

La réactivité du C_{60} est assimilable à celle d'une polyoléfine électro-déficiente tendue qui peut être le siège de réactions d'additions nucléophiles ou de cycloadditions. L'une des réactions les plus utilisées pour la multi-fonctionnalisation du C_{60} est la réaction de Bingel.[3] Cette réaction consiste à l'addition nucléophile d'un α-halomalonate sur le C_{60} et conduit à l'obtention d'un seul dérivé mono-adduit du C_{60}. Cependant, la poly-fonctionnalisation du C_{60} est une tâche ardue et est confrontée à des problèmes de régio- et de stéréochimie.[4,5] En effet, les dérivés mono-fonctionnalisés de C_{60} possèdent neuf liaisons 6-6 différentes (liaisons à la jonction entre deux cycles à six atomes) et un mélange de 9 régioisomères est obtenu lors de deux réactions successives sur le cœur fullerènique (Figure 1). La synthèse de tris-adduits du C_{60} est encore nettement plus difficile car il est théoriquement possible de former jusqu'à 46 régioisomères. L'obtention d'hexa-adduits du C_{60} d'ordre d'addition octaédrique est fortement conditionnée par la régiochimie des précurseurs bis- et tris-adduits. En effet, seul deux bis-adduits et deux tris-adduits du C_{60} ont un motif d'addition adéquat pour l'obtention de ces hexa-adduits de C_{60} (Figure 1).

Les hexa-adduits de fullerène avec une symétrie T_h et un ordre d'addition octaédrique sont une classe unique de molécules tridimensionnelles.[6] Cependant, la synthèse directe d'hexa-adduits de fullerène, à partir de C_{60} et de malonates, reste difficile et est principalement limité à des malonates relativement simple. Ce problème majeur a été récemment résolu par la synthèse d'hexa-adduits du C_{60} facilement accessibles, comportant 12 groupes terminaux post-fonctionnalisables, donnant ainsi accès à des systèmes structurellement plus compliqués.[6–8] Parmi les réactions de post-fonctionnalisation possibles, la cycloaddition 1,3-dipolaire de Huisgen, entre un azoture et un alcyne vrai, s'est révélé être particulièrement intéressante pour incorporer une large variété de groupes fonctionnels autour du corps fullerènique. Actuellement, le développement d'une

méthodologie efficace pour la synthèse d'hexa-adduits de fullerène comportant deux ou plusieurs fonctions périphériques différentes reste un enjeu majeur.

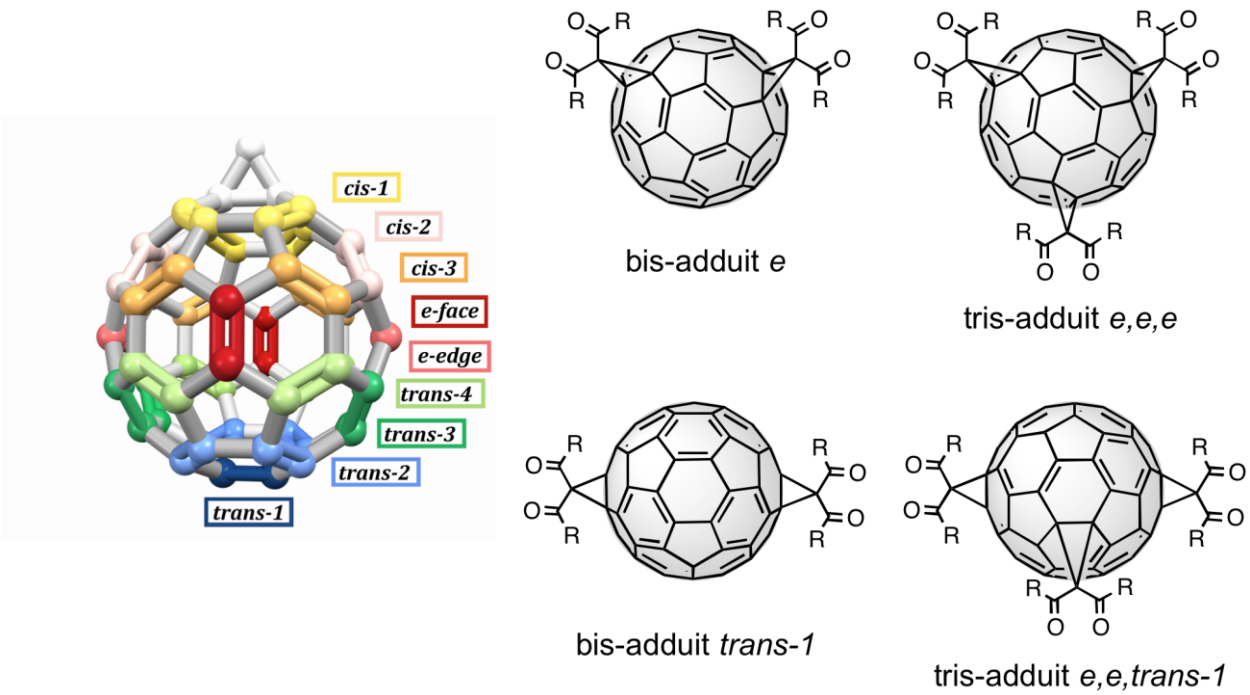

Figure 1: ***A gauche:*** *L'addition d'un second adduit sur un mono-adduit de C_{60} peut en principe mener à 9 régioisomères. Relatif au premier adduit, le second peut être localisé dans le même hémisphère (cis), dans l'autre hémisphère (trans) ou à l'équateur (e).* ***A droite:*** *Les bis- et tris-adduits du C_{60} qui permettent un accès aux hexa-adduits d'ordre d'addition octaédrique.*

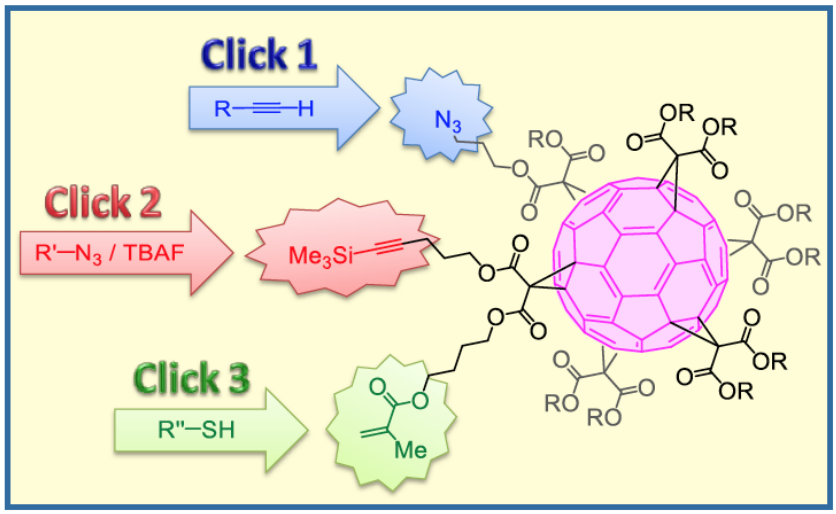

Figure 2: Illustration des possibilités de fonctionnalisation de la sphère du C_{60}.

L'objectif de cette thèse sera dans un premier temps de développer des méthodologies de synthèses régiosélectives de bis- et tris-adduits de C_{60}. Dans un deuxième temps, il sera question de préparer des synthons C_{60} hexa-substitués polyvalents incorporant plusieurs centres réactifs différents et pouvant être sélectivement fonctionnalisés (Figure 2), à partir de

bis- et tris-adduits de C_{60} adaptés à la formation d'hexa-adduits de C_{60} d'ordre d'addition octaédrique.

Afin d'obtenir ce type de supports multifonctionnels, il est essentiel de pouvoir accéder facilement à certain des bis- et tris-adduits du C_{60} possédant un ordre d'addition adéquat (Figure 1). Dans la littérature, deux approches principales ont été mise au point pour la fonctionnalisation régiosélective du C_{60}, une approche dite à « bras directeur ou tête directrice » développée par *Diederich et al*[9] et une approche macrocyclique développée par *Hirsch et al*.[10] Cependant, les travaux effectués jusque-là ne permettaient pas une post-fonctionnalisation aisée de ces dérivés de fullerènes.[11] Dans ce contexte, l'utilisation comme tête directrice ou incorporé dans un macrocycle d'une fonction stable et qui peut être facilement déprotégée semble être une idée prometteuse pour une post-fonctionnalisation aisée.

Notre laboratoire s'est donc intéressé à l'utilisation de groupements silylés. Les groupements silylés sont de bons groupes protecteurs de fonctions alcool ou alcyne vrai et peuvent être facilement enlevés par action de fluorure. Les résultats préliminaires obtenus au sein du laboratoire, nous ont conduits à entreprendre une étude plus approfondie du potentiel des groupements silylés.

Dans un premier temps, c'est l'approche macrocyclique qui a été étudiée. La conception du macrocycle est fondée sur trois éléments, (1) des malonates pour l'ancrage sur le C_{60}, (2) un espaceur pour atteindre une position spécifique sur le C_{60} et (3) des groupements silylés incorporés dans l'espaceur (Figure 3).

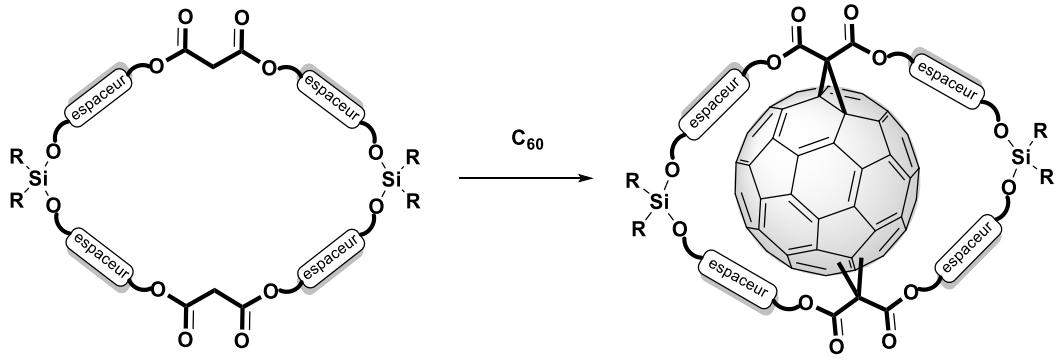

Figure 3: Approche macrocyclique pour la fonctionnalisation régiosélective du C_{60}.

Notre étude sur la régiosélectivité des macrocycles bis-malonates s'est axée sur trois paramètres : (1) la taille des macrocycles, (2) la flexibilité/rigidité des espaceurs et (3) le groupe silylé.

L'élaboration de macrocycles bis-malonates incorporant des groupements silylés, nous a menés vers le développement d'une synthèse dirigée de ces macrocycles à partir d'alcanediols possédant de 4 à 8 atomes de carbone (Figure 4). Dans un premier temps, les alcanediols sont mono-protégés par des groupes p-méthoxybenzyle. S'en suit une deuxième réaction de protection avec du di-*t*-butylsilyl bis(trifluorométhanesulfonate) pour former une

pince. Cette pince est ensuite mono-déprotégée par réaction avec du 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ). Il est à noter que le groupe silylé est inerte dans ces conditions de déprotection. La pince mono-alcool est mise à réagir avec du chlorure de malonyle pour obtenir le mono-malonate, précurseur clé du macrocycle. Une dernière réaction de déprotection avec du DDQ est effectuée pour obtenir le dérivé diol. Finalement, les macrocycles bis-malonates sont obtenus avec de bons rendements (19-50%) par réaction des mono-malonates diols avec du chlorure de malonyle.

Les réactions des macrocycles bis-malonates avec le C_{60} ont donné de bons résultats et différents régioisomères (*cis-2*, *e* et *trans-3*) ont été obtenus selon la taille des macrocycles. Finalement, une réaction de désilylation par traitement avec un excès de $BF_3.Et_2O$ a libéré quatre fonctions alcool pouvant être aisément post-fonctionnalisées.

Le contrôle de la régiochimie par notre méthode macrocyclique est à la fois gouverné par la taille du macrocycle et la différence de réactivité des différentes doubles liaisons du C_{60} après la première fonctionnalisation. Au-delà de la flexibilité/rigidité de l'espaceur, c'est surtout sa longueur et sa forme qui influencent la régiosélectivité mais la fonctionnalisation se fait préférentiellement sur les positions les plus réactives (*e* et *trans-3*). Ce n'est qu'avec les cycles les plus petits que le régioisomère *cis-2* a été obtenue car les positions *e* et *trans-3* sont trop éloignés et ne sont plus accessibles. Le motif O-Si-O joue aussi un rôle non négligeable en apportant une certaine flexibilité au macrocycle. Son hydrolyse permet de générer des synthons tétraalcool. Les bis-adduits *e* formés au cours de cette étude sont de parfaits candidats pour l'élaboration des hexa-adduits de C_{60} multifonctionnels souhaités.

Notre approche macrocyclique ayant donné de bons résultats pour la formation de bis-adduits du C_{60}, la synthèse de tris-adduits du C_{60} a été entreprise en utilisant une stratégie similaire. Pour cela, une synthèse dirigée en 8 étapes de macrocycles tris-malonate a été développée à partir d'alcanediols possédant de 3 à 7 atomes de carbone (Figure 5). Cette stratégie de synthèse fait intervenir jusqu'à trois groupes protecteurs différents, dont les groupements silylés présent dans la structure finale du macrocycle. Ces trois groupes protecteurs ont dû être précautionneusement choisis afin de pouvoir être sélectivement enlevés en présence des autres groupes protecteurs. Par cette méthode, les réactions de macrocyclisation ont donné de bons rendements (21-63%) pour la formation des macrocycles tris-malonates. Pour deux macrocycles tris-malonates, la réaction avec le C_{60} s'est avérée être hautement régiosélective et un seul tris-adduit de C_{60} parmi les 46 régioisomères théoriquement possible a été obtenu. De plus, ces tris-adduits de C_{60} d'ordre d'addition *e,e,e* ont été obtenus avec d'excellents rendements (39 et 61%).

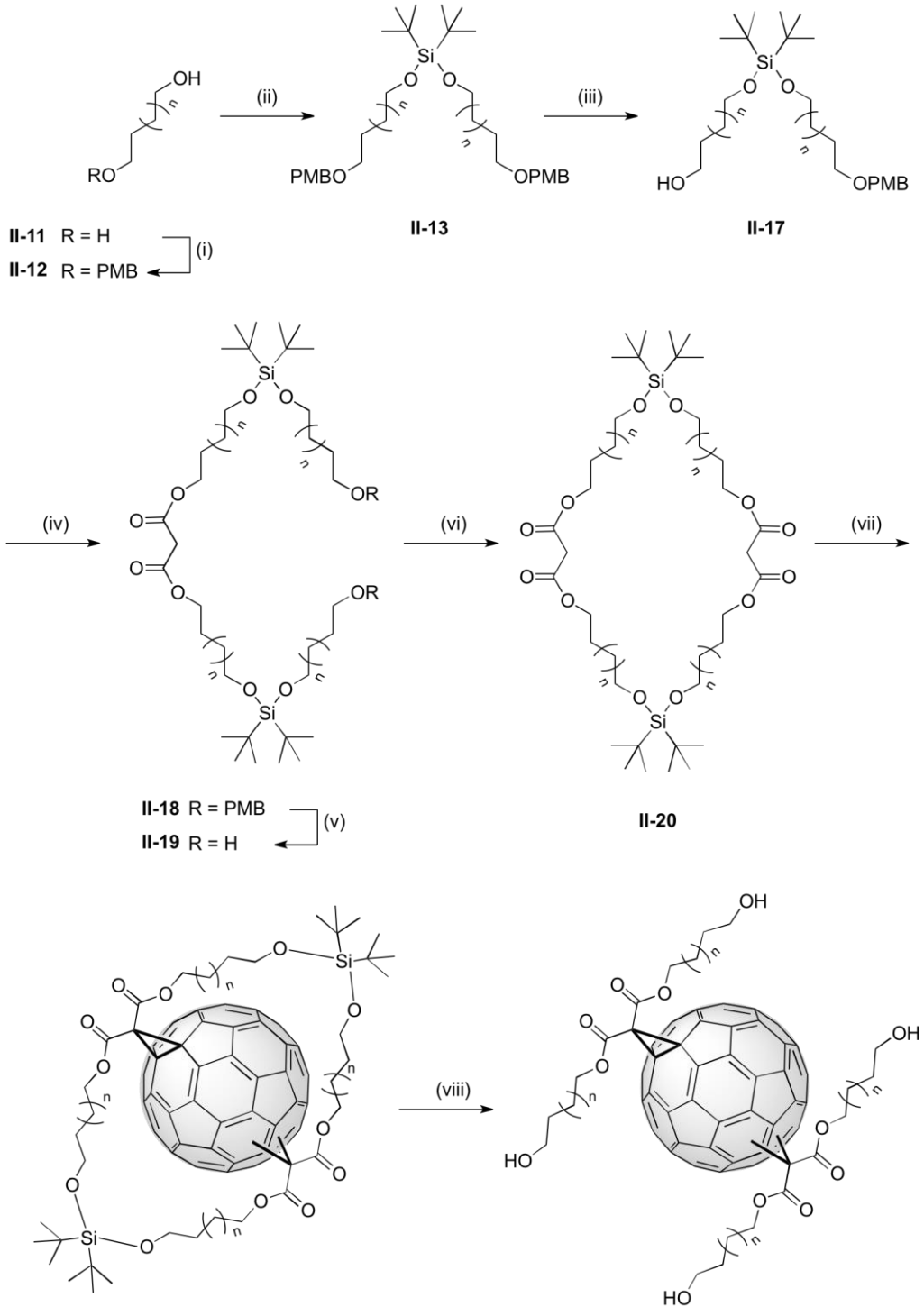

Figure 4: ***Réactifs et conditions*** *: n = 1-5 ;* (i) PMBCl, Ag_2O, CH_2Cl_2, t.a., 48 h (69-95%); (ii) $tBu_2Si(OTf)_2$, DMF, imidazole, t.a., 12 h (60-91%); (iii) DDQ (1 éq), CH_2Cl_2, H_2O, t.a., 6 h (47-50%); (iv) chlorure de malonyle, DMAP, CH_2Cl_2, t.a., 2 h (67-96%); (v) DDQ (2.5 éq), CH_2Cl_2, H_2O, t.a., 2 h (68-85%); (vi) chlorure de malonyle, DMAP, CH_2Cl_2, t.a., 2 h (19-50%); (vii) C_{60}, I_2 and DBU, PhMe, rt, 1 h; (viii) $BF_3.Et_2O$, CH_2Cl_2, CH_3CN, rt, 12 h.

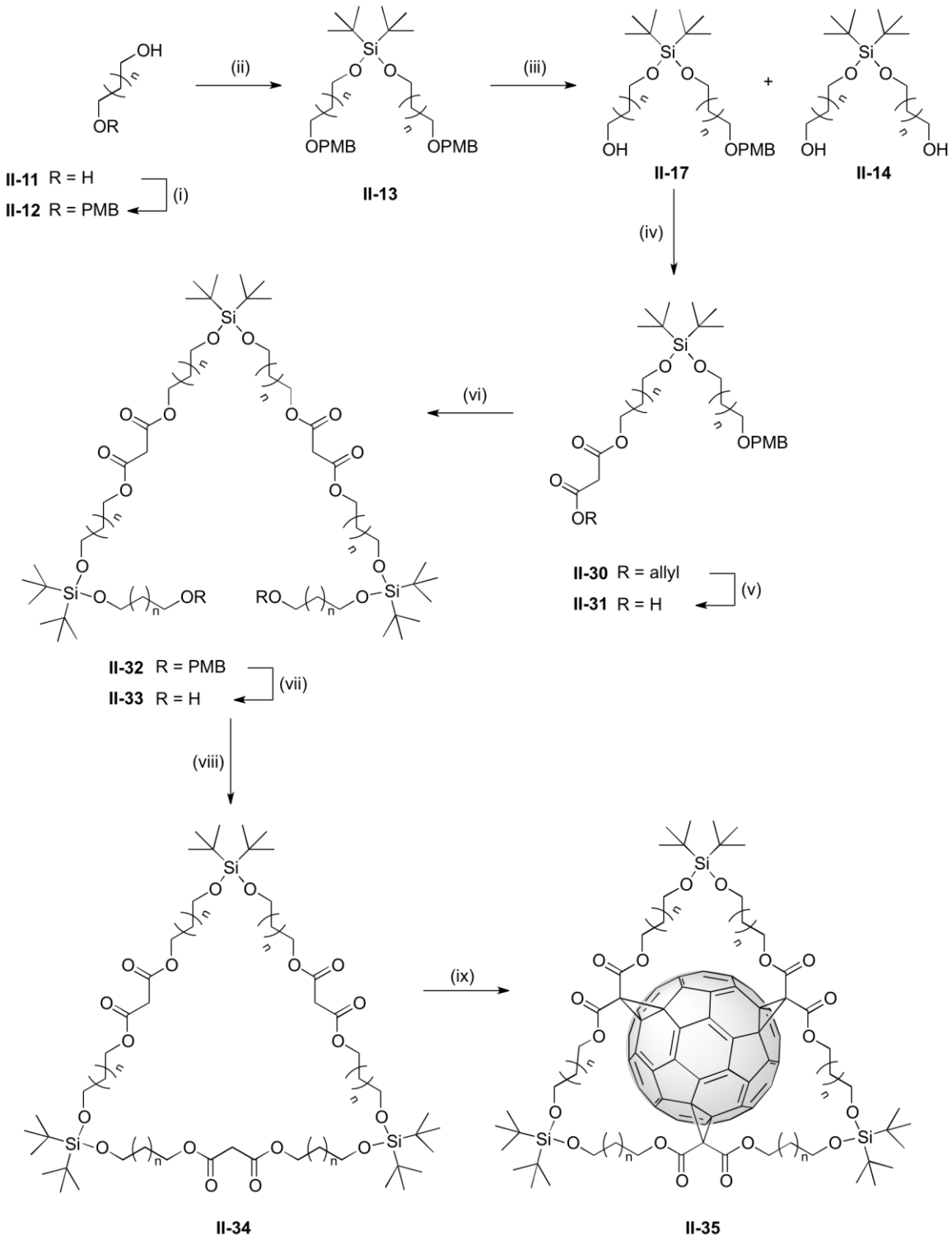

Figure 5: ***Réactifs et conditions*** *:* (i) PMBCl, Ag_2O, CH_2Cl_2, t.a., 12 h; (ii) $tBu_2Si(OTf)_2$, DMF, pyridine, t.a., 12 h (iii) DDQ (1 éq), CH_2Cl_2, H_2O, t.a., 1 h; (iv) **II-28**, DCC, DMAP, CH_2Cl_2, 0°C to t.a., 12 h; (v) $Pd(PPh_3)_4$, morpholine, THF, t.a., 4 h; (vi) **II-14b-e**, DCC, DMAP, CH_2Cl_2, 0°C à t.a., 12 h; (vii) DDQ, CH_2Cl_2, H_2O, t.a., 6 h; (viii) chlorure de malonyle, DMAP, CH_2Cl_2, t.a., 24 h; (ix) C_{60}, I_2, DBU, PhMe, t.a., 1 h.

L'approche macrocyclique s'est avérée être très intéressante pour la fonctionnalisation régiosélective du C_{60} et les produits d'addition sont généralement obtenus avec de bons rendements. Cependant, dans le cas des tris-malonates macrocycliques, le grand nombre d'étapes pour la synthèse des macrocycles ne donne pas un accès rapide au tris-adduits *e,e,e*.

Ceci nous a conduits à développer une approche alternative de type « tête directrice ». Celle-ci repose sur la réaction du C_{60} avec un tris-malonate construit autour d'un motif trialcoxysilane.

Dans ce cas, la préparation des précurseurs tris-malonate est aisée. Elle est réalisée dans un premier temps (Figure 6), par une réaction d'estérification entre du chlorure d'éthyle malonate et un diol. Les mono-malonate-alcools ainsi obtenus sont traités avec du *t*-$BuSiCl_3$ pour former les tripodes tris-malonate correspondant. La faible stabilité de ces produits, nous a amené à effectuer la triple réaction de Bingel avec le C_{60} dans des conditions modifiées. En particulier, il est important de maintenir la température du milieu réactionnel en dessous de -5°C pour éviter des réactions secondaires impliquant le groupement trialcoxysilane. Pour 5 des 8 espaceurs testés, le tris-adduit *e,e,e* a pût être facilement isolé sous forme d'un mélange racémique. La déprotection du groupe silylé a ensuite été effectuée afin d'obtenir des tris-adduits triols post-fonctionnalisables (Figure 6).

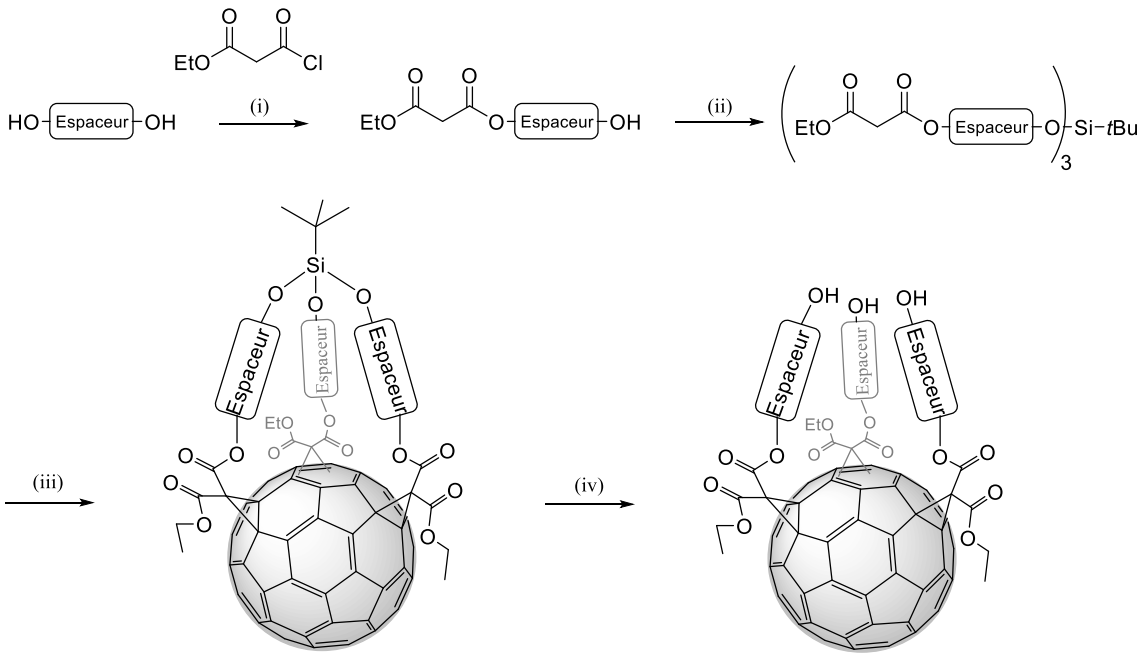

Figure 6 : ***Réactifs et conditions*** *: (i) pyridine, THF, 0°C à t.a., 12 h; (ii) tBuSiCl₃, imidazole, DMF, t.a., 12 h; (iii) C₆₀, I₂, DBU, toluène, -15°C, 1 h.*

Cette méthodologie de synthèse hautement régiosélective a aussi été utilisée pour la préparation de tris-adduits *e,e,e* optiquement pur. Pour cela des diols optiquement purs ont été utilisés selon les mêmes conditions de réaction. La différence par rapport à la synthèse des tris-adduits présentée précédemment est que l'on forme un mélange de

diastéréoisomères et non plus un mélange d'énantiomères. La différence de polarité entre ces diastéréoisomères permet leur séparation par une chromatographie sur colonne de silice classique. L'hydrolyse des esters maloniques a finalement conduit à l'obtention de tris-adduits *e,e,e* optiquement purs et comportant 6 fonctions acides carboxyliques (Figure 7).

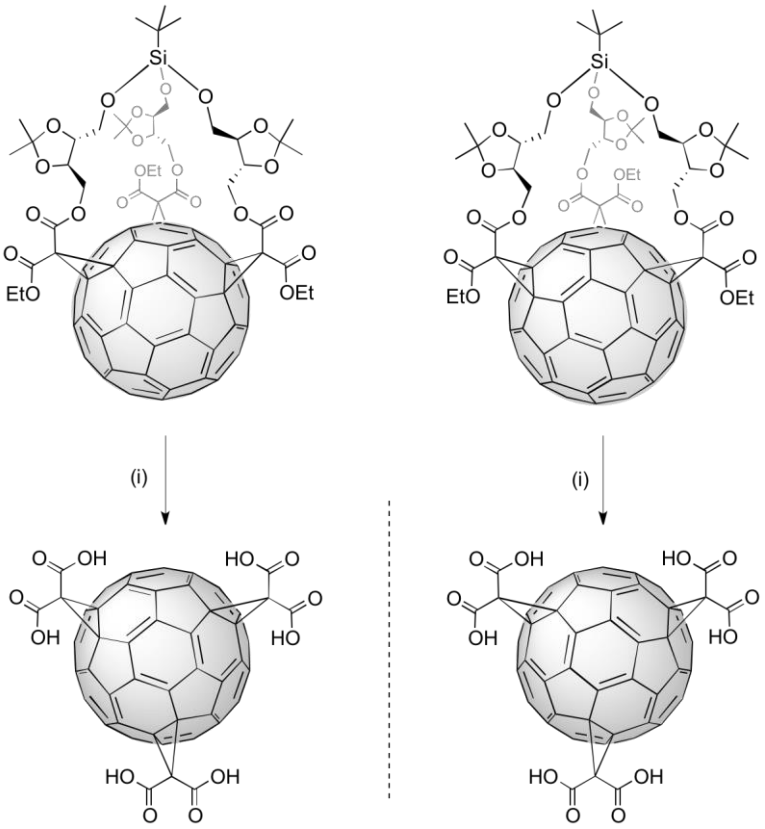

Figure 7: ***Réactifs et conditions*** *: (i)* PhMe, MeOH, NaH, 60 °C.

Cette stratégie « tête directrice » fournit un accès rapide, simple, régio- et stéréo-sélectif à des tris-adduits *e,e,e* approprié à la formation d'hexa-adduits d'ordre d'addition octaédrique. La synthèse des synthons hexa-adduits multifonctionnels a dès lors pu être entreprise.

Dans le but d'avoir des synthons C_{60} hexa-adduits les plus fonctionnalisables possibles, une modification de la chaîne latérale des malonates a été effectuée dans un premier temps (Figure 8). La transformation des synthons bis- et tris-adduits a ensuite été effectué de manière à permettre deux réactions « click » successives après la formation de l'hexa-adduits de C_{60}. Au total, trois synthons « cliquable » d'hexa-adduits mixtes de C_{60} ont été préparé. Par deux réactions « click » successives, l'introduction de deux types de fonctions différentes à la périphérie des hexa-adduits de C_{60} a été effectuée avec de très bons rendements (75-99%). Ces hexa-adduits de C_{60} proposent différents ratio de fonction « clické » (3:6 ; 6:6 et 4:8) dans deux zones distinctement prédéfini.

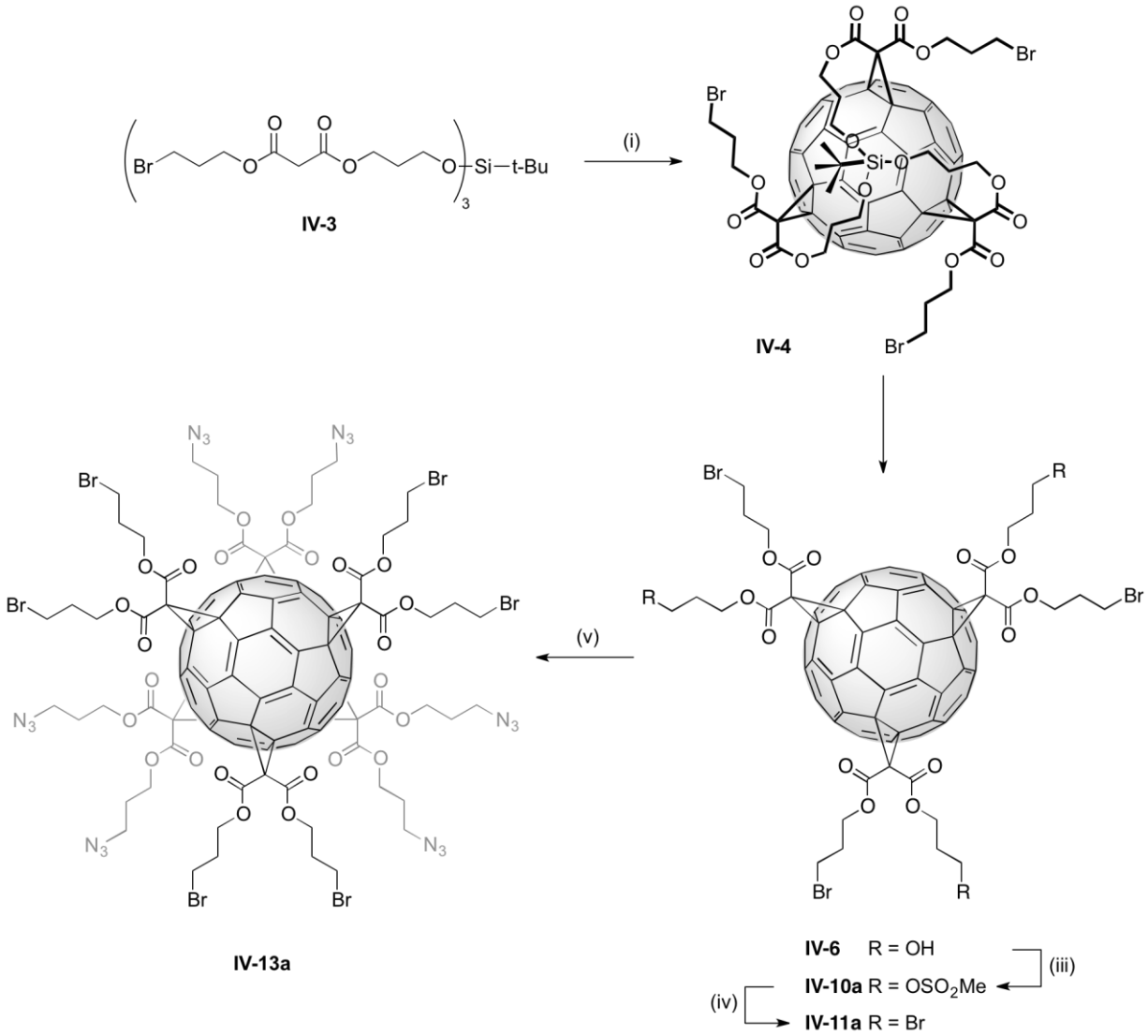

Figure 8: ***Réactifs et conditions*** *:* (i) C_{60}, I_2, DBU, PhMe, -15 °C, 1 h (13%); (ii) $BF_3.Et_2O$, CH_2Cl_2/MeCN 2:1, t.a., 12 h (86%). (iii) $MeSO_2Cl$, Et_3N, CH_2Cl_2, 0 °C, 2 h (86%); (iv) LiBr, THF, 60 °C, 12 h (83%); (v) Malonate azoture, CBr_4, DBU, PhMe, t.a., 12 h (42%).

La post-fonctionnalisation des fonctions alcools du synthon tris-adduit triol (**IV-6**) peut aussi être effectuée par une réaction d'estérification. Cela permet une différenciation supplémentaire des types de fonctions à la périphérie des hexa-adduits (Figure 9). C'est ainsi qu'un troisième hexa-adduits [3:3]-(3:9) à deux types de fonctions a pu être obtenu. Cette méthodologie a ensuite été étendue à la synthèse d'hexa-adduits à trois types de fonctions. Par une réaction d'estérification suivie de deux réactions « click », la post-fonctionnalisation d'un quatrième hexa-adduit [3:3]-(3:3:6) a été achevée. La formation de trois hexa-adduits [3:3] structurellement différent montre la polyvalence de notre méthodologie. Il est aussi à noter que tous les hexa-adduits présentés dans ce travail ont été synthétisé avec un contrôle de la régiochimie et de la stéréochimie, définissant des zones distinctes de fonctionnalités (Figure 9).

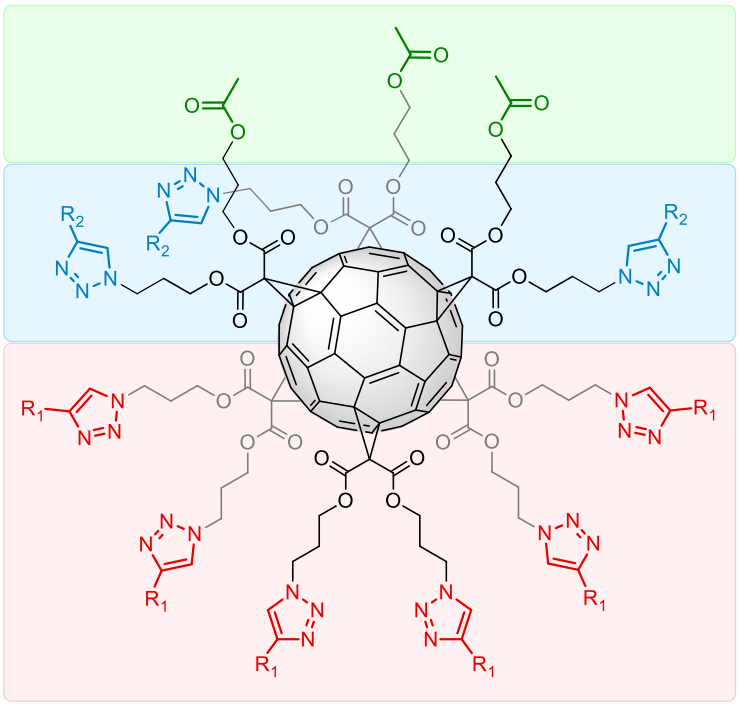

Figure 9: Illustration des trois de distinctes de fonctionnalités de l'hexa-adduit [3:3]-(3:3:6).

A partir des synthons d'hexa-adduits mixtes de C_{60} développés précédemment, l'élaboration d'édifices hyperfonctionnels comportant plusieurs hexa-adduits de C_{60} autour d'un hexa-adduit de C_{60} central a été effectuée.

Dans un premier temps c'est les synthèses de dérivés tri-, tétra- et penta-fullerènes qui ont été réalisées (Figure 10). Pour des raisons d'accessibilité à ces systèmes hyperfonctionnels, un espaceur comportant deux fonctions alcynes vrai à ses extrémités a dû être préparé, afin de pouvoir relier les hexa-adduits périphériques à l'hexa-adduit central. L'utilisation de la cycloaddition 1,3-dipolaire de type Huisgen a permis l'obtention de ces dérivés tri-, tétra- et penta-fullerènes avec de bon rendements. Il est à noter que ces dérivés comportent deux sortes de fonctions, celles de l'hexa-adduit central et celles des hexa-adduits périphériques.

Dans la continuité de ces résultats, un « mégaball » mixte a aussi été préparé (Figure 11). Ce dernier a été préparé à partir d'un hexa-adduit du C_{60} de type [2:4] comme cœur dendritique. Cet hexa-adduit central est fonctionnalisé par deux réactions successives de cycloaddition 1,3-dipolaire de type Huisgen avec des hexa-adduits de C_{60} fonctionnalisés par deux types de fonctions. La première réaction « click » introduit 80 unités de la fonction 1 répartis uniformément sur 8 hexa-adduits périphériques. La deuxième réaction « click » introduit quant à elle 40 unités de la fonction 2. Le mégaball mixte ainsi formé comporte au total 120 fonctions de deux types à sa périphérie.

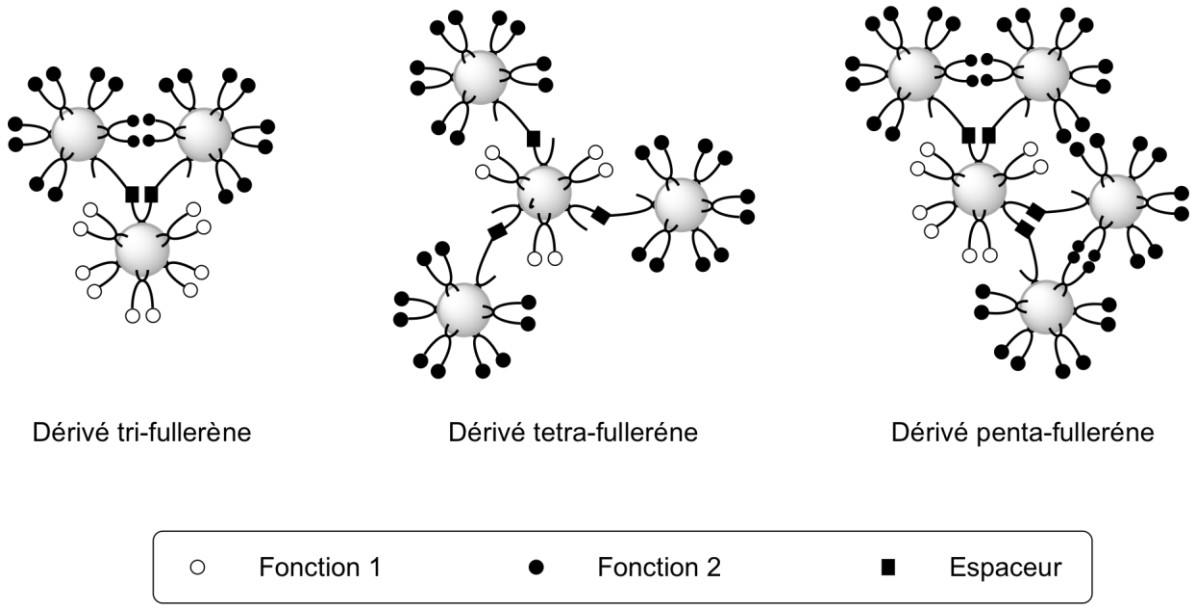

Figure 10: Edifices hyperfonctionnels préparés par assemblage d'hexa-adduits de C_{60}.

Conclusion.

Dans un premier temps, la bis- et tris-fonctionnalisation du C_{60} a été effectuée par une approche macrocyclique. Différents bis- et tris-adduits du C_{60} ont été obtenus avec de bonnes régioselectivités. La régiochimie de notre méthodologie est gouvernée par la taille des macrocycles et par la présence de groupes silylés au sein de la structure des macrocycles. Les dérivés polyols obtenus par déprotection des groupes silylés ouvrent de nouvelles perspectives pour la post-fonctionnalisation de multi-adduits de C_{60}.

Dans un deuxième temps, la tris-fonctionnalisation du C_{60} a été effectué par une approche « tête directrice ». Par cette approche, un accès rapide, simple, régio- et stéréo-sélectif à des tris-adduits *e,e,e* approprié à la formation d'hexa-adduits d'ordre d'addition octaédrique a été obtenu. La synthèse et la séparation de tris-adduits *e,e,e* optiquement purs ont également été réalisées.

A partir de nos méthodologies de synthèse de bis- et tris-adduits de C_{60}, trois synthons d'hexa-adduits mixtes de C_{60} ont été préparés. La post-fonctionnalisation de ces synthons a été effectuée par réaction de cycloaddition 1,3-dipolaire de type *Huisgen* mais aussi par réaction d'estérification, afin d'obtenir des hexa-adduits de C_{60} multifonctionnels avec debons rendements. Le contrôle de la régio- et stéréochimie de notre méthodologie permet de définir jusqu'à trois zones distinctes comportant chacune des fonctions différentes. La post-fonctionnalisation des synthons par chimie « click » donne accès à la préparation contrôlée de nouveaux nanomatériaux globulaires multifonctionnels.

Dans la dernière partie de ce travail de thèse, la méthodologie de synthèse d'hexa-adduits de C_{60} multifonctionnels a été mise à profit pour l'élaboration d'édifices hyperfonctionnels comportant plusieurs hexa-adduits de C_{60} autour d'un hexa-adduit de C_{60}

central. Cette approche dendritique est une voie d'accès à l'élaboration contrôlée de nano-édifices multifonctionnels.

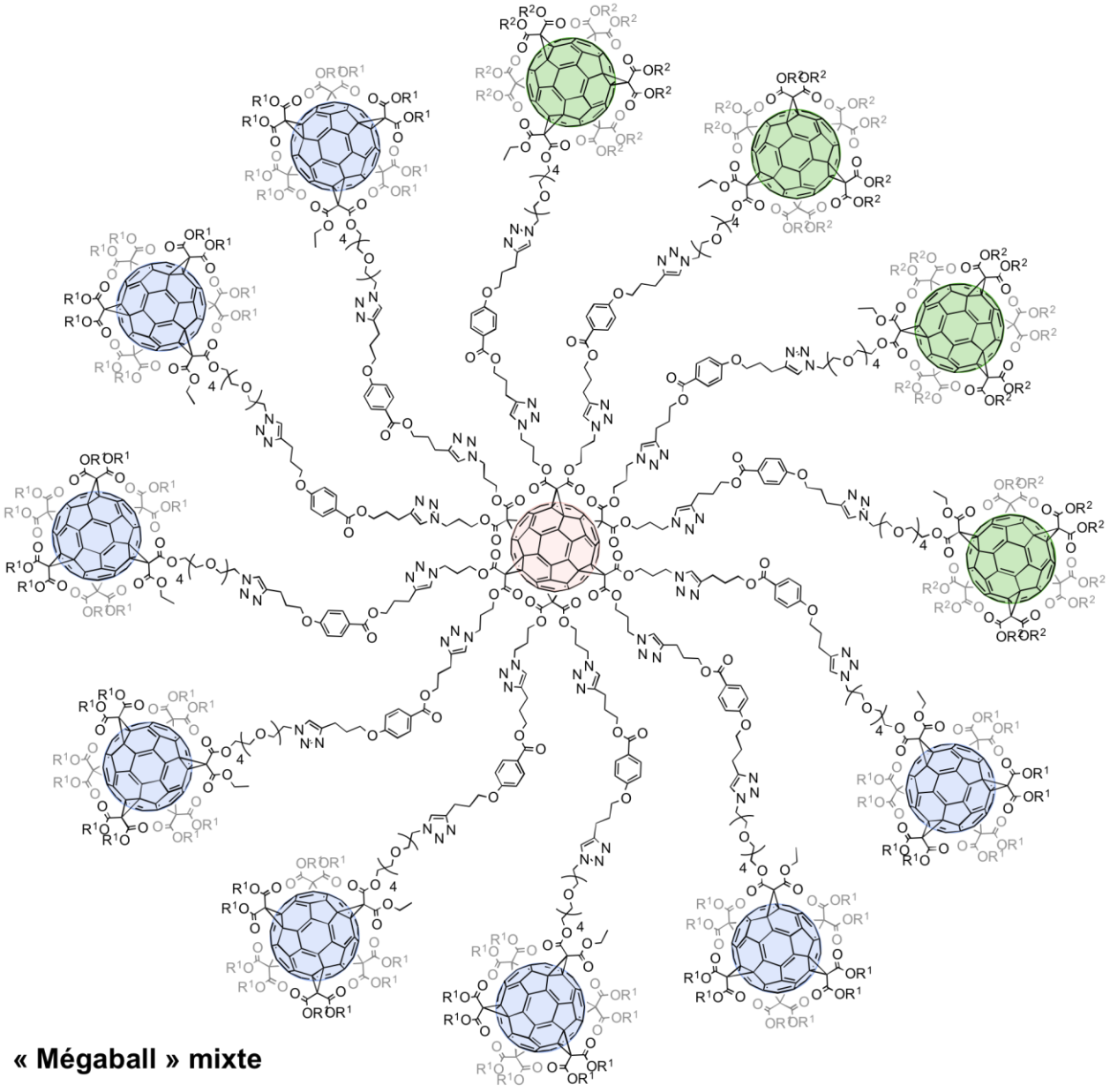

Figure 11: Structure du mégaball mixte comportant au total 120 fonctions de deux types à sa périphérie.

Références :

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Chapter I : General introduction.

1. Generalities.

1.1 Discovery of a new allotropic form of carbon.

Fullerenes are caged molecules exclusively constituted by carbon. After diamond and graphite, they represent the third allotropic form of carbon. The history of this family of compounds began in 1966 when D. E. H. Jones proposed for the first time the idea of large hollow carbon cages[1], later known as giant fullerenes. In the same year, a premise of the structure of fullerenes was drawn by the synthesis of corannulene by G. Lawton et al.[2] Stimulated by the discovery of corannulene, Osawa proposed in 1970 a truncated icosahedral structure for an hypothetical [C_{60}-I_h]fullerene but this structure remained theoretical for many years.[3] The first carbon clusters were produced in 1984 by laser vaporization of graphite. Time-of-flight mass spectrometry analysis revealed that only carbon clusters C_n with an even number and n = 40-190 could be observed.[4] However no specific structure could be proposed for the observed carbon clusters despite the fact that C_{60} was among them. The breakthrough occurred one year later (1985) when Kroto, Curl and Smalley published a Nature article[5] in which they described the production of fullerenes using the same technic.[4] C_{60} and C_{70} were the most abundant fullerenes forms (Figure I-1-a). By optimizing the experimental conditions, they were able to predominantly produce clusters constituted by 60 C atoms (Figure I-1-b). They rationalized these results to a better stability of the C_{60} cluster and proposed a truncated icosahedral structure to explain this extra-stability.

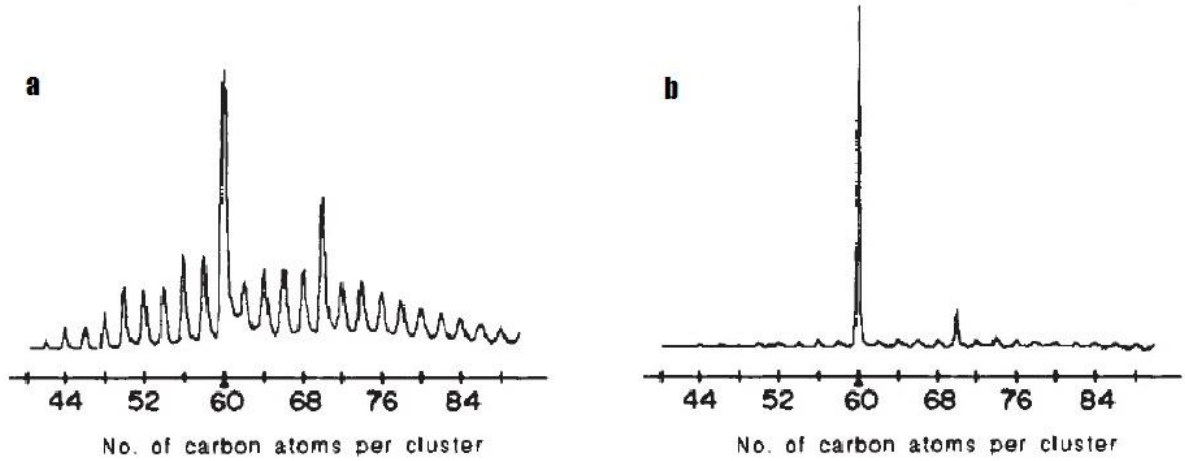


Figure I-1 : "Time of flight mass spectra of carbon clusters prepared by laser vaporization of graphite and cooled in a supersonic beam. a) The spectrum was obtained when roughly 760 torr helium was present over the graphite target at the time of laser vaporization. b) The spectrum was obtained by maximizing these cluster thermalization and cluster-cluster reactions."[5]

A new allotropic form of carbon was born. The most abundant fullerene is C_{60} also called buckminsterfullerene in reference of the geodesic domes created by the architect Buckminster Fuller. After the discovery of other clusters (e.g. C_{70}, C_{76}, C_{80} and C_{82}) the shortest name "Fullerene" was kept to describe this family of compounds.

Two important points contributed to the development of fullerene chemistry: (i) unlike graphite or diamond that are polymeric and insoluble, fullerenes are well-defined molecules soluble in various organic solvents and (ii) their gram-scale production developed by Krätshmer, Huffman et al. in 1990 made them available to the scientific community.[6]

With the development of fullerene chemistry a unified nomenclature was needed. The International Union of Pure and Applied Chemistry (IUPAC) recommended in 2002 the use of (C_{60}-I_h)[5,6]fullerene as systematic name. The number of carbon atoms and the symmetry group of the cluster and the ring size (square bracketed number) in the fullerene are indicated.[7] The recommended systematic numbering of C_{60} is shown in Figure I-2.

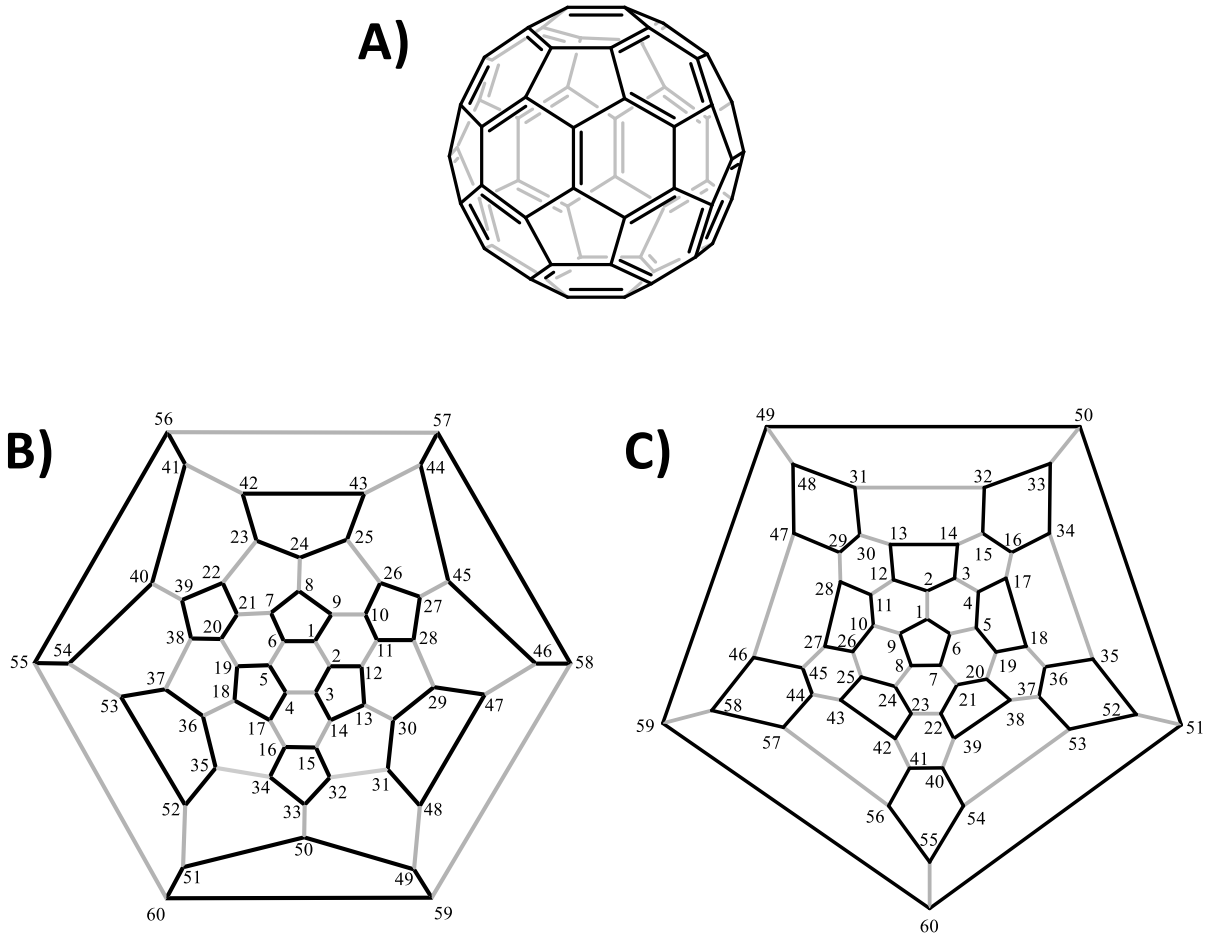


Figure I-2 : Schematic representations of C_{60}. A) Lewis structure; B) Schlegel diagram (hexagon centered) with systematic numbering. ; C) Schlegel diagram (pentagon centered) with systematic numbering.

1.2 Production and Purification.

The macroscopic production of C_{60} was first achieved in 1990 by Kratschmer et al by resistive heating of graphite.[6] In a bell jar under an atmosphere of ~133 mbar of helium, they connected two graphite rods in close contact to two copper electrodes (Figure I-3). For

producing soot, an electric current was applied to evaporate the graphite rods by resistive heating. Purification of the resulting soot afforded a fullerene yield of 5-10%.

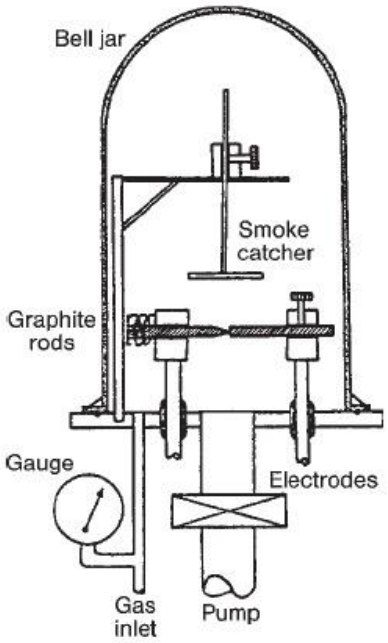


Figure I-3 : Fullerenes production system used by Krätschmer et. al. (from "Fullerenes Chemistry and Reaction", Andreas Hirsch and Michael Brettreich, Willey-VCH, 2002).

Some others technics more or less efficient were also developed to produce fullerenes such as arc heating of graphite[8], solar generators[9] or inductive heating of graphite.[10]

Currently, the most important technic to produce fullerenes is by combustion in optimized sooting flames.[11–13] Fullerenes in hydrocarbon flames were first revealed in 1987 by mass spectrometry.[14] Continuous optimization of this technic allowed later industrial production of fullerenes.

Isolation of fullerenes from soot can be achieved by extraction[6] or by sublimation[15]. Originally purified from soot by extraction in benzene, only a mixture of fullerenes was recovered.[6] Several methods were then developed to separate fullerenes implying especially chromatography technics.[16] A common method is the use of chromatography on alumina, but it can require a big amount of alumina and solvent.[17,18] The use of Soxhlet-chromatography has considerably improved the efficiency of the separation on alumina.[19,20] Another efficient and inexpensive method is chromatography on mixtures of charcoal and silica gel.[21] Instead of chromatography, fractional crystallization can also be used to purify C_{60}.[22]

The development of production and purification methods has allowed industrial scale production of fullerenes. Companies such as *Frontier Carbon Corporation* have produced several tons of fullerenes using an industrial process based on combustion in sooting flames. Concurrently, the cost of fullerenes have considerably decreased from about 5000 $/g at the origin to an affordable price of 20-25 $/g (for C_{60}) nowadays.

1.3 Fullerene C_{60}: Structure and Properties.

1.3.1 Structure

C_{60} Buckminsterfullerene is the smallest stable fullerene and the most abundant. As all fullerenes, it has a ball shape structure and is formed by 20 hexagons and 12 pentagons. Even before its discovery, a truncated icosahedral structure was proposed[3]. Its experimental discovery[5] highlighted the "extra stability" of C_{60}. It has been demonstrated that the more favorable and stable structure is an arrangement with all twelve pentagons isolated by hexagons, leading to the "Isolated Pentagon Rule" (IPR)[23,24]. The juxtaposition of two pentagons increases the strain energy and destabilizes the structure. On the other hand, more the structure is symmetrical and more the strain is uniformly distributed. The structure of choice was therefore a truncated icosahedron. Theoretical calculations were in agreement with this structure[25,26] and it was experimentally confirmed by several technics[27–30]. In particular, the ^{13}C NMR spectrum of C_{60} showing only one signal for the 60 equivalent carbon atoms was in agreement with its high symmetry (I_h).

The diameter of [C_{60}-I_h]fullerene is 10.34 Å if the π electron cloud is considered. At room temperature the C_{60} molecules adopt a face-centered cubic (cfc) organization[28]. The spherical shape of C_{60} implies a pyramidalization of the sp^2 carbons. A consequence of this geometry is a weak π orbital overlap and no real delocalization of the π-electrons preventing a "superaromaticity". Two different bonds can be distinguished (Figure I-4). A [5,6] bond of 1.45 Å at the junction of a pentagon and a hexagon, and a [6,6] bond of 1.38 Å at the junction of two hexagons. The [5,6] bond has a simple bond character and the [6,6] bond has a double bond character. The reactivity of the molecule is centered on this last bond.

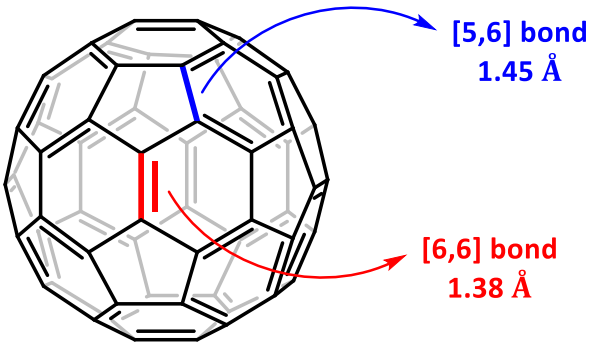


Figure I-4 : Representation of C_{60} and its two different type of bonds.

1.3.2 Solubility

Solubility is an important parameter to take into account for the chemical transformation of compounds. Systematic studies have highlighted the solubility of C_{60} in a large variety of solvents (Table I-1)[31]. The aromatic solvents are the best to solubilize C_{60}, especially naphthalene derivatives. The most used solvents for fullerene chemistry are 1,2-dichlorobenzene and toluene with a solubility of 27 and 2.8 mg/mL respectively. C_{60} is not

soluble in polar solvents and only slightly soluble in alkanes or haloakanes. The low solubility of C_{60} is related to strong π-π interactions and its tendency to aggregate. Even in the best solvent, 1-chloronaphthalene, C_{60} is only moderately soluble (51 mg/mL).

Table I-1 : Solubility of C_{60} in various solvents

Solvent	[C_{60}], mg/mL	mole fraction (x10^4)
alkanes		
n-pentane	0,005	0,008
n-hexane	0,043	0,073
cyclohexane	0,036	0,059
n-decane	0,071	0,19
decalins	4,6	9,8
haloalkanes		
dichloromethane	0,26	0,27
chloroform	0,16	0,22
carbon tetrachloride	0,32	0,4
1,1,2,2-tetrachloroethane	5,3	7,7
polars		
methanol	0,000	0,000
ethanol	0,001	0,001
acetone	0,001	0,001
acetonitrile	0,000	0,000
benzenes		
benzene	1,7	2,1
toluene	2,8	4
benzonitrile	0,41	0,71
chlorobenzene	7	9,9
1,2-dichlorobenzene	27	53
1,2,4-trichlorobenzene	8,5	15
naphthalenes		
1-methylnaphthalene	33	68
1-phenylnaphthalene	50	131
1-chloronaphthalene	51	97
miscellaneous		
carbon disulfide	7,9	6,6
tetrahydrofuran	0,000	0,000
pyridine	0,89	0,99

1.3.3 Photophysical properties.

The photophysical studies of C_{60} in solution have revealed some of its remarkable properties that can most certainly be attributed to its unique geometry[32]. Only a very weak fluorescence was observed for C_{60}[33]. This is due to a nearly quantitative InterSystem Crossing (ISC) from the Singlet excited state to the Triplet excited state. Despite a very high Triplet

quantum yield (ΦT =0.96), no phosphorescence could be observed. The deactivation of the Triplet excited states occurs *via* non-radiative deactivation and/or bimolecular quenching depending on the experimental conditions. In the presence of molecular oxygen, very efficient quenching by O_2 leading to $^1O_2$* occurs. On the other hand, electron transfer is observed in the presence of donor molecules. These deactivation processes are important for various applications in material science[34,35] or in biology[36]. The absorption spectrum of C_{60} is characterized by a strong absorption in UV with representative bands at 211 nm, 256 nm and 328 nm (Figure I-5). The purple color of C_{60} is due to forbidden transitions between 410 and 620 nm[17].

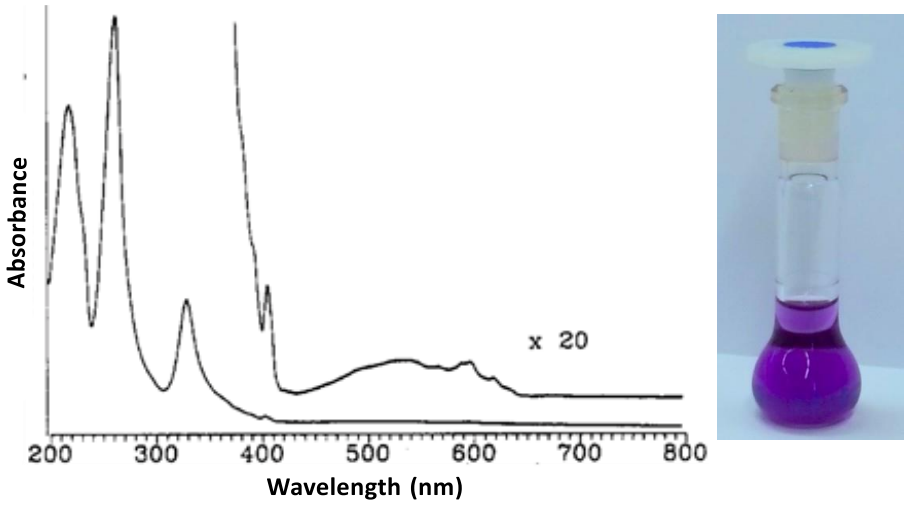


Figure I-5 : Absorption spectrum of C_{60} in n-hexane.

1.3.4 Electrochemical properties.

Huckel molecular orbital (HMO) calculations shows a triply degenerated LUMO orbitals of low energy.[37] In theory C_{60} should be able to accept up to 6 electrons. Six mono-electronic reversible reduction of C_{60} were effectively reported in 1992 by Echegoyen et al.[38] The potentials measured for the six electron reductions relative to Fc/Fc^+ were -0.98, -1.37, -1.87, -2.35, -2.85, -3.26 V in CH_3CN/toluene at -10 °C.[38] According to the authors, C_{60}^{5-} appears to be stable in solution at room temperature and C_{60}^{6-} at -10 °C.

If the reduction of C_{60} is relatively easy, its oxidation is more difficult and requires strict conditions. Oxidation of C_{60} up to C_{60}^{3+} was reported in 2003 by Bruno et al.[39] To be able to generate C_{60}^{3+} species they performed CV experiments at -55 °C with ultra-dry CH_2Cl_2 and $TBAAsF_6$ as electrolytes which has a high oxidation resistance and low nucleophilicity. C_{60}^{2+} and C_{60}^{3+} are unstable and react easily to form electroactive materials.

2. Reactivity of C_{60} and its derivatives.

2.1 Introduction.

The unique geometry of [C_{60}-I_h]Buckminsterfullerene is at the basis of its remarkable reactivity made from strain and electronic arguments. The spherical shape of C_{60} implies a pyramidalization of the carbon atoms. Deviation from planarity modifies the hybridization of the sp^2 σ and π orbitals. It was calculated by π orbital axis vector (POAV) analysis that σ orbitals have a $sp^{2.278}$ hybridization and π orbitals a $s^{0.09}p$ hybridization approximately.[37] This rehybridization disables the aromaticity due to unsuitable orbital geometry and electronic effects. In addition, it also impacts π* orbitals which are lower in energy and exhibit a "considerable s character".[40] With a low lying LUMO level, C_{60} can be easily reduced and be considered as an electronegative molecule. Its electron acceptor character makes it suitable for addition and redox reactions. Moreover, the strain relief when going from a "sp^2" to a sp^3 C atom is a driving force for addition and redox reactions.

It is also interesting to consider the electronic structures of C_{60} in order to explain some structural aspects and the regiochemistry of reactions on C_{60}. As seen before in 1.3.1, there is an alternating of bond length. The reason of this alternating is found in the filling of the angular momentum states for an icosahedral structure by the 60 π-electrons. The angular momentum l = 5 level is the last filled level but it is only partially filled by the 10 remaining π-electrons (50 π-electrons completely fill up through l = 4 level and l = 5 level can have up to 22 electrons)[40,41]. The frontier orbitals are deduced from the irreducible representation of this l = 5 level, from the lowest to the highest in energy, $H_u + T_{1u} + T_{2u}$ for an icosahedral symmetry. The H_u level which correspond to the HOMO is five-fold degenerated and accept the 10 remaining π-electrons. The T_{1u} level is three-fold degenerated and correspond to the LUMO level. It is the filling of HOMO and LUMO levels who have a direct impact on the structure of C_{60}. For the HOMO, the bonding interactions are located preferably at the [6,6] junctions and the anti-bonding interactions at the [5,6] junctions[40] explaining the bond alternation. As for the low lying LUMO level with anti-bonding interactions at the [6,6] junctions[40], it explained the regiochemistry of addition reactions on C_{60} (see 2.2).

2.2 Addition and cycloaddition reactions.

The reactivity of C_{60} can be assimilated to a strained electron deficient polyolefin and is centered on the [6,6] bonds which can react easily with nucleophilic reagents. C_{60} as a good dienophile and dipolarophile can undergo cycloaddition reactions.

The properties of C_{60} have generated a huge interest. However, its poor solubility has limited its utilization. The increase of solubility by functionalizing the C_{60} sphere have greatly contributed to the development of fullerene chemistry. In addition, the main properties of the C_{60} are kept in mono-adduct derivatives. In this context, a lot of nucleophilic (e.g. Bingel

reactions[42], Grignard reactions[43], Organolithium reactions[43]), radical[44] and carbene[45] additions have been developed in order to functionalize C_{60}. For the nucleophilic addition, the nucleophilic intermediate NuC_{60}^- can be quenched by the addition of an electrophile E^+. Addition preferably occurs at 1,2 positions for non-bulky reagents and at 1,4 positions for bulky reagents (Figure I-6).[46,47] An original cyclopentadiene motif can be also formed under specific conditions (Figure I-6).[48–50]

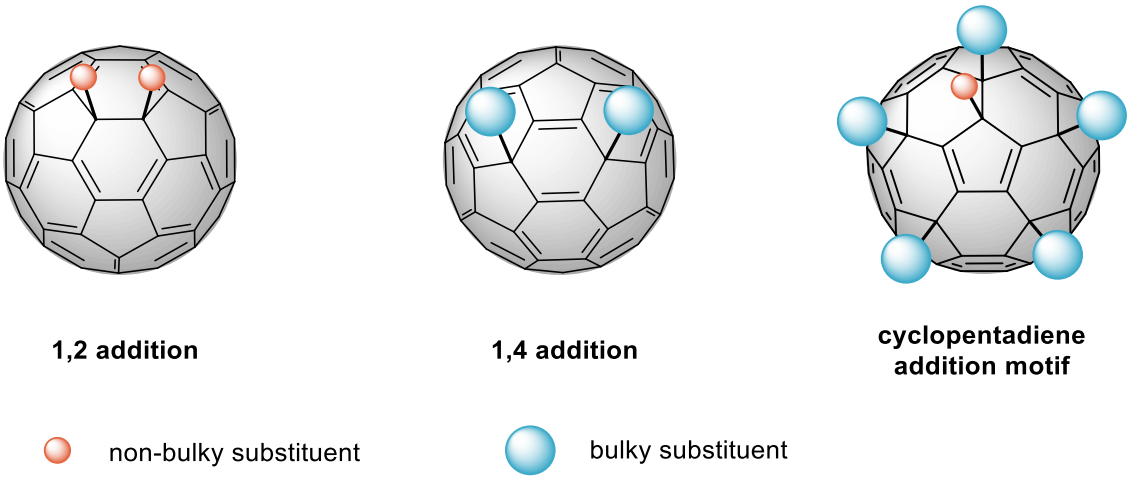


Figure I-6 : Different modes of addition of nucleophilic or radical reagents on C_{60}.

A large number of cycloadditions (e.g. Diels-Alder reactions) and dipolar cycloadditions (e.g. azomethine ylides reactions[51], diazo reactions[52]) have been also published. Cycloaddition always occurs on the [6,6] bond. Nonetheless in the case of diazo reactions, a rearrangement occurs leading to methanofullerenes with a [6,6]-closed isomerism or a [6,5]-open isomerism (Figure I-7) depending on the reaction conditions.[52,53]

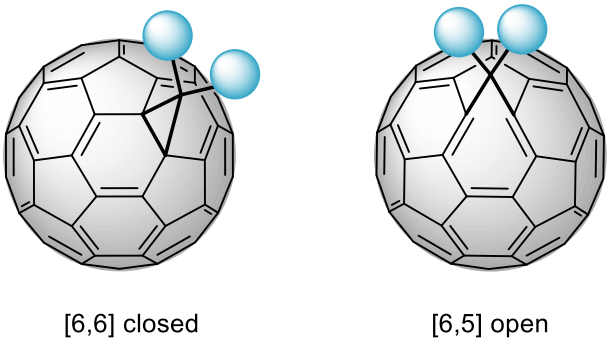


Figure I-7 : Methanofullerenes with a [6,6]-closed isomerism or a [6,5]-open isomerism.

According to the literature, the Bingel and Diels-Alder reactions are the most used conditions for the mutli-functionalization of C_{60}. This is one of the reasons why the present manuscript is mainly focused on the Bingel reactions and in a lesser extend to Diels-Alder reactions.

Bingel reactions:

Discovered in 1993 by Carsten Bingel,[42] it is a nucleophilic addition of a α-halomalonate on C_{60} followed by a nucleophilic intra-molecular substitution that leads to a methanofullerene (Figure I-8). In the initial conditions, a α-halomalonate was used with sodium hydride (NaH) as base.[42] Later some conditions have been developed in order to generate the halogenomalonate *in-situ* with I_2[54] or CBr_4[55] and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base. The use of I_2 is more suitable for the synthesis of lower adducts (up to tris-adducts of C_{60}) and CBr_4 for higher adducts (e.g. hexa-adducts of C_{60}).

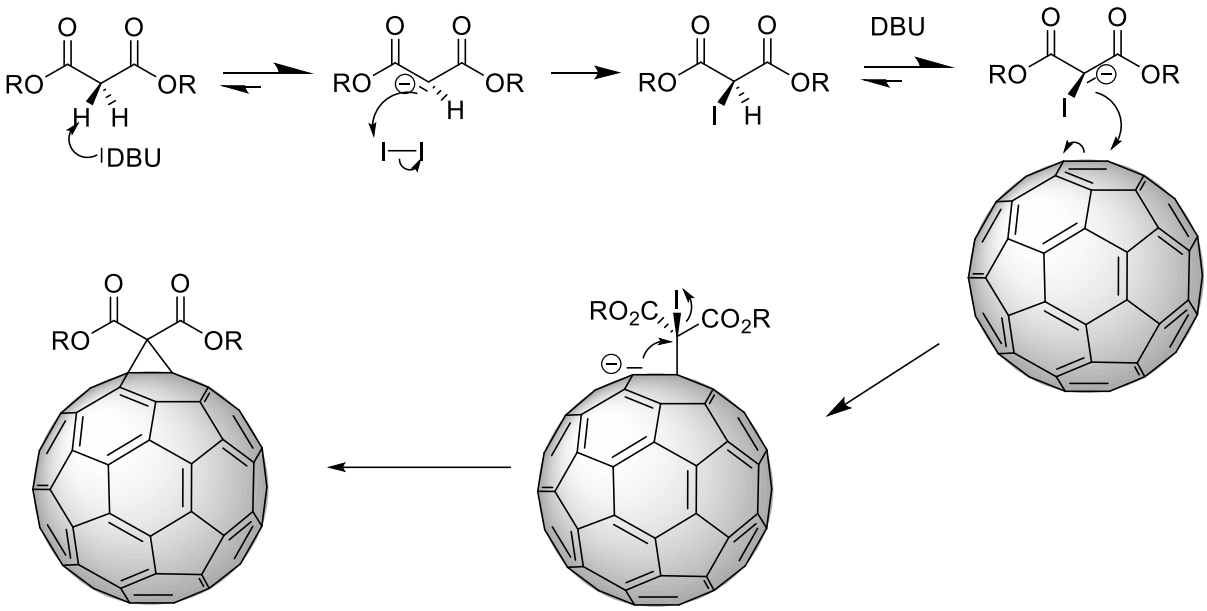


Figure I-8 : Bingel's reaction mechanism with in-situ halogenation.

Diels-Alder reactions:

The Diels-Alder reaction is a [4+2] cycloaddition between a diene and a dienophile. The earliest reported characterized products of a Diels-Alder reaction between a diene and C_{60} was in 1993.[43,56–58] An advantage of the use of Diels-Alder reactions for the functionalization of C_{60} is its reversibility. Diels-Alder adducts can be easily removed by retro-Diels-Alder reactions and thus act as an efficient directing group.[59]

2.3 Multi-functionalization of C_{60}.

2.3.1 Nomenclature.

The 30 double bonds of C_{60} are all equivalents. Therefore a mono-addition will lead to only one product. The remaining 29 double bonds can be energetically differentiated in to nine different sites. Addition of a second addend to a C_{2v}-symmetrical C60 mono-adduct can

in principle lead to nine different regioisomeric bis-addducts. Relative to the first addend, the second one can be located either in the same hemisphere (*cis*), in the opposite hemisphere (*trans*) or on the equatorial belt (*e*) (Figure I-9.).[60] For identical addends, a second attack onto the *e-edge* or *e-face* positions leads to identical products.

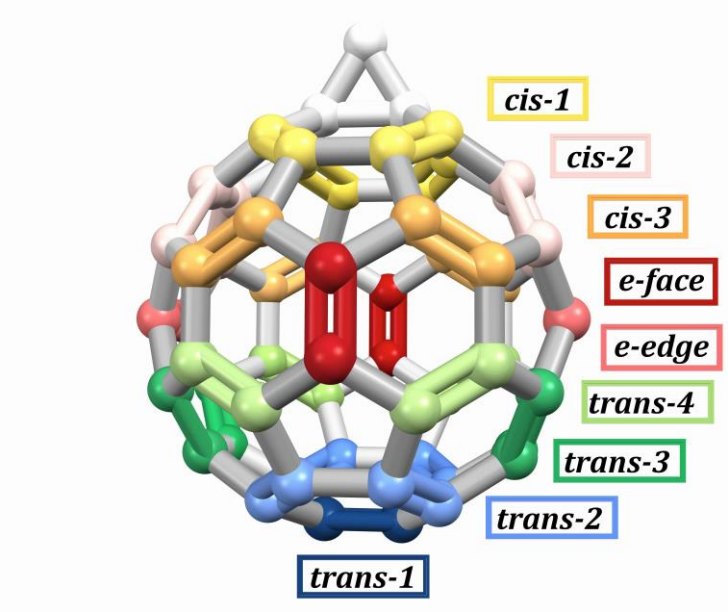
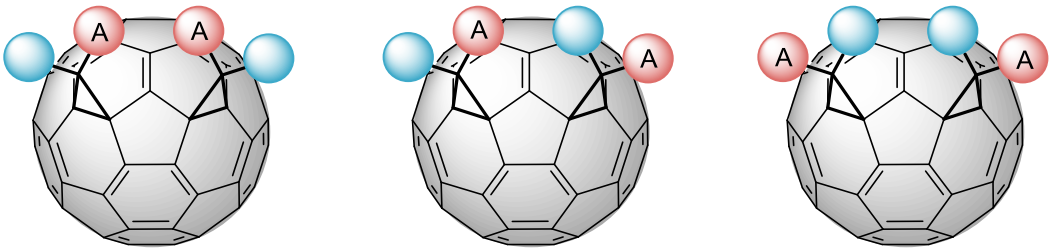


Figure I-9 : Nomenclature of double bonds relative to the first adduct.

In/out descriptor can also be needed, for macrocyclic or dissymmetric compounds, to indicate the direction of the substituents. When considering the substituents A in Figure I-10, there are three possible cases. In case 1 and 3, the two substituents A are together (in/in isomerism) or apart (out/out isomerism). In case 2, the two substituents are mixed (in/out isomerism) considering case 1 and 3.



in / in **1** *in / out* **2** *out / out* **3**

Figure I-10 : Representation of the In/Out Isomerism.

Multiple additions on C_{60} can also lead to chiral addition patterns. To indicate the absolute configuration of inherently chiral fullerene, stereodescriptors (^{f,s}C) and (^{f,s}A) ("f" = fullerene, "s" = systematic numbering, "C" = clockwise, "A" = anti-clockwise) are used. To

determine if it is (^{f,s}C) or (^{f,s}A), the systematic numbering of the adducts must be the smallest possible (Figure I-11).

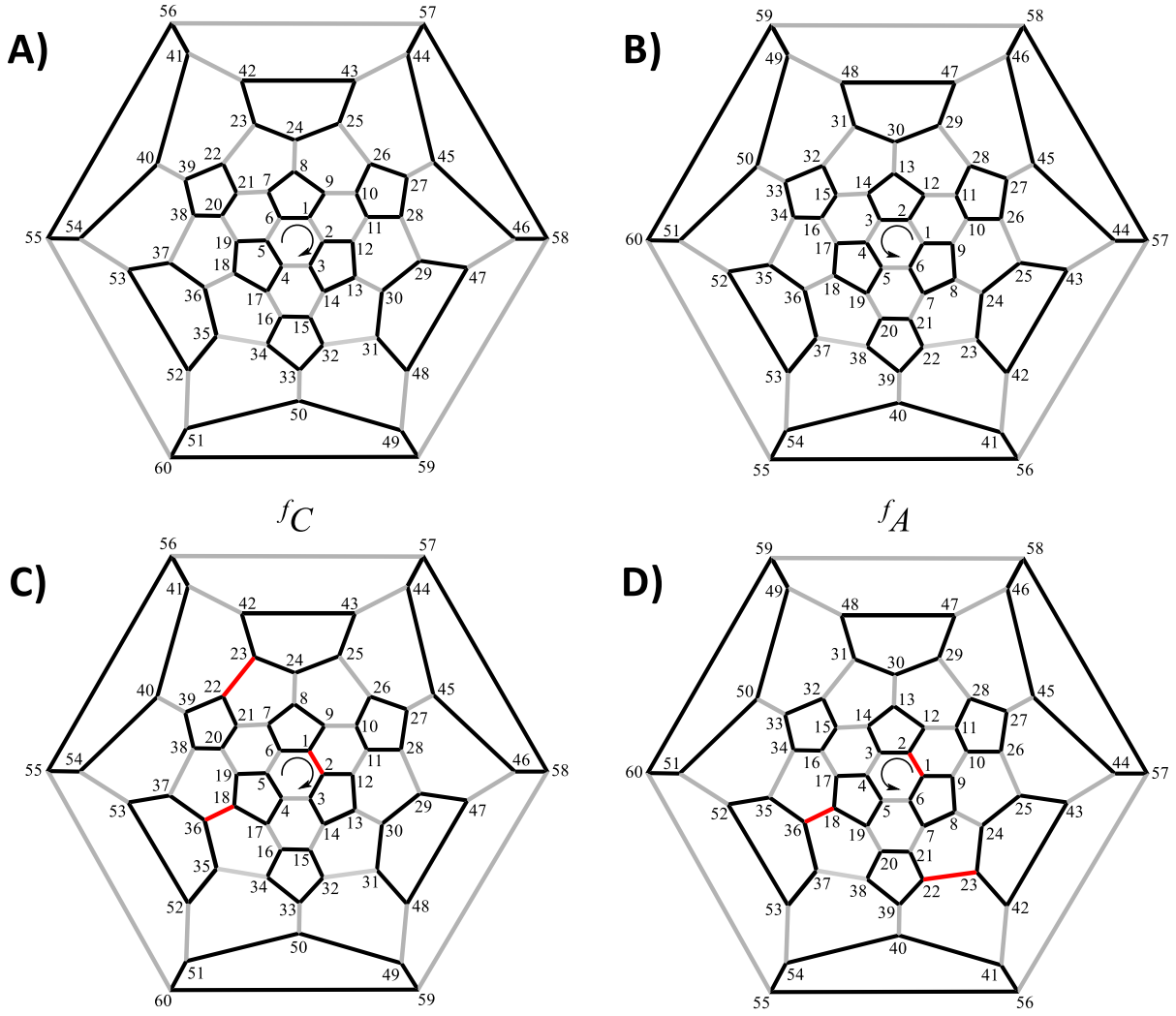


Figure I-11 : Clockwise (A) and Anti-clockwise (B) systematic numbering. C) Representation of ($^{f\text{-}1,2,18,22,23,36}$C) tris-adducts. D) Representation of ($^{f\text{-}1,2,18,22,23,36}$A) tris-adducts.

2.3.2 Symmetry of simple multi-adducts of C_{60}.

When multi-adducts of C_{60} are synthesized, different regioisomers can be formed. In this context, the symmetry of the formed multi-adduct is an important matter in order to attribute the addition pattern and to characterize each regioisomers. The symmetry of all the possible bis-adducts and selected tris- and hexa-adducts with equivalent malonates are given in Figure I-12.

^{13}C NMR analysis can be used to deduce the symmetry of multi-adducts of C_{60}. The important signals on ^{13}C NMR spectrum are signals related to the "C sp^2" of C_{60}.

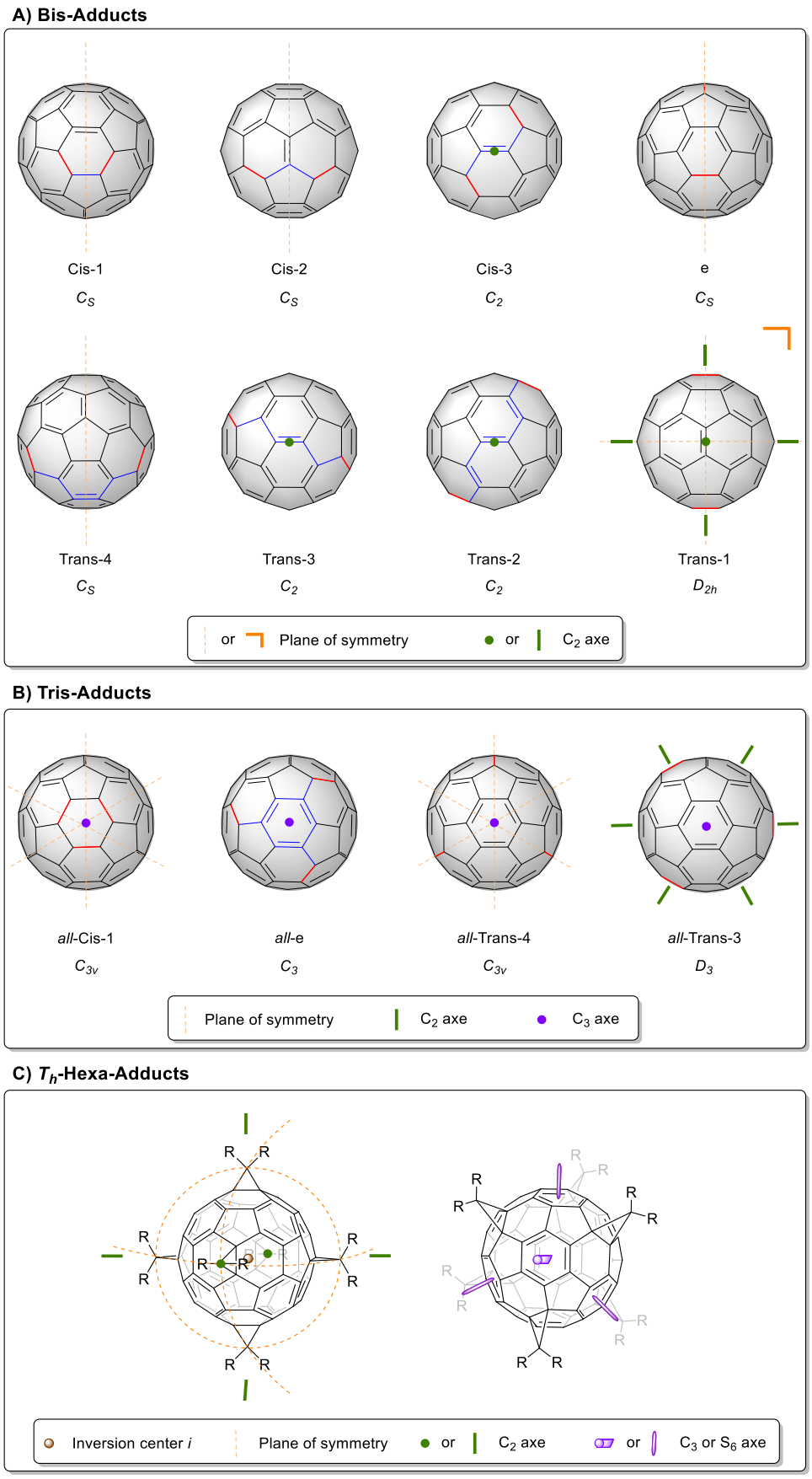
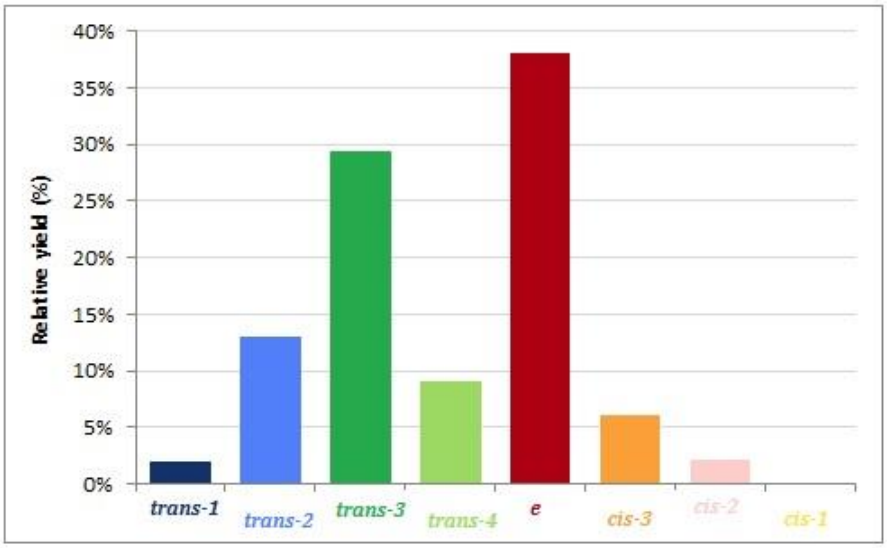


Figure I-12 : Representation of the symmetry of all the possible bis-adducts of C_{60}. Selected examples of tris- and hexa-adducts are also shown.

2.3.3 Regiochemistry of twofold additions.

The regiochemistry of twofold additions of malonates on C_{60} has been studied by Hirsch and coworkers.[60] Starting from the mono-adduct $C_{61}(COOEt)_2$, they isolated seven out of the eight theoretically possible regioisomers $C_{62}(COOEt)_4$. The assignment of each regioisomer was based on both the symmetry deduced from the NMR spectra and the order of elution (polarity) of each product. With the obtained results (Graph 1), an order of reactivity of the double bonds could be established. The *e* double bonds (e_{face} and e_{edge} are equivalent for the addition of identical symmetrical malonates) are the more reactive sites followed by the *trans-3* double bonds. In the case of addition of non-identical or dissymmetrical addends, a difference can be made between e_{face} and e_{edge} double bonds. The e_{edge} double bond is slightly more reactive than the e_{face} double bonds.[61,62] The order of reactivity of the other positions is *trans-2* > *trans-4* > *trans-1* > *cis-3* > *cis-2*. The *trans-1* position is more reactive than the *cis-3* and *cis-2* positions because one should consider the fact that there is only one trans-1 double bond for four double bonds for the *cis-3* or *cis-2* positions. Furthermore, cis positions are susceptible to steric hindrance effects. This is not the case for *e* and *trans* positions. *Cis-1* are not really the least reactive sites, in fact, it should be one of the more reactive positions.[61] In this particular case *cis-1* bis-adducts cannot be formed due to steric effects.



Graph 1 : Relative yields of the different regioisomers.

2.3.4 Multiple additions on C_{60}.

The extreme complexity of the multi-functionnalization of C_{60}, requires a good understanding of the reactivity of the multi-adducts of C_{60} and more particularly their regiochemistry. As seen in the previous paragraphs, 9 regioisomers can be formed for a twofold additon. This number increases to 46 regioisomers for a threefold addition. By a step-by-step procedure, the *e,e,e* tris-adducts (each addends are in a e position relative to each other) and the *trans-3, trans-3, trans-3* tris-adducts, starting from the *e* bis-adducts and the *trans-3* bis-adducts respectively, were the only ones isolated among the multitude of formed

regioisomers.[60] In the continuity of this work, the Hirsch' group has synthesized the T_h-symmetrical hexa-adducts following the same procedure.[62] Starting from the *e,e,e* tris-adducts, only two tetra-adducts were formed. For the fifth and sixth additions, only one penta-adducts and hexa-adducts were formed. Based on this step-by-step synthesis of the T_h-symmetrical hexa-adducts from the mono-adducts (Figure I-13), some important points can be deduced:

- *e* and *trans-3* positions are the preferred reactions sites.
- The regioselectivity is increasing with the degree of addition. The second and third additions have a weak regioselectivity. The fourth and fifth additions are more regioselective and the sixth is totally regioselective.
- This last point can lead to a general rule that says: "*the more addends bound in e positions to a certain double bond, the more favorable is an attack of this bond*".[62]
- In opposition to the regioselectivity, the reactivity of the C_{60} sphere is decreasing with each subsequent addition.

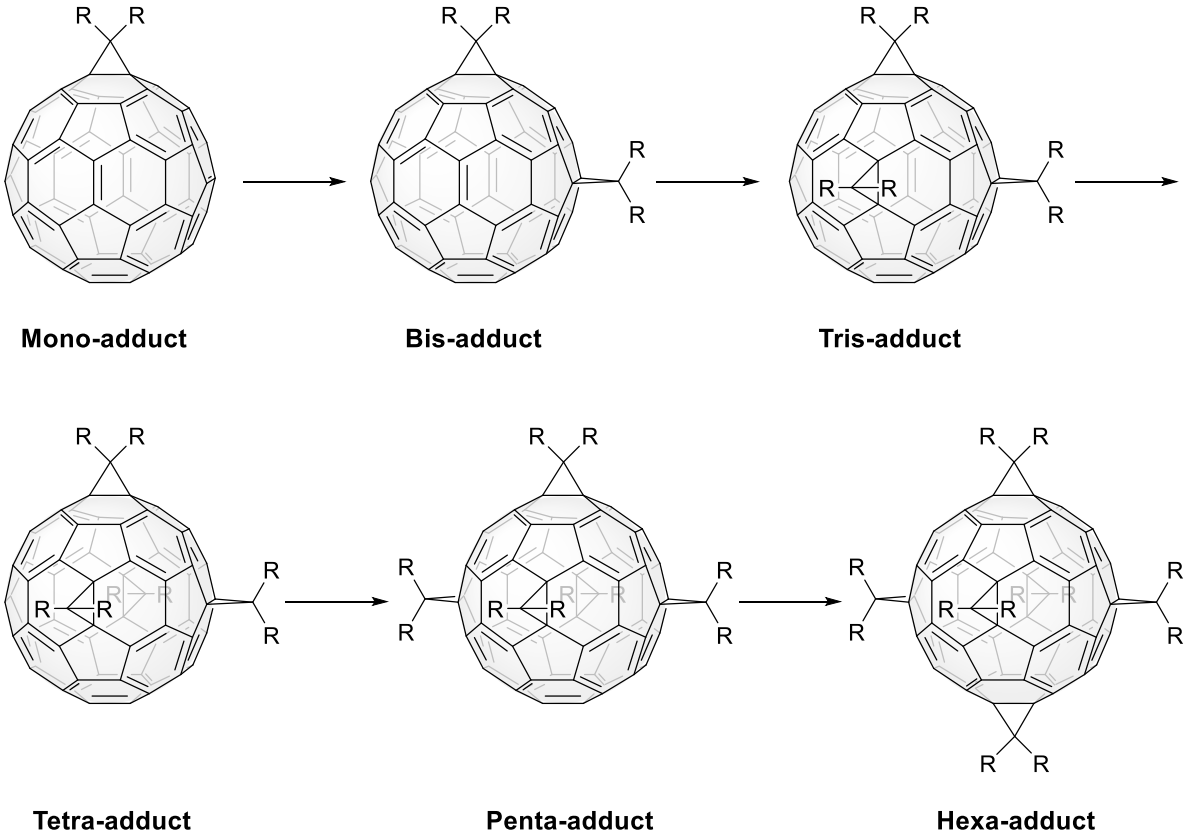


Figure I-13 : Step-by-step synthesis of the T_h*-symmetrical hexa-adducts from the mono-adducts.*

For the formation of T_h-symmetrical hexa-adducts in a one-step synthesis, the high reactivity of e double bonds is definitely an asset but yields are substantially increased with the activation of the *e* positions. The first published example of T_h-hexa-substituted C_{60} has highlighted the importance of the addition reversibility of the addends for the activation of the *e* positions.[63] Malone and coworkers were able to obtain a T_h-hexa-substituted platinium

derivatives $\{[(C_2H_5)_3P]_2Pt\}_6C_{60}$ with an excellent yield of 88% by reversible multiple additions of a Platinum complex $[(C_2H_5)_3P]_4Pt$ on C_{60}. Unfortunately, the addition of malonates on C_{60} are irreversible. In order to have a relatively good yield for the formation of T_h-symmetrical hexa-adducts, the activation of e positions must be done by an auxiliary reagent which add reversibly on C_{60}. In search of such an auxiliary reagent, Hirsch and coworkers have developed conditions with 9,10-dimethylanthracene (DMA).[59] DMA adds reversibly at room temperature to form Diels-Alder adducts $C_{60}(DMA)_n$, acting as templates for the activation of the e positions. Yields are considerably increased with template activation than without.[55,59] Even more efficient conditions have been further developed by Sun and coworkers in 2005.[64] They modified the conditions developed by Hirsch's group[55] with the use of a large excess of CBr_4 (5-10 times more). Under these conditions, they were able to form hexa-adducts from larger malonate reagants. Moreover DMA is not necessary anymore when a large excess of CBr_4 is used,[65] because it was shown that CBr_3^- plays the directing effect owing to its reversible addition onto the fullerene.[66]

Formation of T_h-hexa-adducts are sensitive to steric hindrances. Indeed, when starting from malonates bearing bulky substituents, yields are low or the hexa-adducts are not obtained at all. To resolve this problem, a "click approach" had been proposed (see 3.3).[67,68]

The formation of hepta-adducts or higher adducts are not possible with malonates from the T_h-symmetrical hexa-adducts because all the remaining double bond have a *cis-1* relationship with one already bond malonate. However, it is possible with a suitable addition pattern. Diederich and coworkers have synthesized the C_{60} hexa-adduct **A** with an original addition pattern (Figure I-14). The further functionalization of **A** led to the octa-adduct **B**.[69]

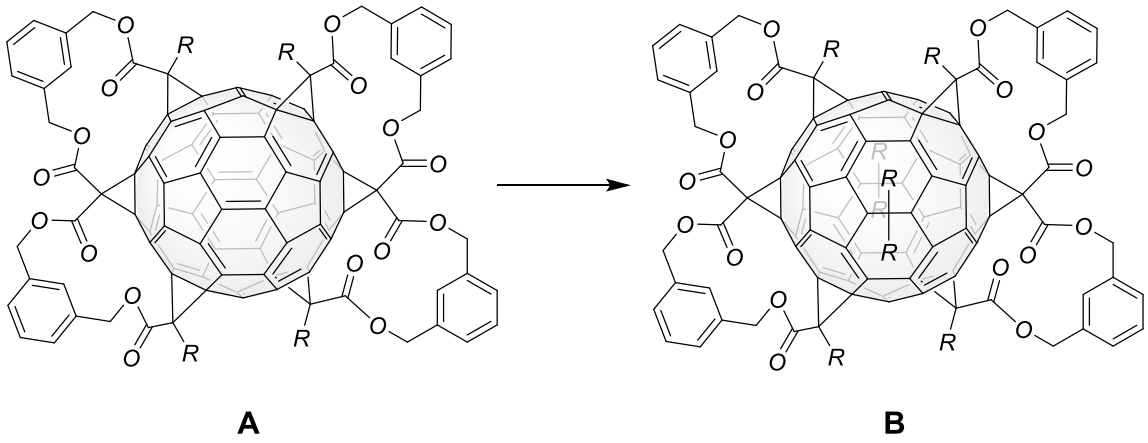


Figure I-14 : C_{60} hexa-adduct with an original addition pattern and its subsequent octa-adduct.

3. The "Click chemistry" in the fullerene chemistry.

3.1 The "click" concept.

The "click" concept was introduced in 2001 by *H. C. Kolb, M. G. Finn* and *K. B. Sharpless*.[70] They defined the "click chemistry" with the following set of requirements that reactions must meet:

- *Modular and wide in scope.*
- *Give very high yields.*
- *Generate only inoffensive byproducts.*
- *Be stereospecific.*
- *Have simple reaction conditions.*
- *Readily available starting materials and reagents.*
- *The use of no solvent or a benign solvent or easily removed.*
- *Simple product isolation.*

To meet these requirements, reactions must be energetically favorable with a high thermodynamic driving force. In this context, "click" reactions can be presented as easy, fast and efficient reactions.

A classification[70,71] of four families of "click" reactions is possible (Figure I-15):

- Cycloaddition reactions, e.g. 1,3-dipolar cycloaddition and Diels-Alder reactions.
- Nucleophilic ring-opening reactions, such as for epoxides, aziridines, cyclic sulfates, cyclic sulfamidates.
- Carbonyl chemistry of the "non-aldol" type, e.g. the formation of oxime ethers, hydrazones and aromatic heterocycles.
- Additions to carbon-carbon multiple bonds, such as epoxidation, dihydroxylation, aziridination, nitrosyl and sulfenyl halide additions, and some Michael addition reactions.

Since its introduction in 2001, the "click chemistry" has generated a large number of articles, crossing different branches of sciences[72] such as materials science or biology. The most famous and most used "click" reaction is certainly the copper catalyzed *Huisgen type* 1,3-dipolar cycloaddition. This reaction has been revealed to be a powerful tool in different fields of chemistry.[73]

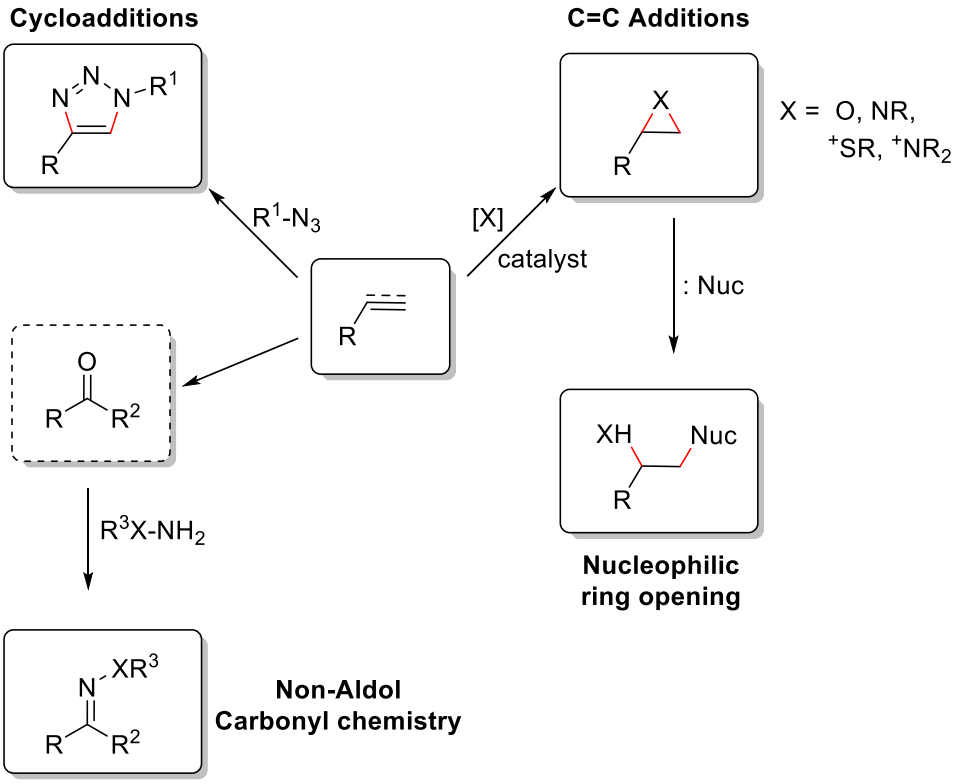


Figure I-15 : Examples of « click » reactions.

3.2 The *Huisgen type* 1,3-dipolar cycloaddition.

The *Huisgen type* 1,3-dipolar cycloaddition corresponds to a cycloaddition reaction between an azide and a terminal alkyne to form a [1,2,3]-triazole. Initially developed by *Rolf Huisgen* in the 60's, a mixture of azides and terminal alkynes was heated at high temperature leading to slow and non-regioselective reactions.[74,75] In 2002, *Meldal and coworkers* revisited this reaction with the use of copper(I) salts as catalyst that leads to a fast and regioselective formation at room temperature of the desired [1,2,3]-triazole.[76] Later *Sharpless and coworkers* had increased the scope of this new found conditions[76] by the use of a more polar solvent such as H_2O and with the *in situ* reduction of Cu^{2+} to Cu^{+}.[77] With the use of copper(I) salts as catalysts, only regioisomers in 1,4 positions are obtained.

Mechanism of copper(I) catalyzed 1,3-dipolar cycloaddition.

The first step is a coordination of a terminal alkyne to the copper(I) complex (Figure I-16). That π-complexation lowers the pKa of the alkyne C–H by up to 9.8 pH units,[78] making possible the formation of copper acetylide in an aqueous media without the addition of a base. In 2013, Folkin and coworkers demonstrated that dinuclear copper intermediates are the active species in azide-alkyne cycloadditions.[79] The direct observation and isolation of bis(copper) key intermediates was published in 2015 by Bertrand and coworkers.[80] In the next step, the substituted N-atom coordinates the second copper atom, followed by

nucleophilic attack at the terminal N-atom of the azide by the β-carbon of the acetylide to form the first covalent C–N bond (Figure I-16).[79] The ring closure happens next to form a triazolide which is subsequently protonated to form the final triazole substituted in 1,4 positions.

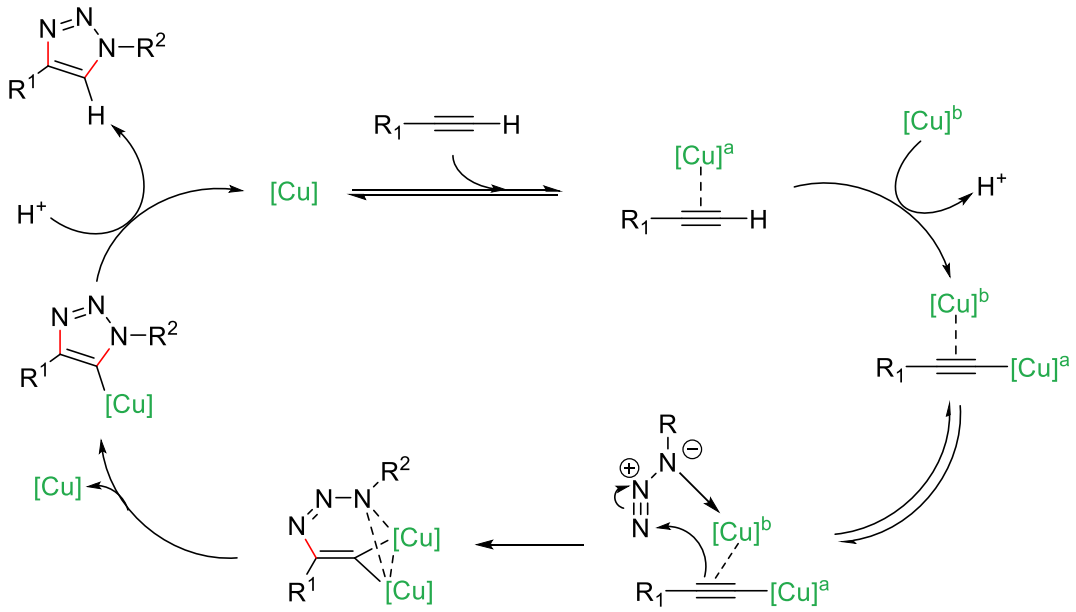


Figure I-16 : Proposed mechanism of copper(I) catalyzed 1,3-dipolar cycloaddition.

3.3 The Copper-catalyzed alkyne-azide 1,3-dipolar cycloaddition in Fullerene chemistry.

3.3.1 Introduction.

The copper-catalyzed alkyne-azide 1,3-dipolar cycloaddition (CuAAC) reaction is a powerful tool for the synthesis of a large variety of molecules from small to macromolecular size with good yields.[73] On the other hand, direct functionalization of C_{60} in one and final step can be limited by steric effects, especially for highly substituted C_{60}.[81] Post-functionalization of quite simple C_{60} building blocks is a solution to form super-functionalized C_{60} derivatives without steric hindrance problems. With its high tolerance to a large variety of functions and its low sensibility to steric effects, the CuAAC reaction arises as a perfect candidate to considerably increase the scope of post-functionalization of C_{60} derivatives in respect to other more restricted reactions such as esterifications,[82,83] amidifications[84] and condensations.[85,86]

The first published article of CuAAC reactions in fullerene chemistry revealed the potential of this kind of reaction for the post-functionalization of C_{60} derivatives.[67] Nakamura and coworkers reported the straightforward synthesis of fullerene-carbohydrate conjugates in very good yields by CuAAC reactions between a pentaalkynylfullerene building block and functionalized azides (Figure I-17). Furthermore, they highlighted the mild conditions of

CuAAC reactions that did not require the protection of the sugar hydroxyl groups, facilitating the synthesis.

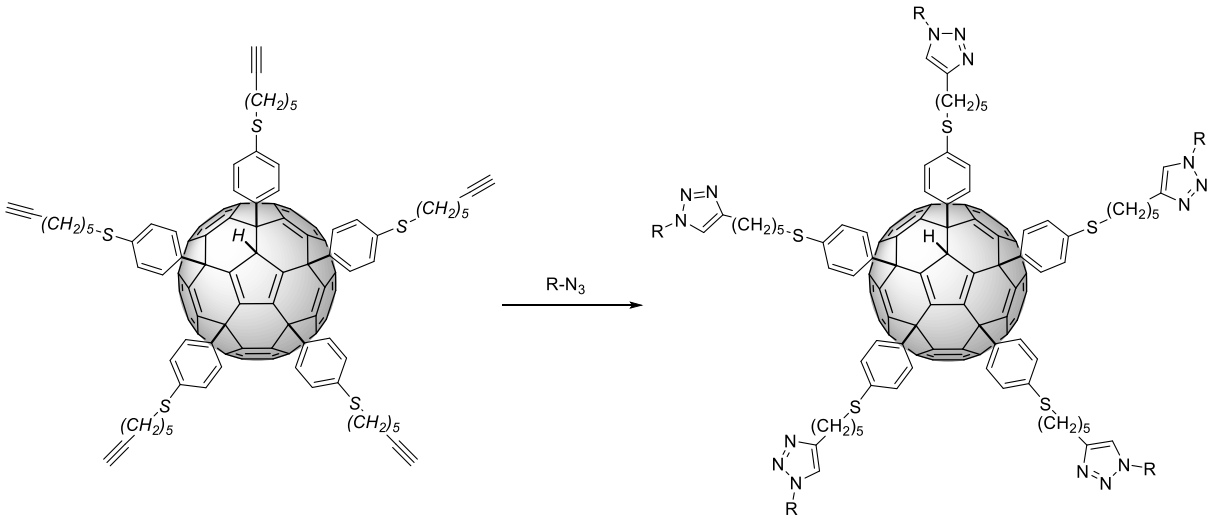


Figure I-17 : First examples of post-functionalization of C60 derivatives by CuAAC reactions.

The potential of CuAAC reactions on different C_{60} derivatives bearing malonates have been investigated in the Nierengarten's group.[87] In the following paragraphs, important results and some examples of this particular field are summarized.

3.3.2 CuAAC reactions with Mono-, Bis- and Tris-adducts of C_{60}.

The elaboration of mono-adducts building blocks (Figure I-18) revealed some limitations for the use of CuAAC reactions in fullerene chemistry. Indeed, organic azides undergo [3+2] cycloadditions with the [6,6] double bonds of fullerenes.[88,89] When the mono-adducts bears terminal alkyne groups, the solubility is an important parameter. Indeed, reactions with moderatly soluble alkyne-substituted mono-adducts are slow and side reactions are observed decreasing the yield (48% with **I-1**).[90] However, when the alkynylated mono-adducts are sufficiently soluble better yields are obtained (80% with **I-2**).[90,91] The use of mono-adducts building blocks bearings azide groups is more delicate. These kind of compounds are very unstable in the solid state.[90] Fullerene azide (**I-3**) requires to be always in solution to avoid polymerization by intermolecular reaction of azide with C_{60}. Under this storage conditions, subsequent CuAAC reactions can be performed with good yields (e.g. 97% with **I-3**).[92]

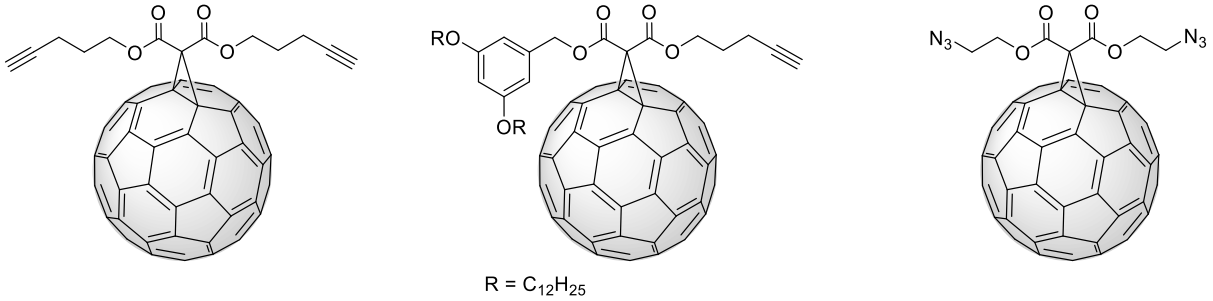


Figure I-18 : Different mono-adduct building blocks used in the literature.

Other examples of post-functionalization of bis- [90,93–95] and tris-adducts[96] were also reported. Bis-adducts building blocks **I-4** afforded yields between 60 to 98% and the Tris-adduct building block **I-5** afforded yields of 36 to 8% (Figure I-19).

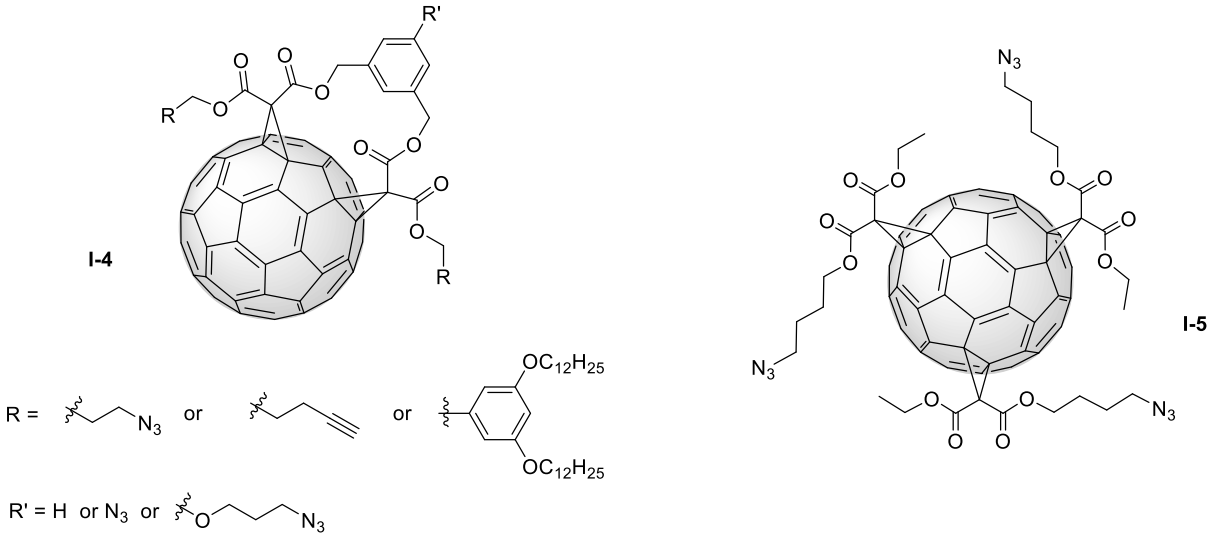


Figure I-19 : Different bis- and tris-adduct building blocks used in the literature.

In summary, yields of CuAAC reactions for post-functionalization of Mono-, Bis- and Tris-adducts building blocks seem to be design dependent and consequently the potential of CuAAC reactions cannot be fully exploited for low multi-adducts of C_{60}.

3.3.3 CuAAC reactions with T_h-addition pattern hexa-adducts.

3.3.3.1 Building blocks

The preparation of hexa-adducts with T_h-addition pattern are sensitive to steric hindrances. Thus, it can be difficult to form highly substituted hexa-adducts by direct additions of bulky malonates. Our group has shown that the post-functionalization of easily accessible hexa-adducts bearing 12 terminal alkyne or azide groups can be easily performed under CuAAC conditions. The hexa-adducts building blocks bearing 12 terminal alkyne (**I-8**) or azide (**I-9**) groups were synthesized with good yields (49% and 62%) starting from malonates **I-6** and **I-7** respectively (Figure I-20).[68,97] For **I-8**, the deprotection of trimethylsilyl (TMS) groups can be performed before the CuAAC reaction. Alternatively, the deprotection can be carried out *in situ* during the CuAAC reaction by adding TBAF to the click mixture. Compound **I-9** is enough stable to be stored 2-3 days at low temperature without intra or intermolecular cycloaddition reaction between the azide and the C_{60} core.

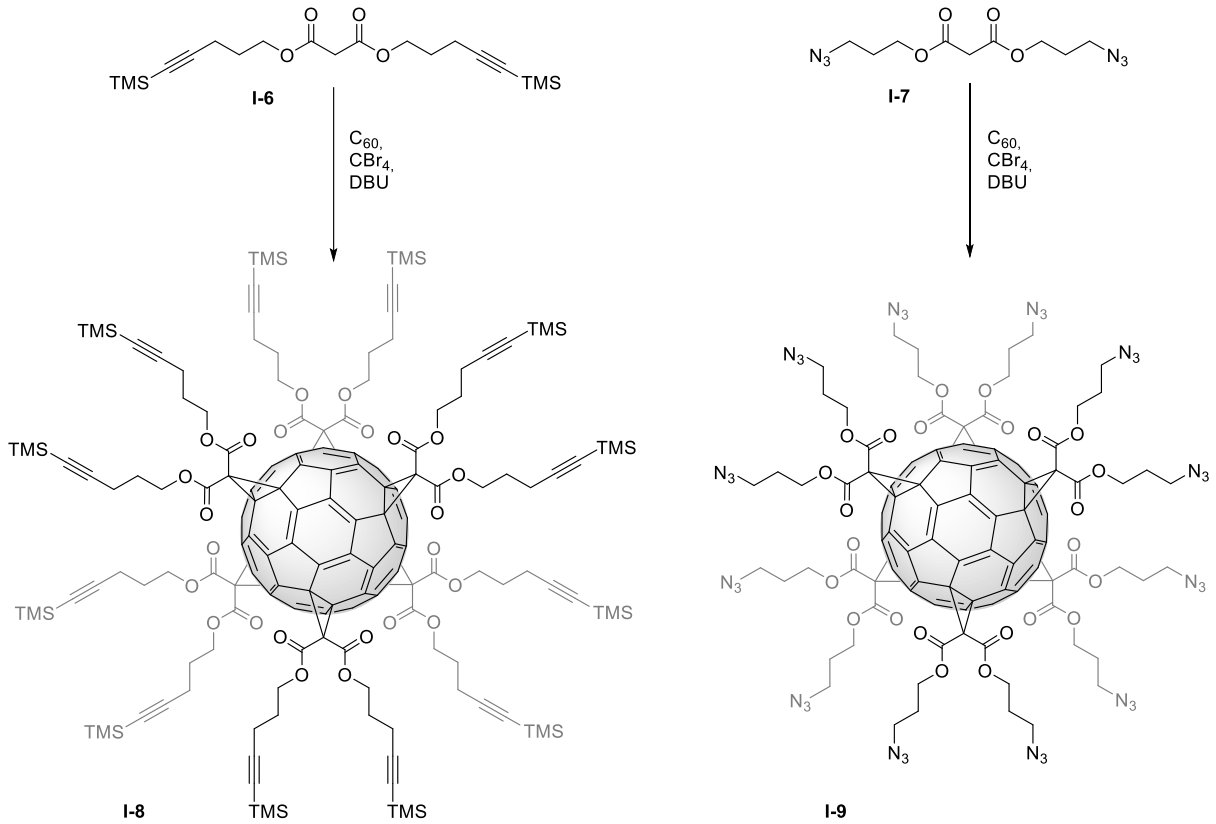


Figure I-20 : Classical T_h-symmetrical hexa-adducts building blocks.

Another example of T_h-symmetrical hexa-adducts has been reported by Bräse and coworkers.[98] In this particular case, the use of macrocyclic malonates bearing an azide function gave rise to hexa-adduct building blocks allowing for the grafting of six peripheral subunits.

The two last examples of reported building blocks with T_h-addition pattern are mixed [5,1] hexa-adducts **I-10** and **I-11** (five malonates are identical and one malonate is

different)(Figure I-21). The particularity of **I-11** is that three successive post-functionalization reactions can be made (two by CuAAC reactions and one by radical thiol-ene click reaction).

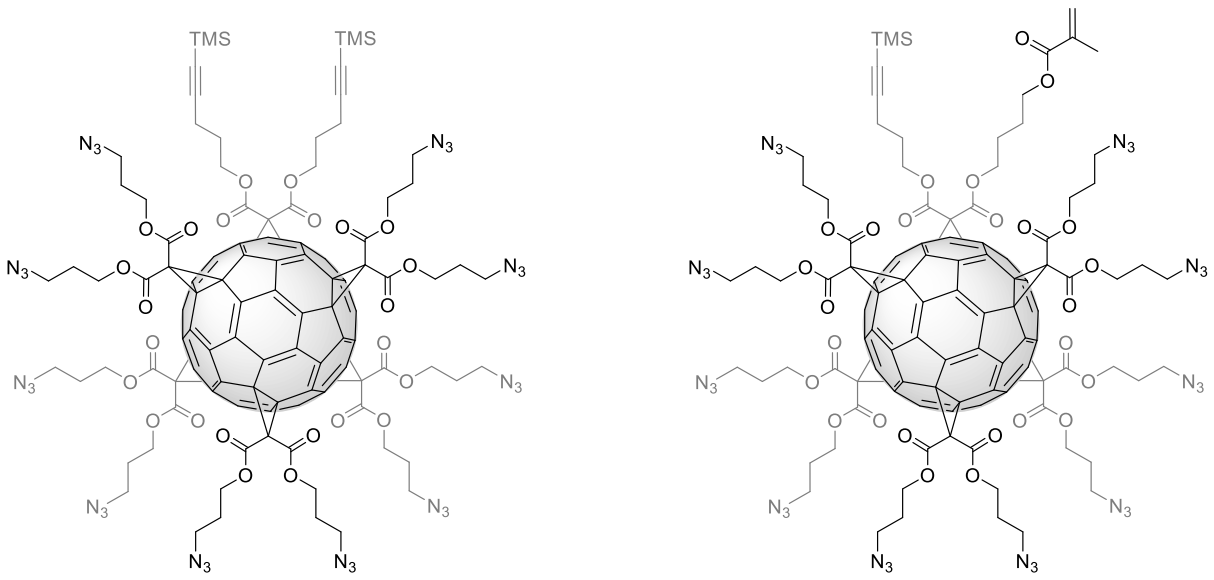


Figure I-21 : Mixed [5,1] hexa-adducts building blocks.

The advantage of this methodology is that the building block can be adequately chosen in order to simplify the synthesis of the "clickable" functions in addition to the formation of highly functionalized hexa-adducts.

3.3.3.2 Applications in various fields.

Fullerene hexa-adducts have been used in various fields. In this section, only a brief overview is given for each application.

All the clicked fullerene hexa-adduct derivatives described in this section were obtained in good yields from ≈ 60% to 90%. For hexa-adducts, electrons or energy transfers on the C_{60} core are very weak.[99,100] In general, the C_{60} hexa-adducts core plays only the role of a scaffold.

Photoactive clicked fullerene derivatives:

Three examples of photoactive derivatives have been published by Nierengarten's group and collaborators.

The interest of hexa-substituted fullerene derivative for photoactive applications is related to the perturbation of both ground- and excited-state energy levels of the carbon sphere. Therefore, the absorption spectra of the central core is blue-shifted and the potential of the first reduction wave is shifted to about 1 V.

Starting from the building block **I-9**, hexa-adducts **I-12**[68] and **I-13** were prepared (Figure I-22). Compound **I-12** has a very strong absorption at 420 nm (Soret band, molar absorptivity: 431×10^4 $M^{-1}.cm^{-1}$) owing to the 12 peripheral Zn^{II}-porphyrin. Photoinduced electron transfer and singlet-singlet energy transfer between the porphyrin and the fullerene core are prevented by the unfavorable electronic states. Thus, **I-12** is attractive for the construction of a supramolecular photosynthetic model by association with a C_{60}-imidazole mono-adducts derivative.[100] In contrast, when hexa-adducts are surrounded by blue emitter chromophores, photoinduced energy transfer to the core can be possible which is not the case for redshifted chromophores. Compound **I-13** bearing 12 stilbene sub-units exhibits efficient light-harvesting properties from the periphery to the core by an efficient singlet-singlet energy transfer. [99]

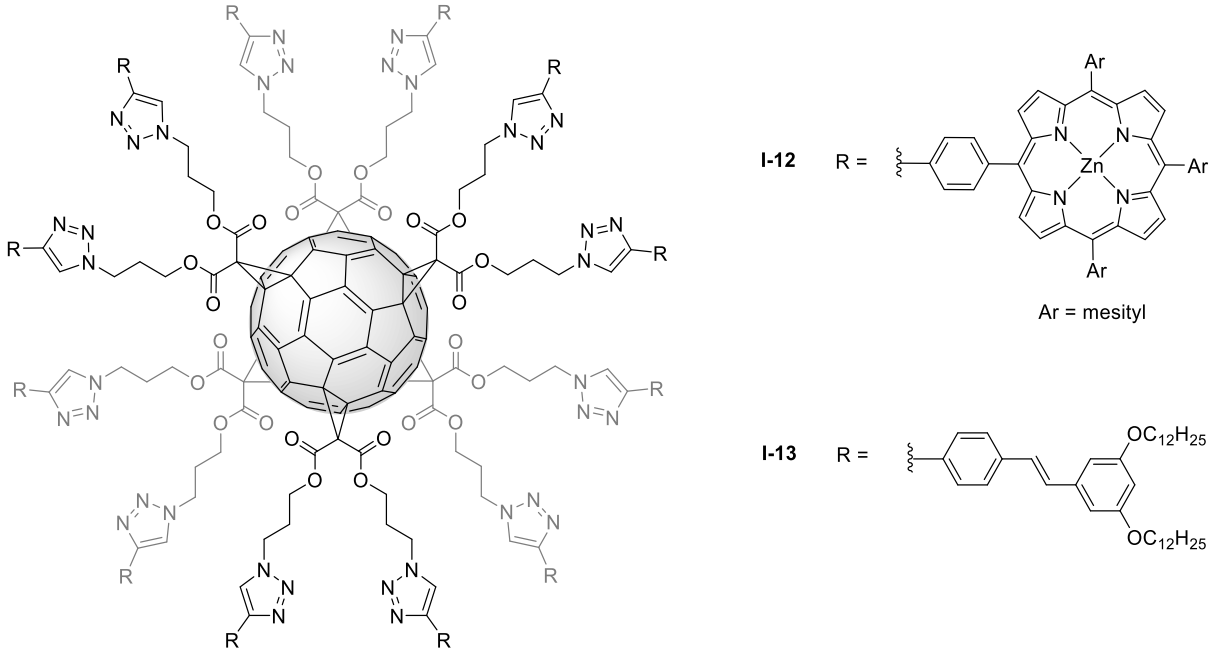


Figure I-22 : Examples of photoactive clicked hexa-adducts.

In the last example,[99] building block **I-10** was used in order to associate ten yellow dyes with two complementary blue dyes to form **I-14** (Figure I-23). Photophysical studies of **I-14** has shown energy transfers from the yellow to the blue dyes resulting to a stronger fluorescence of the blue dyes. **I-14** can be considered as a solar energy concentrator.

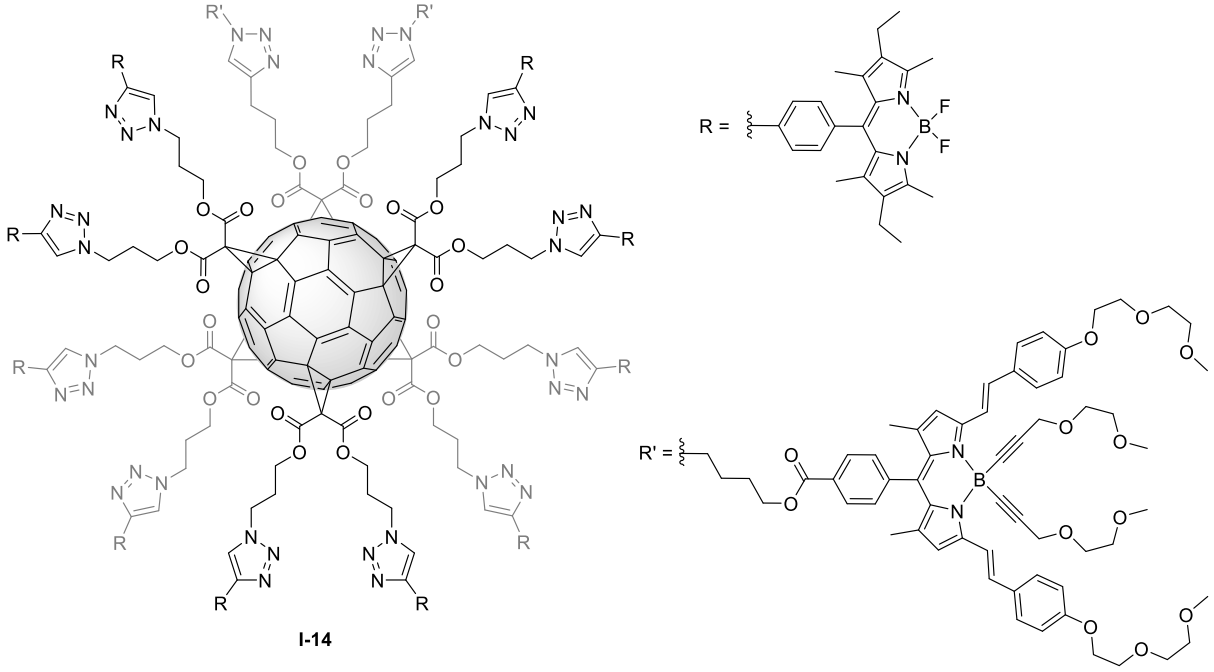


Figure I-23 : Example of photoactive clicked mixed [5,1] hexa-adducts.

Electroactive clicked fullerene derivatives:

In contrast to C_{60}, fullerene hexa-adducts with an octahedral addition pattern are very poor electron acceptors. The C_{60} core of the hexa-adducts is electrochemically silent over a large potential window (from ca. -1.5 to +1.5 V vs. a standard calomel electrode (SCE)). Therefore, the electrochemical properties of fullerene hexa-adduct derivatives are directly related to the substituents.

Molecular motion of **I-15** (Figure I-24) by electrochemical control has been reported.[101] The molecular motion is induced by redox reactions on viologen subunits which π-dimerize when radical cations are produced.

I-16 was functionalized with ten ferrocene and two 1,2-dithiolane units. The dithiolane units served as anchors onto a gold surface (Figure I-24). The electrochemical behavior of **I-16** was investigated by cyclic voltammetry. Depending on the scan rate, all or a fraction of the ferrocene subunits can be oxidized.[102]

Liquid crystalline clicked fullerene derivatives:

Different Percec-type dendrons were grafted onto T_h-symmetrical C_{60} hexa-adduct building blocks (Figure I-25). Mesomorphic propreties were evidenced by Differential Scaning Calorimetry (DSC) and Polarized Optical Microscopy (POM) measurements. These dendronized molecules self-assemble into unprecedent supramolecular discs containing the fulerene at their core. The addition pattern have little if any effects on the liquid crystal phase.[103]

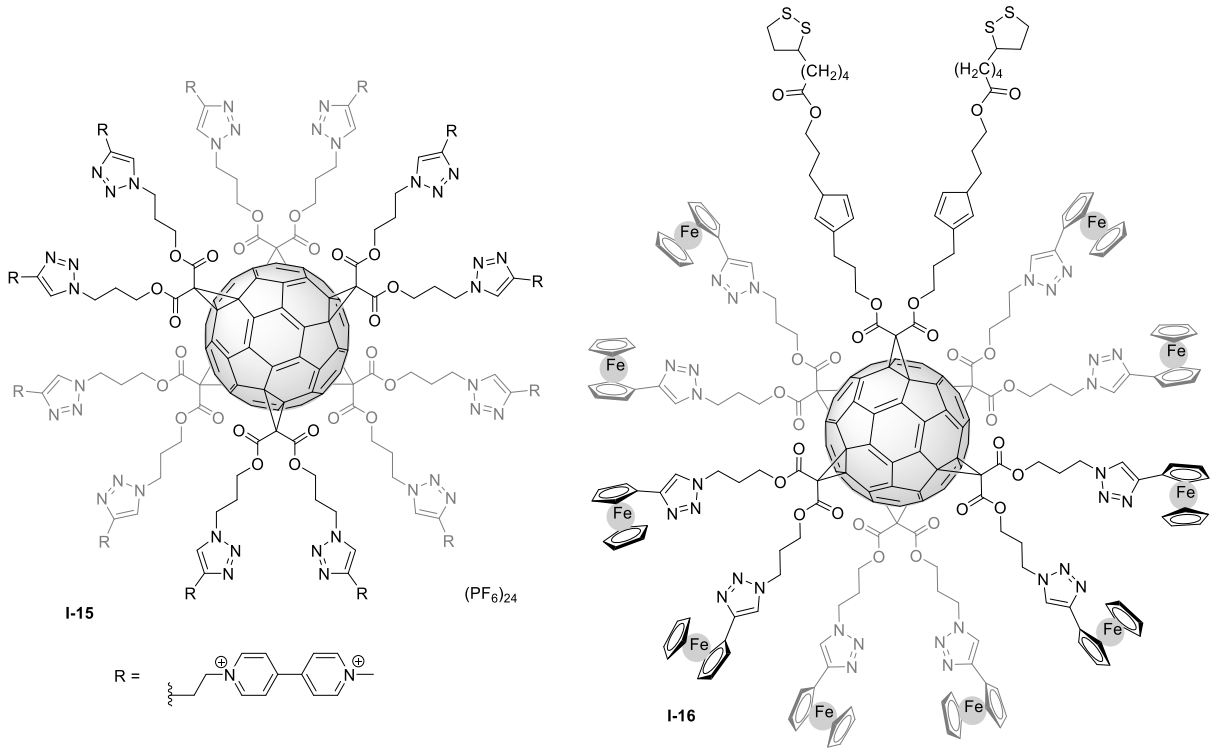


Figure I-24 : Examples of electroactive clicked fullerene derivatives.

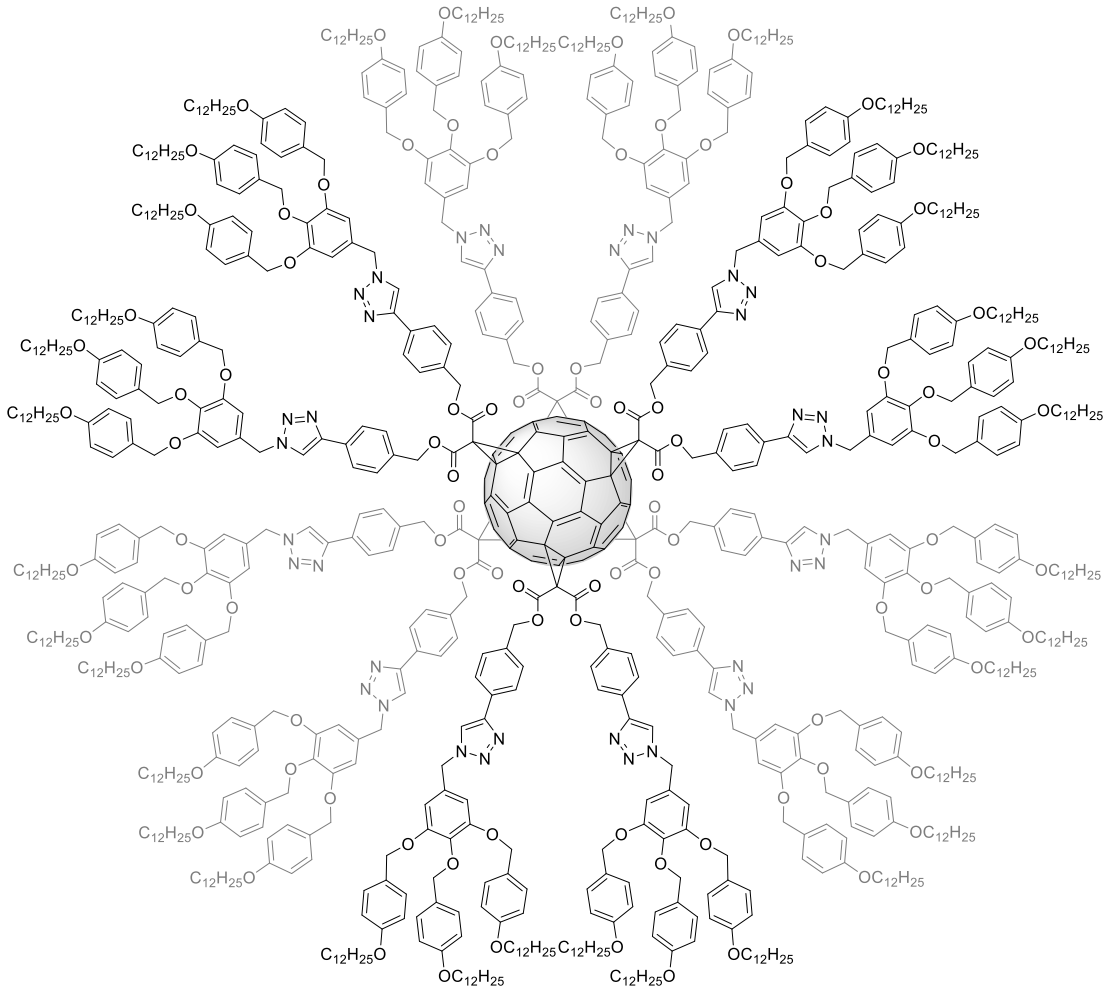


Figure I-25 : Example of a liquid crystal fullerene hexa-adduct derivative.

Bioactive clicked fullerene derivatives:

T_h-symmetrical fullerene hexa-adduct is an interesting scaffold for biological applications. The globular shape is an asset to prevent amphiphilic character and thus possible aggregation in aqueous media. Furthermore, the peripheral function multiplicity of 12 provides a fast dendritic growth.

Preparation of dendronized polycationic hexa-adducts of C_{60} has shown remarkable gene-delivery capabilities (Figure I-26). These compounds exhibit a low toxicity. The polycationic system is more compact with the globular shape of T_h-hexa-adducts. Thus, the efficiency can be good even for low generation dendrons.[104]

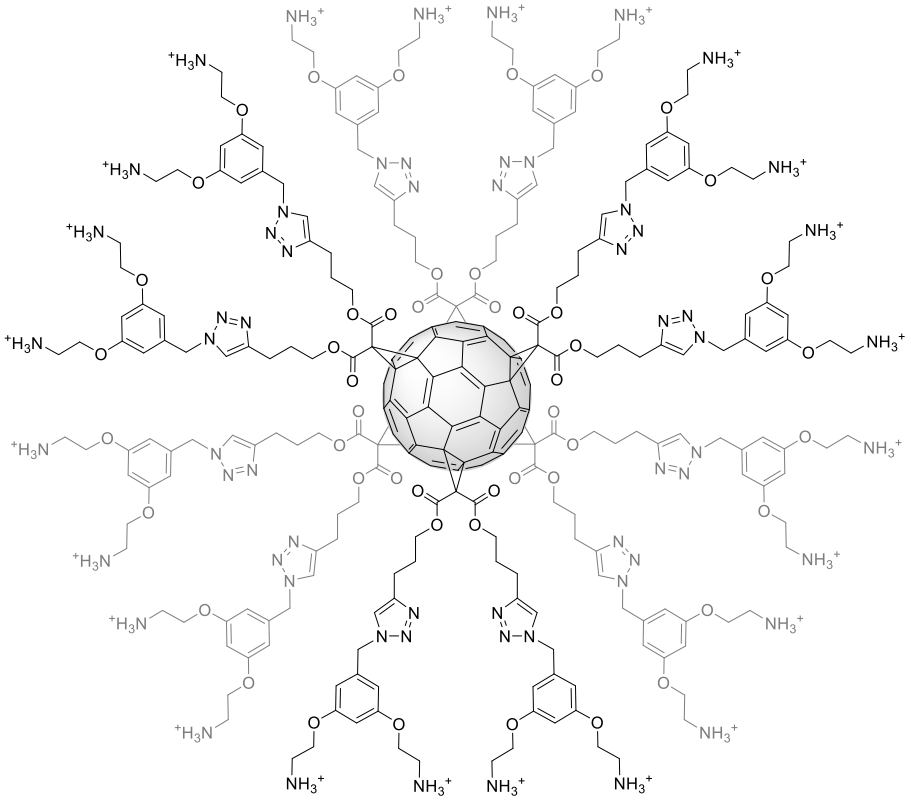


Figure I-26 : Example of a dendronized polycationic hexa-adduct of C_{60}.

Several hexa-adducts of C_{60} bearing sugar units at its periphery (Figure I-27) have been reported.[105–110] Preparation of glycofullerenes are simplified with the use of CuAAC reactions. These fullerenes derivatives have a good solubility in aqueous media and low cytotoxicity. Multivalent effects were observed for enzymatic inhibition.

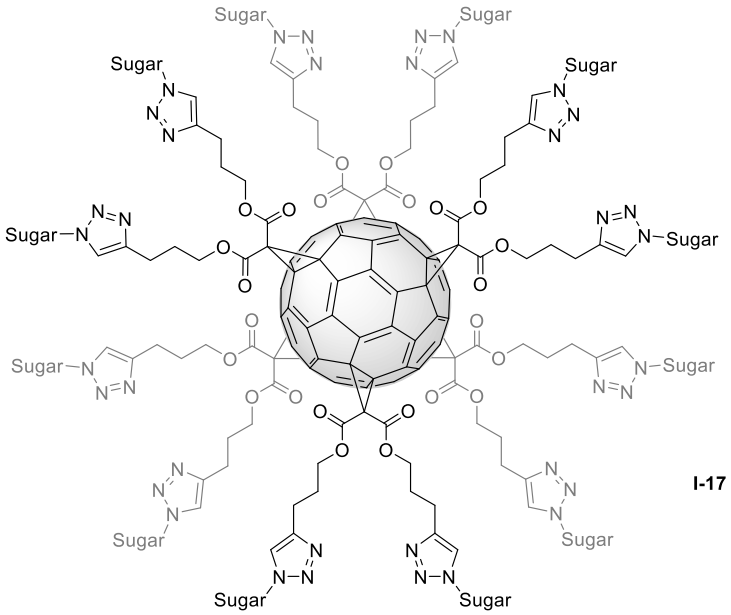


Figure I-27 : Example of bioactive clicked hexa-adducts.

4. Objectives.

Fullerene hexa-adducts with a T_h-symmetrical octahedral addition pattern are a unique class of three dimensional molecules. Their spherical framework is indeed an appealing platform for the preparation of new nanomaterials and bioactive molecules. The direct synthesis of fullerene hexa-adducts from C_{60} and malonates is however difficult and generally restricted to relatively simple malonate derivatives thus limiting their accessibility. This major problem was recently solved by producing easily accessible C_{60} hexa-adduct derivatives bearing 12 terminal groups allowing their further functionalization to generate structurally more complicated systems. Among them, the copper mediated Huisgen 1,3-dipolar cycloaddition of azides and alkynes resulting in 1,2,3-triazoles was found to be particularly interesting as it allows for the incorporation of almost any functional groups around the fullerene core. The development of an efficient toolbox for the synthesis of fullerene hexa-adducts bearing two or more different peripheral functional subunits is now one of the major challenge to produce a unique multifunctional nanomaterials platform.

The aim of this PhD thesis is to develop in a first step a regioselective methodology for the synthesis of bis- and tris-adducts of C_{60}, and in a second step to develop versatile fullerene hexa-adduct building blocks incorporating complementary reactive centers with different and selective reactivity.

The **Chapters II** and **III** were dedicated to the regioselective bis- and tris-functionalization of C_{60} respectively by a macrocyclic approach and by a tether-directed approach. Based on the regioselective syntheses of multi-adducts of C_{60}, the preparation of mixed C_{60} hexa-adducts building blocks and their subsequent post-functionalization were performed in the **Chapter IV**. In the **Chapter V**, the mixed C_{60} hexa-adducts building blocks previously prepared are used for the preparation of original fullerodendrimers.

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Chapter II: Regioselective syntheses of C_{60} derivatives by a macrocyclic approach.

1. Introduction.

The fullerene chemistry is now well understood and a large variety of reactions have been developed to functionalize fullerenes. The 30 double bonds of C_{60} being all equivalents, only one mono-adduct can be formed. In the case of further functionalization, the regiochemistry and the stereochemistry of the formed multi-adducts must be considered.

Problems related to the regiochemistry (achiral and chiral addition patterns) and the stereochemistry (in/out isomerism) considerably complicate the preparation of a specific multi-adducts of C_{60}. However with the specific reactivity of the *e* positions, T_h-hexa-adducts of C_{60} bearing twelve identical functional groups are accessible. Some examples of mixed hexa-adducts of C_{60} have been also reported (see **Chapter IV.1**), but the lack of post-functionalization possibilities, low yields or fastidious syntheses still limits the preparation of highly functionalized mixed hexa-adducts. The straightforward syntheses of mixed hexa-adducts pass through the elaboration of a simple regio- and stereoselective methodology for the formation of bis- or tris-adducts of C_{60} with appropriate addition patterns.

Two main approaches have been developed for the regioselective functionalization of C_{60}, the tether-directed method which will be discussed in **Chapter III** and the macrocyclic-directed method. In this last approach, the malonates are included within a macrocyclic structure (Figure II-1). The conformation and the size of the macrocycle will then play an important role in the regioselectivity of the cyclization on C_{60}.

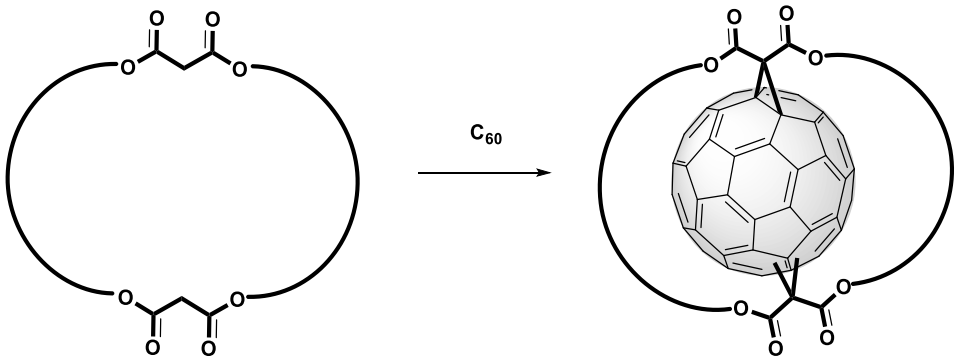


Figure II-1 : Macrocyclic-directed method for the region-functionalization of C_{60}.

The macrocyclic-directed method was introduced in 2002 by Hirsch and coworkers.[1] With this method, they were able to obtain high regioselectivity and good yields for the functionalization of C_{60}. The length of the spacer and more generally the ring size of the macrocycle are determinant to obtain a specific isomer. Indeed for bis-adducts of C_{60}, no regioselectivity was observed for a 26-membered ring macrocyclic bis-malonate. In contrast, by increasing the size of the macrocycle, they were able to obtain the *trans-3* and *trans-1* bis-adducts of C_{60} in a regioselective manner. For example, cyclo-[2]-dodecylmalonate gave exclusively the *trans-3* bis-adducts with a yield of 56% (Figure II-2). They also synthesized mixed macrocycles with two alkyl chains of different length. With unequal distances between

the ester functions, only bis-adducts of C_{60} with C_s-symmetrical addition pattern were obtained. For example, cyclo-[2]-octyl-tetradecylmalonate gave exclusively the *e* bis-adducts in 51% yield.

An increased number of units in the macrocycle play also an important role on the regioselectivity by an enlargement of the ring size. No regioselectivity was observed for the cyclo-[2]-octylmalonate but in contrast, when the reaction was carried out with the cyclo-[3]-octylmalonate, tris-adducts *e,e,e* and *trans-4,trans-4,trans-4* were obtained with 40% and 2% yields, respectively (Figure II-2). Another tris-adducts (*trans-3,trans-3,trans-3*) was obtained in 30% yield with a cyclo-[3]-tetradecylmalonate.

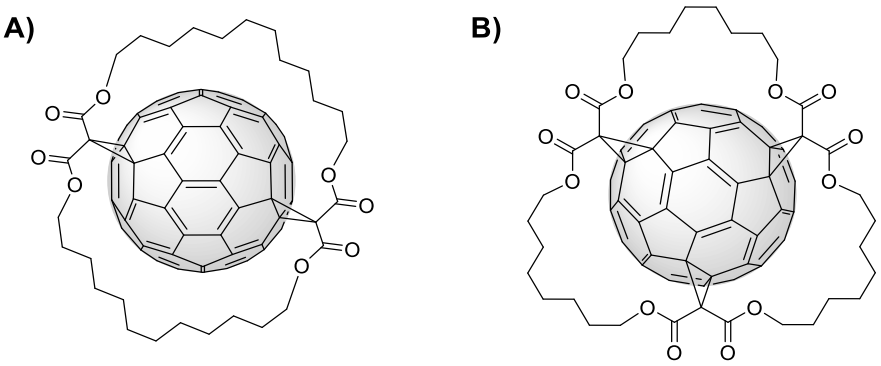


Figure II-2 : Examples of bis- and tris-adducts obtained by a macrocyclic approach. A) Bis-adducts trans-3. B) Tris-adducts e,e,e.

Wilson and coworkers reported syntheses using the same methodology, but instead of alkyl chains, they used oligoglycols as flexible linkers.[2] High regioselectivity and good yields were still obtained. Bis- or tris-adducts with rotational symmetry are favored when symmetric macrocycles are used. Nonetheless, a bis-adducts *e* (C_s-symmetrical addition pattern) (Figure II-3) was also obtained in addition to a *cis-3* bis-adducts with tetraethylene glycol linkers. They also reported an original *trans-4,cis-3,cis-3* tris-adducts that was isolated with a yield of 51%.

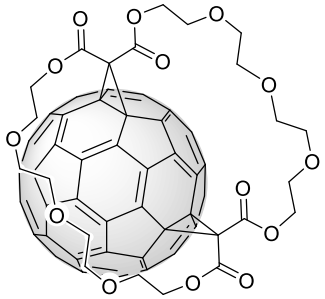


Figure II-3 : Example of a C_s-symmetrical addition pattern of a bis-adducts e.

Some addition patterns are inherently chiral (bis-adducts *cis-3*, *trans-3* and *trans-2* or tris-adducts *e,e,e*) and these fullerene multi-adducts are obtained as racemic mixtures. Purification of enantiomerically pure C_{60} derivatives requires fastidious separations by preparative chromatography (HPLC) on chiral stationary phases.[3]

Chronakis and Hirsch achieved the separation of enantiomerically pure ^{f,s}C and ^{f,s}A addition patterns of *trans-3* and *e,e,e* regioisomers (Figure II-4).[4,5] Starting from optically pure spacers, they synthesized the corresponding chiral cyclo-oligo-malonates. Reaction of the optically pure cyclo-oligo-malonates with C_{60} afforded diastereoisomeric mixtures of bis- or tris-adducts according to the used macrocycle. The difference of polarity of the diastereoisomers made possible the separation of enantiomerically pure *trans-3* and *e,e,e* adddition pattern by classical silica column chromatography. Diastereoselectivity was also observed between the ^{f}C and ^{f}A addition pattern.

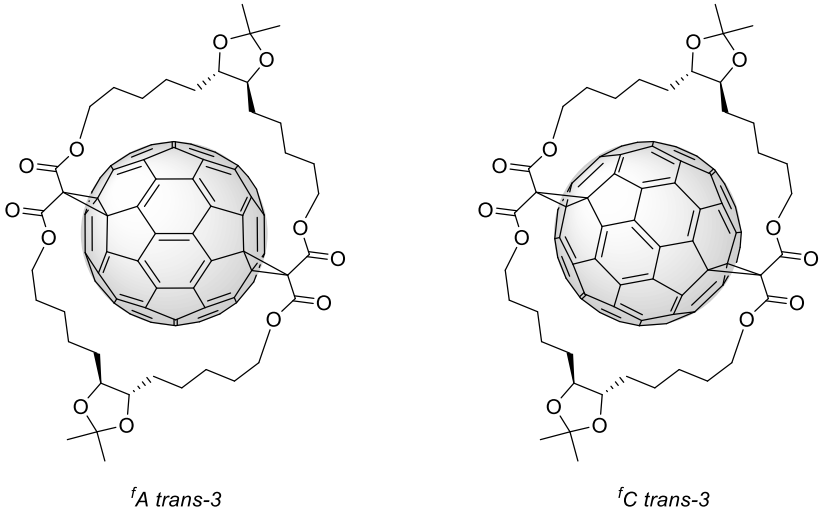


Figure II-4 : Example of inherently chiral addition pattern of C_{60} derivatives.

In the last example, Nierengarten and coworkers have shown that a rigid macrocycle is also suitable for the regioselective functionalization of C_{60}.[6] By the means of a phenylethynyl spacer and a silyl group, a rigid macrocyclic bis-malonate was synthesized. Subsequent reaction with C_{60} afforded the *trans-3* and *trans-1* bis-adducts in a 2:1 ratio (Figure II-5). Unfortunately, it was impossible to remove the silyl groups in this case in order to further functionalize these fullerene bis-adducts.

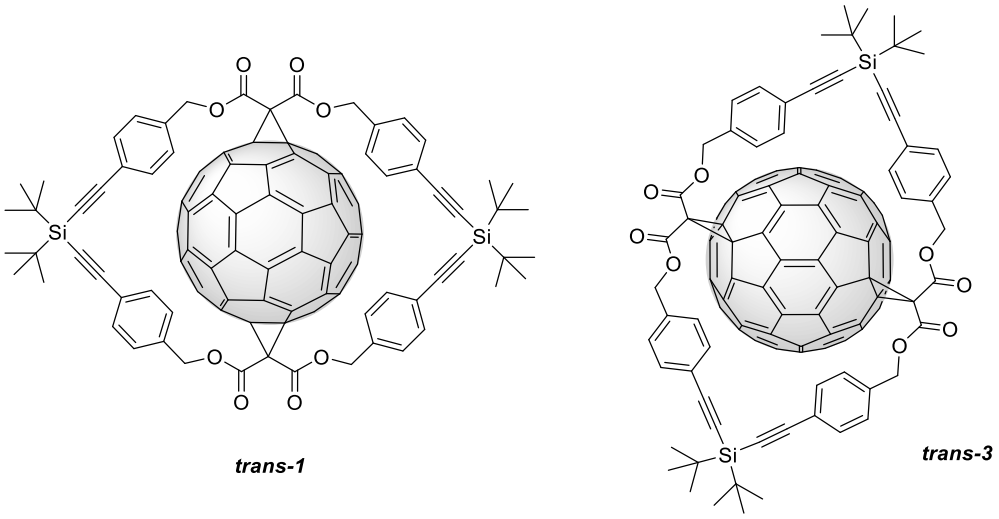


Figure II-5 : Bis-adducts obtained with a rigid macrocycle.

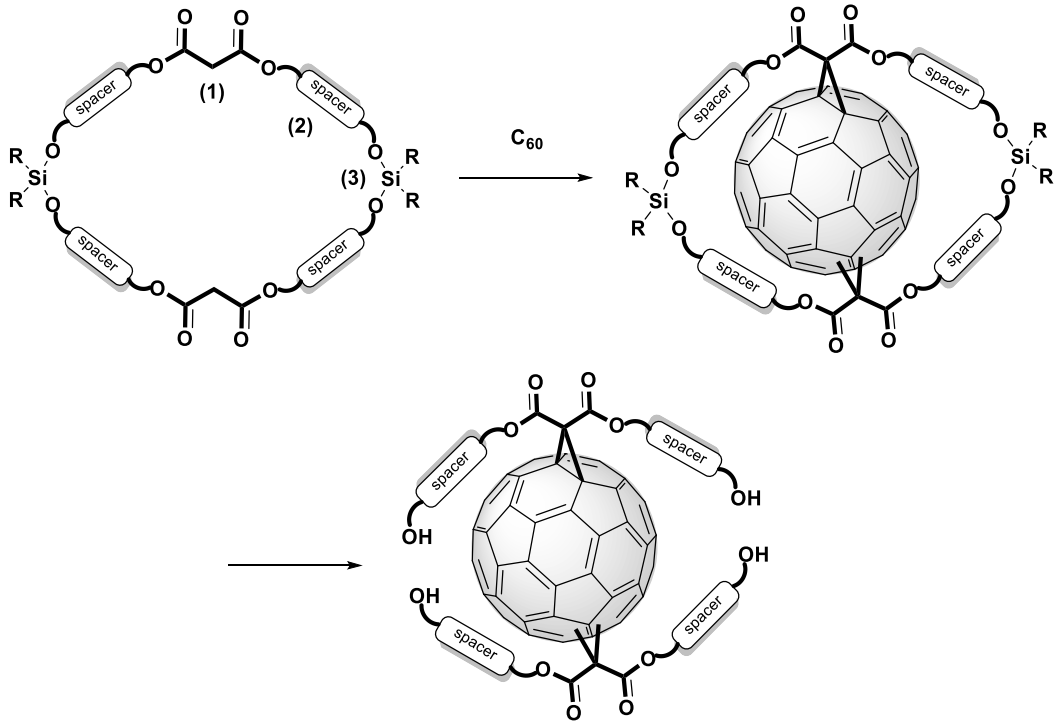


Figure II-6 : Concept of macrocycle incorporating silyl groups.

The macrocyclic approach affords good results for the regioselective functionalization of C_{60}. However, the post-functionalization of the addends bond on the C_{60} is difficult. In this context, the introduction of easily removable sub-units in the macrocycle is needed for an easy post-functionalization of these fullerene derivatives. Preliminary results obtained in our laboratory have shown that silyl groups as alcohol protecting group can be easily removed. In this work, the use of silyl groups as alcohol protecting group within a macrocycle is presented for the regioselective functionalization of C_{60}. The conception of the macrocycle will be based on three elements (Figure II-6): (1) malonates for anchoring on the C_{60}; (2) diol spacers to reach specific positions on the C_{60}; (3) removable silyl groups to allow the post-functionalization of the multi-adducts of C_{60}. In order to study the regioselectivity of macrocyclic bis-malonates incorporating silyl groups, three parameters have been modified: (1) the ring size; (2) the silyl group and (3) the flexibility of the spacer.

2. Regioselective syntheses of Bis-adducts of C_{60} by macrocyclic approach.

2.1 Preparation of macrocyclic bis-malonates.

2.1.1 Synthesis of macrocyclic bis-malonates: the direct approach.

The first challenge has been to develop an efficient synthetic route for the macrocyclic oligo-malonates incorporating silane subunits. A first approach was based on the direct macrocyclization of diols with malonyl chloride (Figure II-7). The diols are either obtained by reduction of the corresponding diesters or by reaction of a monoprotected diol with an appropriated silylating agent followed by deprotection.

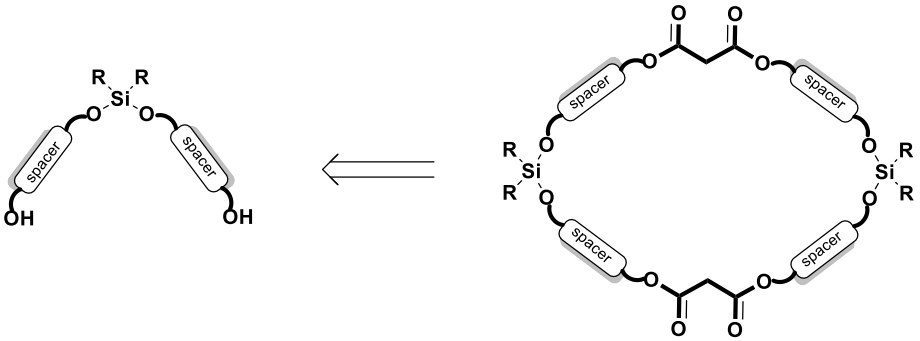
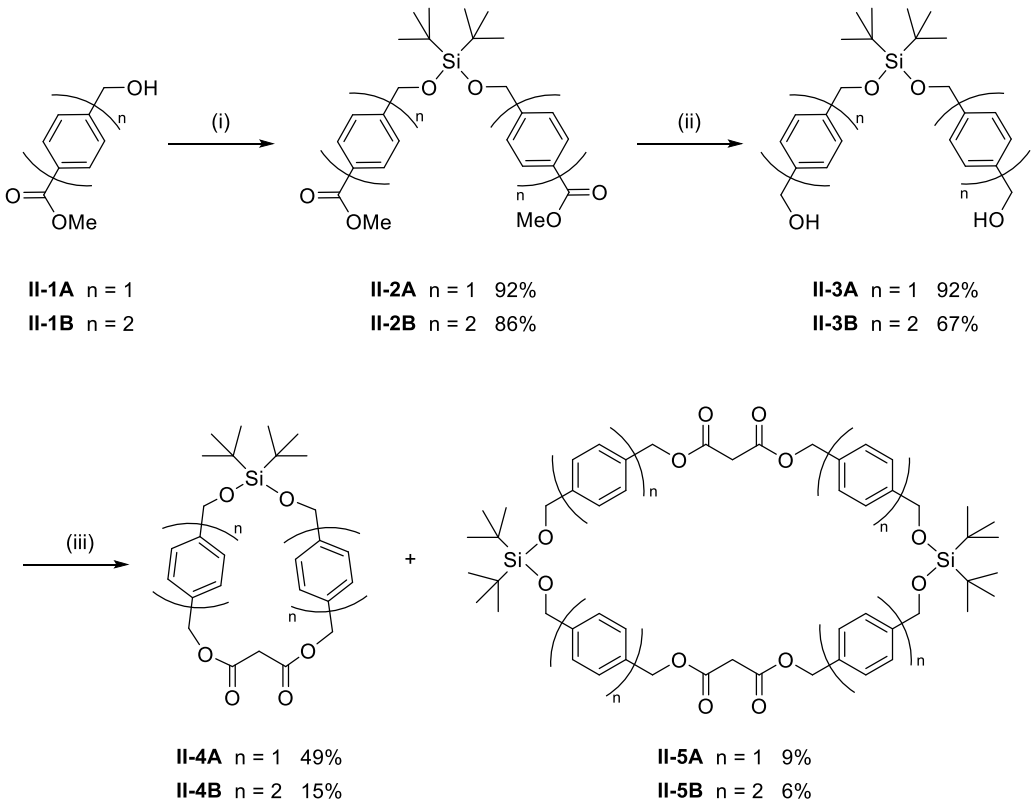


Figure II-7 : Retrosynthetic analysis for the elaboration of cyclo-bis-malonate

The preparation of a first macrocyclic bis-malonate with rigid spacers (**II-5**) is depicted in **Scheme II-1**. Treatment of **II-1** with di-*t*-butylsilylene bis(trifluoromethanesulfonate) (tBu$_2$Si(OTf)$_2$) in DMF in the presence of pyridine gave compounds **II-2**. The reduction of the ester functions of **II-2A** was first attempted with $LiAlH_4$. Under these conditions, the desired diol (II-3A) was not obtained due to the cleavage of the silyl ethers. In contrast, when diisobutylaluminium hydride (DIBAL-H) was used as the reducing agent, compound II-3A was obtained in good yield (92%). Similarly, treatment of II-2B with DIBAL-H in CH_2Cl_2 at -15°C afforded diol **II-3B** in 67% yield. Subsequent reactions of diols **II-3** with malonyl chloride were performed in the presence of 4-dimethylaminopyridine (DMAP) under pseudo high dilution conditions. Based on the order of elution,[1] cyclomonomalonates **II-4** and cyclobismalonates **II-5** were isolated.



II-1A n = 1
II-1B n = 2

II-2A n = 1 92%
II-2B n = 2 86%

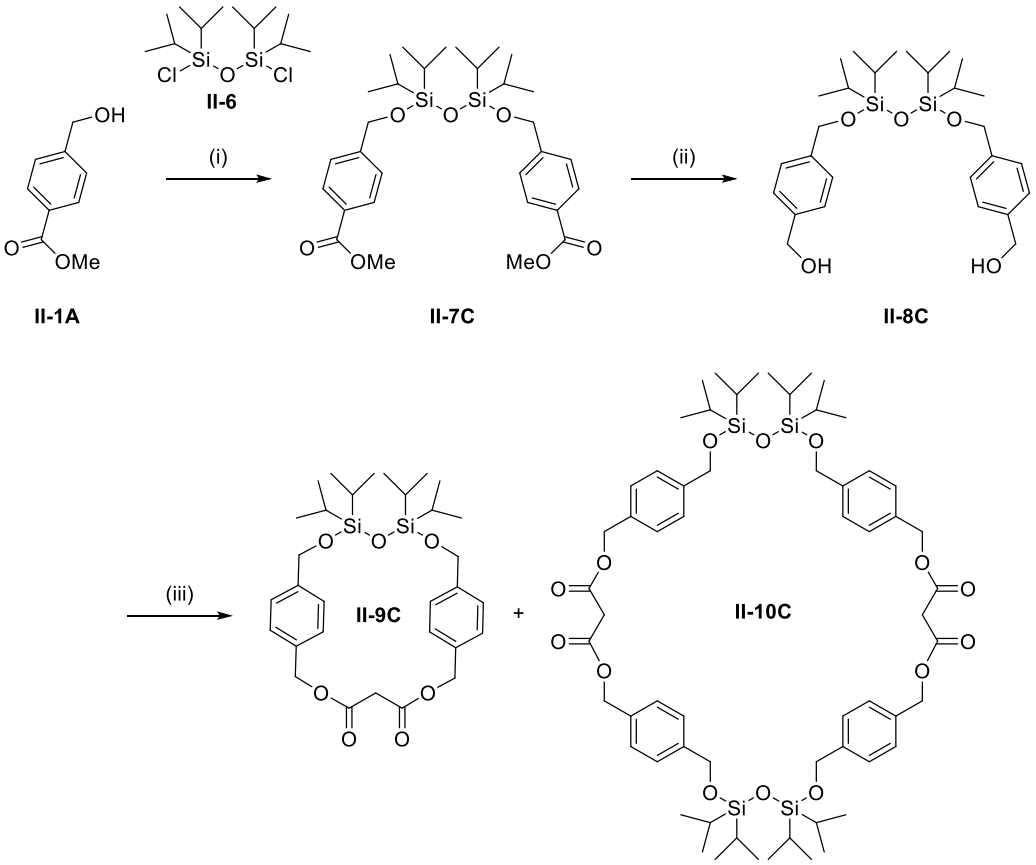
II-3A n = 1 92%
II-3B n = 2 67%

II-4A n = 1 49%
II-4B n = 2 15%

II-5A n = 1 9%
II-5B n = 2 6%

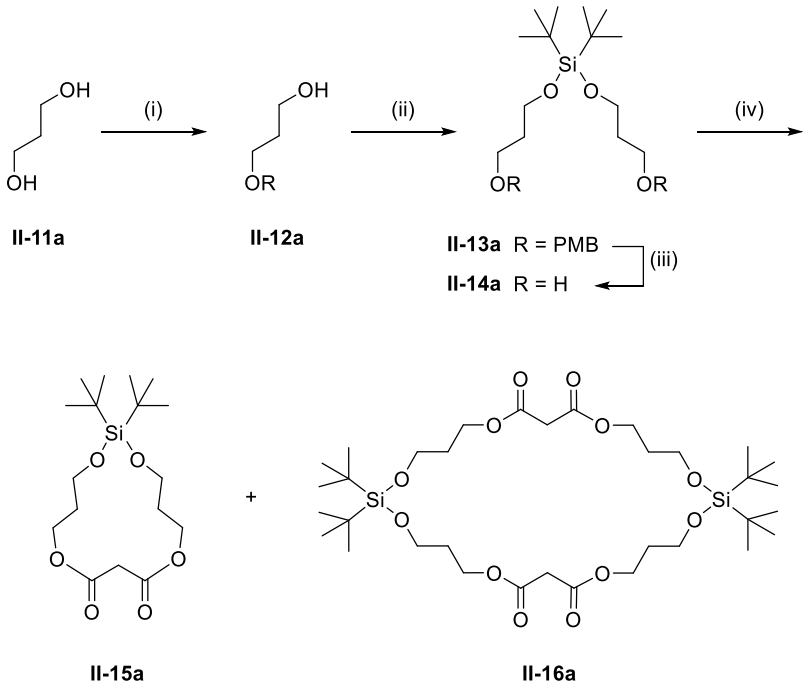
Scheme II-1. Reagents and conditions: (i) *t*$Bu_2Si(OTf)_2$, DMF, pyridine, rt, 12 h; (ii) DIBAL-H, CH_2Cl_2, -15°C, 3 h; (iii) malonyl chloride, DMAP, CH_2Cl_2, rt, 2 h.

To study the influence of the silyl group, the macrocyclic bis-malonates **II-10C** was synthesized from the silyl group 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (**II-6**). Compound **II-10C** was prepared by following the synthetic route developed for the preparation of compounds **II-5** and was obtained in 5% yield (**Scheme II-*2***).



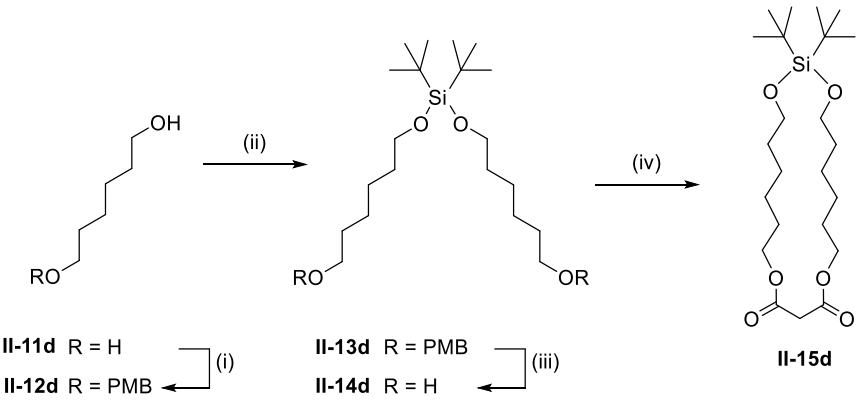
Scheme II-2. Reagents and conditions: (i) **II-6**, DMF, pyridine, rt, 12 h (99%); (ii) DIBAL-H, CH_2Cl_2, -15°C, 3 h (77%); (iii) malonyl chloride, DMAP, CH_2Cl_2, rt, 2 h (**II-9C**: 73%; **II-10C**: 5%).

Macrocycles with alkyl spacers have been also prepared. The synthesis of the macrocyclic bis-malonate **II-16a** shown in **Scheme II-*3*** was first achieved. The selective mono-protection of 1,3-propanediol was carried out by treatment with Ag_2O and *p*-methoxybenzyl chloride (PMBCl) according to the conditions reported by Bouzide and Sauvé.[7] Treatment of the resulting mono-protected derivative **II-12a** with *t*-$Bu_2Si(OTf)_2$ and imidazole in DMF provided **II-13a** in 68% yield. The PMB protecting groups in **II-13a** were conveniently removed by treatment with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in CH_2Cl_2 containing a small amount of water. The di-*t*-butylsilylene group remained unchanged and key building block **II-14a** was thus obtained in good yields (86%). Reaction of diol **II-14a** with malonyl chloride in the presence of DMAP under pseudo high dilution conditions afforded a mixture of cyclooligomers and polymers. Macrocycles **II-15a** and **II-16a** were isolated in a pure form in 24% and 15% yield, respectively. In the case of **II-16a**, the proposed structure was confirmed by MALDI-TOF mass spectrometry.



Scheme II-3. Reagents and conditions: (i) PMBCl, Ag_2O, CH_2Cl_2, 48 h (80%); (ii) *t*$Bu_2Si(OTf)_2$, DMF, imidazole, rt, 12 h (68%); (iii) DDQ, CH_2Cl_2, H_2O, rt, 6 h (86%); (iv) malonyl chloride, DMAP, CH_2Cl_2, rt, 48 h (**II-15a**: 24%; **II-16a**: 15%).

The same synthetic route was then applied from 1,6-hexanediol. Diol **II-14d** was obtained in three steps as shown in **Scheme II-4**. Reaction of **II-14d** with malonyl chloride gave mono-malonate **II-15d** as the major product. The direct synthetic route is therefore not suited for the preparation of larger macrocyclic oligo-malonates. This result prompted us to develop a stepwise synthetic route in which the formation of cyclo-mono-malonates is prevented.

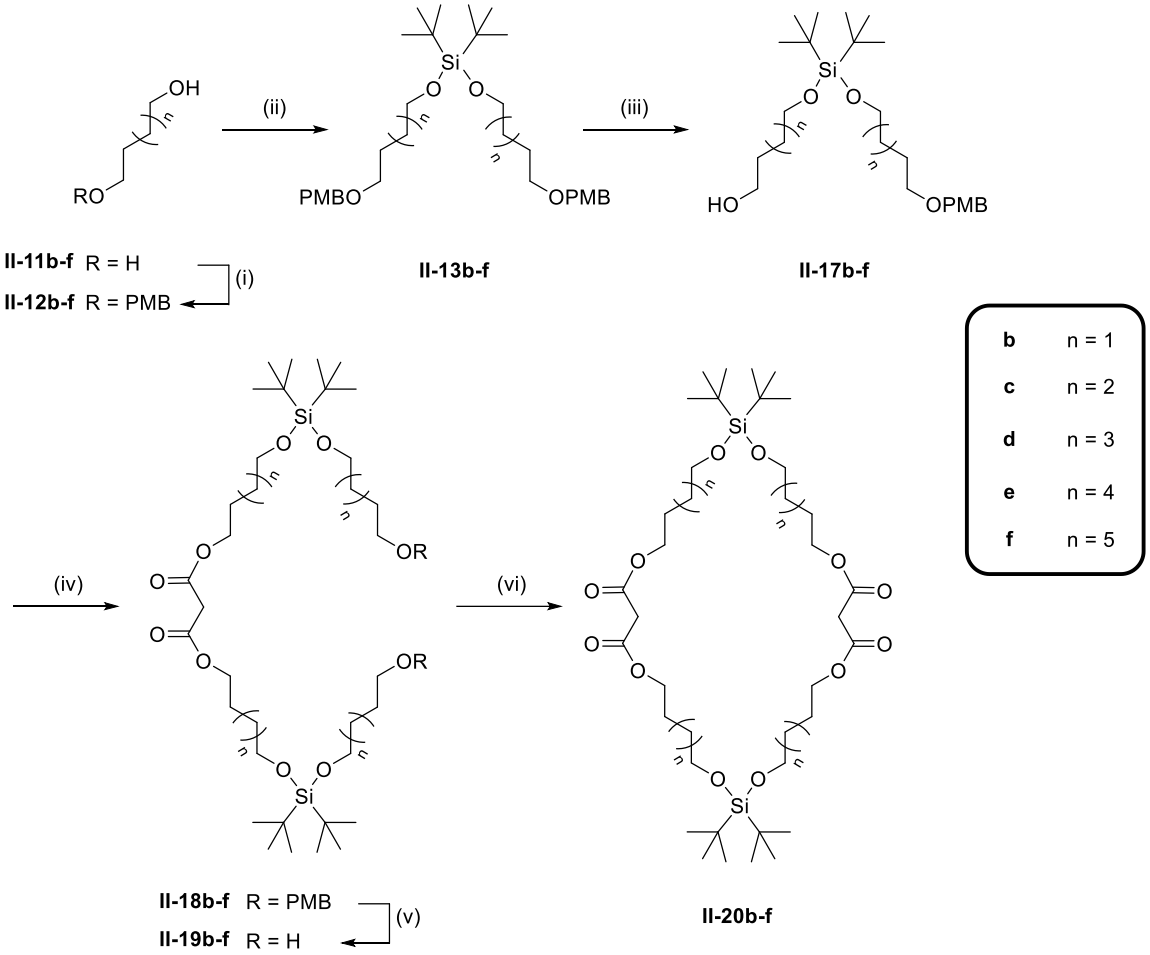


Scheme II-4. Reagents and conditions: (i) PMBCl, Ag_2O, CH_2Cl_2, 48 h (92%); (ii) *t*$Bu_2Si(OTf)_2$, DMF, imidazole, rt, 12 h (59%); (iii) DDQ, CH_2Cl_2, H_2O, rt, 6 h (82%); (iv) malonyl chloride, DMAP, CH_2Cl_2, rt, 48 h (**II-15d**: 38%).

2.1.2 Synthesis of macrocyclic bis-malonates: the stepwise approach.

This work has been done in collaboration with Dr. Thi Minh Nguyet Trinh and Dr. Sebastiano Guerra.

Larger macrocyclic oligo-malonates were prepared with alkanediols with 4 to 8 carbon atoms. The stepwise synthetic route for the preparation of these macrocyclic bis-malonates **II-20** is depicted in **Scheme II-*5***. Mono-protection of diols **II-11b-f** by treatment with PMBCl/Ag_2O followed by silylation (tBu$_2$Si(OTf)$_2$/imidazole) afforded compound **II-13b-f**. Treatment of **II-13** with 1 equiv. of DDQ provided the mono-protected derivatives **II-17**. Subsequent reaction with malonyl chloride in the presence of DMAP gave malonates **II-18**. The PMB protecting groups being removed under neutral conditions by treatment with DDQ, the silyl ether functions remained effectively intact and diols **II-19** were obtained in good yields (68 to 85%). Reaction of **II-19** with malonyl chloride under pseudo high dilution conditions gave cyclobismalonates **II-20** in 19 to 50% yields. Macrocycles **II-20**, which have ring sizes of 32-36-40-44-48 atoms respectively, were characterized by NMR spectroscopy and mass spectrometry.



Scheme II-5. Reagents and conditions: (i) PMBCl, Ag_2O, CH_2Cl_2, 48 h (69-95%); (ii) t$Bu_2Si(OTf)_2$, DMF, imidazole, rt, 12 h (60-91%); (iii) DDQ (1 eq), CH_2Cl_2, H_2O, rt, 6 h (47-50%); (iv) malonyl chloride, DMAP, CH_2Cl_2, rt, 2 h (67-96%); (v) DDQ (2.5 eq), CH_2Cl_2, H_2O, rt, 2 h (68-85%); (vi) malonyl chloride, DMAP, CH_2Cl_2, rt, 2 h (19-50%).

2.2 Regioselective functionalization of C_{60} with macrocyclic bis-malonates.

Reaction of macrocyclic bis-malonates with C_{60} were carried out under the typical conditions developed by Diederich *et. al.* for the preparation of fullerene bis-adducts (**Scheme II-*6***).[8] Specifically, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added to a solution of cyclo-bis-malonates, C_{60} and iodine in toluene at room temperature.

Reaction of **II-5A** with C_{60} was highly regioselective and only the *trans-3* regioisomer was obtained in a good yield of 54%. In contrast, no regioselectivity was observed for the larger macrocycle **II-5B**. Bis-adducts *trans-3*, *e* and *cis-2* were isolated in 15%, 4% and 6% yields, respectively. Traces of other bis-adducts were also observed but too small amounts of products prevented complete characterizations. The Bingel reaction with macrocycle **II-10C** was regioselective and afforded the *trans-3* (**II-21**) and the *e* (**II-22**) bis-adducts in 26% and 15% yields, respectively.

Reaction of the 28 and 32-membered ring macrocyclic bis-malonates (**II-16a** and **II-20b**) with C_{60} were also highly regioselective and gave the *cis-2* C_{60} bis-adduct **II-23** in 27% and 38% yield, respectively. A further increase of the ring size with the 36-48 menbered ring macrocyclic bis-malonates **II-20c-f** afforded the two regioisomeric bis-adducts *trans-3* (**II-21c-f**) and *e* (**II-22c-f**) by reaction with C_{60}.

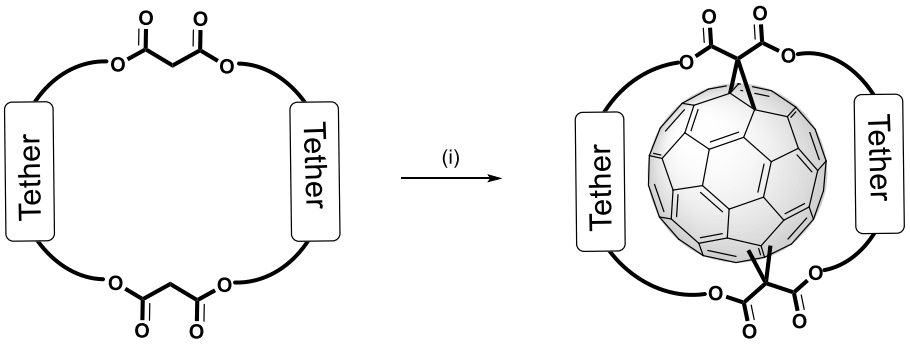
Compounds **II-21-23** have been characterized by ^{1}H and ^{13}C NMR, UV-vis and IR spectroscopies. In addition, the MALDI-TOF mass spectra were also consistent with the proposed structures. The relative position of the two cyclopropane rings on the fullerene core were determined based on the molecular symmetry deduced from the NMR spectra and on the diagnostic features seen in the absorption spectrum.

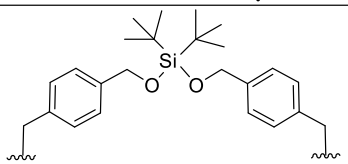
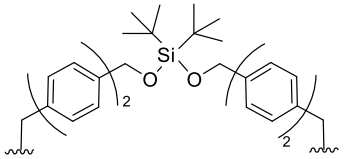
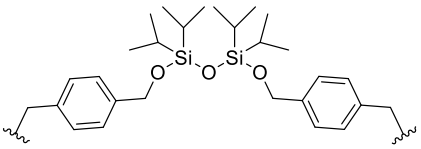
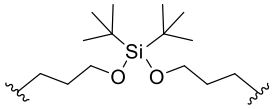
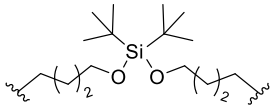
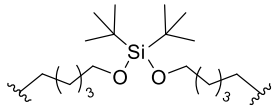
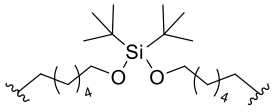
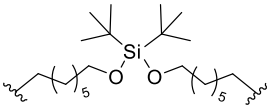
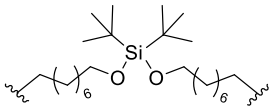
In the case of a bis-functionalization of C_{60} with macrocycles, there are four possible molecular symmetries based on the addition patterns: C_1 (*e*), C_s (*cis-2* and *trans-4*), C_2 (*cis-3*, *trans-3* and *trans-2*) and D_{2h} (*trans-1*). To deduce the molecular symmetry, careful analyses of the fullerene resonances on the ^{13}C NMR spectra of **II-21-23** were performed. As typical examples, the ^{13}C NMR spectra of an *e*, a *trans-3* and a *cis-2* regioisomers are shown in Figure II-8.

In the case of **II-22c**, 60 fullerene resonances were observed: four are observed at δ = 69.7, 71.35, 71.37 and 71.4 ppm (sp^3 C atoms) and 56 between 138.9 and 148.1 ppm (sp^2 C atoms) indicating a C_1 symmetry.

In the case of the *trans-3* bis-adducts **II-21**, 30 fullerene resonances are expected. Indeed, for compound **II-21c** two are observed at δ = 71.0 and 70.9 ppm (sp^3 C atoms) and 28 between δ = 139.4 and 146.7 ppm (sp^2 C atoms) which is in perfect agreement with a C_2 molecular symmetry.

For compound **II-23a**, two fullerene resonances are observed at δ = 67.6 and 70.5 ppm (sp^3 C atoms) and 30 between δ = 135.7 and 148.2 ppm (sp^2 C atoms). The presence of half intensity signals for some of the resonances of the fullerene C atoms seen in the sp^2 region is an unambiguous signature for a C_s symmetrical structure.



	Tether	Regioisomer of C_{60} bis-adduct	Yield
II-5A		***trans-3***	**II-21A** 54%
II-5B		***trans-3*** ***e*** ***cis-2***	**II-21B** 15% **II-22B** 4% **II-23B** 6%
II-10C		***trans-3*** ***e***	**II-21C** 26% **II-22C** 15%
II-16a		***cis-2***	**II-23a** 27%
II-20b		***cis-2***	**II-23b** 38%
II-20c		***trans-3*** ***e***	**II-21c** 44% **II-22c** 12%
II-20d		***trans-3*** ***e***	**II-21d** 33% **II-22d** 27%
II-20e		***trans-3*** ***e***	**II-21e** 30% **II-22e** 20%
II-20f		***e*** ***trans-3***	**II-22f** 21% **II-21f** 16%

Scheme II-6. Reagents and conditions: (i) C_{60}, I_2 and DBU, PhMe, rt, 1 h.

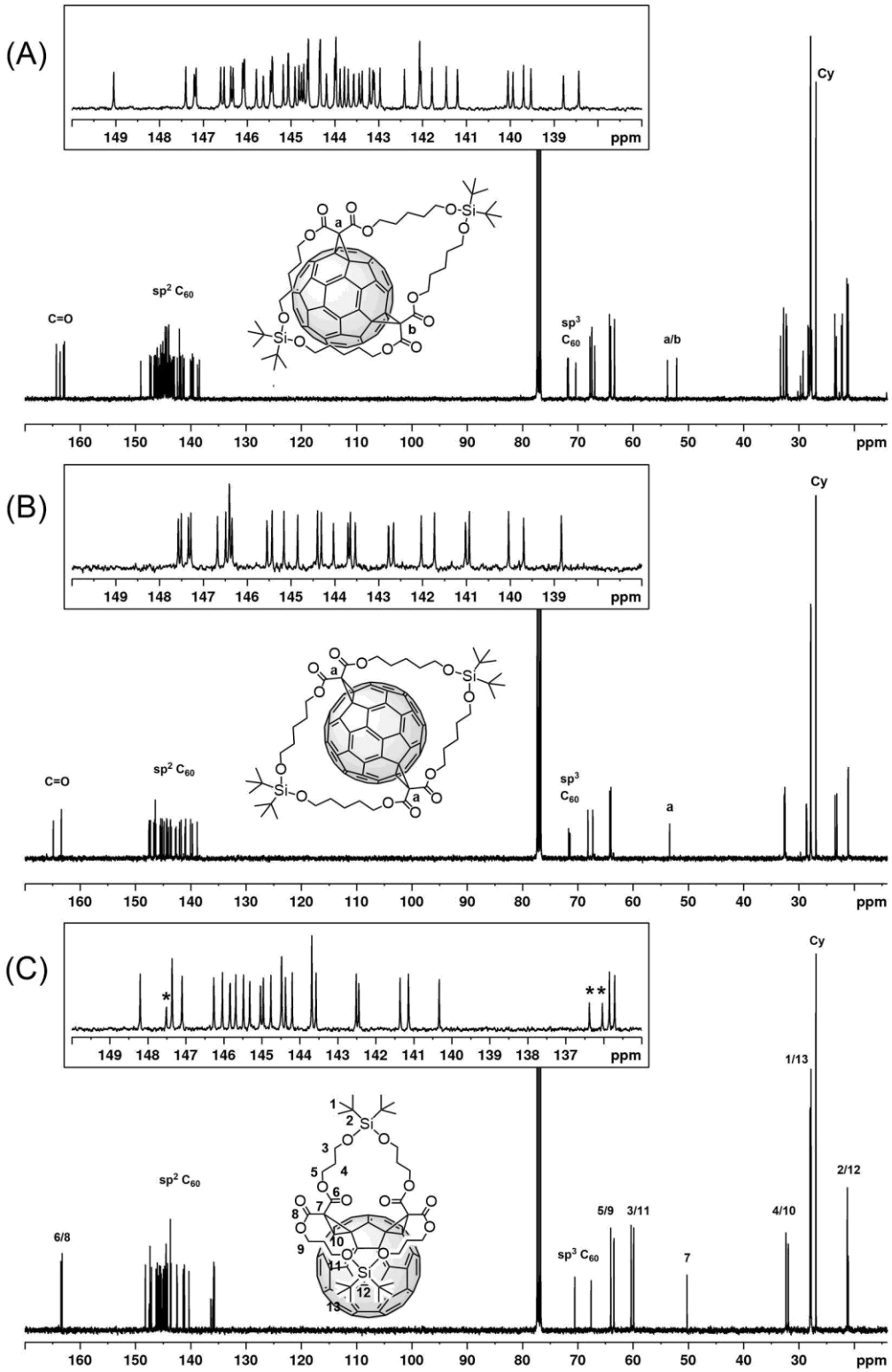


*Figure II-8 : ^{13}C NMR spectra ($CDCl_3$, 100 MHz); (A) C_1-symmetrical e bis-adduct **II-22c**; (B) C_2-symmetrical trans-3 bis-adduct **II-21c**; (C) C_s-symmetrical cis-2 bis-adduct **II-23a**; Inset: detailed view showing the resonances of the fullerene sp^2 C atoms; * indicates the sp^2 fullerene C atoms showing half intensity signals; Cy = cyclohexane.*

The unambiguous assignation of the addition patterns was finally achieved by UV-vis analysis. The absorption spectra of C_{60} multi-adducts are highly dependent on the addition pattern and characteristic for each of the regioisomers (Figure II-9).[8–13] The absorption spectra of **II-21-23** were recorded in CH_2Cl_2 and clearly revealed the diagnostic features of *trans-3*, *e* and *cis-2* addition patterns, respectively.

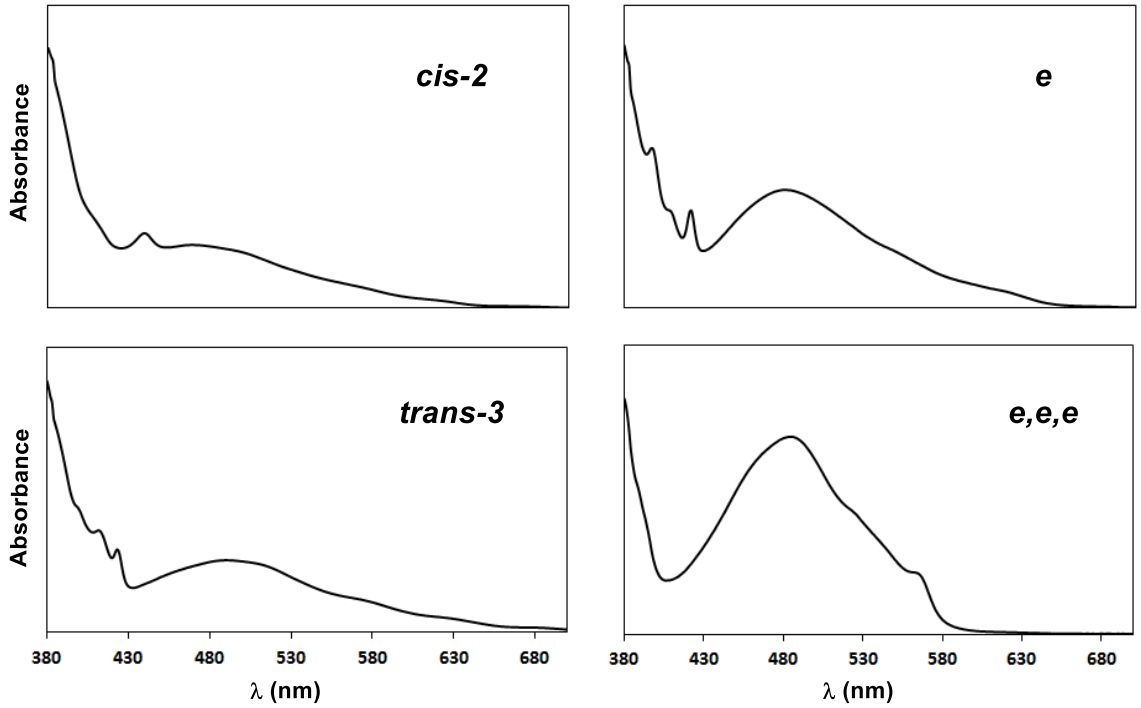


Figure II-9 : Characteristic UV/vis spectra of four multi-adducts of C_{60}.

The regioselectivity of the bis-addition on the C_{60} is clearly governed by the ring size of the macrocycle. Indeed, an increase of the macrocycle size induces a decrease in the regioselectivity.

The silyl group has also an impact on the regioselectivity. The fact that three different regioisomers were isolated with the macrocycle **II-5B** shows that the O-Si-O sequence introduces too much flexibility into the macrocycle. Indeed, the macrocycle must adopted different conformations in order to form these regioisomers. To adopt these different conformations, the necessary degrees of freedom are provided by the silyl groups. This is further validated by the formation the *e* and *trans-3* regioisomers with macrocycle **II-10C**.

The influence of the rigidity/flexibility of the spacer on the regioselectivity is only minor to the fact that the silyl groups provide flexibility to the macrocycle.

The preferential formation of the *e* and *trans-3* C_{60} bis-adducts is explained by the reactivity of the C_{60} sphere. For C_{60} mono-adduct derivatives, the *e* and *trans-3* positions are the most reactive sites.[9,14] Therefore bis-adducts *e* and *trans-3* are kinetic products. In counterpart, the thermodynamic product is formed when the formation of *e* and *trans-3* bis-adducts are energetically disfavored by strain arguments relative to the conformation of the

macrocycle. In the case of the cyclo-alkylmalonates, computational calculations at the AM1 semi-empirical level were performed with Spartan'10 Macintosh Parallel Edition (Wavefunction Inc., USA) (Table II-1). As shown in Table II-1, the *e* and *trans-3* isomers are low in energy for $(CH_2)_{5\text{-}8}$ and confirmed the observed regioselectivity. The preference for the C_2-symmetrical C_{60} bis-adducts *trans-3* can be explained by the higher molecular symmetry. In general, more a molecule is symmetric, more the strain is uniformly distributed and thus provides a more stable compound. In the case of $(CH_2)_{3\text{-}4}$, the formation of the *e* and *trans-3* isomers are energetically disfavored compared to the *cis-2* isomer and thus only the *cis-2* bis-adduct of C_{60} were formed.

	$(CH_2)_3$ **II-16a**	$(CH_2)_4$ **II-20b**	$(CH_2)_5$ **II-20c**	$(CH_2)_6$ **II-20d**	$(CH_2)_7$ **II-20e**	$(CH_2)_8$ **II-20f**
cis-2 C_s	0	0	0	0	+3	+20.6
cis-3 C_2	+180.3	+97.2	+121	+91.5	+79.8	+85.7
e C_1	+76.3	+30.8	+18.1	+7.3	+1.1	+12.1
trans-4 C_s	326.5	+57.2	+28.4	+16.2	+14.5	+23.1
trans-3 C_2	+83.4	+30.3	+15.3	+21.3	0	+6.5
trans-2 C_2		+219.2	+77.1	+53.2	+28	+36.8
trans-1 D_{2h}			+71.3	+5.8	+39	+0

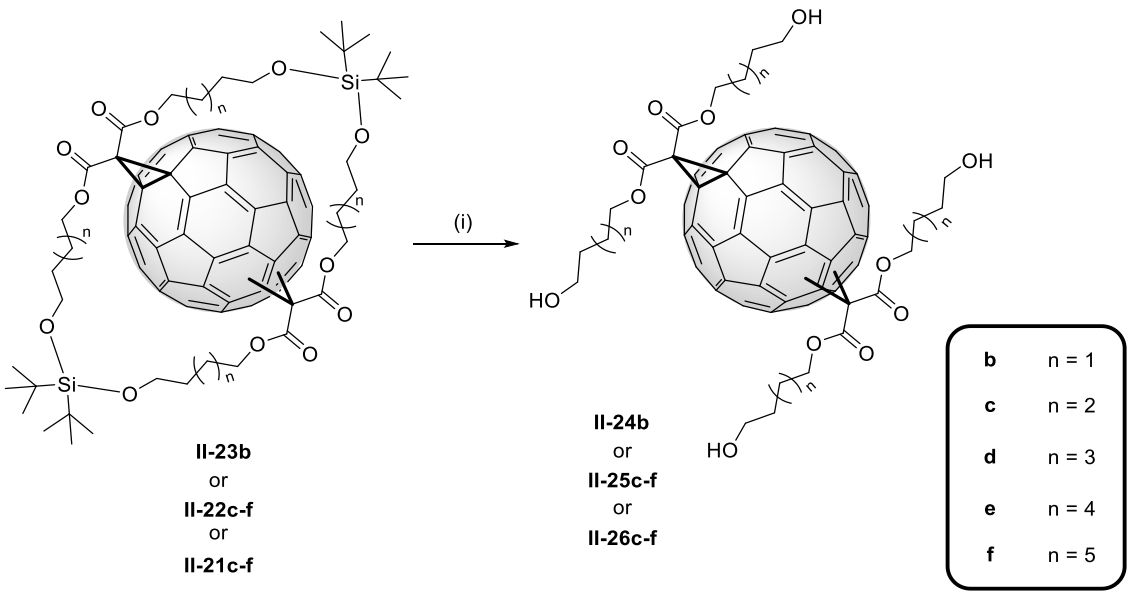
Table II-1 : Calculated ΔE heat of formation in kJ/mol at the AM1 semi-empirical level. In green the major formed regioisomer and in orange the minor formed regioisomer.

2.3 Deprotection.

As seen previously, the silyl groups have an impact on the regioselectivity. However, the principal interest to integrate them into a macrocycle structure is their easy deprotection. In order to preserve the ester functions, basic deprotection conditions are excluded. The deprotection of compounds **II-23b**, **II-22c-f** and **II-21c-f** were carried out with an excess of $BF_3.Et_2O$ in CH_2Cl_2/CH_3CN (**Scheme II-*7***). With acidic conditions, the ester functions remained unchanged and C_{60} bis-adducts **II-24**, **II-25** and **II-26** were obtained in good yields (56-89%). The removal of the silyl groups was confirmed by the spectroscopic and spectrometric data. In the case of C_1-symmetrical bis-adducts **II-22**, the removal of the silyl groups led to an increase of the molecular symmetry. A C_s-symmetry was deduced from their ^{13}C NMR spectra.

As typical example, the ^{13}C NMR spectrum of **II-22c** is shown in Figure II-10. Out of the 32 expected fullerene resonances, three are observed at δ = 70.4, 71.58 and 71.65 ppm for the sp^3 C atoms and 28 between δ = 138.7 and 147.6 ppm for the sp^2 C atoms. The presence of a half intensity signal in the sp^2 region is an unambiguous proof for the C_s-symmetry of compound **II-22c**. Furthermore, the presence of three sp^3 fullerene C atoms resonances is an unambiguous confirmation of the *equatorial* addition pattern. The *e* C_{60} bis-adduct is the sole C_s-symmetrical regioisomer for which three sp^3 fullerene C atoms resonances are expected. Only two signals are expected for the two other possible C_s-symmetrical regioisomers (*cis-2* and *trans-4*).

Our macrocyclic bis-malonates approach have furnished three regioisomers with good regioselectivity. The silyl groups can be readily cleaved to afford the corresponding acyclic fullerene polyols. With their four alcohol functions, compound **II-24-26** are valuable building blocks for further chemical modifications. Bis-adducts **II-25** with its *e* addition pattern can also be used as precursor for the preparation of hexa-adducts of C_{60} with an octahedral addition pattern.



Scheme II-7. Reagents and conditions: (i) $BF_3.Et_2O$, CH_2Cl_2, CH_3CN, rt, 12 h (**II-24**: 88%; **II-25**: 70-85%; **II-26**: 56-89%)

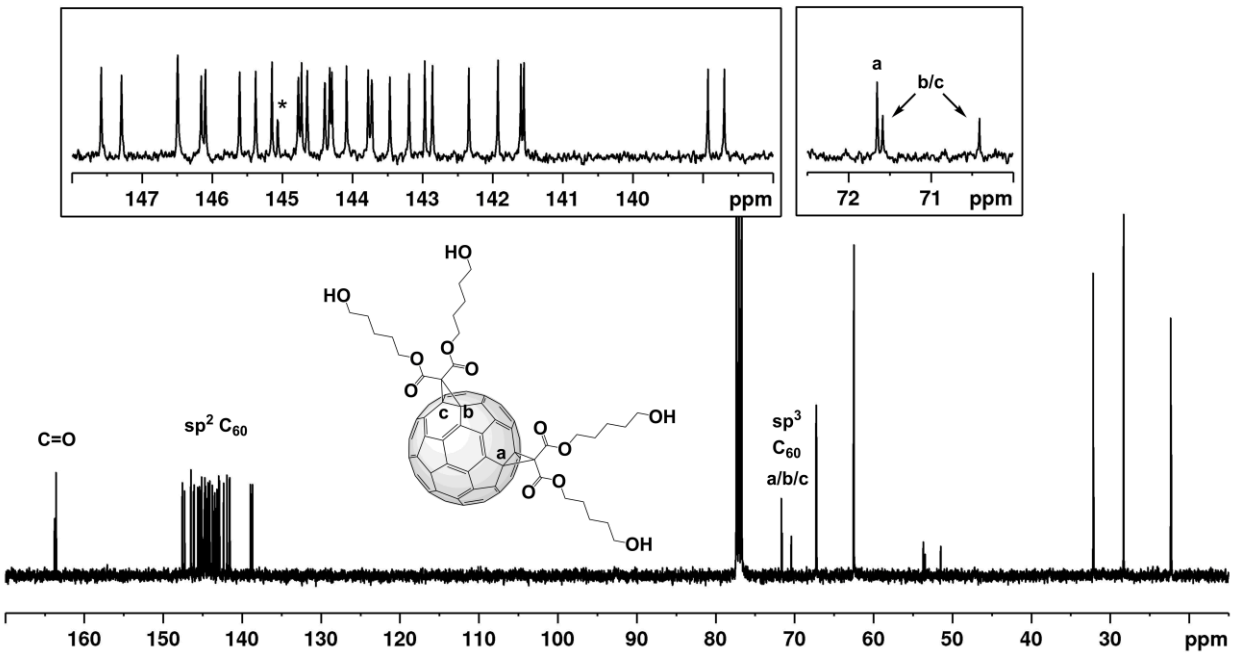


*Figure II-10 : ^{13}C NMR spectra ($CDCl_3$, 100 MHz) of C_s-symmetrical e bis-adduct **II-25c**; Inset: detailed view showing the resonances of the fullerene sp^2 C atoms; * indicates the sp^2 fullerene C atoms showing half intensity signals.*

3. Regioselective syntheses of Tris-adducts of C_{60} by macrocyclic approach.

3.1 Stepwise preparation of cyclo-tris-malonates.

This work has been done in collaboration with Eric Meischner.

Following the successful preparation of fullerene bis-adducts from macrocyclic bis-malonates, we became interested in extending our work to the synthesis of macrocyclic tris-malonates to prepare specific fullerene tris-adducts. For this purpose, an efficient synthetic route allowing the preparation of macrocyclic tris-malonates had to be developed first.

To selectively prepare cyclo-tris-malonates, we proposed to synthesize step-by-step the diol **II-33** containing two malonate sub-units (Figure II-11). The third malonate sub-unit being introduced by macrocyclisation reaction with malonyl chloride. In principle, diol **II-33** can be prepared from compounds **II-17** and **II-27** by an esterification reaction followed by deprotection. This last compounds are obtained from the protected derivative **II-13**. In a first instance, the synthesis of the cyclo-tris-malonate will be optimize with the $(CH_2)_3$ spacer.

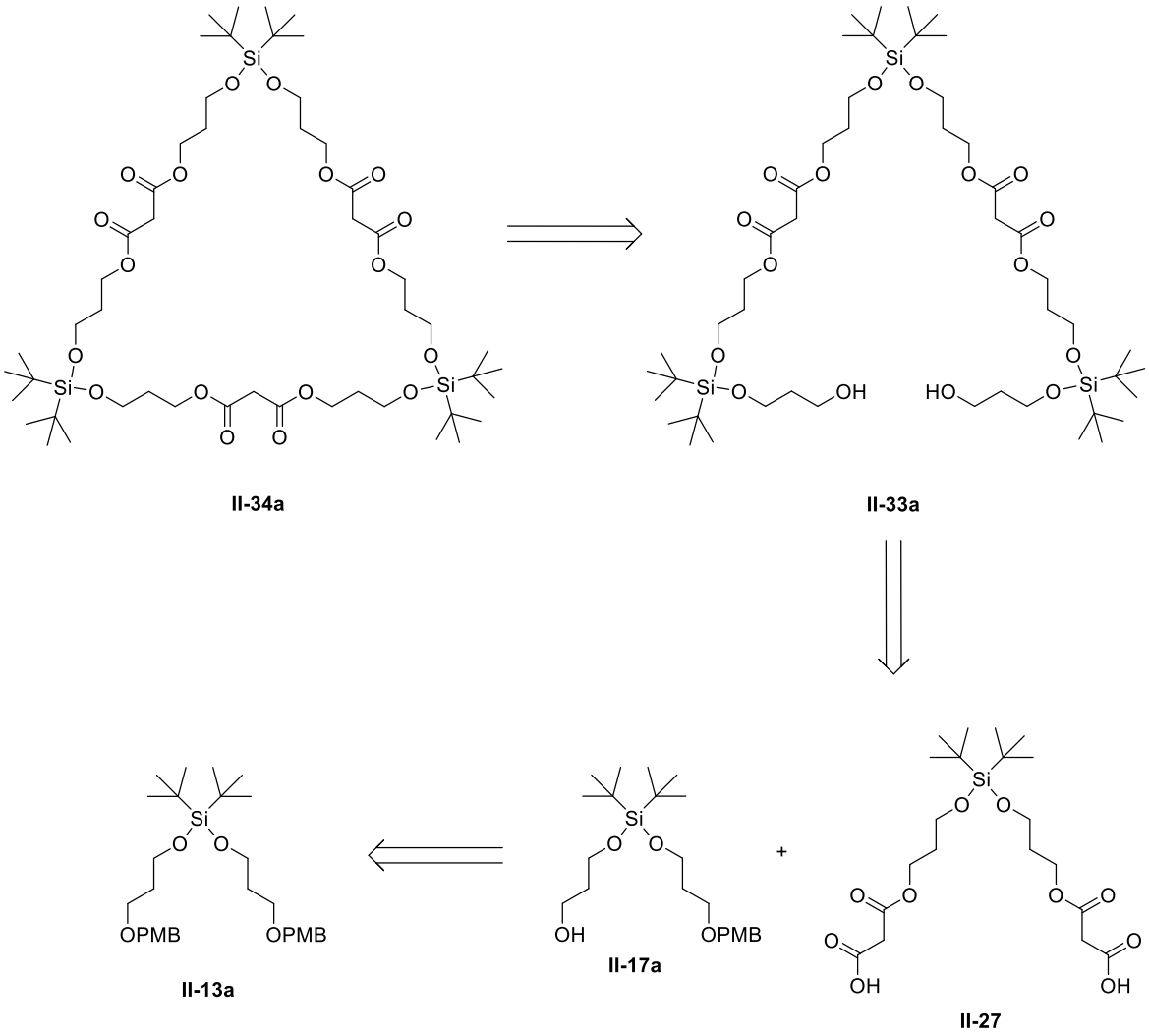
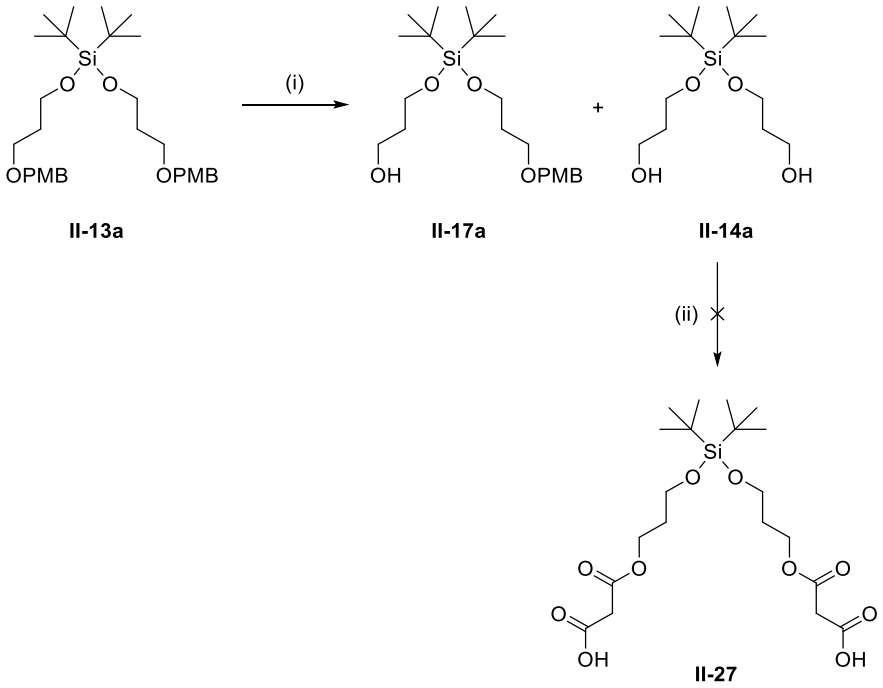


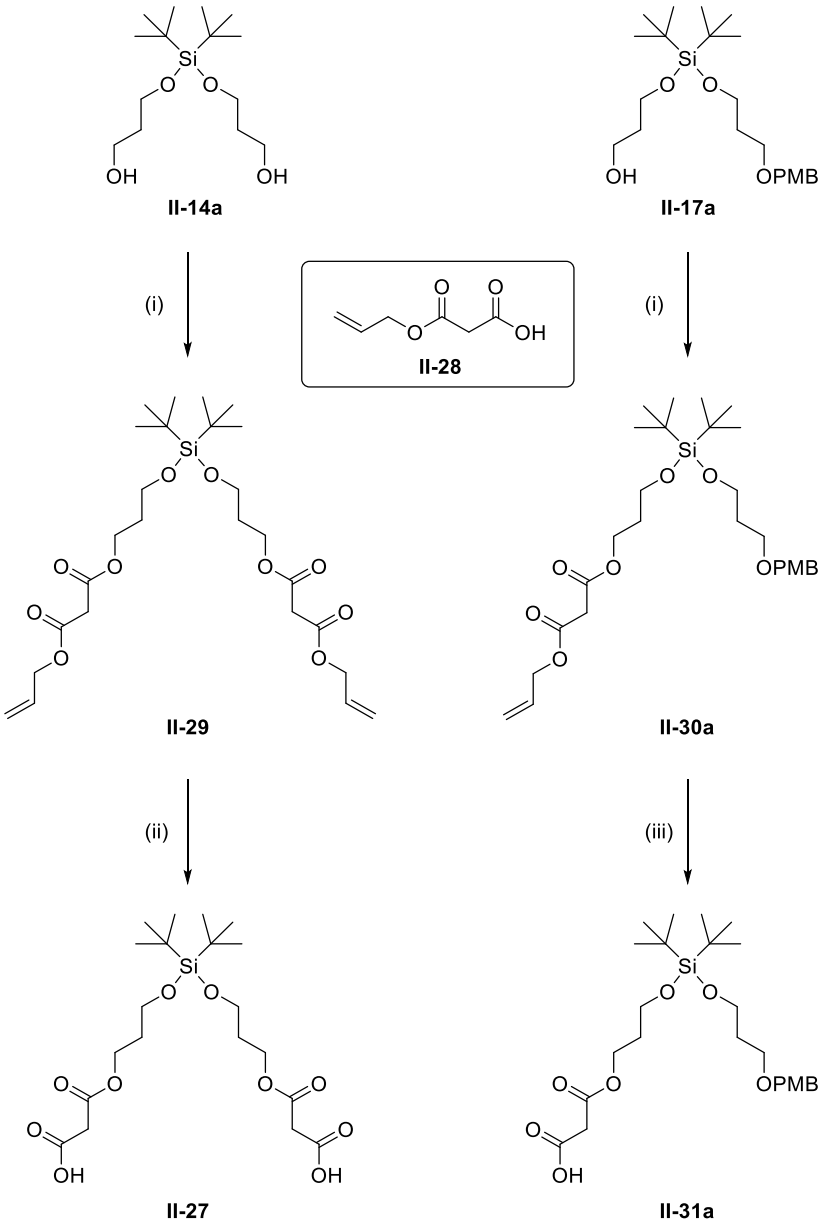
Figure II-11: Retrosynthetic analysis for the elaboration of cyclo-tris-malonate.

Treatment of **II-13** with 1 equiv. of DDQ provided the mono-protected derivative **II-17**, but also the diol **II-14** (**Scheme II-*8***). The introduction of malonate moieties was initially attempted by reaction of **II-14** with Meldrum's acid at 120°C. However, the ether group was not stable under these conditions.



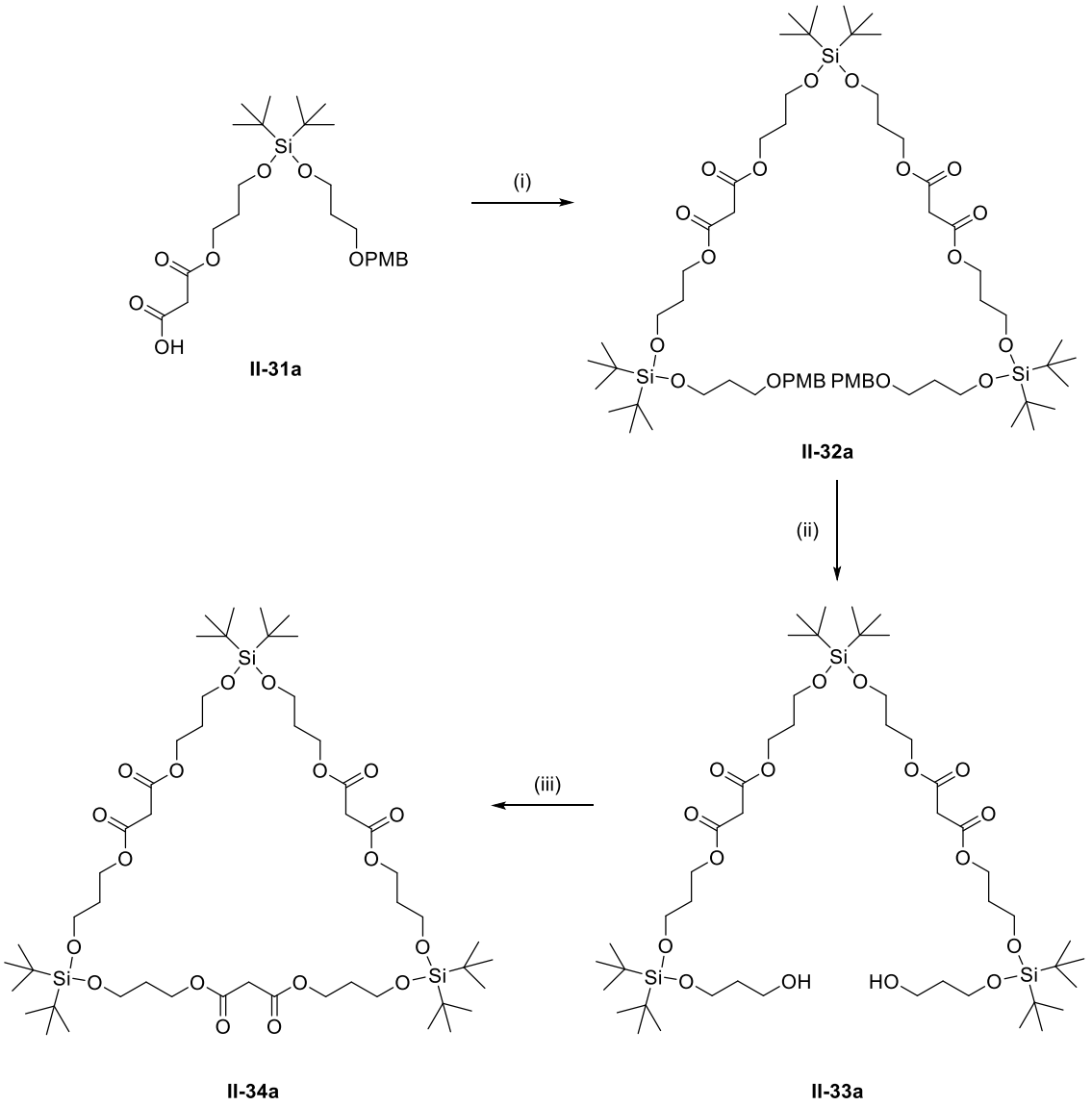
Scheme II-8. Reagents and conditions: (i) DDQ (1 eq), CH_2Cl_2, H_2O, rt, 1 h; (ii) Meldrum's acid, 120°C, (degradation).

In order to prevent the degradation of the starting material, an esterification reaction was carried out with **II-14** and malonic acid monoallyl ester **II-28** under the Steglich conditions (**Scheme II-*9***).[15] The bis-protected derivative **II-29** was obtained in 74% yield. The esterification reaction was also performed with **II-17** to afford compound **II-30** in 73% yield. The choice of the appropriate protecting groups for the malonic acid functions was the key for this synthesis. The deprotection conditions must not be acidic or imply a fluorine reagent in order to preserve the bridging di-*t*-butylsilylene groups, may not be basic to preserve the ester functions and they should be inert toward the PMB protecting group. The allyl protecting groups were removed under neutral conditions by treatment with $Pd(PPh_3)_4$ in the presence of an excess of morpholine.[16] Under these conditions the two other protecting groups (Si and PMB) and the ester functions remained effectively intact and the acidic derivatives **II-27** and **II-31** were obtained.



Scheme II-9. Reagents and conditions: (i) **II-28**, DCC, DMAP, CH_2Cl_2, 0°C to rt, 12 h (**II-29**: 74%, **II-30a**: 73%); (ii) $Pd(PPh_3)_4$, piperidine, THF, rt, 4 h; (iii) $Pd(PPh_3)_4$, morpholine, THF, rt, 4 h.

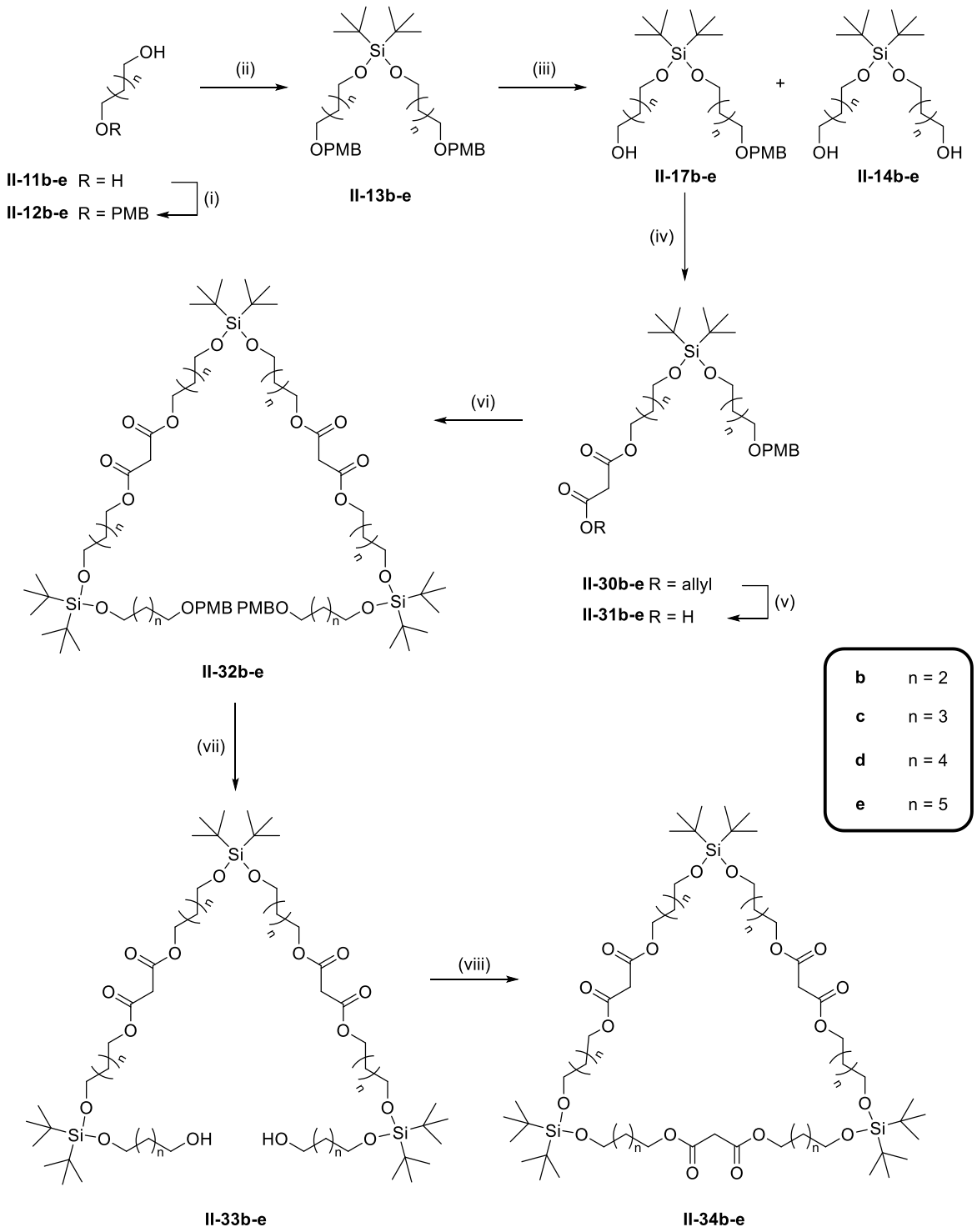
The bis-carboxylic acid derivative **II-27** being difficult to handle, only the mono-acidic derivative **II-31** was used (**Scheme II-*10***). Treatment of **II-31a** with diol **II-14a** under esterification conditions using dicyclohexylcarbodiimide (DCC) and DMAP afforded **II-32a** in 61% yield. Subsequent deprotection of the PMB protecting group with DDQ gave the key product **II-33a** in a nearly quantitative yield (98%). Final macrocyclisation of **II-33a** with malonyl dichloride afforded the cyclo-tris-malonates **II-34a** in an excellent yield of 53%. It is also important to note that **II-34a** is the only formed cyclooligomer. By-product being polymers, the isolation of **II-34a** was easy to perform.



II-31a **II-32a** **II-33a** **II-34a**

Scheme II-10. Reagents and conditions: (i) **II-14a**, DCC, DMAP, CH_2Cl_2, 0°C to rt, 12 h (61%); (ii) DDQ, CH_2Cl_2, H_2O, rt, 6 h (98%); (iii) malonyl chloride, DMAP, CH_2Cl_2, rt, 24 h (53%).

By following the same synthetic route, four others macrocyclic tris-malonates **II-34b-e** were synthetized starting from alkanediol possessing 4 to 7 carbon atoms (**Scheme II-*11***). The 48-54-60 and 66 membered ring macrocycles **II-34b-e** were thus obtained in good yields (21-63%) considering their ring size.

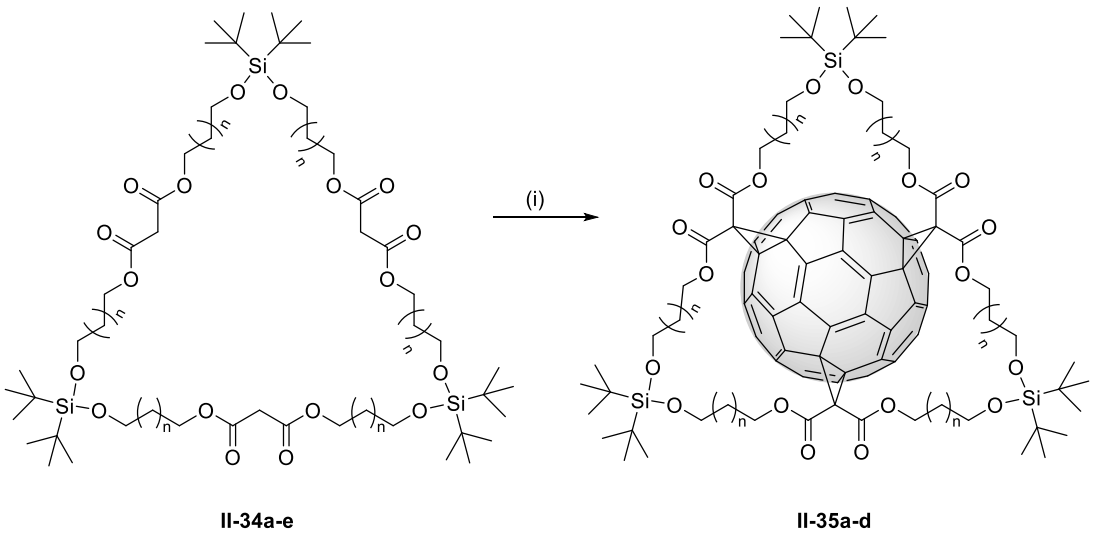


Scheme II-11. Reagents and conditions: (n= 2-5) (i) PMBCl, Ag_2O, CH_2Cl_2, rt, 12 h; (ii) $tBu_2Si(OTf)_2$, DMF, pyridine, rt, 12 h (iii) DDQ (1 eq), CH_2Cl_2, H_2O, rt, 1 h; (iv) **II-28**, DCC, DMAP, CH_2Cl_2, 0°C to rt, 12 h; (v) $Pd(PPh_3)_4$, morpholine, THF, rt, 4 h; (vi) **II-14b-e**, DCC, DMAP, CH_2Cl_2, 0°C to rt, 12 h; (vii) DDQ, CH_2Cl_2, H_2O, rt, 6 h; (viii) malonyl chloride, DMAP, CH_2Cl_2, rt, 24 h.

3.2 Regioselective tris-functionalization of C_{60}.

This work has been done in collaboration with Eric Meischner.

The reaction of the macrocyclic tris-malonates **II-34a-e** with C_{60} was carried out in the presence of I_2 and DBU (**Scheme II-*12***). The results are reported in Table II-2. A poor regioselectivity was observed for the largest macrocycles. For the 66 membered macrocyclic tris-malonates **II-34e**, no C_{60} tris-adducts could be isolated in a pure form from the mixture of products. In the case of **II-34c-d**, mixtures were also obtained but one specific regioisomer could be isolated in moderate yields. The large ring size and the relative flexibility of the O-Si-O motif bring a too high degree of freedom and consequently allows the formation of numerous tris-adducts and thus reduces the regioselectivity. For macrocycles **II-34a-b**, the reactions were highly regioselective and only the fullerene tris-adduct with an *e,e,e*-addition pattern was thus obtained. The relative position of the three cyclopropane rings on the C_{60} were determined based on the C_3 symmetry deduced from the ^1H and ^{13}C NMR spectra. As shown in Figure II-12, the 18 fullerene resonances of the sp^2 C atoms and the 2 fullerene resonances of the sp^3 C atoms observed in the ^{13}C NMR spectrum of **II-35a** are fully consistent with a threefold symmetrical compound. The cherry-red color and the UV-vis spectrum (Figure II-9) are also in complete agreement with the proposed *e,e,e*-addition pattern for compound **II-35**.



Scheme II-12. Reagents and conditions: (n= 1-5) (i) C_{60}, I_2, DBU, PhMe, rt, 1 h.

The *e* positions are the most reactive sites (kinetic products). Furthermore, the *e,e,e* tris-adducts of C_{60} are the most stable regioisomers (thermodynamics products) for the macrocycles **II-34a-b** (Table II-3). The formation of the *e,e,e* tris-adducts of C_{60} were optimal with the macrocycles **II-34a-b** and were thus obtained in excellent yields of 61% and 39%, respectively.

	$(CH_2)_3$ **II-34a**	$(CH_2)_4$ **II-34b**	$(CH_2)_5$ **II-34c**	$(CH_2)_6$ **II-34d**	$(CH_2)_7$ **II-34e**
e,e,e C_3	61	39	8	5	-
undefined C_1	-	-	35	26	-

Table II-2 : Results of the reactions of **II-34a-e** with C_{60} (%).

	e,e,e C_3	*all-trans-4* C_{3v}	*all-trans-3* D_3
$(CH_2)_3$ **II-34a**	0	+15	+115
$(CH_2)_4$ **II-34b**	0	+48	+26

Table II-3 : Calculated ΔE heat of formation in kJ/mol at the AM1 semi-empirical level.

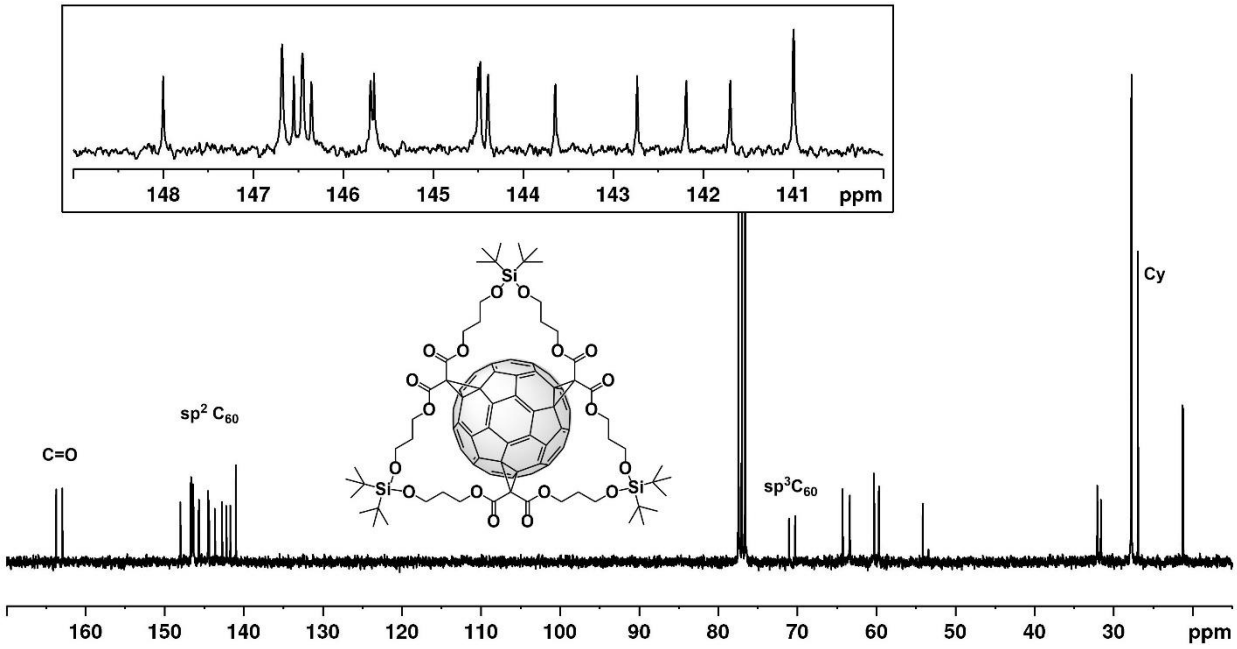


*Figure II-12 : ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of compound **II-34a** showing its C_3 symmetry; Inset: detailed view showing the resonances of the fullerene sp^2 Catoms; Cy = cyclohexane.*

4. Conclusion.

The reaction of macrocyclic di-*t*-butylsilylene-tethered bis- and tris-malonates with C_{60} gave access to fullerene bis- and tris-adducts with an excellent regioselectivity. By the modification of the rigidity and the length of the spacer units linking the malonate subunits to the di-*t*-butylsilylene moieties, fullerene bis-adducts with different addition patterns were obtained.

The control of the regiochemistry is primarly governed by the ring size of the macrocycle. The O-Si-O motif play also an important role in the regioselectivity by introducing flexibility in the macrocycle. Beyond the flexibility/rigidity of the spacer, the regioselectivity is mainly influenced by the relative reactivity of the different double bonds of the mono-substituted fullerene intermediate. In most of the cases, the macrocyclisation on the fullerene core occurs under kinetic control. For this reason, mainly *e* and *trans-3* bis-adducts are formed in the case of the fullerene bis-adducts. Similarly, the fullerene tris-adducts with an all-e addition pattern are also preferentially formed owing to the higher reactivity of the equatorial positions.

The silyl groups are also protecting groups that can be readily cleaved to afford the corresponding acyclic fullerene polyols. This new strategy opens therefore new perspectives for the post-functionalization of fullerene multi-adducts derivatives. Furthermore, the obtained bis-adducts *e* and tris-adducts *e,e,e* are totally suited for the preparation of multi-functionalized C_{60} hexa-adducts with an octahedral addition pattern.

5. Bibliography.

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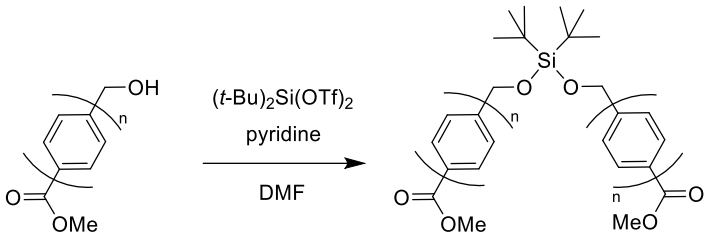
6. Experimental part.

General: Reagents and solvents were purchased as reagent grade and used without further purification. All reactions were performed in standard glassware under an inert Ar atmosphere. Evaporation and concentration were done at water aspirator pressure and drying in vacuo at 10^{-2} Torr. Column chromatography: silica gel 60 (230-400 mesh, 0.040-0.063 mm) was purchased from E. Merck. Thin Layer Chromatography (TLC) was performed on aluminum sheets coated with silica gel 60 F_{254} purchased from E. Merck. IR spectra (cm^{-1}) were recorded on a Perkin–Elmer Spectrum One Spectrophotometer. UV/Visible spectra were recorded on a Perkin-Elmer Lamda 35 UV/Vis Spectrometer. NMR spectra were recorded on a Bruker AC 300 or AC 400 with solvent peaks as reference at 25°C. MALDI-TOF-MS were obtained on a Bruker ULTRAFLEX TOF/TOF mass spectrometer with a dithranol matrix.

Synthesis.

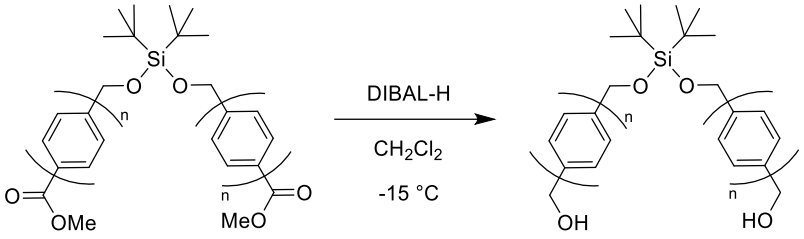


II-1A n = 1
II-1B n = 2

II-2A n = 1 92%
II-2B n = 2 86%

Compound II-2A: Di-tert-butylsilyl-bis(trifluoromethanesulfonate) (, 12.4mmol) was added slowly to a solution of **II-1A** (3.96 g, 24.8 mmol) and pyridine (2.1 mL, 26.1 mmol) in DMF (13 mL). The resulting mixture was stirred overnight at room temperature, then water was added and the aqueous layer extracted with Et_2O. The organic layer was washed, dried ($MgSO_4$) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2) yielded **II-2A** (4.94 g, 92%). IR (neat): $\upsilon = 1723$ (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, J = 8 Hz, 4H), 7.36 (d, J = 8 Hz, 4H), 4.96 (s, 4H), 3.92 (s, 6H), 1.11 (s, 18H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.0, 146.2, 129.6, 128.9, 125.5, 65.2, 52.0, 27.9, 21.4 ppm.

Compound II-2B: Di-tert-butylsilyl-bis(trifluoromethanesulfonate) (2.0 mL, 6.3 mmol) was added to a solution of **II-1B** (3.19 g, 13.2 mmol) and pyridine (1.1 mL, 13.5 mmol) in DMF (2 mL). The resulting mixture was stirred overnight at room temperature, then water was added and the aqueous layer extracted with CH_2Cl_2. The organic layer was washed, dried ($MgSO_4$) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 7:3) yielded **II-2B** (3.31 g, 5.3 mmol, 86%) as a white solid. IR (neat): υ = 1721 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.09 (d, *J* = 8 Hz, 4 H), 7.66 (d, *J* = 8 Hz, 4 H), 7.60 (d, *J* = 8 Hz, 4 H), 7.43 (d, *J* = 8 Hz, 4 H), 5.01 (s, 4 H), 3.94 (s, 6 H), 1.14 (s, 18 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 167.0, 145.4, 141.3, 138.6, 130.1, 128.8, 127.1, 126.9, 126.3, 65.3, 52.1, 28.0, 21.4 ppm.

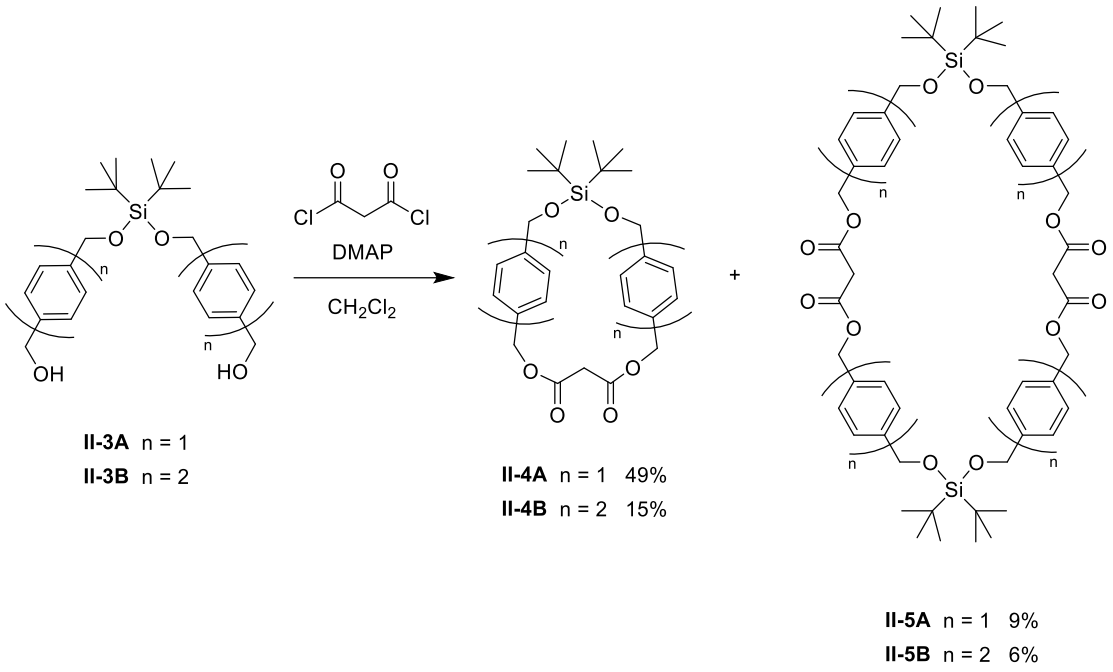


II-2A n = 1
II-2B n = 2

II-3A n = 1 92%
II-3B n = 2 67%

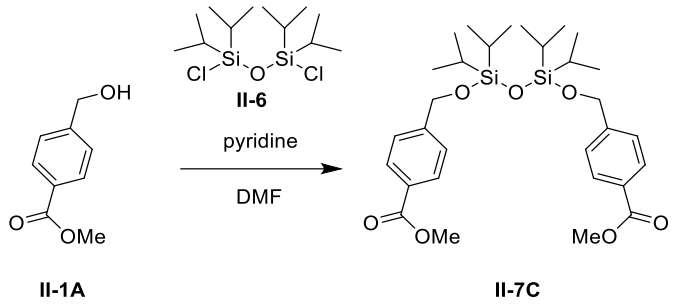
Compound II-3A: A solution of **II-2A** (2.42 g, 5.1 mmol) in dry CH_2Cl_2 (20 mL) was added dropwise to a stirred 0.5 M DIBAL-H solution in dry CH_2Cl_2 (22 mL, 22 mmol) at -15°C. The resulting mixture was stirred for 3 h, then MeOH and NH_4Cl (aq) were carefully added. The resulting mixture was filtered (Celite) and evaporated. Column chromatography on SiO2 (CH_2Cl_2/Cyclohexane 9:1 to CH_2Cl_2/MeOH, 98:2) yielded **II-3A** (1.97 g, 92%) as a white solid. IR (neat): υ = 3321 (O-H) cm^{-1}. ^1H-NMR (400 MHz, $CDCl_3$): δ = 7.32 (s, 8H), 4.93 (s, 4H), 4.68 (s, 4H), 1.10 (s, 18H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 140.7, 139.5, 127.0, 126.0, 65.4, 65.3, 28.0, 21.4 ppm.

Compound II-3B: A solution of **II-2B** (3.03 g, 4.8 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a stirred 1M DIBAL-H solution in THF (20.3 mL, 20.3 mmol) at -15°C. The resulting mixture was stirred for 3h, then quenched with MeOH and NH_4Cl (aq), filtered on celite and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 96:4) yielded **II-3B** (1.85 g, 3.2 mmol, 67%) as a white solid. IR (neat): υ = 3311 (br, O-H) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.59 (d, *J* = 8 Hz, 4 H), 7.56 (d, *J* = 8 Hz, 4 H), 7.43 (d, *J* = 8 Hz, 4 H), 7.41 (d, *J* = 8 Hz, 4 H), 5.01 (s, 4 H), 4.74 (s, 4 H), 1.14 (s, 18 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.5, 140.4, 139.7, 139.4, 127.5, 127.2, 126.9, 126.3, 65.4, 65.1, 28.0, 21.4 ppm.

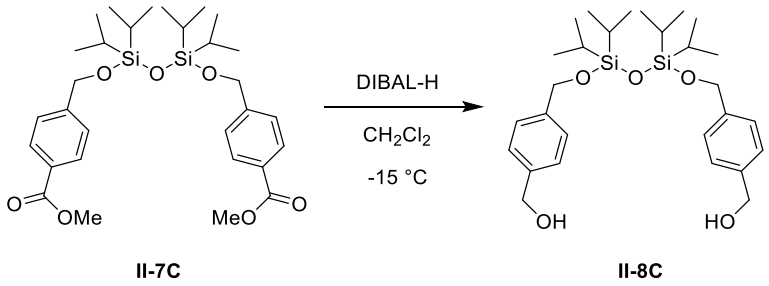


Compound II-4A & II-5A: A solution of malonyl chloride (0.5 mL, 5.2 mmol) in CH_2Cl_2 (100 mL) was added dropwise to a solution of **II-3A** (1.97 g, 4.7 mmol) and DMAP (1.27 g, 10.4 mmol) in CH_2Cl_2 (430 mL). The resulting mixture was stirred at room temperature for 2 h, then filtered on SiO_2 (CH_2Cl_2) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2 to CH_2Cl_2/cyclohexane, 9:1) yielded **II-4A** (1.12 g, 2.3 mmol, 49%) as a white solid and **II-5A** (0.20 g, 0.2 mmol, 9%) as a white solid. **II-4A:** IR (neat): υ = 1732 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.01 (s, 8 H), 5.13 (s, 4 H), 4.88 (s, 4 H), 3.51 (s, 2 H), 1.14 (s, 18 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.0, 141.0, 133.5, 127.3, 126.0, 66.8, 65.7, 42.4, 28.2, 21.3 ppm. **II-5A:** ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.25 (s, 16 H), 5.14 (s, 8 H), 4.87 (s, 8 H), 3.47 (s, 4 H), 1.10 (s, 36 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.2, 141.4, 133.8, 128.2, 125.9, 67.1, 65.2, 41.7, 28.0, 21.4 ppm.

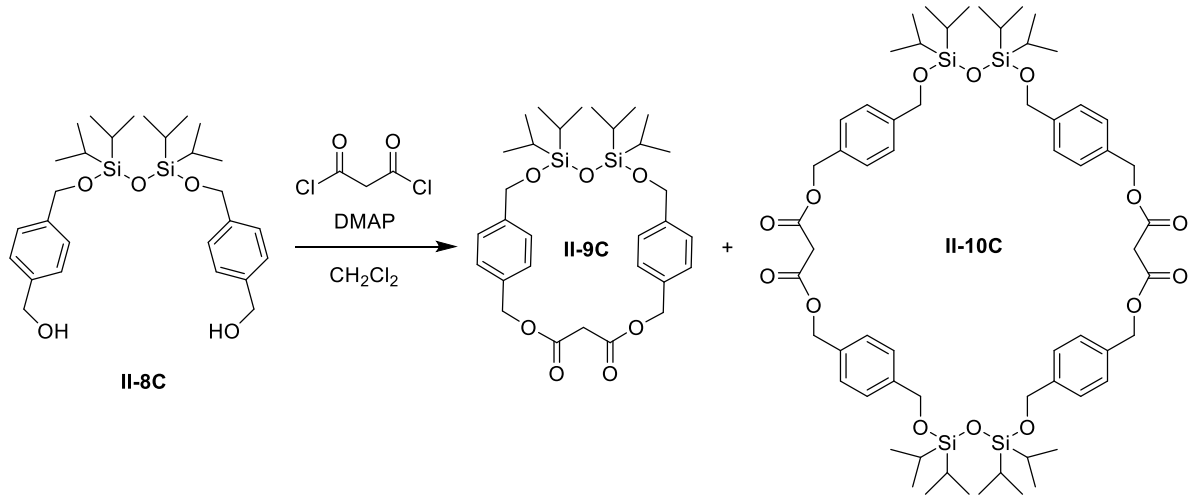
Compound II-4B & II-5B: A solution of malonyl chloride (0.32 mL, 3.2 mmol) in CH_2Cl_2 (100 mL) was added dropwise to a solution of **II-3B** (1.85 g, 3.2 mmol) and DMAP (1.47 g, 12 mmol) in CH_2Cl_2 (300 mL). The resulting mixture was stirred at room temperature for 2 h, then filtered on SiO_2 (CH_2Cl_2) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane/ether, 7:2:1) yielded **II-4B** (250 mg, 0.39 mmol, 12%) as a white solid and **II-5B** (170 mg, 0.13 mmol, 8%) as a white solid. **II-4B:** IR (neat): υ = 1754 (C=O), 1725 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.29 (d, *J* = 8 Hz, 4 H), 7.21 (d, *J* = 8Hz, 4 H), 7.19 (d, *J* = 8 Hz, 4 H), 7.07 (d, *J* = 8 Hz, 4 H), 5.22 (s, 4 H), 4.98 (s, 4 H), 3.56 (s, 2 H), 1.17 (s, 18 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.1, 140.7, 140.3, 138.5, 133.8, 128.2, 127.0, 126.4 (two peaks), 67.0, 66.0, 42.3, 28.3, 21.5 ppm. **II-5B**: ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.54-7.46 (m, 16 H), 7.40-7.32 (m, 16 H), 5.21 (s, 8 H), 4.99 (s, 8 H), 3.53 (s, 4 H), 1.16 (s, 36 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.2, 141.1, 140.4, 139.1, 134.0, 128.9, 128.8, 127.1, 126.9, 126.3, 67.0, 65.4, 41.9, 28.1, 21.5 ppm.



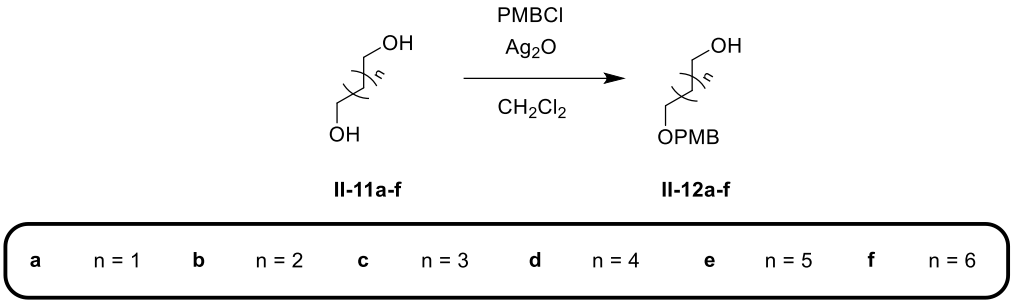
Compound II-7C: 1,3-Dichloro-1,1,3,3-tetraisopropyldisiloxane (**II-6**) (2.47 mL, 7.9mmol) was added to a solution of **II-1A** (2.77 g, 16.6 mmol) and pyridine (1.5 mL, 18.5 mmol) in DMF (9 mL). The mixture was stirred overnight at room temperature, then H_2O was added and the product was extracted with ether and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2) yielded **II-7C** (4.53 g, 7.87 mmol, 99%) as a white solid. IR (neat): υ = 1724 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.98 (d, *J* = 8 Hz, 4 H), 7.34 (d, *J* = 8 Hz, 4 H), 4.88 (s, 4 H), 3.91 (s, 6 H), 1.06 (m, 28 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 167.0, 146.3, 129.5, 128.8, 125.5, 63.8, 52.0, 17.4, 17.3, 13.0 ppm.



Compound II-8C: A solution of **II-7C** (4.51 g, 7.85 mmol) in dry THF (35 mL) was added dropwise to a stirred 0.5 M DIBAL-H solution in dry THF (33 mL, 33 mmol) at -15°C. The resulting mixture was stirred for 3 h, then MeOH and NH_4Cl (aq) were carefully added. The resulting mixture was filtered (Celite) and evaporated. Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2 to CH_2Cl_2/MeOH, 95:5) yielded **II-8C** (3.16 g, 6.1 mmol, 77%) as a white solid. IR (neat): υ = 3325 (O-H) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.27 (s, 8 H), 4.84 (s, 4 H), 4.65 (s, 4 H), 1.08 (m, 28 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.7, 139.4, 126.9, 126.1, 65.2, 64.0, 17.4, 17.4, 13.1 ppm.



Compound II-9C & II-10C: A solution of malonyl chloride (0.94 g, 6.6 mmol) in CH_2Cl_2 (100 mL) was added dropwise to a solution of **II-8C** (3.14 g, 6.1 mmol) and DMAP (1.77g, 14.5 mmol) in CH_2Cl_2 (590 mL). After 2 h, the resulting mixture was filtered on SiO_2 (CH_2Cl_2) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 7:3 to CH_2Cl_2/cyclohexane, 9:1) yielded **II-9C** (2.59 g, 4.4 mmol, 73%) as a white solid and **II-10C** (170 mg, 0.14 mmol, 5%) as a white solid. **II-9C:** IR (neat): $\upsilon = 1734$ (C=O) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.13 (d, *J* = 8 Hz, 4 H), 7.04 (d, *J* = 8Hz, 4 H), 5.12 (s, 4 H), 4.85 (s, 4 H), 3.49 (s, 2 H), 1.11 (s, 28 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.0, 141.1, 133.4, 127.8, 125.9, 67.0, 63.9, 42.3, 17.4 (two peaks), 13.1 ppm. **II-10C:** ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.22 (m, 16 H), 5.12 (s, 8 H), 4.77 (s, 8 H), 3.44 (s, 4H), 1.07 (s, 56 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.3, 141.7, 133.7, 128.2, 125.9, 67.1, 63.8, 41.5, 17.4, 13.0 ppm.



General Procedure for the mono-Protection of diols (II-12a-f) (GP I): A solution of PMB-Cl (1eq.) in CH_2Cl_2 was added dropwise to a solution of the appropriate diol (**II-11a-f**) (2-3 eq.) and Ag_2O (1 eq.) in CH_2Cl_2. The resulting mixture was stirred overnight at room temperature, then filtered on SiO_2 (CH_2Cl_2/EtOAc, 9:1) and concentrated. Column chromatography on SiO_2 gave **II-12a-f**.

Compound II-12a: II-12a was synthetized from 1,3-propoanediol (13.5 mL, 187 mmol), PMB-Cl (8.5 mL, 62.4 mmol) and Ag_2O (14.5 g, 62.4 mmol) in CH_2Cl_2 (250 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2 to CH_2Cl_2/EtOAc, 9:1) yielded **II-12a** (9.77 g,

49.8 mmol, 80%) as a colorless oil. IR (neat): υ = 3391 (br, OH) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, *J* = 8 Hz, 2 H), 6.81 (d, *J* = 8 Hz, 2 H), 4.39 (s, 2 H), 3.74 (s, 3 H), 3.71 (t, *J* = 6 Hz, 2 H), 3.58 (t, *J* = 6 Hz, 2 H), 1.78 (quint., *J* = 6 Hz, 2 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 159.3, 130.1, 129.3, 113.9, 73.0, 69.3, 62.1, 55.3, 32.1 ppm.

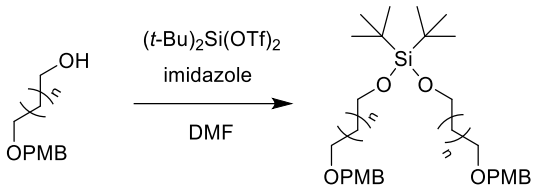
Compound II-12b: II-12b was synthetized from 1,4-butanediol (10.0 g, 111 mmol), PMB-Cl (5.0 mL, 37.0 mmol) and Ag_2O (8.6 g, 37.0 mmol) in CH_2Cl_2 (150 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2 to CH_2Cl_2/EtOAc, 95:5) yielded **II-12b** (7.4 g, 35.1 mmol, 95%) as a colorless oil. IR (neat): υ = 3392 (br, OH) cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8 Hz, 2 H), 6.87 (d, *J* = 8 Hz, 2 H), 4.43 (s, 2 H), 3.80 (s, 3 H), 3.62 (t, *J* = 7 Hz, 2 H), 3.45 (t, *J* = 7 Hz, 4 H), 1.79 (m, 4 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 159.2, 130.2, 129.3, 113.8, 72.7, 70.1, 62.7, 55.3, 30.2, 26.8 ppm.

Compound II-12c: II-12c was synthetized from 1,5-pentanediol (10.0 g, 96 mmol), PMB-Cl (4.4 mL, 32.0 mmol) and Ag_2O (7.4 g, 32.0 mmol) in CH_2Cl_2 (150 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2 to CH_2Cl_2/EtOAc, 95:5) yielded **II-12c** (6.5 g, 29.1 mmol, 91%) as a colorless oil. IR (neat): υ = 3392 (br, OH) cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8 Hz, 2 H), 6.87 (d, *J* = 8 Hz, 2 H), 4.43 (s, 2 H), 3.80 (s, 3 H), 3.62 (t, *J* = 7 Hz, 2 H), 3.45 (t, *J* = 7 Hz, 4 H), 1.58 (m, 4 H), 1.43 (m, 2 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 159.1, 130.7, 129.1, 113.7, 72.6, 70.0, 62.8, 55.3, 32.5, 29.5, 22.4 ppm.

Compound II-12d: II-12d was synthetized from 1,6-hexanediol (10.0 g, 85 mmol), PMB-Cl (3.8 mL, 28.2 mmol) and Ag_2O (6.6 g, 28.2 mmol) in CH_2Cl_2 (200 mL). Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/EtOAc, 93:7) yielded **II-12d** (6.2 g, 26.1 mmol, 92%) as a colorless oil. IR (neat): υ = 3378 (br, OH) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8 Hz, 2 H), 6.87 (d, *J* = 8 Hz, 2 H), 4.43 (s, 2 H), 3.80 (s, 3 H), 3.62 (t, *J* = 7 Hz, 2 H), 3.44 (t, *J* = 7 Hz, 4 H), 1.58 (m, 4 H), 1.37 (m, 4 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 159.1, 130.7, 129.2, 113.7, 72.6, 70.0, 63.0, 55.3, 32.7, 29.7, 26.0, 25.6 ppm.

Compound II-12e: II-12e was synthetized from 1,7-hepatanediol (10.0 g, 76 mmol), PMB-Cl (4.1 mL, 30.3 mmol) and Ag_2O (7.7 g, 33.3 mmol) in CH_2Cl_2 (200 mL). Column chromatography on SiO_2 (CH_2Cl_2/EtOAc, 95:5) yielded **II-12e** (6.9 g, 27.4 mmol, 90%) as a colorless oil. IR (neat): υ = 3378 (br, OH) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 8 Hz, 2 H), 6.87 (d, *J* = 8 Hz, 2 H), 4.43 (s, 2 H), 3.80 (s, 3 H), 3.63 (t, *J* = 7 Hz, 2 H), 3.43 (t, *J* = 7 Hz, 4 H), 1.58 (m, 4 H), 1.34 (m, 6 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 159.1, 130.7, 129.2, 113.7, 72.5, 70.1, 63.0, 55.3, 32.7, 29.7, 29.2, 26.0, 25.7 ppm.

Compound II-12f: II-12f was synthetized from 1,8-octanediol (13.8 g, 95 mmol), PMB-Cl (4.3 mL, 31.6 mmol) and Ag_2O (8.0 g, 34.7 mmol) in CH_2Cl_2 (270 mL). Column chromatography on SiO_2 (CH_2Cl_2/EtOAc, 95:5) yielded **II-12f** (5.8 g, 21.8 mmol, 69%) as a colorless oil. IR (neat): υ = 3400 (br, OH) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 8 Hz, 2 H), 6.87 (d, *J* = 8 Hz, 2 H), 4.43 (s, 2 H), 3.80 (s, 3 H), 3.63 (t, *J* = 7 Hz, 2 H), 3.43 (t, *J* = 7 Hz, 4 H), 1.57 (m, 4 H), 1.32 (m, 8 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 159.1, 130.8, 129.2, 113.7, 72.5, 70.2, 63.1, 55.3, 32.8, 29.8, 29.4, 29.3, 26.1, 25.7 ppm.



II-12a-f **II-13a-f**

General Procedure for silylation of mono-protected diols (II-12a-f) (GP II): Di-*tert*-butylsilyl-bis(trifluoromethanesulfonate) (1 eq.) was added slowly to a solution of **II-12a-f** (2 eq.) and pyridine (or imidazole) (2 eq.) in DMF. The resulting mixture was stirred overnight at room temperature, then water was added and the aqueous layer extracted with Et_2O. The organic layer was washed, dried ($MgSO_4$) and concentrated. Column chromatography on SiO_2 gave **II-13a-f**.

Compound II-13a: II-13a was synthetized from **II-12a** (9.8 g, 49.8 mmol), (*t*-Bu)$_2$Si(OTf)$_2$ (8.1 mL, 24.9 mmol) and imidazole (4.2 g, 62.2 mmol) in DMF (10 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2 to CH_2Cl_2) yielded **II-13a** (9.0 g, 17.0 mmol, 68%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.18 (d, *J* = 8 Hz, 4 H), 6.79 (d, *J* = 8 Hz, 4 H), 4.35 (s, 4 H), 3.84 (t, *J* = 6 Hz, 4 H), 3.72 (s, 6 H), 3.50 (t, *J* = 6 Hz, 4 H), 1.76 (quint., *J* = 6 Hz, 4 H), 0.91 (s, 18 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 159.1, 130.7, 129.6, 113.8, 72.7, 66.8, 60.7, 55.3, 33.1, 27.9, 21.2 ppm.

Compound II-13b: II-13b was synthetized from **II-12b** (7.3 g, 34.6 mmol), (*t*-Bu)$_2$Si(OTf)$_2$ (5.1 mL, 15.7 mmol) and imidazole (2.4 g, 34.6 mmol) in DMF (20 mL). Column chromatography on SiO_2 (CH_2Cl_2) yielded **II-13b** (5.3 g, 9.5 mmol, 60%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8 Hz, 4 H), 6.87 (d, *J* = 8 Hz, 4 H), 4.43 (s, 4 H), 3,81(t, *J* = 6 Hz, 4 H), 3,80 (s, 6 H), 3.47 (t, *J* = 6 Hz, 4 H), 1,69 (m, 4 H), 1,61 (m, 4 H), 0.98 (s, 18 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 159.0, 130.7, 129.2, 113.7, 72.5, 70.0, 63.6, 55.3, 29.6, 27.9, 26.2, 21.1 ppm.

Compound II-13c: II-13c was synthetized from **II-12c** (5.6 g, 25.0 mmol), (*t*-Bu)$_2$Si(OTf)$_2$ (3.7 mL, 11.4 mmol) and pyridine (2.0 mL, 25.0 mmol) in DMF (20 mL). Column chromatography on SiO_2 (CH_2Cl_2) yielded **II-13c** (6.0 g, 10.3 mmol, 91%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8 Hz, 4 H), 6.87 (d, *J* = 8 Hz, 4 H), 4.43 (s, 4 H), 3.80 (s, 6 H), 3.79 (t, *J* = 7 Hz, 4 H), 3.45 (t, *J* = 7 Hz, 4 H), 1.59 (m, 4 H), 1.45 (m, 2 H), 0.99 (s, 18 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): □ = 159.1, 130.8, 129.1, 113.7, 72.5, 70.2, 63.7, 55.3, 32.7, 29.6, 27.9, 22.5, 21.2 ppm.

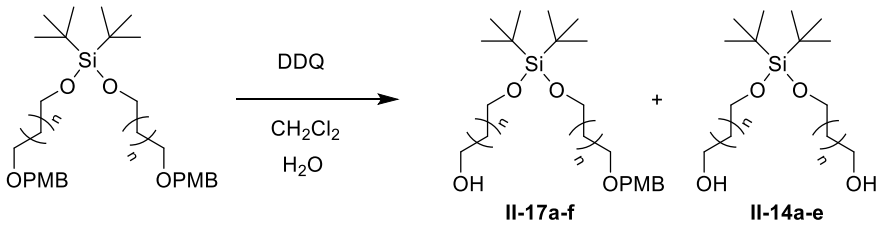
Compound II-13d: II-13d was synthetized from **II-12d** (6.4 g, 26.9 mmol), (*t*-Bu)$_2$Si(OTf)$_2$ (4.0 mL, 12.3 mmol) and imidazole (2.2 g, 32.6 mmol) in DMF (20 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 10:3) yielded **II-13d** (4.0 g, 6.5 mmol, 59%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8 Hz, 4 H), 6.87 (d, *J* = 8 Hz, 4 H), 4.43 (s, 4 H), 3.80 (s, 6 H), 3.79 (t, *J* = 6 Hz, 4 H), 3.44 (t, *J* = 6 Hz, 4 H), 1.63 (m, 2 H), 1.58 (m, 4 H), 1.40 (m, 4 H), 0.99 (s, 18 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 159.1, 130.8, 129.2, 113.7, 72.6, 70.2, 63.7, 55.3, 32.9, 29.9, 27.9, 26.1, 25.7, 21.1 ppm.

Compound II-13e: II-13e was synthetized from **II-12e** (6.3 g, 25.0 mmol), (*t*-Bu)$_2$Si(OTf)$_2$ (5.0 mL, 11.4 mmol) and pyridine (1.9 mL, 23.8 mmol) in DMF (20 mL). Column chromatography on SiO_2 (CH_2Cl_2) yielded **II-13e** (5.8 g, 9.0 mmol, 79%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, *J* = 8 Hz, 4 H), 6.87 (d, *J* = 8 Hz, 4 H), 4.43 (s, 4 H), 3,80 (s, 6 H), 3,79 (t, *J* = 6 Hz, 4 H), 3.43 (t, *J* = 6 Hz, 4 H), 1.56 (m, 8 H), 1.34 (m, 12 H), 0.99 (s, 18 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 159.0, 130.8, 129.2, 113.7, 72.5, 70.2, 63.8, 55.3, 32.9, 29.8, 29.3, 27.9, 26.3, 25.8, 21.2 ppm.

Compound II-13f: II-13f was synthetized from **II-12f** (5.8 g, 21.8 mmol), (*t*-Bu)$_2$Si(OTf)$_2$ (3.2 mL, 9.9 mmol) and pyridine (1.7 mL, 20.8 mmol) in DMF (20 mL). Column chromatography on SiO_2 (CH_2Cl_2) yielded **II-13f** (5.5 g, 8.2 mmol, 83%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8 Hz, 4 H), 6.87 (d, *J* = 8 Hz, 4 H), 4.43 (s, 4 H), 3,80 (s, 6 H), 3.79 (t, *J* = 6 Hz, 4 H), 3.43 (t, *J* = 6 Hz, 4 H), 1.55 (m, 8 H), 1.32 (m, 16 H), 0.99 (s, 18 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 159.0, 130.8, 129.2, 113.7, 72.5, 70.3, 63.8, 55.3, 32.9, 29.9, 29.5, 29.4, 27.9, 26.2, 25.8, 21.2 ppm.

Compound II-14a: A solution of **II-13a** (2.54 g, 4.8 mmol) and DDQ (2.27 g, 10.0 mmol) in CH_2Cl_2/H_2O (170/4 mL) was stirred at room temperature for 6 h, then filtered on SiO_2 (CH_2Cl_2/MeOH, 96:4) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 98:2) yielded **II-14a** (1.19 g, 4.1 mmol, 86%) as a colorless oil. IR (neat): υ = 3326 (br, OH) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.98 (t, *J* = 6 Hz, 4 H), 3.76 (t, *J* = 6 Hz, 4 H), 1.98 (br s, 2 H), 1.78 (quint., *J* = 6 Hz, 4 H), 0.97 (s, 18 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 62.5, 61.1, 34.7, 27.9, 21.1 ppm.

Compound II-14d: A solution of **II-13d** (4.00 g, 6.5 mmol) and DDQ (3.68 g, 16.2 mmol) in CH_2Cl_2/H_2O (180/10 mL) was stirred overnight at room temperature, then filtered on SiO_2 (CH_2Cl_2/MeOH, 9:1) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 94:6) yielded **II-14d** (2.00 g, 5.3 mmol, 82%) as a colorless oil. IR (neat): υ = 3325 (br, OH) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.81 (t, *J* = 6 Hz, 4 H), 3.65 (t, *J* = 6 Hz, 4 H), 1.58 (m, 8 H), 1.40 (m, 8 H) 0.99 (s, 18 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 63.7, 63.0, 32.9, 32.8, 27.9, 25.6, 25.5, 21.2 ppm.



General procedure for the synthesis of compounds II-14a-e & II-17a-f: Water (20 eq) was added to a solution of **II-13a-f** (1 eq) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 1 eq) in CH_2Cl_2 at room temperature. After 1 h, the crude was filtered on SiO_2 (CH_2Cl_2/MeOH, 95:5) and concentrated. Column chromatography on SiO_2 gave **II-14a-e** and **II-17a-f**.

Compound II-14a & II-17a: **II-14a** and **II-17a** were synthetized from water (6 mL), **II-13a** (6.56 g, 12.3 mmol) and DDQ (2.80 g, 12.3 mmol) in CH_2Cl_2 (450 mL). Column chromatography (SiO_2, CH_2Cl_2/EtOAc, 8:2 to CH_2Cl_2/MeOH, 95:5) gave **II-17a** (2.22 g, 44%) and **II-14a** (0.82 g, 2.8 mmol, 23%) as colorless oils. **II-17a**: IR (neat): υ = 3448 (O-H) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8 Hz, 2 H), 6.87 (d, *J* = 8 Hz, 2 H), 4.43 (s, 2 H), 4.00 (t, *J* = 6 Hz, 2 H), 3.95 (t, *J* = 6 Hz, 2 H), 3.80 (s, 3 H), 3.79 (t, *J* = 6 Hz, 2 H), 1.86 (m, *J* = 6 Hz, 2 H), 1.78 (m, *J* = 6 Hz, 2 H), 1.62 (s br, 1 H), 1.01 (s, 18 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 130.6, 129.3, 113.8, 72.7, 66.5, 62.6, 61.4, 60.9, 55.3, 34.6, 33.0, 27.8, 21.1 ppm.

Compound II-14b & II-17b: **II-14b** and **II-17b** were synthetized from water (3 mL), **II-13b** (6.00 g, 10.7 mmol) and DDQ (2.43 g, 10.7 mmol) in CH_2Cl_2 (270 mL). Column chromatography (SiO_2, CH_2Cl_2/EtOAc, 9:1 to CH_2Cl_2/MeOH, 95:5) gave **II-17b** (2.22 g, 5.0 mmol, 47%) and **II-14b** (0.75 g, 2.3 mmol, 22%) as colorless oils. **II-14b**: IR (neat): υ = 3327 (O-H) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.88 (t, *J* = 6 Hz, 4 H), 3.68 (t, *J* = 6 Hz, 4 H), 2.00 (s br, 2 H), 1.68 (m, 8 H), 1.01 (s, 18 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 64.0, 62.9, 29.9, 29.7, 28.0, 21.3 ppm. **II-17b**: IR (neat): υ = 3400 (O-H) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.26 (t, *J* = 8.5 Hz, 2 H), 6.87 (t, *J* = 8.5 Hz, 2 H), 4.44 (s, 2 H), 3.85 (m, 4 H), 3.80 (s, 3 H), 3.66 (t, *J* = 6 Hz, 2 H), 3.48 (t, *J* = 6 Hz, 2 H), 1.66 (m, 9 H), 1.00 (s, 18 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 130.9, 129.4, 113.9, 72.7, 70.1, 63.9, 63.9, 63.0, 55.4, 30.0, 29.8, 29.7, 28.0, 26.4, 21.3 ppm.

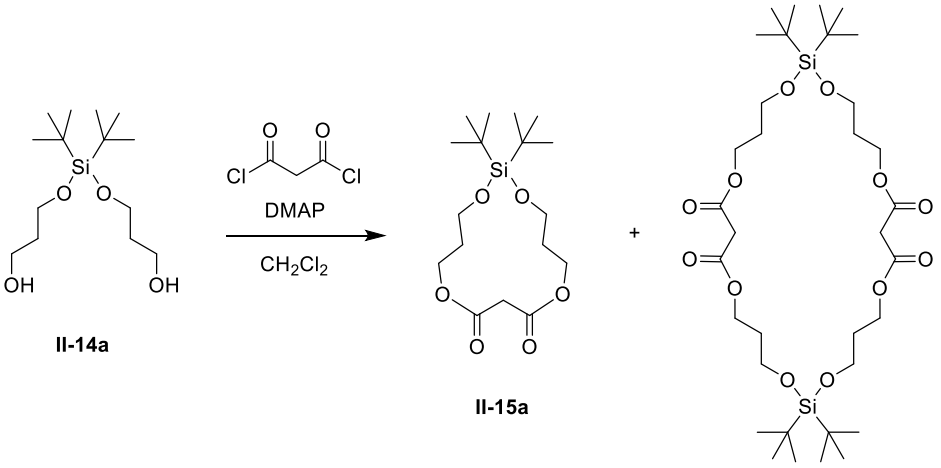
Compound II-14c & II-17c: **II-14c** and **II-17c** were synthetized from water (3 mL), **II-13c** (6.32 g, 10.7 mmol) and DDQ (2.44 g, 10.7 mmol) in CH_2Cl_2 (270 mL). Column chromatography (SiO_2, CH_2Cl_2/EtOAc, 9:1 to CH_2Cl_2/MeOH, 95:5) gave **II-17c** (2.38 g, 5.1 mmol, 47%) and **II-14c** (0.77 g, 2.2 mmol, 21%) as colorless oils. **II-14c:** IR (neat): υ = 3327 (O-H) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 3.83 (t, *J* = 6 Hz, 4 H), 3.65 (t, *J* = 6 Hz, 4 H), 1.58 (m, 8 H), 1.45 (m, 4 H), 1.00 (s, 18 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 63.8, 63.1, 32.8, 32.6, 28.0, 22.2, 21.3 ppm. **II-17c**: IR (neat): υ = 3399 (O-H) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) : δ = 7.25 (d, *J* = 8 Hz, 2 H), 6.87 (d, *J* = 8 Hz, 2 H), 4.43 (s, 2 H), 3.81 (m, 7 H), 3.63 (t, *J* = 7 Hz, 2 H), 3.44 (t, *J* = 7 Hz, 2 H), 1.59 (m, 8 H), 1.43 (m, 4 H), 1.00 (s, 18 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.1, 130.7, 129.2, 113.7, 72.5, 70.2, 63.7, 63.6, 62.9, 55.3, 32.8, 32.6, 32.5, 29.6, 27.9, 22.5, 22.0, 21.2 ppm.

Compound II-14d & II-17d: **II-14d** and **II-17d** were synthetized from water (3 mL), **II-13d** (4.30 g, 7.0 mmol) and DDQ (1.58 g, 7.0 mmol) in CH_2Cl_2 (250 mL). Column chromatography (SiO_2, CH_2Cl_2) gave **II-17d** (1.51 g, 3.0 mmol, 43%) and **II-14d** (0.58 g, 1.5mmol, 22%) as colorless oils. **II-14d**: IR (neat): υ = 3325 (br, OH) cm^{-1}. ^1H-NMR (400 MHz, $CDCl_3$): δ = 3.81 (t, *J* = 6 Hz, 4 H), 3.65 (t, *J* = 6 Hz, 4 H), 1.58 (m, 8 H), 1.40 (m, 8 H) 0.99 (s, 18 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 63.7, 63.0, 32.9, 32.8, 27.9, 25.6, 25.5, 21.2 ppm. **II-17d**: IR (neat): υ = 3399 (O-H) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 8.5 Hz, 2 H), 6.87 (d, *J* = 8.5 Hz, 2 H), 4.43 (s, 2 H), 3.80 (m, 7 H), 3.63 (t, *J* = 6.5 Hz, 2 H), 3.44 (t, *J* = 6.5 Hz, 2 H), 1.57 (m, 8 H), 1.38 (m, 9 H), 0.99 (s,

18 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.2, 130.9, 129.4, 113.9, 72.7, 70.3, 63.9, 63.8, 63.0, 55.4, 33.0, 33.0, 32.9, 29.9, 28.0, 26.2, 25.9, 25.8, 25.7, 21.3 ppm.

Compound II-14e & II-17e: **II-14e** and **II-17e** were synthetized from water (3 mL), **II-13e** (5.00 g, 7.8 mmol) and DDQ (1.76 g, 7.8 mmol) in CH_2Cl_2 (200 mL). Column chromatography (SiO_2, CH_2Cl_2/EtOAc, 9:1 to CH_2Cl_2/MeOH, 97:3) gave **II-17e** (2.08 g, 3.9 mmol 51%) and **II-14e** (0.65 g, 1.6 mmol, 21%) as colorless oils. **II-14e**: IR (neat): υ = 3327 (O-H) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.80 (t, *J* = 6.5 Hz, 4H), 3.64 (t, *J* = 6.5 Hz, 4 H), 1.56 (m, 8 H), 1.39 (m, 12 H), 0.99 (s, 18 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 63.9, 63.2, 33.0, 32.9, 29.4, 28.0, 26.0, 25.9, 21.3 ppm. **II-17e**: IR (neat): υ = 3387 (O-H) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 8.5 Hz, 2 H), 6.88 (d, *J* = 8.5 Hz, 2 H), 4.43 (s, 2 H), 3.80 (m, 7 H), 3.63 (t, *J* = 6.5 Hz, 2 H), 3.43 (t, *J* = 6.5 Hz, 2 H), 1.55 (m, 8 H), 1.36 (m, 12 H), 0.99 (s, 18 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 130.9, 129.4, 113.9, 72.7, 70.4, 64.0, 63.9, 63.2, 55.4, 33.0, 33.0, 32.9, 29.9, 29.5, 29.4, 28.0, 26.4, 26.0, 25.9, 21.3 ppm.

Compound II-17f: II-17f was synthetized from water (15 mL), **II-13f** (5.4 g, 8.1 mmol) and DDQ (1.8 g, 8.1 mmol) in CH_2Cl_2 (270 mL)**.** Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/EtOAc, 95:5) yielded **II-17f** (2.3 g, 4.1 mmol, 50%) as a colorless oil. IR (neat): υ = 3388 (br, OH) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, *J* = 8 Hz, 2 H), 6.87 (d, *J* = 8 Hz, 2 H), 4.43 (s, 2 H), 3.80 (m, 7 H), 3.63 (t, *J* = 6 Hz, 2 H), 3.43 (t, *J* = 6 Hz, 2 H), 1.55 (m, 8 H), 1.33 (m, 16 H), 0.99 (s, 18 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 159.1, 130.7, 129.2, 113.7, 72.5, 70.2, 63.8, 63.1, 55.3, 32.9, 32.8, 29.8, 29.5, 29.4 (two peaks), 27.9, 27.5, 26.2, 25.8, 25.7, 21.2 ppm.

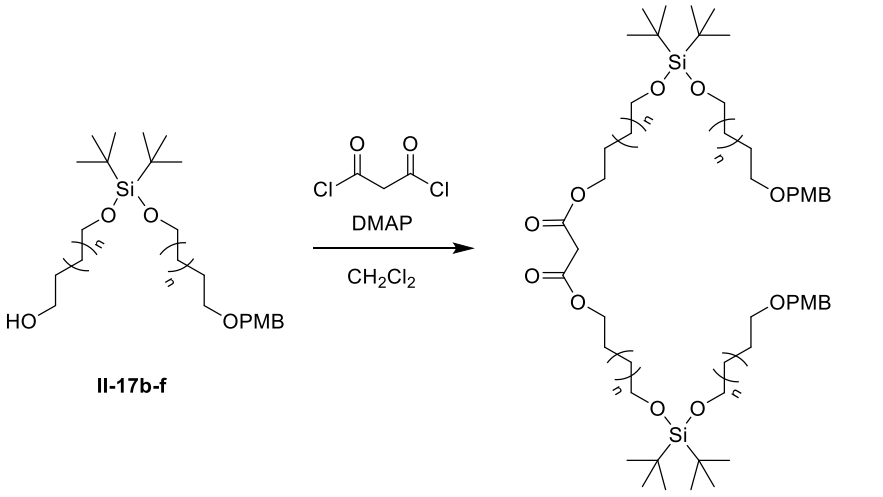


II-14a **II-15a** **II-16a**

Compounds II-15a & II-16a: A solution of DMAP (1.42 g, 11.6 mmol) in CH_2Cl_2 (100 mL) was added dropwise to a solution of **II-14a** (1.56 g, 5.3 mmol) and malonyl chloride (0.57 mL, 5.8 mmol) in CH_2Cl_2 (480 mL). The resulting mixture was stirred overnight at room temperature, then filtered on SiO_2 (CH_2Cl_2) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2 to CH_2Cl_2) yielded **II-15a** (0.45 g, 1.3 mmol, 24%) as a colorless oil, **II-16a** (0.29 g, 0.4 mmol, 15%) as a colorless oil. **II-15a:** IR (neat): υ = 1735 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.29 (t, *J* = 6 Hz, 4 H), 3.86 (t, *J* = 6 Hz, 4 H), 3.37 (s, 2 H), 1.91 (quint., *J* =

6 Hz, 4 H), 1.01 (s, 18 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.2, 61.6, 59.3, 42.5, 31.7, 27.8, 20.8 ppm. **II-16a:** IR (neat): υ = 1736 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.29 (t, *J* = 6 Hz, 8 H), 3.90 (t, *J* = 6 Hz, 8 H), 3.37 (s, 4 H), 1.89 (quint., *J* = 6 Hz, 8 H), 1.00 (s, 36 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.6, 62.4, 60.0, 41.6, 31.7, 27.8, 21.1 ppm. MALDI-TOF-MS: 720.9 ([M]$^+$, calcd for $C_{34}H_{64}O_{12}Si_2$: 720.4).

Compound II-15d: A solution of DMAP (1.54 g, 12.6 mmol) in CH_2Cl_2 (100 mL) was added dropwise to a solution of **II-14d** (1.90 g, 5.0 mmol) and malonyl chloride (0.54 mL, 5.5 mmol) in CH_2Cl_2 (400 mL). The resulting mixture was stirred overnight at room temperature, then filtered on SiO_2 (CH_2Cl_2) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2) yielded **II-15d** (0.86 g, 1.9 mmol, 38%) as a colorless oil. IR (neat): υ = 1751 (C=O), 1734 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.15 (t, *J* = 6 Hz, 4 H), 3.82 (t, *J* = 6 Hz, 4 H), 3.36 (s, 2 H), 1.65 (m, 4 H), 1.59 (m, 4H), 1.39 (m, 8 H), 1.01 (s, 18 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 165.5, 65.5, 63.8, 42.3, 32.7, 28.6, 27.9, 25.5, 25.4, 21.1 ppm.



II-17b-f

II-18b-f

b n = 1 **c** n = 2 **d** n = 3 **e** n = 4 **f** n = 5

General Procedure for the preparation of compounds II-18b-f : Malonyl chloride (1 eq.) was added to a solution of **II-17b-f** (2 eq.) and DMAP (2.2 eq) in CH_2Cl_2. The resulting mixture was stirred at room temperature for 2 h, then filtered on SiO_2 (CH_2Cl_2/EtOAc, 9:1) and concentrated. Column chromatography on SiO_2 gave **II-18b-f**.

Compound II-18b: II-18b was synthetized from **II-17b** (1.9 g, 4.3 mmol), malonyl chloride (0.21 mL, 2.2 mmol) and DMAP (0.58 g, 4.7 mmol) in CH_2Cl_2 (200 mL). Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/EtOAc, 98:2) yielded **II-18b** (1.4 g, 1.4 mmol, 67%) as a colorless oil. IR (neat): υ = 1752 (C=O), 1735 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8 Hz, 4 H), 6.87 (d, *J* = 8 Hz, 4 H), 4.43 (s, 4 H), 4.17 (t, *J* = 6 Hz, 4 H), 3.82(t, *J* = 6 Hz, 8 H), 3,80 (s, 6 H),

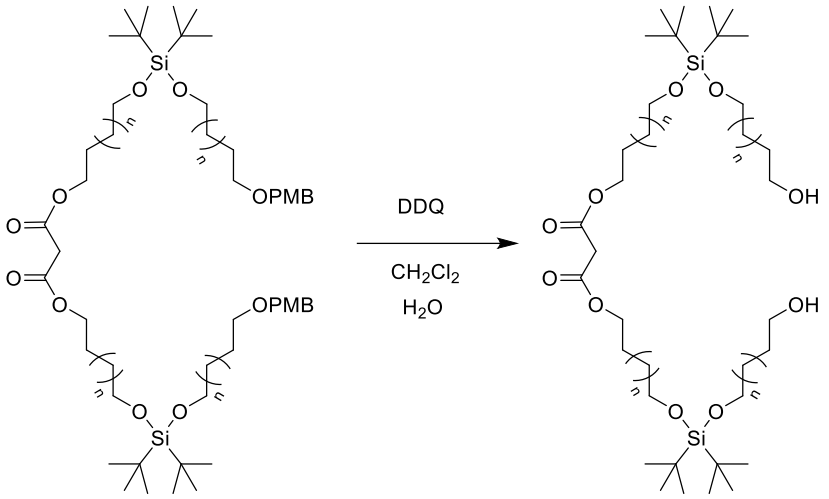
3.47 (t, *J* = 6 Hz, 4 H), 3,37 (s, 2 H), 1.77 – 1.59 (m, 16 H), 0.97 (s, 18 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 166.1, 159.1, 130.7, 129.2, 113.7, 72.5, 70.0, 65.5, 63.6, 63.1, 55.3, 41.6, 29.6, 29.1, 27.9, 26.3, 25.15, 21.2 ppm.

Compound II-18c: II-18c was synthetized from **II-17c** (2.3 g, 4.8 mmol), malonyl chloride (0.23 mL, 2.4 mmol) and DMAP (0.65 g, 5.3 mmol) in CH_2Cl_2 (100 mL). Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/EtOAc, 9:1) yielded **II-18c** (2.3 g, 2.3 mmol, 94%) as a colorless oil. IR (neat): υ = 1753 (C=O), 1736 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 7.25 (d, *J* = 8 Hz, 4 H), 6.87 (d, *J* = 8 Hz, 4 H), 4.43 (s, 4 H), 4.14 (t, *J* = 7 Hz, 4 H), 3.80 (s, 6 H), 3.79 (t, *J* = 7 Hz, 8 H), 3.45 (t, *J* = 7 Hz, 4 H), 3.35 (s, 2 H), 1.69 – 1.50 (m, 16 H), 1.38 (m, 8 H), 0.99 (s, 36 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 166.6, 159.0, 130.7, 129.1, 113.7, 72.5, 70.2, 65.6, 63.7, 63.4, 55.3, 41.6, 32.9, 32.7, 29.8, 28.5, 27.9, 26.1, 25.7, 25.6, 25.5, 21.2 ppm.

Compound II-18d: II-18d was synthetized from **II-17d** (1.2 g, 2.3 mmol), malonyl chloride (0.16 g, 1.2 mmol) and DMAP (0.31 g, 2.6 mmol) in CH_2Cl_2 (120 mL). Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/EtOAc, 95:5) yielded **II-18d** (1.1 g, 1.1 mmol, 93%) as a colorless oil. IR (neat): υ = 1753 (C=O), 1736 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 7.25 (d, *J* = 8 Hz, 4 H), 6.87 (d, *J* = 8 Hz, 4 H), 4.43 (s, 4 H), 4.14 (t, *J* = 7 Hz, 4 H), 3,80 (s, 6 H), 3.79 (t, *J* = 6 Hz, 8 H), 3.44 (t, *J* = 6 Hz, 4 H), 3,36 (s, 2 H), 1.69 – 1.50 (m, 22 H), 1.38 (m, 16 H), 0.99 (s, 36 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 166.6, 159.0, 130.7, 129.2, 113.7, 72.5, 70.2, 65.6, 63.8, 63.6, 55.3, 41.6, 32.7, 32.4, 29.6, 28.3, 27.9, 22.5, 22.1, 21.2 ppm.

Compound II-18e: II-18e was synthetized from **II-17e** (2.3 g, 4.3 mmol), malonyl chloride (0.31 g, 2.2 mmol) and DMAP (0.58 g, 4.7 mmol) in CH_2Cl_2 (150 mL). Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/EtOAc, 98:2) yielded **II-18e** (2.3 g, 2.1 mmol, 96%) as a colorless oil. IR (neat): υ = 1753 (C=O), 1736 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 7.26 (d, *J* = 8 Hz, 4 H), 6.87 (d, *J* = 8 Hz, 4 H), 4.43 (s, 4 H), 4.13 (t, *J* = 7 Hz, 4 H), 3.80 (s, 6 H), 3.79 (t, *J* = 6 Hz, 8 H), 3.43 (t, *J* = 6 Hz, 4 H), 3.36 (s, 2 H), 1.66 – 1.51 (m, 16 H), 1.35 (m, 24 H), 0.99 (s, 36 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 166.6, 159.1, 130.8, 129.1, 113.7, 72.5, 70.2, 65.6, 63.8, 63.7, 55.3, 41.6, 32.9, 32.8, 29.8, 29.3, 29.0, 28.5, 28.0, 26.3, 25.8, 25.7, 21.2 ppm.

Compound II-18f: II-18f was synthetized from **II-17f** (2.3 g, 4.1 mmol), malonyl chloride (0.29 g, 2.0 mmol) and DMAP (1.1 g, 9.0 mmol) in CH_2Cl_2 (150 mL). Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/EtOAc, 98:2) yielded **II-18f** (2.1 g, 1.8 mmol, 90%) as a colorless oil. IR (neat): υ = 1753 (C=O), 1736 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 7.25 (d, *J* = 8 Hz, 4 H), 6.87 (d, *J* = 8 Hz, 4 H), 4.43 (s, 4 H), 4.13 (t, *J* = 7 Hz, 4 H), 3.80 (s, 6 H), 3.79 (t, *J* = 6 Hz, 8 H), 3.43 (t, *J* = 6 Hz, 4 H), 3.36 (s, 2 H), 1.66 – 1.50 (m, 16 H), 1.32 (m, 32 H), 0.99 (s, 36 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.7, 159.0, 130.8, 129.2, 113.7, 72.5, 70.2, 65.7, 63.8 (two peaks), 55.3, 41.7, 32.9, 29.8, 29.5, 29.4, 29.3, 29.2, 28.7, 27.5, 26.2, 25.8, 21.2 ppm.



II-18b-f **II-19b-f**

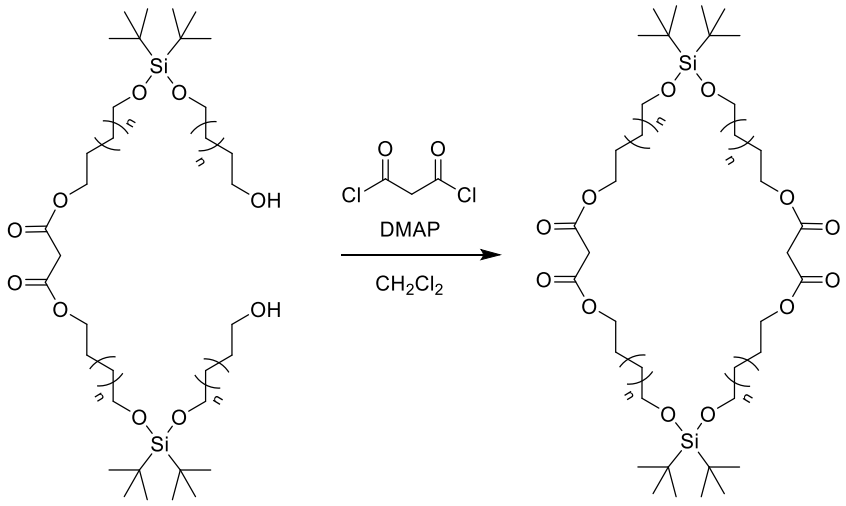
General Procedure for the preparation of compounds II-19b-f : DDQ (2.5 eq.) was added to a solution of **II-18b-f** (1 eq.) in CH_2Cl_2/H_2O. The resulting mixture was stirred at room temperature for 2 h, then filtered on SiO_2 (CH_2Cl_2/MeOH, 95:5) and concentrated. Column chromatography on SiO_2 gave **II-19b-f**.

Compound II-19b: II-19b was synthetized from **II-18b** (1.3 g, 1.4 mmol) and DDQ (0.78 g, 3.4 mmol) in CH_2Cl_2/H_2O (135/7.5 mL). Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 95:5) yielded **II-19b** (0.70 g, 0.99 mmol, 68%) as a colorless oil. IR (neat): $\upsilon =$ 3388 (br, OH), 1752 (C=O), 1737 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.21 (t, *J* = 7 Hz, 4 H), 3.88 (m, 8 H), 3.70 (t, *J* = 6 Hz, 4 H), 3.40 (s, 2 H), 1.80 (quint., *J* = 7 Hz, 4 H), 1.73 – 1.61 (m, 12 H), 1.03 (s, 36 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.7, 65.5, 63.9, 63.2, 62.8, 41.6, 29.8, 29.6, 29.1, 27.9, 25.1, 21.2 ppm.

Compound II-19c: II-19c was synthetized from **II-18c** (2.3 g, 2.3 mmol) and DDQ (1.3 g, 5.6 mmol) in CH_2Cl_2/H_2O (150/5.5 mL). Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/EtOAc, 9:1) yielded **II-19c** (1.4 g, 1.8 mmol, 81 %) as a colorless oil. IR (neat): $\upsilon =$ 3361 (br, OH), 1753 (C=O), 1736 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.15 (t, *J* = 7 Hz, 4 H), 3.82 (t, *J* = 7 Hz, 4 H), 3.81 (t, *J* = 7 Hz, 4 H), 3.65 (t, *J* = 7 Hz, 4 H), 3.36 (s, 2 H), 1.66 (quint, *J* = 7 Hz, 4 H), 1.68 (m, 4 H), 1.58 (m, 12 H), 1.40 (m, 8 H), 0.99 (s, 36 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.7, 65.6, 63.7, 63.4, 62.9, 41.6, 32.6, 32.5, 32.4, 28.2, 27.9, 22.1, 22.0, 21.2 ppm.

Compound II-19d: II-19d was synthetized from **II-18d** (1.1 g, 1.0 mmol) and DDQ (0.52 g, 2.3 mmol) in CH_2Cl_2/H_2O (90/5 mL). Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 95:5) yielded **II-19d** (0.69 g, 0.83 mmol, 80%) as a colorless oil. IR (neat): $\upsilon =$ 3363 (br, OH), 1753 (C=O), 1737 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.14 (t, *J* = 7 Hz, 4 H), 3.81 (t, *J* = 6 Hz, 4 H), 3.80 (t, *J* = 6 Hz, 4 H), 3.66 (t, *J* = 6 Hz, 4 H), 3.37 (s, 2 H), 1.66 (quint, *J* = 7 Hz, 4 H), 1.60 – 1.50 (m, 18 H), 1.40 (m, 16 H), 0.99 (s, 36 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.7, 65.6, 63.7, 63.6, 62.9, 41.6, 32.8 (three peaks), 28.5, 27.9, 25.6 (three peaks), 25.5, 21.2 ppm.

Compound II-19e: II-19e was synthetized from **II-18e** (2.3 g, 2.0 mmol) and DDQ (1.0 g, 4.5 mmol) in CH_2Cl_2/H_2O (150/8.4 mL). Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 95:5) yielded **II-19e** (1.5 g, 1.7 mmol, 84%) as a colorless oil. IR (neat): υ = 3378 (br, OH), 1756 (C=O) 1732 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.14 (t, *J* = 7 Hz, 4 H), 3,80 (t, *J* = 6 Hz, 8 H), 3.64 (t, *J* = 6 Hz, 4 H), 3,37 (s, 2 H), 1.65 (t, *J* = 6 Hz, 4 H), 1.56 (m, 16 H), 1.35 (m, 24 H), 0.99 (s, 36 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.7, 65.7, 63.8, 63.7, 63.0, 41.7, 32.9, 32.8 (two peaks), 29.4 (two peaks), 29.3, 29.0, 28.4, 27.9, 25.8 (two peaks), 25.7, 21.2 ppm.
Compound II-19f: II-19f was synthetized from **II-18f** (2.0 g, 1.7 mmol) and DDQ (0.87 g, 3.8 mmol) in CH_2Cl_2/H_2O (135/7.5 mL). Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 95:5) yielded **II-19f** (1.4 g, 1.5 mmol, 85%) as a colorless oil. IR (neat): υ = 3378 (br, OH), 1756 (C=O), 1732 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.13 (t, *J* = 7 Hz, 4 H), 3.80 (t, *J* = 6 Hz, 8 H), 3.64 (t, *J* = 6 Hz, 4 H), 3.36 (s, 2 H), 1.64 (t, *J* = 6 Hz, 4 H), 1.55 (m, 16 H), 1.33 (m, 32 H), 0.99 (s, 36 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.7, 65.7, 63.8 (two peaks), 63.0, 41.7, 32.9, 32.8, 29.4 (two peaks), 29.3, 29.2, 28.4, 27.9, 27.5, 25.7 (two peaks), 21.2 ppm.



II-19b-f **II-20b-f**

General Procedure for the preparation of Macrocycles II-20b-f : A solution of DMAP (2.2 eq.) in CH_2Cl_2 was added dropwise to a solution of **II-19b-f** (1 eq.) and malonyl chloride (1.1 eq.) in CH_2Cl_2. The resulting mixture was stirred at room temperature for 2 h, then filtered on SiO_2 (CH_2Cl_2/EtOAc, 9:1) and concentrated. Column chromatography on SiO_2 gave **II-20b-f**.

Compound II-20b: II-20b was synthetized from **II-19b** (670 mg, 0.94 mmol), malonyl chloride (0.1 mL, 1.04 mmol) and DMAP (138 mg, 1.13 mmol) in CH_2Cl_2 (90 mL). Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/EtOAc, 97:3) yielded **II-20b** (367 mg, 0.47 mmol, 50%) as a colorless oil. IR (neat): υ = 1736 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.15 (t, *J* = 7 Hz, 8 H), 3.81 (t, *J* = 7 Hz, 8 H), 3.34 (s, 4 H), 1.73 (quint, *J* = 7 Hz, 8 H), 1.59 (quint., *J* = 6 Hz, 8 H), 0.96 (s, 36 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.6, 65.4, 63.1, 41.7, 29.2, 27.8, 25.1, 21.2 ppm. MALDI-TOF-MS: 799.46 (100%, $[M+Na]^+$, calcd. for $C_{38}H_{72}O_{12}Si_2Na$: 799.45),

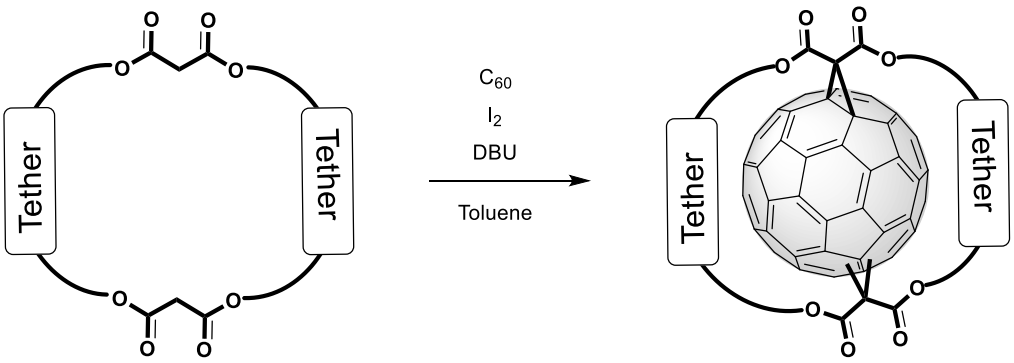
777.38 (24%, $[M+H]^+$, calcd. for $C_{38}H_{73}O_{12}Si_2$: 777.46), 815.38 (20%, $[M+K]^+$, calcd. for $C_{38}H_{72}O_{12}Si_2K$: 815.42).

Compound II-20c: II-20c was synthetized from **II-19c** (1.40 g, 1.83 mmol), malonyl chloride (0.2 mL, 2.01 mmol) and DMAP (0.27 g, 2.20 mmol) in CH_2Cl_2 (160 mL). Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/EtOAc, 97:3) yielded **II-20c** (430 mg, 0.52 mmol, 28%) as a colorless oil. IR (neat): $\upsilon =$ 1752 (C=O), 1734 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.15 (t, *J* = 7 Hz, 8 H), 3.81 (t, *J* = 7 Hz, 8 H), 3.36 (s, 4 H), 1.68 (quint, *J* = 7 Hz, 8 H), 1.58 (quint., *J* = 7 Hz, 8 H), 1,45 (m, 16 H), 0.99 (s, 36 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.6, 65.5, 63.5, 41.7, 32.4, 28.3, 27.9, 22.1, 21.2 ppm. MALDI-TOF-MS: 833.37 (100%, $[M+H]^+$, calcd. for $C_{42}H_{81}O_{12}Si_2$: 833.53), 855.51 (61%, $[M+Na]^+$, calcd for $C_{42}H_{80}O_{12}Si_2Na$: 855.51).

Compound II-20d: II-20d was synthetized from **II-19d** (660 mg, 0.80 mmol), malonyl chloride (0.09 mL, 0.88 mmol) and DMAP (118 mg, 0.96 mmol) in CH_2Cl_2 (80 mL). Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/EtOAc, 98:2) yielded **II-20d** (212 mg, 0.24 mmol, 30%) as a colorless oil. IR (neat): $\upsilon =$ 1753 (C=O), 1735 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.15 (t, *J* = 7 Hz, 8 H), 3.80 (t, *J* = 7 Hz, 8 H), 3.36 (s, 4H), 1.66 (quint, *J* = 7 Hz, 8 H), 1.56 (quint., *J* = 7 Hz, 8 H), 1,39 (m, 16 H), 0.99 (s, 36 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.6, 65.5, 63.6, 41.8, 32.7, 28.5, 27.9, 25.6, 25.4, 21.2 ppm. MALDI-TOF-MS: 889.73 ($[M+H]^+$, calcd. for $C_{46}H_{89}O_{12}Si_2$: 889.59).

Compound II-20e: II-20e was synthetized from **II-19e** (1.47 g, 1.68 mmol), malonyl chloride (0.17 mL, 1.76 mmol) and DMAP (0.43 g, 3.52 mmol) in CH_2Cl_2 (150 mL). Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/EtOAc, 98:2) yielded **II-20e** (298 mg, 0.32 mmol, 19%) as a colorless oil. IR (neat): $\upsilon =$ 1752 (C=O), 1736 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.14 (t, *J* = 7 Hz, 8 H), 3.80 (t, *J* = 7 Hz, 8 H), 3.36 (s, 4 H), 1.65 (quint, *J* = 7 Hz, 8 H), 1.55 (m, 8 H), 1.35 (m, 24 H), 1.00 (s, 36 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.6, 65.6, 63.7, 41.8, 32.8, 29.0, 28.4, 25.8, 25.7, 21.1 ppm. MALDI-TOF-MS: 967.68 (100%, $[M+Na]^+$, calcd. for $C_{50}H_{96}O_{12}Si_2Na$: 967.63), 983.60 (28%, $[M+K]^+$, calcd. for $C_{50}H_{96}O_{12}Si_2K$: 983.61), 945.57 (26%, $[M]^+$, calcd. for $C_{50}H_{96}O_{12}Si_2$: 945.65).

Compound II-20f: II-20f was synthetized from **II-19f** (1.30 g, 1.39 mmol), malonyl chloride (0.15 mL, 1.53 mmol) and DMAP (0.37 g, 3.06 mmol) in CH_2Cl_2 (200 mL). Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/EtOAc, 98:2) yielded **II-20f** (287 mg, 0.29 mmol, 19%) as a colorless oil. IR (neat): $\upsilon =$ 1752 (C=O), 1736 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.14 (t, *J* = 7 Hz, 8 H), 3.80 (t, *J* = 7 Hz, 8 H), 3.36 (s, 4 H), 1.73 (quint, *J* = 7 Hz, 8 H), 1.64 (quint., *J* = 6 Hz, 8 H), 1.55 (m, 32 H), 1.00 (s, 36 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.6, 65.6, 63.8, 41.8, 32.9, 29.3, 29.2, 28.5, 27.9, 25.7, 25.7, 21.2 ppm. MALDI-TOF-MS: 1023.72 (100%, $[M+Na]^+$, calcd. for $C_{54}H_{104}O_{12}Si_2Na$: 1023.70), 1039.69 (30%, $[M+K]^+$, calcd. for $C_{54}H_{104}O_{12}Si_2K$: 1039.67), 1000.63 (12%, $[M]^+$, calcd. for $C_{54}H_{104}O_{12}Si_2$: 1000.71).



General Procedure for the formation of bis-adducts : DBU (5 eq.) was added to a solution of C_{60} (1 eq.), macrocycle bis-malonate (1 eq.) and I_2 (2.5 eq.) in toluene (2 mL/mg of C_{60}). The resulting mixture was stirred at room temperature for 1 h, then filtered on SiO_2 (CH_2Cl_2) and concentrated. Column chromatography on SiO_2 gave **II-21** and/or **II-22** and/or **II-23.**

Compound II-21A: II-21A was synthetized from **II-5A** (190 mg, 0.2 mmol), C_{60} (141 mg, 0.2 mmol), I_2 (124 mg, 0.5 mmol) and DBU (0.15 mL, 1.0 mmol) in toluene (280 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 5:5) yielded **II-21A** (179 mg, 0.1 mmol, 54%) as a brown glassy solid. IR (neat): υ = 1748 (C=O), 1729 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 252 ($6x10^4$), 322 (sh, $2x10^4$), 413 ($2x10^3$), 423 ($2x10^3$), 493 ($1x10^3$), 579 (sh, $6x10^2$), 635 (sh, $3x10^2$) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.47 (d, ^3J = 8 Hz, 4 H), 7.26 (d, ^3J = 8 Hz, 8 H), 7.13 (d, ^3J = 8 Hz, 4 H), 5.78 (d, ^2J = 11 Hz, 2 H), 5.46 (d, ^2J = 11 Hz, 2 H), 5.35 (d, ^2J = 11 Hz, 2 H), 5.33 (d, ^2J = 11 Hz, 2 H), 4.91 (d, ^2J = 14 Hz, 2 H), 4.88 (d, ^2J = 14 Hz, 2 H), 4.77 (d, ^2J = 14 Hz, 2 H), 4.72 (d, ^2J = 14 Hz, 2 H), 1.07 (s, 18 H), 1.06 (s, 18 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.8, 163.2, 146.7, 146.5, 146.3 (two peaks), 145.7, 145.3, 145.2, 145.1, 144.8, 144.6, 144.5, 144.4, 144.1, 143.8, 143.6, 143.2, 143.0, 142.9, 142.6, 142.3, 142.1, 142.0, 141.8, 141.6, 141.3, 141.0, 139.3, 138.6, 137.9, 133.3, 132.6, 130.6, 130.3, 125.6 (two peaks), 70.9 (two peaks), 69.4, 68.8, 65.3, 65.1, 51.3, 27.9 (two peaks), 26.9, 21.6, 21.4 ppm. MS-MALDI-TOF: 1686.7 ([M]$^+$, calcd for $C_{114}H_{69}O_{12}Si_2$: 1686.4).

Compound II-21B & II-22B & II-23B: II-21B & II-22B & II-23B were synthetized from **II-5B** (170 mg, 0.14 mmol), C_{60} (100 mg, 0.14 mmol), I_2 (89 mg, 0.35 mmol) and DBU (0.1 mL, 0.7 mmol) in toluene (200 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 5:5) yielded **II-21B** (40 mg, 20 μmol, 15%) as a brown glassy solid, **II-22B** (12 mg, 6 μmol, 4%) as a brown glassy solid and **II-23B** (16 mg, 8 μmol, 6%) as a brown glassy solid. **II-21B:** IR (neat): υ = 1749 (C=O), 1728 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 253, 317 (sh), 412, 423, 489 nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.57 (d, ^3J = 8 Hz, 4 H), 7.52 (d, ^3J = 8 Hz, 4 H), 7.41 (s, 8 H), 7.38 (d, ^3J = 8 Hz, 4 H), 7.33 (d, ^3J = 8 Hz, 4 H), 7.21 (d, ^3J = 8 Hz, 4 H), 7.13 (d, ^3J = 8 Hz, 4 H), 5.73 (d, ^2J = 12 Hz, 2 H), 5.63 (d, ^2J = 12 Hz, 2 H), 5.49 (d, ^2J = 12 Hz, 2 H), 5.40 (d, ^2J = 12 Hz, 2 H), 4.83 (d, ^2J = 14 Hz, 2 H), 4.80 (d, ^2J = 14 Hz, 2 H), 4.71 (d, ^2J = 13 Hz, 2 H), 4.65 (d, ^2J = 13 Hz, 2 H), 1.14 (s, 18 H), 1.10 (s, 18 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.5, 163.4, 146.8, 146.6, 146.2, 146.1, 145.1, 145.8, 145.7, 145.6, 145.5, 145.4, 145.1, 145.0, 144.4, 144.1, 143.7, 143.5, 143.3, 143.2,

143.1, 142.5, 142.2, 142.0, 141.9, 141.8 (two peaks), 141.6, 141.3, 140.5, 140.0, 139.3, 139.0, 138.8, 137.8, 133.5, 133.2, 130.4, 129.9, 127.4, 127.1, 126.9, 126.8 (two peaks), 126.4, 71.4, 70.9, 69.1, 68.9, 65.5, 65.3, 51.7, 28.2, 28.1, 21.3, 21.2 ppm. MS-MALDI-TOF: 1990.3 ($[M+H]^+$, calcd for $C_{138}H_{85}O_{12}Si_2$: 1990.5). **II-22B:** IR (neat): υ = 1747 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 256, 311 (sh), 398 (sh), 409 (sh), 422, 479 nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.53 (d, ^3J = 8 Hz, 2 H), 7.49 (d, ^3J = 8 Hz, 2 H), 7.48-7.45 (m, 4 H), 7.44 (d, ^3J = 8 Hz, 2 H), 7.41 (d, ^3J = 8 Hz, 2 H), 7.33 (d, ^3J = 8 Hz, 2 H), 7.30 (d, ^3J = 8 Hz, 2 H), 7.29 (d, ^3J = 8 Hz, 2 H), 7.24 (d, ^3J = 8 Hz, 2 H), 7.18 (d, ^3J = 8 Hz, 2 H), 7.16 (d, ^3J = 8 Hz, 2 H), 7.04 (d, ^3J = 8 Hz, 2 H), 6.99 (d, ^3J = 8 Hz, 2 H), 5.85 (d, ^2J = 11 Hz, 1 H), 5.77 (d, ^2J = 12 Hz, 1 H), 5.60 (d, ^2J = 12 Hz, 1 H), 5.59 (d, ^2J = 11 Hz, 1 H), 5.47 (d, ^2J = 12 Hz, 1 H), 5.33 (d, ^2J = 11 Hz, 1 H), 5.17 (d, ^2J = 11 Hz, 1 H), 5.07 (d, ^2J = 12 Hz, 1 H), 5.03 (s, 2 H), 4.84 (d, ^2J = 13 Hz, 1 H), 4.74 (d, ^2J = 13 Hz, 1 H), 4.68 (s, 2 H), 4.45 (d, ^2J = 13 Hz, 1 H), 4.34 (d, ^2J = 13 Hz, 1 H), 1.15 (s, 18 H), 1.10 (s, 18 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.9, 163.7, 163.4, 162.6, 147.6, 147.4, 147.1 (two peaks), 146.4, 146.3 (two peaks), 146.2, 146.0, 145.9, 145.8, 145.5 (two peaks), 145.4, 145.2, 145.1, 145.0, 144.6 (two peaks), 144.5 (three peaks), 144.4, 144.3 (three peaks), 144.0 (two peaks), 143.7 (two peaks), 143.6, 143.4, 143.3, 143.2 (two peaks), 143.0 (two peaks), 142.9, 142.8, 142.7, 142.5, 142.3, 142.2, 142.0, 141.9, 141.7, 141.6, 141.5, 141.4, 141.3, 141.0, 140.8, 140.7, 140.6, 140.5 (two peaks), 139.4, 138.8, 138.7, 138.4, 138.3, 138.1, 133.7, 133.4 (two peaks), 133.1, 130.9, 130.2, 129.0, 128.9, 127.5, 127.4, 127.3, 127.2, 127.1, 126.9, 126.8, 126.6 (two peaks), 126.4, 125.9, 71.4 (three peaks), 69.0, 68.9, 68.7, 68.6, 66.2, 65.7, 65.3, 65.1, 51.0, 48.3, 28.3, 28.2, 28.1 (two peaks), 21.4, 21.2 (two peaks) ppm. **II-23B:** IR (neat): υ = 1746 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 412 (sh), 438, 471 nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.42 (d, ^3J = 8 Hz, 4 H), 7.28 (d, ^3J = 8 Hz, 4 H), 7.20 (s, 8 H), 7.18 (d, ^3J = 8 Hz, 4 H), 7.09 (d, ^3J = 8 Hz, 4 H), 7.06 (d, ^3J = 8 Hz, 4 H), 6.95 (d, ^3J = 8 Hz, 4 H), 5.70 (d, ^2J = 12 Hz, 2 H), 5.69 (d, ^2J = 12 Hz, 2 H), 5.35 (d, ^2J = 12 Hz, 2 H), 5.03 (s, 4 H), 4.90 (d, ^2J = 12 Hz, 2 H), 4.83 (d, ^2J = 13 Hz, 2 H), 4.74 (d, ^2J = 13 Hz, 2 H), 1.23 (s, 9 H), 1.21 (s, 9 H), 1.18 (s, 9 H), 1.15 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.3, 162.4, 147.4, 146.2, 145.9 (two peaks), 145.7, 145.4, 145.3 (two peaks), 145.1, 145.0, 144.7, 144.6, 144.4, 144.2, 143.8, 143.6, 143.2, 142.5, 142.0, 141.0 (two peaks), 140.9, 140.5, 140.2, 139.4, 138.7 (two peaks), 138.4, 138.2, 137.5, 133.5, 133.4, 129.5, 128.3, 127.1, 127.0, 126.6 (three peaks), 126.5, 70.1, 68.6, 68.0, 67.7, 66.0, 65.6, 49.0, 28.5, 28.3, 28.2 (two peaks), 21.6, 21.5, 21.4, 21.2 ppm.

Compound II-21C & II-22C: II-21C & II-22C were synthetized from **II-10C** (170 mg, 0.14 mmol), C_{60} (104 mg, 0.14 mmol), I_2 (89 mg, 0.35 mmol) and DBU (0.1 mL, 0.7 mmol) in toluene (210 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 5:5) yielded **II-21C** (42 mg, 22 μmol, 15%) as a brown glassy solid and **II-22C** (72 mg, 38 μmol, 26%) as a brown glassy solid. **II-21C:** IR (neat): υ = 1751 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 254 (1.3x105), 311 (sh, 5x104), 397, 409 (sh), 422, 481 nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.41 (d, ^3J = 8 Hz, 2 H), 7.35 (d, ^3J = 8 Hz, 2 H), 7.33 (d, ^3J = 8 Hz, 2 H), 7.28 (d, ^3J = 8 Hz, 2 H), 7.26 (d, ^3J = 8 Hz, 2 H), 7.21 (d, ^3J = 8 Hz, 2 H), 7.04 (d, ^3J = 8 Hz, 2 H), 6.98 (d, ^3J = 8 Hz, 2 H), 5.73 (d, ^2J = 11 Hz, 1 H), 5.67 (d, ^2J = 11

Hz, 1 H), 5.61 (d, ^2J = 12 Hz, 1 H), 5.49 (d, ^2J = 12 Hz, 1 H), 5.37 (d, ^2J = 12 Hz, 1 H), 5.19 (d, ^2J = 12 Hz, 1 H), 5.11 (d, ^2J = 11 Hz, 1 H), 5.00 (d, ^2J = 11 Hz, 1 H), 4.84 (s, 2 H), 4.77 (s, 2 H), 4.65 (d, ^2J = 13 Hz, 1 H), 4.58 (d, ^2J = 13 Hz, 1 H), 4.56 (s, 2 H), 1.06-0.80 (m, 56 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 163.6, 163.5, 163.3, 162.6, 148.1, 147.3, 147.2, 147.1, 146.4 (two peaks), 146.2, 146.1, 145.9, 145.5 (two peaks), 145.3, 145.2, 144.9, 144.8, 144.7, 144.6 (two peaks), 144.5 (two peaks), 144.4, 144.3 (three peaks), 144.0, 143.9, 143.8, 143.7, 143.6, 143.5, 143.4, 143.3 (two peaks), 143.1 (two peaks), 142.9, 142.8 (two peaks), 142.5, 142.3, 142.2, 142.1, 142.0 (three peaks), 141.9, 141.8, 141.5 (two peaks), 141.3, 141.0, 140.7, 138.9, 138.8, 138.3, 138.2, 133.9, 133.3, 132.7, 132.5, 129.9, 129.0, 128.7, 128.5, 126.7, 126.1, 125.9, 125.5, 71.4, 71.3 (two peaks), 69.7, 68.9, 68.8 (two peaks), 68.7, 64.4, 63.9, 63.8, 63.5, 53.7, 51.0, 17.4 (two peaks), 17.3 (four peaks), 17.2 (three peaks), 13.1, 13.0 (two peaks), 12.9 (two peaks), 12.8 ppm. MS-MALDI-TOF: 1889.3 ([M]$^+$, calcd for $C_{122}H_{88}O_{14}Si_4$: 1889.5). **II-22C:** IR (neat): υ = 1747 (C=O), 1728 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 251 (1.3x10^5), 319 (sh, 5x10^4), 399 (sh), 412, 423, 473, 489 nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.44 (d, ^3J = 8 Hz, 4 H, ArH), 7.28 (d, ^3J = 8 Hz, 4 H, ArH), 7.26 (d, ^3J = 8 Hz, 4 H, ArH), 7.14 (d, ^3J = 8 Hz, 4 H), 5.77 (d, ^2J = 11 Hz, 2 H), 5.43 (d, ^2J = 11 Hz, 2 H), 5.40 (d, ^2J = 11 Hz, 2 H), 5.30 (d, ^2J = 11 Hz, 2 H), 4.80 (d, ^2J = 13 Hz, 2 H), 4.76 (d, ^2J = 13 Hz, 2 H), 4.72 (d, ^2J = 13 Hz, 2 H), 4.68 (d, ^2J = 13 Hz, 2 H), 1.05-0.97 (m, 56 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 163.8, 163.3, 146.8, 146.3 (three peaks), 145.8, 145.4, 145.3, 145.2, 145.1, 145.0, 144.9, 144.6 (two peaks), 144.4, 144.1, 144.0, 143.8, 143.6, 143.4, 143.2, 143.1, 143.0, 142.8, 142.6, 142.5 (two peaks), 142.1, 142.0, 141.9, 141.7, 141.4, 141.2, 140.7, 139.6, 138.8 (two peaks), 137.9, 133.3, 132.9, 132.7, 130.9, 130.3, 129.8, 126.1, 126.0, 125.9, 71.0, 70.9, 69.3, 68.9, 64.1, 63.9, 51.4, 17.4 (two peaks), 17.3, 13.0, 12.9 (two peaks) ppm. MS-MALDI-TOF: 1890.3 ([M+H]$^+$, calcd for $C_{122}H_{89}O_{14}Si_4$: 1890.5).

Compounds II-23a: II-23a was synthetized from **II-16a** (220 mg, 0.3 mmol), C_{60} (219 mg, 0.3 mmol), I_2 (190 mg, 0.8 mmol) and DBU (0.21 mL, 1.4 mmol) in toluene (440 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 5:5 to CH_2Cl_2) yielded **II-23a** (115 mg, 0.08 mmol, 27%) as a brown glassy solid. IR (neat): υ = 1748 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon$ = 259 (84200), 323 (sh, 24700), 439 (2500), 476 (2100), 622 (sh, 250) nm. ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 4.71-4.62 (m, 4 H), 4.50-4.41 (m, 4 H), 4.03 (m, 4 H), 3.88 (m, 4 H), 2.10 (m, 4 H), 1.98 (m, 4 H), 1.11 (s, 9 H), 1.04 (s, 18 H), 0.87 (s, 9 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.5, 163.3, 148.2, 147.5, 147.4 (two peaks), 147.1, 146.3, 146.0, 145.8, 145.7, 145.5, 145.3, 145.05, 145.0, 144.8, 144.5 (two peaks), 144.4, 144.2, 143.7 (two peaks), 143.6, 142.5, 142.45, 141.4, 141.1, 140.3, 136.4, 136.0, 135.9, 135.7, 70.6, 67.69, 64.0, 63.5 ,60.4, 59.9, 50.2, 32.3, 31.9, 28.0, 27.95, 27.85, 27.8, 21.3, 21.1, 21.05 ppm. MALDI-TOF-MS: 1438.4 ([M+H]$^+$, calcd for $C_{94}H_{61}O_{12}Si_2$: 1438.4).

Compound II-23b: II-23b was synthetized from **II-20b** (286 mg, 0.37 mmol), C_{60} (265 mg, 0.37 mmol), I_2 (234 mg, 0.92 mmol) and DBU (0.25 mL, 1.7 mmol) in toluene (530 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 5:2 to 4:1) followed by gel permeation

chromatography (Biobeads SX-1, CH_2Cl_2) yielded **II-23b** (212 mg, 0.14 mmol, 39%) as a brown glassy solid. IR (neat): υ = 1746 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 259 (143000), 319 (sh, 43000), 380 (sh, 15000), 438 (3900), 488 (sh, 3700), 622 (sh, 400) nm. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.57 (m, 2 H), 4.50 (m, 2 H), 4.39 (m, 2 H), 4.26 (m, 2 H), 1.99 (quint, *J* = 7 Hz, 4 H), 1.84 (quint., *J* = 7 Hz, 4 H), 1.75 (quint., *J* = 7 Hz, 4 H), 1.63 (quint., *J* = 7 Hz, 4 H), 1.07 (s, 9 H), 1.04 (s, 9 H), 1.03 (s, 9 H) , 0.95 (s, 9 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.3, 163.2, 148.2, 147.4, 147.3 (two peaks), 146.8, 146.2, 146.0, 145.8, 145.7, 145.5, 145.3, 145.0 (two peaks), 144.7, 144.6, 144.4 (two peaks), 144.1, 143.6 (two peaks), 143.5, 142.5, 142.4, 141.3, 141.1, 140.1, 137.1, 136.4, 136.1, 135.6, 70.6, 67.7, 66.7 (two peaks), 63.2, 62.8, 50.3, 28.8, 28.5, 27.9 (three peaks), 27.8, 26.9, 25.5, 25.0, 21.4, 21.3, 21.2 ppm. MALDI-TOF-MS: 1515.38 (100%, $[M+Na]^+$, calcd. for $C_{98}H_{68}O_{12}Si_2Na$: 1515.41), 1493.33 (81%, $[M+H]^+$, calcd. for $C_{98}H_{69}O_{12}Si_2$: 1493.43), 1531.36 (26%, $[M+K]^+$, calcd. for $C_{98}H_{68}O_{12}Si_2K$: 1531.39).

Compounds II-22c & II-21c: II-22c & II-21c were synthetized from **II-20c** (430 mg, 0.52 mmol), C_{60} (374 mg, 0.52 mmol), I_2 (330 mg, 1.3 mmol) and DBU (0.36 mL, 2.3 mmol) in toluene (800 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 5:5 to 75:25) yielded **II-22c** (95 mg, 0.06 mmol, 12%) as a red-brown glassy solid and **II-21c** (350 mg, 0.23 mmol, 44%) as a brown glassy solid. **II-22c:** IR (neat): υ = 1744 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 249 (48200), 308 (sh, 17200), 398 (3000), 409 (sh, 1800), 422 (1800), 480 (2100), 620 (sh, 300) nm. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.73-4.53 (m, 4 H), 4.36 (m, 2 H), 4.25 (m, 2 H), 3.88 (m, 2 H), 3.83-3.66 (m, 5 H), 3.54 (m, 1 H), 1.77 (m, 8 H), 1.66 – 1.50 (m, 16 H), 1.00 (s, 9 H), 0.97 (s, 18 H) , 0.90 (s, 9 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 164.3, 163.6, 163.0, 162.8, 149.0, 147.4, 147.2, 147.1, 146.6, 146.5, 146.3 (two peaks), 146.1, 146.0 (two peaks), 145.7, 145.6, 145.4 (two peaks), 145.1, 145.0, 144.9, 144.8, 144.7 (two peaks), 144.6 (two peaks), 144.3 (two peaks), 144.1, 143.9 (two peaks), 143.8, 143.7 (two peaks), 143.5, 143.4, 143.3, 143.2, 143.1 (two peaks), 142.9, 142.4, 142.0, 141.7, 141.4, 141.2, 140.0, 139.9, 139.7, 139.5, 138.7, 138.4, 71.9, 71.8, 71.7, 70.4, 67.8, 67.4, 66.9, 64.3, 64.0, 63.4 (two peaks), 53.8, 53.1, 33.3, 32.8, 32.3, 32.2, 29.2, 28.3, 28.2, 27.9 (several peaks), 27.7, 23.5, 23.2, 22.3, 22.2, 21.3 (two peaks), 21.1 (two peaks) ppm. MALDI-TOF-MS: 1571.82 ($[M+Na]^+$, calcd. for $C_{102}H_{76}O_{12}Si_2Na$: 1571.48). **II-21c:** IR (neat): υ = 1749 (C=O), 1724 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 250 (49300), 319 (sh, 15300), 399 (sh, 3400), 412 (2800), 424 (2300), 493 (2000), 574 (sh, 900), 628 (sh, 400), 686 (sh, 200) nm. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.81 (m, 2 H), 4.57 (m, 2 H), 4.40 (m, 4 H), 3.62-2.52 (m, 8 H), 1.90 (m, 2 H), 1.75 (m, 6 H), 1.50 – 1.34 (m, 16 H), 0.93 (s, 18 H), 0.92 (s, 18 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 164.8, 163.4, 147.5 (two peaks), 147.3, 147.2, 146.6, 146.4 (two peaks), 146.3, 145.5, 145.4, 145.1, 144.8, 144.4, 144.3, 144.0, 143.7, 143.6, 143.5, 142.7, 142.6, 142.0, 141.7, 141.1 (two peaks), 140.0, 139.6, 138.8, 71.7, 71.4, 68.2, 67.3, 64.2, 64.0, 53.4, 32.7, 32.5, 28.7, 27.9, 27.8, 26.9, 23.4, 21.1 (two peaks) ppm. MALDI-TOF-MS: 1571.80 ($[M+Na]^+$, calcd. for $C_{102}H_{76}O_{12}Si_2Na$: 1571.48).

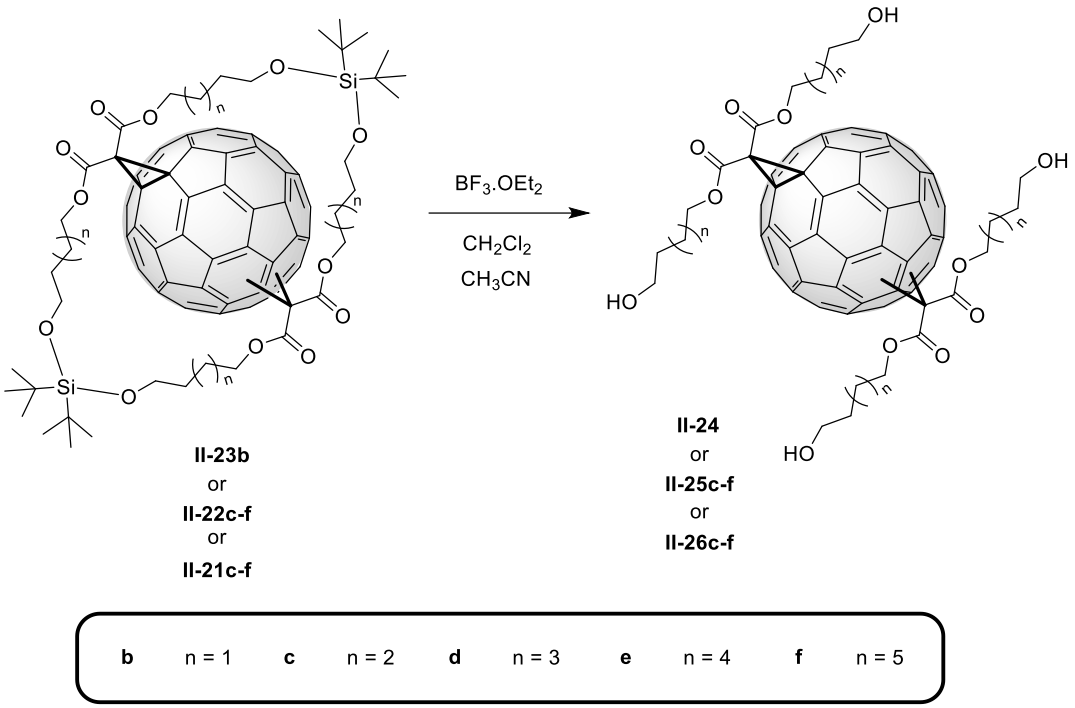
Compounds II-22d & II-21d: II-22d & II-21d were synthetized from **II-20d** (210 mg, 0.24 mmol), C_{60} (170 mg, 0.24 mmol), I_2 (149 mg, 0.59 mmol) and DBU (0.16 mL, 1.1 mmol) in toluene (340

mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 2:3 to 3:2) yielded **II-22d** (102 mg, 0.06 mmol, 27%) as a red-brown glassy solid and **II-21d** (125 mg, 0.07 mmol, 33%) as a brown glassy solid. **II-22d:** IR (neat): υ = 1745 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 253 (137000), 309 (sh, 53200), 356 (sh, 21300), 397 (5000), 409 (sh, 3100), 420 (3000), 481 (3700), 618 (sh, 600) nm. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.72 (m, 1 H), 4.57 (m, 3 H), 4.33 (m, 2 H), 4.16 (m, 2 H), 3.80 (m, 7 H), 3.71 (m, 1 H), 1.77 (m, 8 H), 1.64 – 1.13 (m, 24 H), 1.00 (s, 9 H), 0.97 (s, 18 H) , 0.91 (s, 9 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.7, 163.5, 163.2, 147.4, 147.2, 146.6, 146.4, 146.1, 145.7, 145.6, 145.4, 145.2, 144.8, 144.7, 144.6, 144.4, 144.1, 144.0, 143.9 (two peaks), 143.5 (two peaks), 143.3, 142.5, 142.1, 141.6 (two peaks), 140.6, 139.6 (two peaks), 138.6 (two peaks), 71.8, 67.7, 67.3, 66.9 (two peaks), 64.2, 63.6, 63.4, 51.9, 33.2, 32.8, 32.7 (two peaks), 28.6, 28.2, 28.0, 27.9, 27.2, 26.9, 26.5, 26.1, 25.5, 25.2, 25.1 (two peaks), 25.0 (two peaks), 21.1 (three peaks) ppm. MALDI-TOF-MS: 1627.65 (100%, $[M+Na]^+$, calcd. for $C_{106}H_{84}O_{12}Si_2Na$: 1627.54), 1643.59 (30%, $[M+K]^+$, calcd. for $C_{106}H_{84}O_{12}Si_2K$: 1643.51), 1605.61 (12%, $[M]^+$, calcd. for $C_{106}H_{85}O_{12}Si_2$: 1605.56). **II-21d:** IR (neat): υ = 1749 (C=O), 1727 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 248 (172800), 322 (sh, 52000), 376 (sh, 17000), 399 (sh, 5000), 412 (5100), 424 (4300), 490 (3600), 570 (sh, 1800), 632 (sh, 700), 694 (sh, 260) nm. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.78 (m, 2 H), 4.52 (m, 2 H), 4.38 (m, 4 H), 3.64 (m, 8 H), 1.80 (m, 4 H), 1.69 (m, 4 H), 1.50 – 1.19 (m, 24 H), 0.93 (s, 18 H), 0.91 (s, 18 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 164.4, 163.8, 147.3, 147.2, 147.0, 146.9, 146.7 (two peaks), 146.5, 146.4 (two peaks), 145.8, 145.4, 145.3, 144.7, 144.4, 144.3, 144.0, 143.6 (two peaks), 143.0, 142.6, 142.0, 141.7 (two peaks), 141.6, 140.2, 139.0, 138.2, 71.7, 71.6, 67.5, 63.8, 63.7, 53.1, 33.0, 32.9, 29.7, 28.8, 28.7, 27.6, 26.5, 26.3, 25.6, 25.4, 21.2, 21.1 ppm. MALDI-TOF-MS: 1627.56 ($[M+Na]^+$, calcd. for $C_{106}H_{84}O_{12}Si_2Na$: 1627.54).

Compounds II-22e & II-21e: II-22e & II-21e were synthetized from **II-20e** (288 mg, 0.30 mmol), C_{60} (220 mg, 0.30 mmol), I_2 (193 mg, 0.76 mmol) and DBU (0.21 mL, 1.4 mmol) in toluene (440 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 3:2 to 2:1) yielded **II-22e** (150 mg, 0.09 mmol, 30%) as a red-brown glassy solid and **II-21e** (102 mg, 0.06 mmol, 20%) as a brown glassy solid. **II-22e:** IR (neat): υ = 1747 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 252 (135000), 307 (sh, 52000), 356 (sh, 20000), 397 (5300), 408 (sh, 3300), 421 (3000), 482 (3700), 617 (sh, 600) nm. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.68 – 4.46 (m, 4 H), 4.35 – 4.19 (m, 4 H), 3.82 – 3.74 (m, 6 H), 3.67 (t, *J* = 7 Hz, 8 H), 1.76 (m, 8 H), 1.53 (m, 8 H), 1.49 – 1.13 (m, 24 H), 0.99 (s, 9 H), 0.98 (s, 9 H), 0.97 (s, 9 H), 0.93 (s, 9 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.9, 163.6, 163.5, 163.3, 148.6, 147.5, 147.3, 147.2, 146.5 (two peaks), 146.4, 146.2, 146.1 (two peaks), 146.0, 145.6, 145.5, 145.2, 145.1 (two peaks), 145.0 (two peaks), 144.8, 144.7 (two peaks), 144.6 (three peaks), 144.5, 144.3 (two peaks), 144.1, 144.0, 143.8 (two peaks), 143.7 (three peaks), 143.5, 143.3 (two peaks), 143.0 (two peaks), 142.7, 142.3, 142.3, 142.2, 142.1, 141.9 (two peaks), 141.6, 141.5, 141.1, 140.8, 139.3, 138.6 (two peaks), 71.8, 70.4, 67.4, 67.3, 67.2, 63.9 (two peaks), 63.7, 63.6, 53.8, 51.9, 33.1, 32.8, 32.8, 32.7, 32.3, 29.5, 29.0, 28.7, 28.6 (two peaks), 28.4 (two peaks), 28.2, 27.9 (two peaks), 26.8, 26.0, 25.9, 25.8, 25.7, 25.5, 25.4, 21.2, 21.1 (two peaks) ppm. MALDI-TOF-MS: 1683.61 (100%, $[M+Na]^+$, calcd. for $C_{110}H_{93}O_{12}Si_2Na$:

1683.60), 1663.64 (77%, $[M]^+$, calcd. for $C_{110}H_{93}O_{12}Si_2$: 1662.62). **II-21e:** IR (neat): υ = 1742 (C=O), 1728 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 254 (134500), 330 (sh, 35700), 399 (sh, 5300), 409 (4200), 424 (3300), 488 (2800), 583 (sh, 1100), 627 (sh, 500), 688 (sh, 200) nm. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.77 (m, 2 H), 4.43 (m, 6 H), 3.66 (m, 8 H), 1.82 (m, 4 H), 1.70 (m, 4 H), 1.50 – 1.19 (m, 32 H), 0.93 (s, 36 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.9 (two peaks), 147.2, 147.0, 146.8, 146.6 (two peaks), 146.5, 146.4, 146.3 (two peaks), 146.0, 145.5, 145.4, 144.6, 144.3, 144.2, 143.9, 143.6, 143.4, 142.9, 142.5, 142.2 (two peaks), 141.9, 141.6, 140.3, 138.5, 137.8, 71.9, 71.6, 67.5, 67.3, 63.8, 63.7, 53.0, 32.8, 32.7, 29.0, 28.8, 28.7, 28.6, 27.9 (two peaks), 26.4, 26.0, 25.9, 25.6, 21.1 (two peaks) ppm. MALDI-TOF-MS: 1661.66 (100%, $[M]^+$, calcd. for $C_{110}H_{93}O_{12}Si_2$: 1662.62), 1683.66 (52%, $[M+Na]^+$, calcd. for $C_{110}H_{93}O_{12}Si_2Na$: 1683.60).

Compound II-22f & II-38f: II-22f & II-21f were synthetized from **II-20f** (280 mg, 0.28 mmol), C_{60} (201 mg, 0.28 mmol), I_2 (178 mg, 0.70 mmol) and DBU (0.19 mL, 1.3 mmol) in toluene (400 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 3:2 to 2:1) yielded **II-22f** (102 mg, 0.06 mmol, 21%) as a red-brown glassy solid and **II-21f** (79 mg, 0.05 mmol, 16%) as a brown glassy solid. **II-22f:** IR (neat): υ = 1744 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 256 (112000), 313 (sh, 42000), 356 (sh, 17000), 393 (4600), 407 (sh, 3000), 422 (2700), 480 (3200), 628 (sh, 300) nm. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.63 – 4.23 (m, 8 H), 3.79 (m, 4 H), 3.69 (t, *J* = 7 Hz, 4 H), 1.75 (m, 8 H), 1.56 (m, 8 H), 1.48 – 1.13 (m, 40 H), 1.00 (s, 9 H), 0.99 (s, 9 H), 0.96 (s, 9 H), 0.94 (s, 9 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.9, 163.6, 163.4, 148.5, 147.5, 147.3, 147.2, 146.4 (two peaks), 146.2, 146.1 (two peaks), 146.0, 145.6, 145.5, 145.3, 145.2 (two peaks), 145.0, 144.9, 144.8, 144.7 (two peaks), 144.6, 144.5, 144.4, 144.2, 144.1, 144.0 (two peaks), 143.8, 143.7, 143.5, 143.3 (two peaks), 142.9 (two peaks), 142.8, 142.6, 142.3, 142.0, 141.9, 141.6, 141.5, 141.2, 140.8, 138.9 (two peaks), 138.6 (two peaks), 71.9, 71.6, 70.4, 67.4, 67.3, 67.2, 63.9, 63.8, 63.5, 53.8, 51.9, 33.1, 32.9, 32.8, 29.7, 29.4, 29.3 (two peaks), 29.2 (two peaks), 28.9 (two peaks), 28.8, 28.7, 28.4 (two peaks), 27.9, 26.5, 26.3, 26.0, 25.7, 25.6 (two peaks), 25.0 (two peaks), 21.1 (three peaks) ppm. MALDI-TOF-MS: 1718.00 ($[M+H]^+$, calcd. for $C_{114}H_{101}O_{12}Si_2$: 1718.69). **II-21f:** IR (neat): υ = 1751 (C=O), 1732 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 249 (132000), 318 (sh, 41000), 397 (sh, 5300), 410 (4200), 424 (3300), 487 (2900), 573 (sh, 1300), 627 (sh, 500), 688 (sh, 100) nm. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.73 (m, 2 H), 4.41 (m, 6 H), 3.70 (m, 8 H), 1.82 (m, 4 H), 1.69 (m, 4 H), 1.50 – 1.19 (m, 40 H), 0.95 (s, 36 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.9, 163.8, 147.2, 147.0, 146.8, 146.6, 146.5, 146.3 (two peaks), 146.1, 145.5, 145.4, 144.6, 144.4, 144.1, 143.8, 143.5, 143.4, 143.0, 142.5, 142.2, 141.9, 141.6, 140.4, 138.6, 138.4, 137.7, 71.8, 71.6, 67.5, 67.2, 63.8, 52.9, 32.9 (two peaks), 29.4 (two peaks), 29.1, 29.0, 28.7, 28.6, 27.9 (two peaks), 26.2, 26.0, 25.9, 25.7, 21.1 (two peaks) ppm. MALDI-TOF-MS: 1719.83 ($[M+H]^+$, calcd. for $C_{114}H_{101}O_{12}Si_2$: 1718.69).



General Procedure for the desilylation of bis-adducts II-23b or II-22c-f or II-21c-f : $BF_3.OEt_2$ (10-15 eq.) was added to a solution of the appropiate bis-adducts (1 eq.) in CH_2Cl_2/CH_3CN (2:1). The resulting mixture was stirred overnight at room temperature, then filtered on SiO_2 (CH_2Cl_2/MeOH, 95:5) and concentrated. Column chromatography on SiO_2 gave **II-24 or II-25c-f and II-26c-f.**

Compound II-24: II-24 was synthetized from **II-23b** (77 mg, 52 µmol) and $BF_3.OEt_2$ (0.1 mL, 790 µmol) in CH_2Cl_2/CH_3CN (3/1.5 mL). Column chromatography on SiO_2 (CH_2Cl_2/MeOH, 97:3 to 92:8) yielded **II-24** (52 mg, 43 µmol, 88%) as a brown glassy solid. IR (neat): υ = 3340 (br, OH), 1741 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 257 (150000), 320 (sh, 47000), 379 (sh, 16000), 437 (4100), 490 (sh, 2900), 624 (sh, 500) nm. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.40 (m, 8 H), 3.68 (m, 8 H), 1.96 – 1.62 (m, 16 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$) : δ = 163.4, 163.1, 148.4, 147.4 (two peaks), 147.3, 146.2, 145.9 (two peaks), 145.8, 145.7, 145.4, 145.3, 145.1, 145.0, 144.7, 144.4 (two peaks), 144.2, 143.7, 143.6, 143.4, 142.5, 142.4, 141.3, 141.0, 139.7, 137.8, 137.1, 136.7, 135.2, 70.5, 67.7, 67.1, 62.2, 62.1, 49.6, 29.2, 29.1, 25.1, 25.0 ppm. MALDI-TOF-MS: 1212.44 ($[M]^+$, calcd. for $C_{82}H_{36}O_{12}$: 1212.22).

Compound II-25c: II-25c was synthetized from **II-22c** (82 mg, 53 µmol) and $BF_3.OEt_2$ (0.1 mL, 790 µmol) in CH_2Cl_2/CH_3CN (3/1.5 mL). Column chromatography on SiO_2 (CH_2Cl_2/THF, 3:1 to THF/MeOH, 95:5) yielded **II-25c** (57 mg, 45 µmol, 85%) as a red-brown glassy solid. IR (neat): υ = 3339 (br, OH), 1739 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 240 (29400), 308 (sh, 11600), 398 (1900), 410 (sh, 1200), 422 (1200), 481 (1400), 620 (sh, 200) nm. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.43 (m, 8 H), 3.64 (m, 8 H), 1.85 (m, 12 H), 1.60 (m, 8 H), 1.51 (m, 8 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$) : δ = 163.7, 163.6, 163.5, 147.5, 147.2, 146.4, 146.1 (two peaks), 145.6,

145.3, 145.1, 145.0, 144.7 (two peaks), 144.6, 144.3 (two peaks), 144.2, 144.0, 143.7 (two peaks), 143.4, 143.1, 142.9, 142.8, 142.3, 141.9, 141.6 (two peaks), 138.9, 138.7, 71.7, 71.6, 70.4, 67.3, 67.2, 62.5, 53.7, 53.44, 51.5, 32.2, 32.1, 28.3, 22.3 (two peaks) ppm. MALDI-TOF-MS: 1286.47 ($[M]^+$, calcd for $C_{86}H_{44}O_{12}$: 1268.28).

Compound II-25d: II-25d was synthetized from **II-22d** (82 mg, 51 µmol) and $BF_3.OEt_2$ (0.1 mL, 790 µmol) in CH_2Cl_2/CH_3CN (3/1.5 mL). Column chromatography on SiO_2 (CH_2Cl_2/MeOH, 92:8) yielded **II-25d** (54 mg, 41 µmol, 80%): red-brown glassy solid. IR (neat): υ = 3338 (br, OH), 1741 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 251 (133600), 310 (sh, 50600), 358 (sh, 19100), 396 (sh, 5000), 406 (3100), 421 (2900), 482 (3600), 620 (sh, 500) nm. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.42 (m, 8 H), 3.64 (m, 8 H), 1.81(m, 8 H), 1.58 (m, 8 H), 1.51 – 1.38 (m, 12 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.7, 163.6 (two peaks), 147.6, 147.3, 146.5, 146.2, 146.1, 145.6, 145.4, 145.2, 145.1, 144.7(two peaks), 144.6, 144.4 (two peaks), 144.2, 144.1, 143.8, 143.7, 143.5, 143.2, 143.0, 142.4, 141.9, 141.6 (two peaks), 138.9, 138.7, 71.7, 71.6, 70.4, 67.3, 62.7, 53.7, 51.5, 32.6 (two peaks), 28.5 (two peaks), 28.4, 25.8 (two peaks), 25.7, 25.4 (two peaks), 25.3 ppm. MALDI-TOF-MS: 1324.45 (100%, $[M]^+$, calcd for $C_{90}H_{52}O_{12}$: 1324.34), 1347.35 (15%, $[M+Na]^+$, calcd. for $C_{90}H_{52}O_{12}Na$: 1347.34), 1363.26 (20%, $[M+K]^+$, calcd. for $C_{90}H_{52}O_{12}K$: 1363.31).

Compound II-25e: II-25e was synthetized from **II-22e** (95 mg, 57 µmol) and $BF_3.OEt_2$ (0.1 mL, 790 µmol) in CH_2Cl_2/CH_3CN (3/1.5 mL). Column chromatography on SiO_2 (CH_2Cl_2/MeOH, 93:7) yielded **II-25e** (55 mg, 40 µmol, 70%) as a red-brown glassy solid. IR (neat): υ = 3316 (br, OH), 1741 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 251 (151000), 309 (sh, 58700), 356 (sh, 23300), 396 (sh, 5000), 398 (5300), 409 (sh, 3400), 422 (3100), 480 (sh, 3800), 626 (sh, 500) nm. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.40 (m, 8 H), 3.64 (m, 8 H), 1.79 (m, 8 H), 1.58 (m, 16 H), 1.48 – 1.34 (m, 24 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.6, 163.5, 147.6, 147.2, 146.4, 146.1, 146.0, 145.5, 145.3, 145.1, 145.0, 144.7 (two peaks), 144.6, 144.4 (two peaks), 144.1, 144.0, 143.7 (two peaks), 143.4, 143.3, 143.1, 142.9, 142.3, 141.9, 141.6, 141.5, 138.7, 138.6, 71.7, 70.5, 67.3, 62.8, 53.7, 51.5, 32.6, 28.9 (two peaks), 28.5, 25.8 (two peaks), 25.9, 25.8, 25.7 ppm. MALDI-TOF-MS: 1380.36 ($[M]^+$, calcd for $C_{94}H_{60}O_{12}$: 1380.41).

Compound II-25f: II-25f was synthetized from **II-22f** (73 mg, 43 µmol) and $BF_3.OEt_2$ (0.1 mL, 790 µmol) in CH_2Cl_2/CH_3CN (3/1.5 mL). Column chromatography on SiO_2 (CH_2Cl_2/MeOH, 94:6) yielded **II-25f** (50 mg, 35 µmol, 82%) as a red-brown glassy solid. IR (neat): υ = 3330 (br, OH), 1741 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 257 (82000), 315 (sh, 31500), 398 (sh, 3500), 410 (sh, 2200), 423 (2000), 483 (sh, 2600), 636 (sh, 190) nm. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.40 (m, 8 H), 3.64 (m, 8 H), 1.79 (m, 8 H), 1.58 (m, 16 H), 1.45 – 1.34 (m, 32 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.6 (two peaks), 163.5, 147.6, 147.2, 146.4, 146.1, 146.0, 145.5, 145.3, 145.1, 145.0, 144.7, 144.6, 144.5, 144.4, 144.0 (two peaks), 143.8, 143.7, 143.4, 143.3, 143.2, 142.9, 142.3, 141.8, 141.6, 141.5, 138.6, 71.7, 70.4, 67.3, 62.9, 53.7, 51.5, 32.7, 29.3 (two peaks), 29.2 (two peaks), 29.1, 28.5 (two peaks), 28.4, 25.9 (two peaks), 25.8, 25.7 (two peaks), 25.6 ppm. MALDI-TOF-MS: 1436.26 ($[M]^+$, calcd for $C_{98}H_{68}O_{12}$: 1436.47).

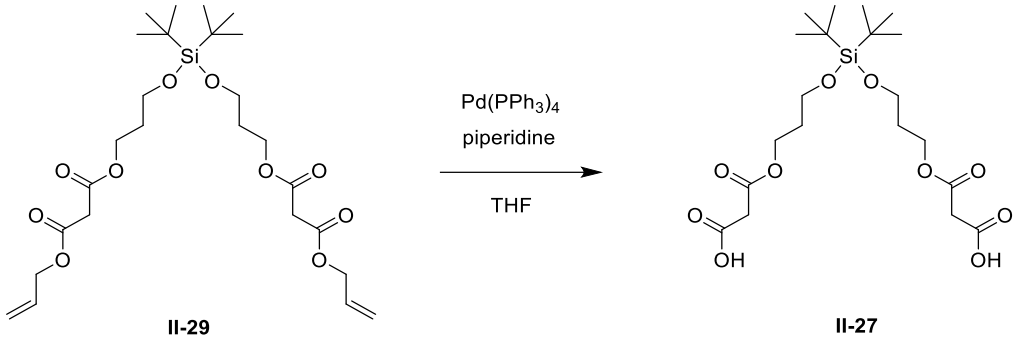
Compound II-26c: II-26c was synthetized from **II-21c** (118 mg, 76 µmol) and $BF_3.OEt_2$ (0.2 mL, 1.5 mmol) in CH_2Cl_2/CH_3CN (3/1.5 mL). Column chromatography on SiO_2 (THF to THF/MeOH, 95:5) yielded **II-26c** (78 mg, 61 µmol, 81%) as a brown glassy solid. IR (neat): υ = 3326 (br, OH), 1737 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 248 (60200), 319 (sh, 27300), 400 (sh, 3000), 412 (2500), 424 (2100), 490 (1700), 576 (sh, 800), 633 (sh, 330), 689 (sh, 100) nm. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.52 (t, *J* = 7 Hz, 4 H), 4.42 (2t, *J* = 7 Hz, 4 H), 3.68 (t, *J* = 7 Hz, 4 H), 3.62 (t, *J* = 7 Hz, 4 H), 1.90 (m, 4 H), 1.80 (m, 4 H), 1.75 (OH, 4 H), 1.65 – 1.47 (m, 16 H). ^{13}C-NMR (100 MHz, $CDCl_3$) : δ = 163.6 (two peaks), 147.2, 147.0, 146.6, 146.5, 146.4 (two peaks), 146.1, 146.0, 145.6, 145.5, 145.3, 144.6, 144.4, 144.2, 143.8, 143.5, 143.4, 143.0, 142.5, 142.2, 142.1, 141.9, 141.6, 140.3, 139.1, 138.4, 71.8, 71.3, 67.3, 67.2, 62.5 (two peaks), 51.8, 32.2, 32.1, 28.4, 28.3, 22.4, 22.3 ppm. MALDI-TOF-MS: 1286.35 (100%, $[M]^+$, calcd for $C_{86}H_{44}O_{12}$: 1268.28), 1291.34 (27%, $[M+Na]^+$, calcd. $C_{86}H_{44}O_{12}$: 1291.27).

Compound II-26d: II-26d was synthetized from **II-21d** (96 mg, 60 µmol) and $BF_3.OEt_2$ (0.1 mL, 790 µmol) in CH_2Cl_2/CH_3CN (3/1.5 mL). Column chromatography on SiO_2 (CH_2Cl_2/MeOH, 92:8) yielded **II-26d** (70 mg, 53 µmol, 89%) as a brown glassy solid. IR (neat): υ = 3325 (br, OH), 1741 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 248 (132500), 319 (sh, 40700), 381 (sh, 10900), 400 (sh, 4900), 411 (4100), 422 (3300), 490 (2800), 576 (sh, 1300), 632 (sh, 500), 693 (sh, 180) nm. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.51 (t, *J* = 7 Hz, 4 H), 4.40 (t, *J* = 7 Hz, 4 H), 3.66 (t, *J* = 6 Hz, 4 H), 3.62 (t, *J* = 6 Hz, 4 H), 1.91 – 1.73 (m, 12 H), 1.65 – 1.38 (m, 20 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$) : δ = 163.6 (two peaks), 147.2, 147.0, 146.6, 146.5 (two peaks), 146.4, 146.2, 146.1, 145.6, 145.5, 145.4, 144.7, 144.4, 144.2, 143.9, 143.6, 143.4, 143.1, 142.6, 142.2, 142.1, 142.0, 141.7, 140.4, 139.2, 138.5, 71.8, 71.3, 67.4, 67.3, 62.8 (two peaks), 51.8, 32.6 (two peaks), 28.6, 28.5, 25.9, 25.8, 25.5, 25.4 ppm. MALDI-TOF-MS: 1324.38 ($[M]^+$, calcd for $C_{90}H_{52}O_{12}$: 1324.35).

Compound II-26e: II-26e was synthetized from **II-21e** (70 mg, 42 µmol) and $BF_3.OEt_2$ (0.1 mL, 790 µmol) in CH_2Cl_2/CH_3CN (3/1.5 mL). Column chromatography on SiO_2 (CH_2Cl_2/MeOH, 95:5) yielded **II-26e** (36 mg, 26 µmol, 66%) as a brown glassy solid. IR (neat): υ = 3336 (br, OH), 1743 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 248 (137000), 317 (sh, 43000), 397 (sh, 5400), 411 (4400), 422 (3600), 492 (3000), 581 (sh, 1200), 635 (sh, 500), 689 (sh, 160) nm. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.51 (t, *J* = 7 Hz, 4 H), 4.40 (t, *J* = 7 Hz, 4 H), 3.65 (t, *J* = 7 Hz, 4 H), 3.62 (t, *J* = 7 Hz, 4 H), 1.87 (m, 4 H), 1.77 (m, 4 H), 1.56 (m, 16 H), 1.43 – 1.34 (m, 20 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$) : δ = 163.6 (two peaks), 147.2, 146.9, 146.5 (two peaks), 146.4, 146.1, 146.0, 145.6, 145.5, 145.3, 144.6, 144.4, 144.1, 143.8, 143.5 (two peaks), 143.4, 143.0, 142.5, 142.2, 142.1, 141.9, 140.6, 140.3, 139.1, 138.4, 71.8, 71.4, 67.4, 67.3, 62.8 (two peaks), 51.9, 32.6 (two peaks), 29.0 (two peaks), 28.6, 28.5, 25.9 (two peaks), 25.8, 25.7 ppm. MALDI-TOF-MS: 1380.40 ($[M]^+$, calcd for $C_{94}H_{60}O_{12}$: 1380.41).

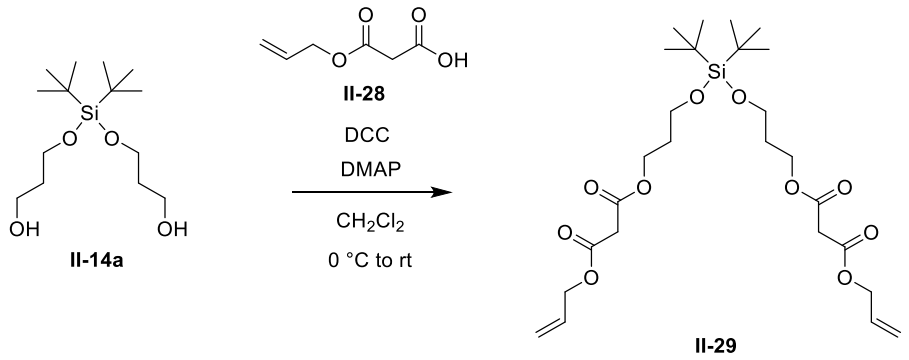
Compound II-26f: II-26f was synthetized from **II-21f** (60 mg, 35 µmol) and $BF_3.OEt_2$ (0.1 mL, 790 µmol) in CH_2Cl_2/CH_3CN (3/1.5 mL). Column chromatography on SiO_2 (CH_2Cl_2/MeOH, 94:6) yielded **II-26f** (28 mg, 19 µmol, 56%) as a brown glassy solid. IR (neat): υ = 3330 (br, OH), 1746 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 248 (126000), 319 (sh, 41000), 398 (sh, 5000), 410 (4200), 423 (3400), 488 (sh, 3000), 579 (sh, 1200), 632 (sh, 500), 689 (sh, 150) nm. ^{1}H-NMR

(400 MHz, $CDCl_3$): δ= 4.51 (t, *J* = 7 Hz, 4 H), 4.40 (t, *J* = 7 Hz, 4 H), 3.64 (t, *J* = 7 Hz, 4 H), 3.63 (t, *J* = 7 Hz, 4 H), 1.86 (m, 4 H), 1.77 (m, 4 H), 1.56 (m, 16 H), 1.43 – 1.31 (m, 28 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$) : δ= 163.6 (two peaks), 147.2, 146.9, 146.5, 146.4 (two peaks), 146.2, 146.0, 145.6, 145.5, 145.3, 144.6, 144.4, 144.1, 143.8, 143.5 (two peaks), 143.4, 143.0, 142.5, 142.2, 142.1, 141.9, 141.6, 140.3, 139.1, 138.4, 71.8, 71.4, 67.4, 67.3, 62.9 (two peaks), 51.9, 32.7 (two peaks), 29.4 (two peaks), 29.2 (two peaks), 28.6, 28.5, 26.0, 25.9, 25.7 (two peaks) ppm. MALDI-TOF-MS: 1436.46 ([M]$^+$, calcd for $C_{98}H_{68}O_{12}$: 1436.47).

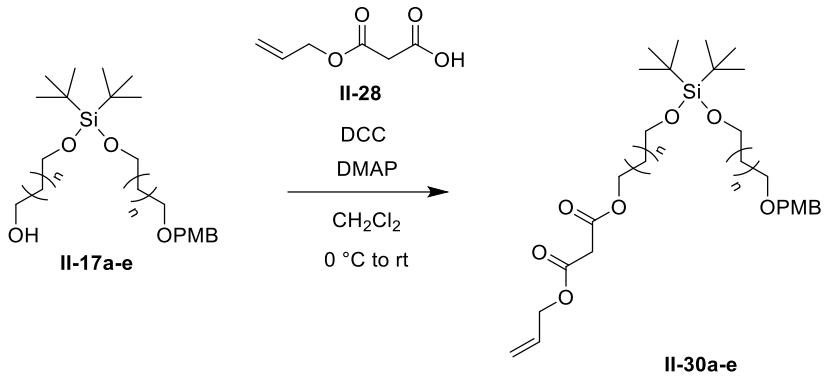


Compound II-27: Piperidine (5.8 mL, 58 mmol) and $Pd(PPh_3)_4$ (0.54 g, 0.47 mmol) were added to a solution of **II-29** (1.28 g, 2.3 mmol) in THF (10 mL). After 4 h, the solvent was removed under vacuum. The crude was dissolved in CH_2Cl_2 then the solution was acidified with HCl 2M (10 mL). The organic layer was washed with water and the solvent was removed under vacuum to give **II-27.**

Compound II-28: II-28 was prepared as described in Tetrahedron Letters, Vol. 38, No. 44, pp. 7737-7740, 1997.



Compound II-29: DCC (1.97 g, 9.55 mmol) was added to a solution of **II-14a** (0.93 g, 3.2 mmol), 10 (0.98 g, 6.8 mmol) and DMAP (0.39 g, 3.2 mmol) in CH_2Cl_2 (40 mL) at 0°C. The resulting mixture was stirred overnight at room temperature, then filtered on SiO2 (CH2Cl2/Ethyl acetate, 9:1) and concentrated. Column chromatography on SiO2 (CH2Cl2/cyclohexane, 8:2) yielded **II-29** (1.27 g, 2.3 mmol, 74%) as a colorless oil.



General procedure for the synthesis of compounds II-30a-e: Dicyclohexylcarbodiimide (DCC, 2 eq) was added to a solution of **II-17a-e** (1 eq), **II-28** (1 eq) and 4-dimethylaminopyridine (DMAP, 1 eq) in CH_2Cl_2 at 0 °C under argon. After 12 h the crude was filtered on SiO_2 (CH_2Cl_2) and concentrated. Column chromatography on SiO_2 gave **II-30a-e**.

Compound II-30a: **II-30a** was synthetized from DCC (2.22 g, 10.8 mmol), **II-17a** (2.22 g, 5.38 mmol), **II-28** (0.853 g, 5.92 mmol) and DMAP (0.657 g, 5.38 mmol) in CH_2Cl_2 (20 mL). Column chromatography (SiO_2, CH_2Cl_2) gave **II-30a** (2.10 g, 73%) as a colorless oil. IR (neat): υ = 1753 (C=O), 1736 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8.5 Hz, 2 H), 6.87 (d, *J* = 8.5 Hz, 2 H), 5.90 (m, 1 H), 5.30 (m, 2 H), 4.64 (td, *J* = 5.5 Hz, 1.5 Hz, 2 H), 4.43 (s, 2 H), 4.29 (t, *J* = 6.5 Hz, 2 H), 3.92 (t, *J* = 6 Hz, 2 H), 3.88 (t, *J* = 6 Hz, 2 H), 3.80 (s, 3 H), 3.58 (t, *J* = 6.5 Hz, 2 H), 3.39 (s, 2 H), 1.86 (m, 4 H), 0.99 (s, 18 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.5, 166.3, 159.2, 131.6, 130.8, 129.3, 188.8, 113.8, 72.8, 66.7, 66.1, 62.7, 60.8, 60.1, 55.3, 41.6, 33.2, 31.8, 27.9, 21.2 ppm.

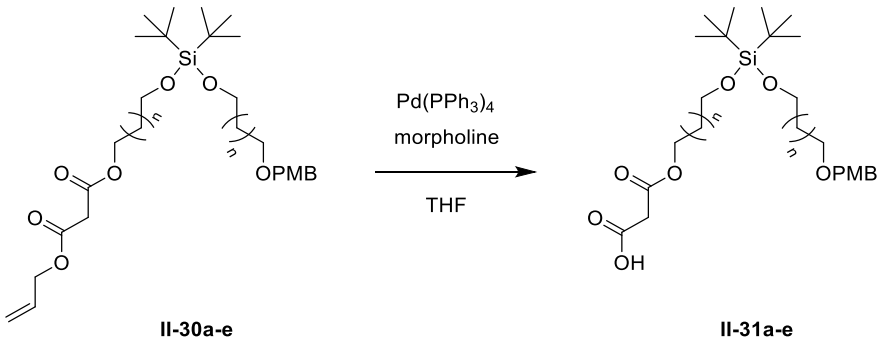
Compound II-30b: **II-30b** was synthetized from DCC (2.06 g, 10.0 mmol), **II-17b** (2.21 g, 5.02 mmol), **II-28** (0.796 g, 5.52 mmol) and DMAP (0.610 g, 5.02 mmol) in CH_2Cl_2 (40 mL). Column chromatography (SiO_2, CH_2Cl_2) gave **II-30b** (2.04 g, 71%) as a colorless oil. IR (neat): υ = 1754 (C=O), 1737 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 8.5 Hz, 2 H), 6.87 (d, *J* = 8.5 Hz, 2 H), 5.91 (ddt, *J* = 17 Hz, 10.5 Hz, 6 Hz, 5.5 Hz, 1 H), 5.29 (m, 2 H), 4.65 (m, 2 H), 4.44 (s, 2 H), 4.18 (t, *J* = 6.5 Hz, 2 H), 3.82 (t, *J* = 6 Hz, 2 H), 3.80 (s, 3 H), 3.48 (t, *J* = 6.5 Hz, 2 H), 3.40 (s, 2 H), 1.68 (m, 8 H), 0.99 (s, 18 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 166.4, 159.3, 131.7, 130.9, 129.4, 118.9, 113.9, 72.6, 70.1, 66.2, 65.7, 63.8, 63.2, 55.4, 41.7, 29.8, 29.3, 28.0, 26.4, 25.3, 21.3 ppm.

Compound II-30c: **II-30c** was synthetized from DCC (2.08 g, 10.1 mmol), **II-17c** (2.36 g, 5.04 mmol), **II-28** (0.80 g, 5.54 mmol) and DMAP (0.62 g, 5.04 mmol) in CH_2Cl_2 (20 mL). Column chromatography (SiO_2, CH_2Cl_2/cyclohexane/MeOH, 49:49:2) gave **II-30c** (3.01 g, 100%) as a light yellow oil. IR (neat): υ = 1754 (C=O), 1737 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) : δ = 7.26 (d, *J* = 8.5 Hz, 2 H), 8.87 (d, *J* = 8.5 Hz, 2 H), 5.90 (m, 1 H), 5.30 (m, 2 H), 4.65 (m, 2 H), 4.43 (s, 2 H), 4.15 (t, *J* = 6.5 Hz, 2 H), 3.80 (m, 7 H), 3.45 (t, *J* = 6.5 Hz, 2 H), 3.39 (s, 2 H), 1.59 (m, 8 H), 1.44 (m, 4 H), 0.99 (s, 18 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7, 166.4, 159.3, 131.7,

131.0, 129.3, 118.9, 113.9, 72.7, 70.3, 66.2, 65.8, 63.9, 63.6, 55.4, 41.7, 32.9, 32.5, 29.7, 28.4, 28.0, 22.7, 22.3, 21.3 ppm.

Compound II-30d: **II-30d** was synthetized from DCC (1.25 g, 6.1 mmol), **II-17d** (1.51 g, 3.03 mmol), **II-28** (0.44 g, 3.03 mmol) and DMAP (0.37 g, 3.0 mmol) in CH_2Cl_2 (8 mL). Column chromatography (SiO_2, CH_2Cl_2/cyclohexane, 7:3) gave **II-30d** (1.81 g, 96%) as a light yellow oil. IR (neat): υ = 1754 (C=O), 1737 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 8.5 Hz, 2 H), 6.87 (d, *J* = 8.5 Hz, 2 H), 5.91 (m, 1 H), 5.30 (m, 2 H), 4.64 (m, 2 H), 4.43 (s, 2 H), 4.14 (t, *J* = 6.5 Hz, 2 H), 3.80 (m, 7 H), 3.44 (t, *J* = 6.5 Hz, 2 H), 3.40 (s, 2 H), 1.61 (m, 8 H), 1.38 (m, 8 H), 0.99 (s, 18 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.7, 166.4, 159.2, 131.7, 130.9, 129.3, 118.9, 113.9, 72.7, 70.3, 66.2, 65.8, 63.9, 63.7, 55.4, 41.7, 33.0, 32.9, 30.0, 28.6, 28.0, 26.2, 25.9, 25.8, 25.6, 21.3 ppm.

Compound II-30e: **II-30e** was synthetized from DCC (1.63 g, 7.90 mmol), **II-17e** (2.07 g, 3.93 mmol), **II-28** (0.62 g, 4.33 mmol) and DMAP (0.48 g, 3.9 mmol) in CH_2Cl_2 (15 mL). Column chromatography (SiO_2, CH_2Cl_2/cyclohexane, 9:1) gave **II-30e** as a light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 8.5 Hz, 2 H), 6.87 (d, *J* = 8.5 Hz, 2 H), 5.91 (m, 1 H), 5.30 (m, 2 H), 4.65 (d, *J* = 5.5 Hz, 2 H), 4.43 (s, 2 H), 4.14 (t, *J* = 6.5 Hz, 2 H), 3.80 (s, 3 H), 3.79 (t, *J* = 6.5 Hz, 4 H), 3.43 (t, *J* = 6.5 Hz, 2 H), 3.40 (s, 2 H), 1.58 (m, 8 H), 1.35 (m, 12 H), 0.99 (s, 18 H) ppm.



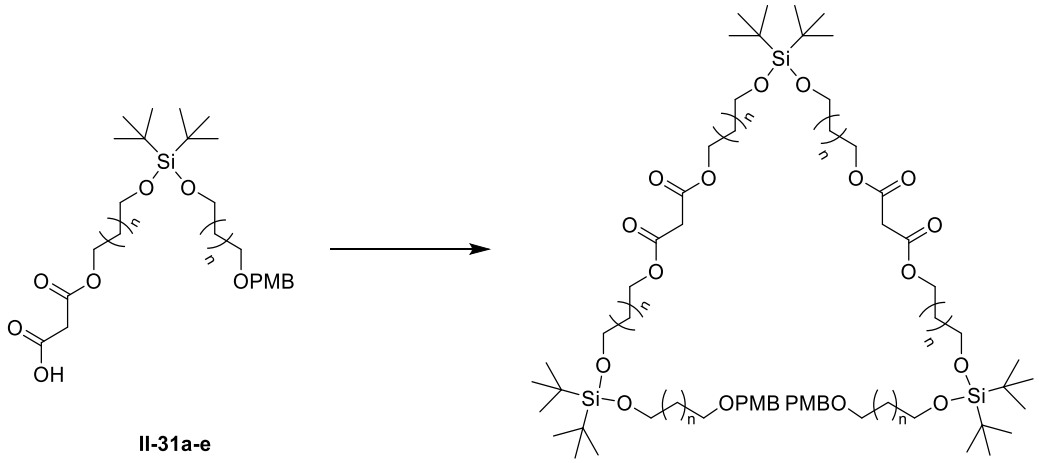
II-30a-e **II-31a-e**

General procedure for the synthesis of compounds II-31a-e: Morpholine (5 eq) and $Pd(PPh_3)_4$ (0.05 eq) were added to a solution of **II-30a-e** (1 eq) in dry THF under argon. After 4 h, the solvent was removed under vacuum. The crude was dissolved in CH_2Cl_2 then the solution was acidified with HCl 2M (10 mL). The organic layer was washed with water and the solvent was removed under vacuum to give **II-31a-e**. The crude was used without purification.

Compound II-31a: **II-31a** was synthetized from morpholine (2.0 mL, 22.9 mmol), $Pd(PPh_3)_4$ (0.21 g, 0.18 mmol) and **II-430a** (0.49 g, 0.92 mmol) in dry THF (5 mL). **II-30a** was isolated as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 8.5 Hz, 2 H), 6.87 (d, *J* = 8.5 Hz, 2 H), 4.49 (s, 2 H), 4.30 (t, *J* = 6 Hz, 2 H), 3.90 (m, 4 H), 3.80 (s, 3 H), 3.61 (t, *J* = 6 Hz, 2 H), 3.37 (s, 2 H), 1.87 (m, 4 H), 0.98 (s, 18 H) ppm.

Compound II-31b: **II-31b** was synthetized from morpholine (2.9 mL, 34.0 mmol), $Pd(PPh_3)_4$ (0.20 g, 0.17 mmol) and **II-30b** (2.04 g, 3.42 mmol) in dry THF (20 mL).

Compound II-31c: **II-31c** was synthetized from morpholine (6.61 mL, 75.9 mmol), $Pd(PPh_3)_4$ (0.585 g, 0.506 mmol) and **II-30c** (3.01 g, 5.06 mmol) in dry THF (20 mL).
Compound II-31d: **II-31d** was synthetized from morpholine (1.3 mL, 14.5 mmol), $Pd(PPh_3)_4$ (0.17 g, 0.145 mmol) and **II-30d** (1.81 g, 2.91 mmol) in dry THF (10 mL). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 4.45 (s, 2H), 4.16 (t, J = 6.5 Hz, 2H), 3.80 (m, 7H), 3.45 (t, J = 6.5 Hz, 2H), 3.39 (s, 2H), 1.59 (m, 8H), 1.38 (m, 8H), 0.99 (s, 18H) ppm.
Compound II-31e: **II-31e** was synthetized from morpholine (4.3 mL, 48.8 mmol), $Pd(PPh_3)_4$ (0.45 g, 0.39 mmol) and **II-30e** in dry THF (20 mL).



II-31a-e → **II-32a-e**

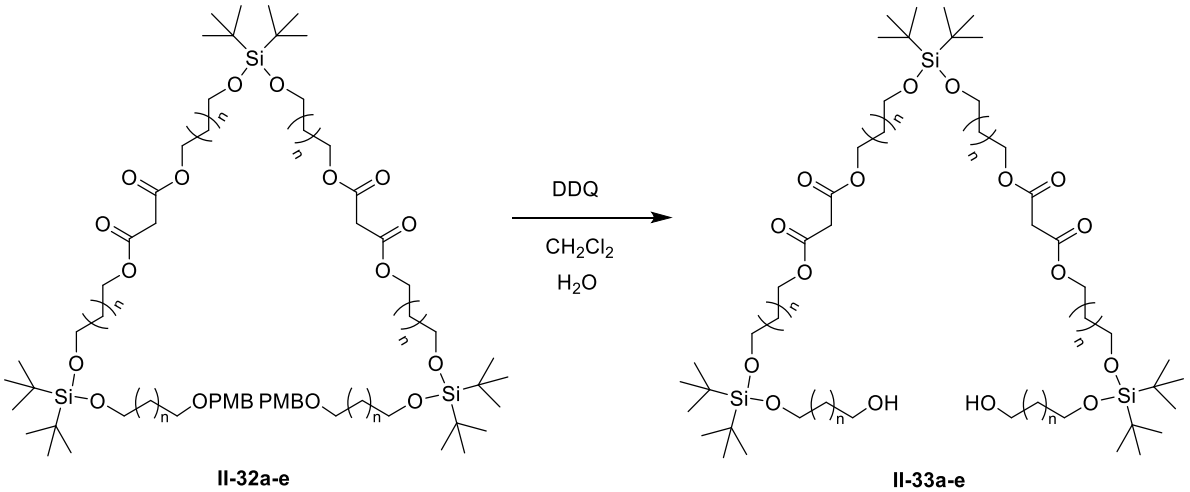
General procedure for the synthesis of compounds II-32a-e: Dicyclohexylcarbodiimide (DCC, 4.5 eq) was added to a solution of **II-14a-e** (1 eq), **II-31a-e** and 4-dimethylaminopyridine (DMAP, 2 eq) in CH_2Cl_2 at 0 °C under argon. After 12 h the crude was filtered on SiO_2 (CH_2Cl_2). Column chromatography (SiO_2) gave **II-32a-e**.

Compound II-32a: **II-32a** was synthetized from DCC (0.28 g, 1.37 mmol), **II-14a** (0.13 g, 0.458 mmol), **II-31a** (0.46 g, 0.915 mmol) and DMAP (0.056 g, 0.458 mmol) in CH_2Cl_2 (10 mL). Column chromatography (SiO_2, cyclohexane/diethyl ether, 9:1) gave **II-32a** (0.35 g, 61% calc. for two steps) as a colorless oil. IR (neat): υ = 1753 (C=O), 1736 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8.5 Hz, 4 H), 6.87 (d, *J* = 8.5 Hz, 4 H), 4.43 (s, 4 H), 4.29 (t, *J* = 6.5 Hz, 4 H), 4.27 (t, *J* = 6.5 Hz, 4 H), 3.90 (m, 12 H), 3.80 (s, 6 H), 3.58 (t, *J* = 6 Hz, 4 H), 3.36 (s, 4 H), 1.87 (m, 12 H), 0.99 (s, 54 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7, 159.3, 130.8, 129.4, 113.9, 72.8, 66.8, 62.8, 62.7, 60.3, 60.2, 55.4, 41.6, 33.2, 31.9, 28.0, 27.9, 21.3 ppm.
Compound II-32b: II-32b was synthetized from DCC (0.87 g, 4.20 mmol), **II-14b** (0.38 g, 1.20 mmol), **II-31b** and DMAP (0.15 g, 1.20 mmol) in CH_2Cl_2 (60 mL). Column chromatography (SiO_2, CH_2Cl_2/EtOAc, 9:1) gave **II-32b** (1.70 g, 99%) as a colorless oil. IR (neat): υ = 1753 (C=O), 1736 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 8.5 Hz, 4 H), 6.87 (d, *J* = 8.5 Hz, 4 H), 4.43 (s, 4 H), 4.17 (m, 8 H), 3.82 (m, 18 H), 3.47 (t, *J* = 6.5 Hz, 4 H), 3.37 (s, 4 H), 1.68 (m, 24 H), 0.99 (s, 54 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 159.3, 130.9, 129.4, 113.9, 72.6, 70.1, 65.6, 65.6, 63.8, 63.3, 63.2, 55.4, 41.7, 29.8, 29.3, 28.0, 27.0, 26.4, 25.3, 21.3 ppm.

Compound II-32c: **II-32c** was synthetized from DCC (DCC, 1.36 g, 6.57 mmol), **II-14c** (0.76 g, 2.19 mmol), **II-31c** and DMAP (0.54 g, 4.38 mmol) in CH_2Cl_2 (10 mL). Column chromatography (SiO_2, cyclohexane/diethyl ether, 85:15) gave **II-32c** (2.06 g, 66%, calc. for two steps) as a colorless oil. IR (neat): υ = 1753 (C=O), 1736 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.26 (t, *J* = 8.5 Hz, 4 H), 6.87 (t, *J* = 8.5 HZ, 4 H), 4.43 (s, 4 H), 4.15 (m, 8 H), 3.80 (m, 18 H), 3.45 (t, J = 6.5 Hz, 4 H), 3.55 (s, 4 H), 1.59 (m, 24 H), 1.44 (m, 12 H), 0.99 (s, 54 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 159.3, 131.0, 129.3, 113.9, 75.7, 70.3, 65.7, 63.9, 63.6, 63.6, 55.4, 41.7, 32.9, 32.5, 29.7, 28.4, 28.0, 27.1, 22.7, 22.3, 21.3 ppm.

Compound II-32d: **II-32d** was synthetized from DCC (DCC, 1.44 g, 7.00 mmol), **II-14d** (0.58 g, 1.53 mmol), **II-31d** and DMAP (0.38 g, 3.11 mmol) in CH_2Cl_2 (10 mL). Column chromatography (SiO_2, cyclohexane/diethyl ether, 8:2) gave **II-32d** (1.26 g, 54%, calc. for two steps) as a colorless oil. IR (neat): υ = 1753 (C=O), 1736 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, J = 8.5 Hz, 4 H), 6.67 (d, J = 8.5 Hz, 4 H), 4.43 (s, 4 H), 4.14 (t, J = 6.5 Hz, 8 H), 3.80 (m, 18 H), 3.44 (t, J = 6.5 Hz, 4 H), 3.36 (s, 4 H), 1.60 (m, 24 H), 1.38 (m, 24 H), 0.99 (s, 54 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 159.3, 131.0, 129.3, 113.9, 72.7, 70.3, 65.8, 63.9, 63.8, 55.4, 41.8, 33.0, 32.9, 30.0, 28.7, 28.0, 26.2, 25.9, 25.8, 25.7, 21.3 ppm.

Compound II-32e: **II-32e** was synthetized from DCC (DCC, 0.83 g, 4.00 mmol), **II-14e** (0.65 g, 1.61 mmol), **II-31e** and DMAP (0.20 g, 1.61 mmol) in CH_2Cl_2 (60 mL). Column chromatography (SiO_2, CH_2Cl_2) gave **II-32e** (0.75 g, 29%, calc. for three steps) as a colorless oil. IR (neat): υ = 1753 (C=O), 1737 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 8.5 Hz, 4 H), 6.87 (d, *J* = 8.5 Hz, 4 H), 4.43 (s, 4 H), 4.13 (t, *J* = 6.5 Hz, 8 H), 3.80 (s, 6 H), 3.79 (t, *J* = 6.5 Hz, 12 H), 3.43 (t, *J* = 6.5 Hz, 4 H), 3.36 (s, 4 H), 1.58 (m, 26 H), 1.35 (m, 34 H), 0.99 (s, 54 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 159.3, 131.0, 129.3, 113.9, 72.7, 70.4, 65.8, 64.0, 63.9, 55.4, 41.8, 33.0, 33.0, 29.9, 29.5, 29.2, 28.6, 28.0, 26.4, 26.0, 25.9, 21.3 ppm.



II-32a-e **II-33a-e**

General procedure for the synthesis of compounds II-33a-e: Water (20 eq) was added to a solution of **II-32a-e** (1 eq) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 2.2 eq) in CH_2Cl_2 at room temperature. After 6 h, the crude was filtered on SiO_2 and concentrated. Column chromatography (SiO_2) gave **II-33a-e**.

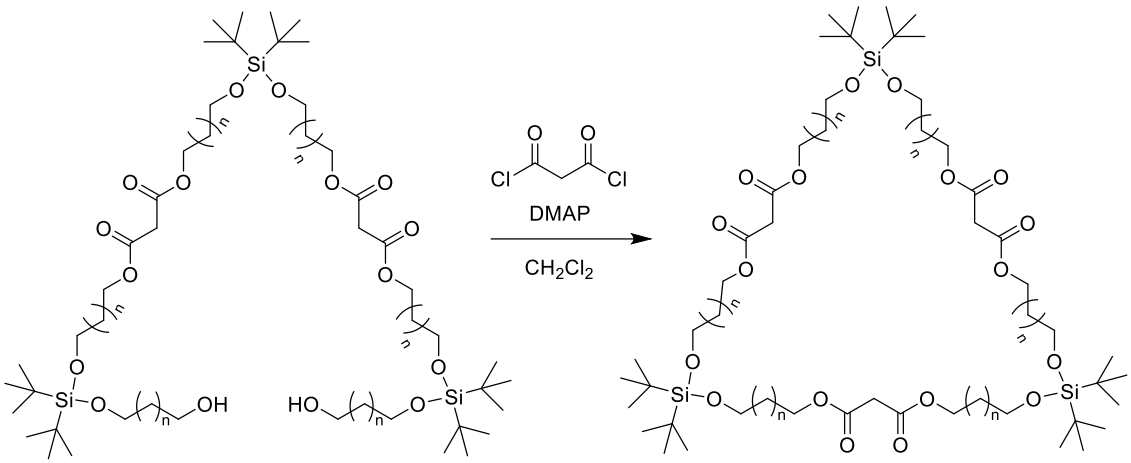
Compound II-33a: **II-33a** was synthetized from water (1 mL), **II-32a** (0.348 g, 0.277 mmol) and DDQ (0.139 g, 0.610 mmol) in CH_2Cl_2 (10 mL). Filtration (SiO_2, CH_2Cl_2/MeOH, 95:5) and column chromatography (SiO_2, CH_2Cl_2/MeOH, 98:2) gave **II-33a** (0.274 g, 98%) as a colorless oil. IR (neat): $\tilde{\upsilon}$ = 3459 (O-H), 1752 (C=O), 1737 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.30 (t, *J* = 6.5 Hz, 4 H), 4.29 (t, *J* = 6.5 Hz, 4 H), 4.02 (t, *J* = 5.5 Hz, 4 H), 3.92 (m, 8 H), 3.81 (t, *J* = 6 Hz, 4 H), 3.37 (s, 4 H), 2.05 (s br, 2 H), 1.90 (m, 8 H), 1.81 (m, *J* = 5.5 Hz, 4 H), 1.01 (s, 36 H), 0.99 (s, 54 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 166.7, 62.8, 62.8, 62.7, 61.5, 60.4, 60.3, 41.6, 34.8, 31.9, 28.0, 27.9, 21.3 ppm.

Compound II-33b: **II-33b** was synthetized from water (1.5 mL), **II-32b** (1.68 g, 1.26 mmol) and DDQ (0.571 g, 2.51 mmol) in CH_2Cl_2 (80 mL). Filtration (SiO_2, CH_2Cl_2/MeOH, 97:3) and column chromatography (SiO_2, CH_2Cl_2/MeOH, 97:3) gave **II-33b** (1.23 g, 89%) as a colorless oil. IR (neat): $\tilde{\upsilon}$ = 3454 (O-H), 1752 (C=O), 1736 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.19 (t, *J* = 6.5 Hz, 8 H), 3.85 (m, 12 H), 3.67 (t, *J* = 6 Hz, 4 H), 3.38 (s, 4 H), 1.67 (m, 26 H), 1.00 (s, 36 H), 0.99 (s, 54 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 65.6, 64.0, 63.3, 62.9, 41.7, 30.0, 29.7, 29.3, 29.2, 28.0, 25.3, 25.2, 21.3 ppm.

Compound II-33c: **II-33c** was synthetized from water (5 mL), **II-32c** (2.06 g, 1.45 mmol) and DDQ (0.658 g, 2.90 mmol) in CH_2Cl_2 (50 mL). Filtration (SiO_2, CH_2Cl_2) and column chromatography (SiO_2, CH_2Cl_2/ diethyl ether, 8:2) gave **II-33c** (0.916 g, 53%) as a colorless oil. IR (neat): $\tilde{\upsilon}$ = 3454 (O-H), 1752 (C=O), 1736 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.15 (t, *J* = 6.5 Hz, 8 H), 3.81 (m, 12 H), 3.65 (t, *J* = 6.5 Hz, 4 H), 3.35 (s, 4 H), 1.58 (m, 36 H), 0.99 (s, 54 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 65.7, 63.8, 63.6, 63.1, 41.7, 32.8, 32.7, 32.5, 28.4, 28.0, 22.3, 22.2, 21.3 ppm.

Compound II-33d: **II-33d** was synthetized from water (3 mL), **II-32d** (1.26 g, 0.834 mmol) and DDQ (0.417 g, 1.83 mmol) in CH_2Cl_2 (30 mL). Filtration (SiO_2, CH_2Cl_2/MeOH, 99:1) and column chromatography (SiO_2, CH_2Cl_2/ diethyl ether, 1:1 and 0.1% MeOH) gave **II-33d** (0.683 g, 65%) as a colorless oil. IR (neat): $\tilde{\upsilon}$ = 3418 (O-H), 1752 (C=O), 1737 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.14 (t, J = 7 Hz, 8 H), 3.81 (m, 12 H), 3.64 (t, J = 6.5 Hz, 4 H), 3.36 (s, 4 H), 1.66 (m, 8 H), 1.56 (m, 16 H), 1.40 (m, 26 H), 0.99 (s, 54 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 65.8, 63.9, 63.8, 63.1, 41.8, 33.0, 33.0, 32.9, 28.7, 28.0, 25.8, 25.8, 25.8, 25.7, 25.6, 25.6, 21.3 ppm.

Compound II-33e: **II-33e** was synthetized from water (1 mL), **II-32e** (0.744 g, 0.468 mmol) and DDQ (0.213 g, 0.938 mmol) in CH_2Cl_2 (35 mL). Filtration (SiO_2, CH_2Cl_2/MeOH, 95:5) and column chromatography (SiO_2, CH_2Cl_2/MeOH, 99:1) gave **II-33e** (0.450 g, 71%) as a colorless oil. IR (neat): $\tilde{\upsilon}$ = 3454 (O-H), 1753 (C=O), 1737 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.14 (t, *J* = 7 Hz, 8 H), 3.80 (t, *J* = 6.5 Hz, 12 H), 3.64 (t, *J* = 6.5 Hz, 4 H), 3.37 (s, 4 H), 1.65 (m, 8 H), 1.55 (m, 18 H), 1.35 (m, 34 H), 0.99 (s, 54 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 65.8, 63.9, 63.9, 63.2, 41.8, 33.0, 33.0, 33.0, 29.4, 29.2, 28.6, 28.0, 26.0, 26.0, 25.9, 21.3 ppm.



II-33a-e **II-34a-e**

General procedure for the synthesis of compounds II-34a-e: Malonyl chloride (1.1 eq) was added to a solution of **II-33a-e** (1 eq) and DMAP (2 eq) in CH_2Cl_2 under argon. After 24 h the mixture was filtered on SiO_2 and concentrated. Column chromatography (SiO_2) gave **II-34b-e**.

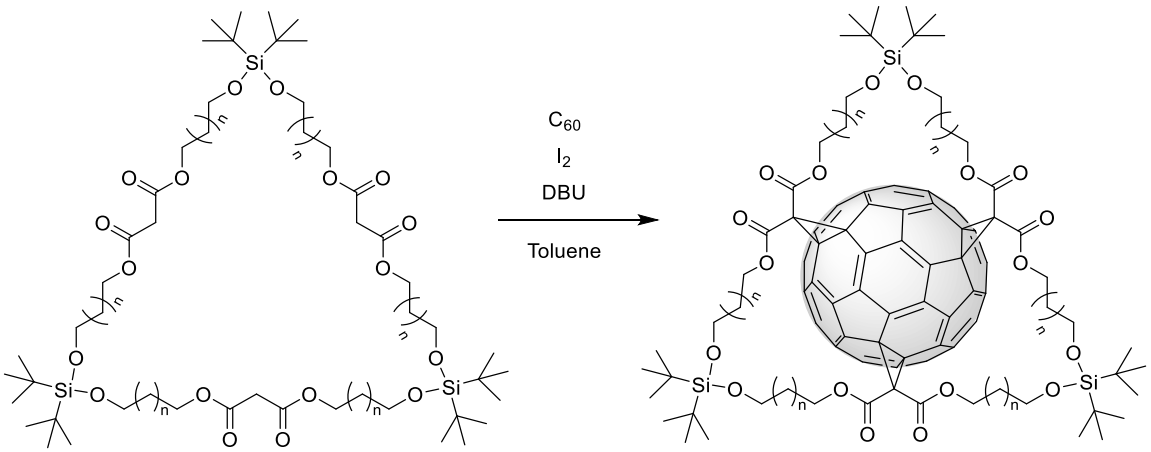
Compound II-34a: **II-34a** was synthetized from malonyl chloride (0.0564 g, 0.400 mmol), **II-33a** (0.405 g, 0.400 mmol) and DMAP (0.0977 g, 0.800 mmol) in CH_2Cl_2 (50 mL). Filtration (SiO_2, CH_2Cl_2/ diethyl ether, 9:1) and column chromatography (SiO_2, CH_2Cl_2/ diethyl ether, 9:1) gave **II-34a** (0.229 g, 53 %) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.22 (t, *J* = 6 Hz, 12 H), 3.84 (t, *J* = 6 Hz, 12 H), 3.30 (s, 6 H), 1.83 (quint., *J* = 6 Hz, 12 H), 0.93 (s, 54 H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.6, 62.5, 60.1, 41.5, 31.7, 27.8, 21.1 ppm. MALDI-TOF-MS: 1103.5 (100%, $[M+Na]^+$, calcd for $C_{51}H_{96}O_{18}Si_3Na$: 1103.6), 1081.5 (47%, $[M+H]^+$, calcd for $C_{51}H_{97}O_{18}Si_3$: 1081.6).

Compound II-34b: **II-34b** was synthetized from malonyl chloride (0.156 g, 1.11 mmol), **II-33b** (1.22 g, 1.11 mmol) and DMAP (0.305 g, 2.50 mmol) in CH_2Cl_2 (300 mL). Filtration (SiO_2, CH_2Cl_2/ EtOAc, 9:1) and column chromatography (SiO_2, CH_2Cl_2) gave **II-34b** (0.331 g, 26 %) as a colorless oil. IR (neat): $\tilde{\upsilon}$ = 1752 (C=O), 1735 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.18 (t, *J* = 6.5 Hz, 12 H), 3.84 (t, *J* = 6 Hz, 12 H), 3.37 (s, 6 H), 1.76 (q, *J* = 6.5 Hz, 12 H), 1.61 (t, *J* = 6 Hz, 12 H), 0.99 (s, 54 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 65.5, 63.3, 41.8, 29.3, 28.0, 25.3, 21.3 ppm. MALDI-TOF MS: *m/z* = 1417.740 $[M+H]^+$, calcd for $C_{75}H_{145}O_{18}Si_3$: 1417.97.

Compound II-34c: **II-34c** was synthetized from malonyl chloride (0.109 g, 0.775 mmol), **II-33c** (0.916 g, 0.775 mmol) and DMAP (0.189 g, 1.55 mmol) in CH_2Cl_2 (250 mL). Filtration (SiO_2, CH_2Cl_2/diethyl ether, 1:1) and column chromatography (SiO_2, cyclohexane / diethyl ether, 1:1) gave **II-34c** (0.612 g, 63%) as a colorless oil. IR (neat): $\tilde{\upsilon}$ = 1753 (C=O), 1736 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.15 (t, *J* = 6.5 Hz, 12 H), 3.81 (t, *J* = 6.5 Hz, 12 H), 3.35 (s, 6 H), 1.68 (m, 12 H), 1.58 (m, 12 H), 1.45 (m, 12 H), 0.99 (s, 54 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.8, 65.7, 63.6, 41.7, 32.5, 28.4, 28.0, 22.8, 21.3 ppm. MALDI-TOF MS: *m/z* = 1271.6 $[M+Na]^+$, calcd for $C_{63}H_{120}NaO_{18}Si_3$: 1271.77.

Compound II-34d: **II-34d** was synthetized from malonyl chloride (0.0835 g, 0.592 mmol), **II-33d** (0.682 g, 0.539 mmol) and DMAP (0.132 g, 1.08 mmol) in CH_2Cl_2 (70 mL). Filtration (SiO_2, CH_2Cl_2/diethyl ether, 1:1) and column chromatography (SiO_2, CH_2Cl_2/ diethyl ether, 7:3) gave **II-34d** (0.307 g, 43%) as a colorless oil. IR (neat): $\tilde{\upsilon}$ = 1753 (C=O), 1736 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.14 (t, *J* = 6.5 Hz, 12 H), 3.80 (t, *J* = 6 Hz, 12 H), 3.36 (s, 6 H), 1.66 (m, 12 H), 1.55 (m, 12 H), 1.39 (m, 24 H), 0.99 (s, 54 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 65.7, 63.8, 41.8, 32.9, 28.7, 28.0, 25.8, 25.6, 21.3 ppm. MALDI-TOF MS: *m/z* = 1355.8 $[M+Na]^+$ calcd for $C_{69}H_{132}NaO_{18}Si_3$: 1355.86.

Compound II-34e: **II-34e** was synthetized from malonyl chloride (0.0470 g, 0.333 mmol), **II-33e** (0.450 g, 0.333 mmol) and DMAP (0.122 g, 1.00 mmol) in CH_2Cl_2 (200 mL). Filtration (SiO_2, CH_2Cl_2) and column chromatography (SiO_2, CH_2Cl_2) gave **II-34e** (0.099 g, 21%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.17 (t, *J* = 6.5 Hz, 12 H), 3.83 (t, *J* = 6.5 Hz, 12 H), 3.40 (s, 6 H), 1.62 (m, 24 H), 1.39 (m, 36 H), 1.03 (m, 54 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7, 65.7, 63.8, 41.8, 32.9, 29.1, 28.5, 28.0, 25.9, 25.8, 21.2 ppm. MALDI-TOF MS: *m/z* = 1417.740 $[M+H]^+$, calcd for $C_{75}H_{145}O_{18}Si_3$: 1417.97.



II-34a-e **II-35a-d**

General procedure for the synthesis of compounds II-35a-d: DBU (7.5 eq) was added to a solution of **II-34** (1 eq), [60]fullerene (C_{60}) (1 eq) and I_2 (3.5 eq) in toluene. The mixture was stirred at room temperature for 1 h 30 min, then filtered on SiO_2 (cyclohexane, then CH_2Cl_2) and concentrated. Column chromatography (SiO_2) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) gave **II-35a-d**.

Compound II-35a: **II-35a** was synthetized from DBU (0.15 mL, 1.00 mmol), **II-34a** (0.58 g, 0.15 mmol), C_{60} (0.108 g, 0.15 mmol) and I_2 (0.131 g, 0.52 mmol) in toluene (400 mL). Column chromatography (SiO_2, CH_2Cl_2/cyclohexane, 1:1) gave **II-35a** as a cherry-red glassy solid (tris-adduct *e,e,e*, 0.055 g, 61%). IR (neat): $\tilde{\upsilon}$ = 1751 (C=O) cm^{-1}; UV/Vis (CH_2Cl_2): 252 ($1.6x10^5$), 281 ($1.1x10^5$), 304 (sh, $9x10^4$), 482 ($6x10^4$), 564 (sh, $2X10^4$); ^1H NMR ($CDCl_3$, 400 MHz): δ= 4.70 (m, 3 H), 4.60 (m, 3 H), 4.36 (m, 6 H), 3.95-3.77 (m, 12 H), 1.94 (m, 12 H), 0.98 (s, 36 H), 0.90 (s, 36

H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = ppm. MALDI-TOF-MS: 1797.0 ([M+H]$^+$, calcd for $C_{98}H_{91}O_{18}Si_3$: 1796.5).

Compound II-35b: **II-35b** was synthetized from DBU (0.299 mL, 1.96 mmol), **II-34b** (0.326 g, 0.280 mmol), C_{60} (0.201 g, 0.280 mmol) and I_2 (0.248 g, 0.978 mmol) in toluene (400 mL). Column chromatography (SiO_2, CH_2Cl_2/cyclohexane, 1:1) gave **II-35b** as a cherry-red glassy solid (tris-adduct *e,e,e*, 0.204 g, 39%). IR (neat): $\breve{\upsilon}$ = 1748 (C=O), 1728 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): 237 (1.2x10^5), 251 (1.2x10^5), 281 (9x10^4), 304 (sh, 7x10^4), 484 (6x10^3), 568 (sh, 2x10^3) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 4.53 (m, 6 H), 4.21 (m, 6 H), 3.79 (m, 12 H), 1.77 (m, 12 H), 1.57 (m, 12 H), 1.00 (s, 27 H), 0.96 (s, 27 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 163.6, 163.2, 147.8, 146.8, 146.8 (two peaks), 146.8, 146.6, 146.6, 146.5, 145.8, 145.7, 144.7, 144.6, 144.2, 143.7, 142.7, 142.5, 142.4, 141.7, 141.2, 71.0, 70.4, 67.3, 67.1, 63.2, 62.9, 53.9, 29.5, 29.2, 28.0, 25.5, 25.4, 21.4, 21.2 ppm. MALDI-TOF-MS: 1881.7 ([M+2H]$^+$, calcd for $C_{117}H_{104}O_{18}Si_3$: 1881.3).

Compound II-35c: **II-35c** was synthetized from DBU (0.557 mL, 3.68 mmol), **II-34c** (0.326 g, 0.280 mmol), C_{60} (0.353 g, 0.490 mmol) and I_2 (0.435 g, 1.72 mmol) in toluene (700 mL). Column chromatography (SiO_2, CH_2Cl_2/cyclohexane, 1:1) followed by gel permeation chromatography gave **II-35c** as a cherry-red glassy solid (tris-adduct *e,e,e*, 77 mg, 8%). IR (neat): $\breve{\upsilon}$ = 1746 (C=O) cm^{-1}. UV/vis (CH_2Cl_2): 239 (9x10^4), 250 (9x10^4), 281 (6x10^4), 307 (sh, 5x10^4), 484 (4x10^3), 564 (sh, 1x10^3) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.49 (m, 2 H), 4.19 (m, 2 H), 3.81-3.70 (m, 4 H), 1.70 (m, 4 H), 1.55 (m, 4 H), 1.41 (m, 4 H), 0.98 (s, 18 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.6, 163.6, 147.8, 146.9, 146.8, 146.8, 146.6, 146.5, 146.5, 145.8, 145.8, 144.8, 144.6, 144.5, 143.7, 143.0, 142.4, 142.3, 141.8, 141.0, 71.1, 70.4, 67.3, 67.2, 63.5, 63.4, 53.7, 32.3, 32.2, 28.3, 28.1, 28.0, 22.2, 22.1, 21.3, 21.2 ppm. MALDI-TOF-MS: 1963.942 ([M+H]$^+$, calcd for $C_{123}H_{114}O_{18}Si_3$: 1962.73).

Compound II-35d: **II-35d** was synthetized from DBU (0.250 mL, 1.65 mmol), **II-34d** (0.293 g, 0.219 mmol), C_{60} (0.158 g, 0.219 mmol) and I_2 (0.195 g, 0.768 mmol) in toluene (316 mL). Column chromatography (SiO_2, CH_2Cl_2/cyclohexane, 1:1) followed by gel permeation chromatography gave **II-35d** as a cherry-red glassy solid (tris-adduct *e,e,e*, 25.4 mg, 5.7%). IR (neat): $\breve{\upsilon}$ = 1748 (C=O) cm^{-1}. UV/vis (CH_2Cl_2): 242 (1.0x10^5), 248 (1.0x10^5), 285 (sh, 6x10^4), 483 (4x10^3), 564 (sh, 1x10^3) nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.70 (m, 4 H), 4.41 (m, 4 H), 4.23 (m, 4 H), 3.78 (m, 12 H), 1.70 (m, 12 H), 1.39 (m, 36 H), 0.99 (m, 54 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.6, 163.5, 147.6, 146.9, 146.9, 146.7, 146.6, 146.6, 146.5, 145.9, 145.8, 144.8, 144.5 (two peaks), 143.6, 143.0, 142.5, 142.3, 141.9, 141.0, 129.2, 128.4, 125.4, 71.1, 70.4, 67.1, 67.1, 63.7, 63.7, 53.6, 32.7, 28.6, 28.0, 25.6, 25.5, 25.4, 25.2, 21.3, 21.3 ppm. MALDI-TOF MS: *m/z* = 2047.948 [M+H]$^+$, calcd for $C_{129}H_{127}O_{18}Si_3$: 2047.83

Chapter III: Regioselective syntheses of C_{60} Tris-adducts by a tethered-directed approach.

1. Introduction.

The first regioselective formation of a C_{60} tris-adduct was reported in 1994 by Diederich and coworkers, introducing the tethered-directed remote functionalization concept.[1] Their methodology was based on three elements: (1) an anchor; (2) a tether and (3) a reactive group. The anchor is the first addend attached to the C_{60} core. It is linked to the reactive groups by the tethers. The length and the shape of the tether will then induce the regioselective attack of the reactive group onto the C_{60} core to form regioselectively a C_{60} derivative. A malonate moiety was chosen as anchor, a 4-substituted benzyl alcohol as tether and a 2-substituted 1,3-butadiene as reactive group. Reaction of **III-1** with C_{60} in a two steps synthesis led only to the tris-adducts *e,e,trans-1* **III-2** in an excellent yield of 48% (Figure III-1).

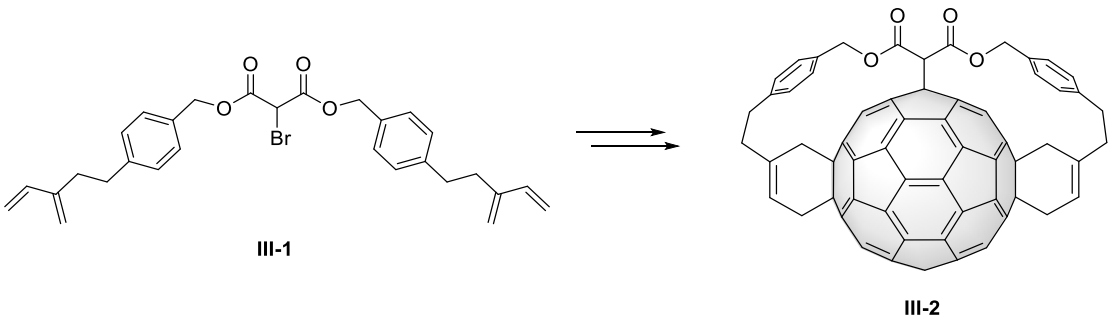


Figure III-1 : First regioselective synthesis of C_{60} tris-adducts by tethered-directed remote functionalization.

This tether-directed approach has been also extensively used for the regioselective synthesis of C_{60} bis-adducts.[2] Based on double Bingel reactions, 7 out of the 8 possible regioisomers of C_{60} bis-adducts could be obtained. These syntheses were achieved with xylylene,[3] crown ether,[4] porphyrin,[5] Tröger's base,[6] phenantroline[3], spirobifluorene[3] and chiral[7] tethers (Figure III-2). For steric reasons, this strategy is not suitable for the preparation of the *cis-1* regioisomer.

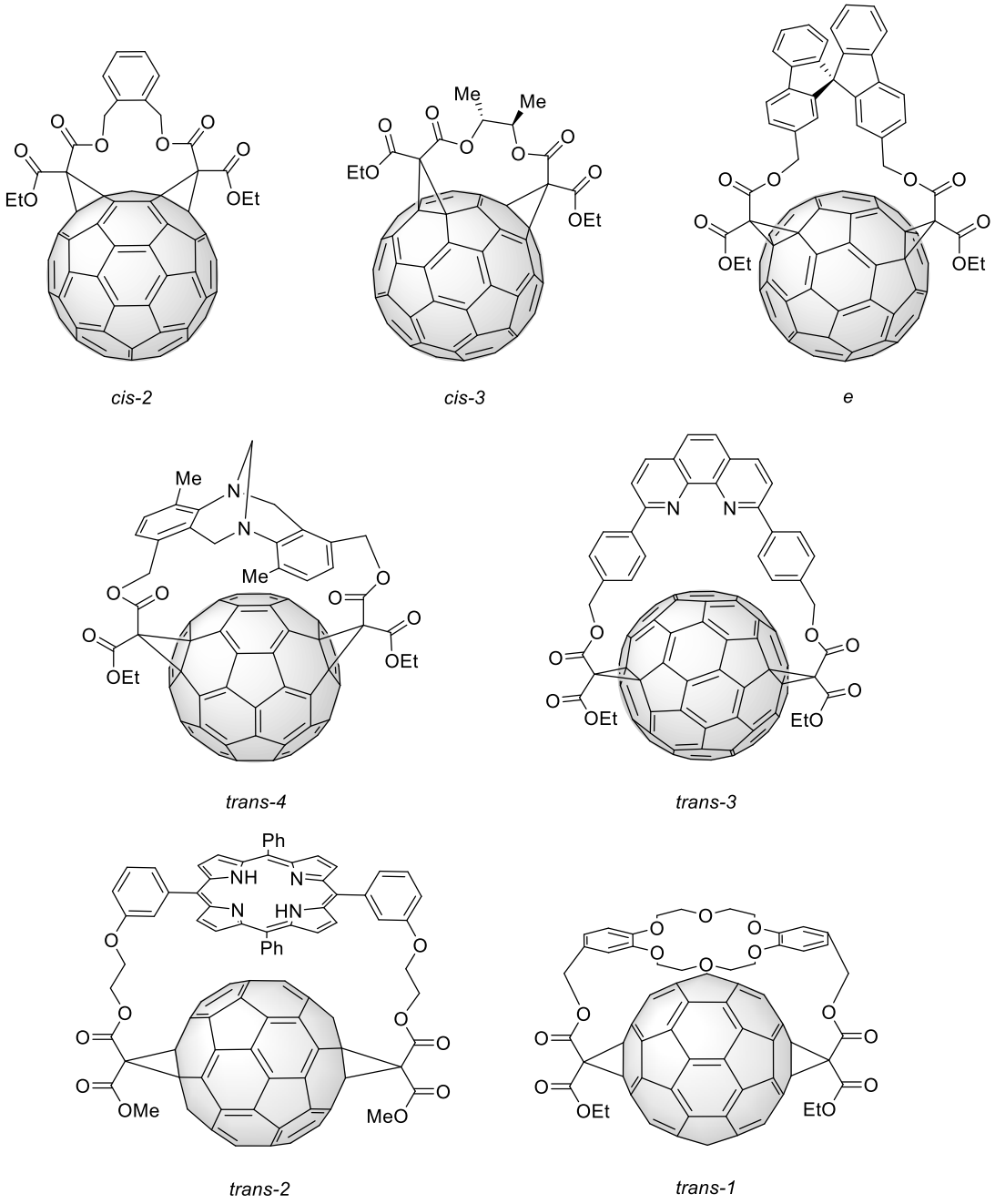
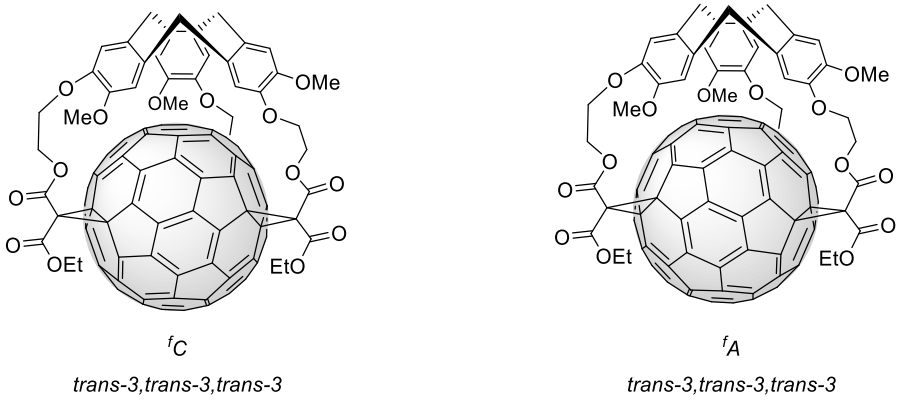


Figure III-2 : Examples of tethers for the regioselective bis-functionalization of C_{60}.

Theoretically, it is more complicated to obtain C_{60} tris-adducts in a pure form due to the 46 possible addition patterns. This problem has been partially solved by the tether-directed remote functionalization methodology as the number of possible regioisomers is considerably reduced. Different tethers have been developed in order to prepare selected fullerene tris-adducts.

Diederich and coworkers reported in 1999 a tether-directed methodology based on a cyclotriveratrylene (CTV) tether.[8] The CTV core was selected for its favorable π-π charge transfer interaction with C_{60} and the resulting host-guest complex CTV-C_{60} may play the role of a template.[9] Subsequent C_{60} regioselective functionalization was enabled by grafting

malonates on the CTV and afforded two pairs of diastereomeric *trans-3,trans-3,trans-3* tris-adducts in 11% and 9% yields, respectively (Figure III-3).[8,10] Due to the chirality of the CTV tether, the unambiguous assignation of the compounds was difficult. In opposition to the previously reported tris-adducts,[11] the formation of those tris-adducts were achieved in a one-step synthesis and isolated by classical silica column chromatography.



^{f}C — *trans-3,trans-3,trans-3*

^{f}A — *trans-3,trans-3,trans-3*

Figure III-3 : Regioselective tris-functionalization of fullerene with a CTV tether. Only one pair of diastereoisomers is showed.

Hirsch and coworkers reported a regioselective synthesis of *e,e,e* tris-adducts with a tripodal tether that could be removed after the formation of the tris-adducts.[12,13] In a 7-steps synthesis, they obtained a tripodal benzyl tether bearings three malonates. Subsequent reaction of the tripodal malonates with C_{60} afforded the *e,e,e* tris-adducts in addition to an inseparable mixture of other tris-adducts. Deprotection of the benzyl tether was then achieved to obtain the resulting tris-adducts triol or tribromide that allowed further functionalization of the tris-adducts (Figure III-4). Furthermore, the regioselectivity could be increased by using another tripodal tether with shorter distances between the tether and the malonates moieties. This result showed the influence of the spacer between the tether and the malonates moieties on the regioselectivity. Moreover, they also modified the side chain of the malonate moieties in order to obtain tris-adducts with functionalizable side chains. In addition to being regioselective, this methodology is also stereoselective. Indeed, it provides two defined addend zones. However, the high number of steps for the preparation of the tripodal tether discouraged the use of this methodology.

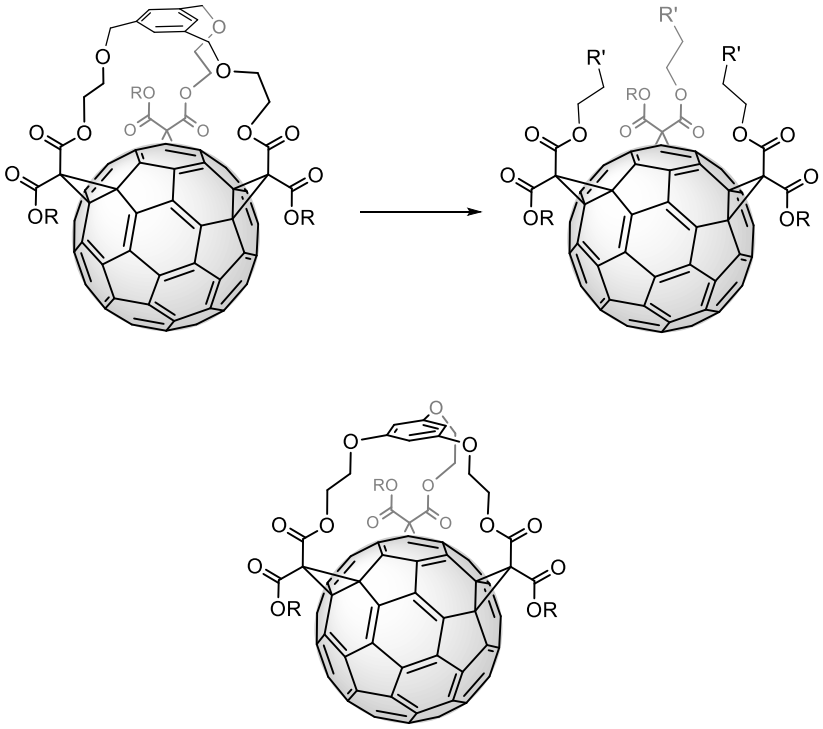


Figure III-4 : (top) Deprotectable tether allowing further functionalization. (bottom) Non-deprotectable tether which afford better regioselectivity.

Chronakis and coworkers designed the structurally new tris-malonates tether **III-3** in which two malonates are included in two crown ether type macrocycles. Reaction of **III-3** with C_{60} gave only the *e,e,trans-1* tris-adducts **III-4** in an excellent yield of 65% (Figure III-5). The assignation of the addition pattern was supported by an X-Ray crystal structures.

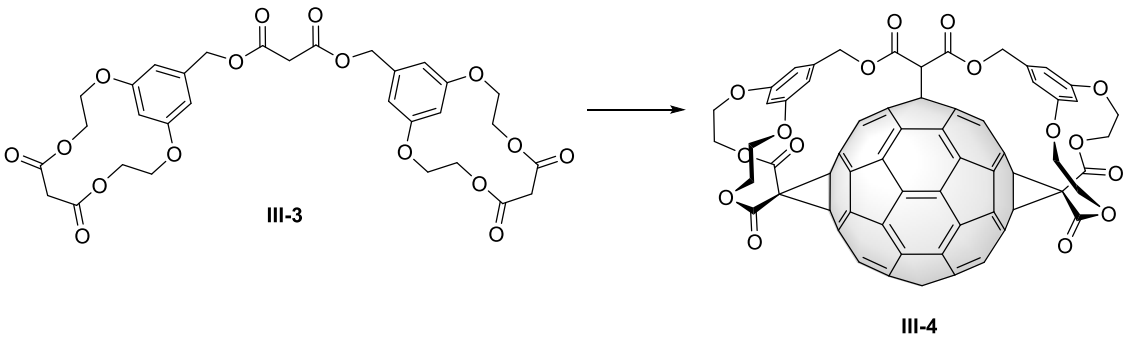


Figure III-5 : Original tether for the regioselective functionalization of C_{60}.

Rubin and Qian proposed a different approach for the regioselective formation of *e,e,trans-1* tris-adducts.[14] They designed a removable tether that led to the formation of *trans-1* bis-adducts via a double Diels-Alder reaction. This C_{60} bis-adduct served as a template. Indeed, this *trans-1* addition pattern has a high directing effects for the *equatorial* positions.[15] By masking an *equatorial* position with the tether, the functionalization of the three remaining

equatorial positions afforded a temporary penta-adducts **III-5** (Figure III-6)**.** The tris-adduct **III-6** was obtained by removal of the tether by a retro-Diels-Alder procedure.

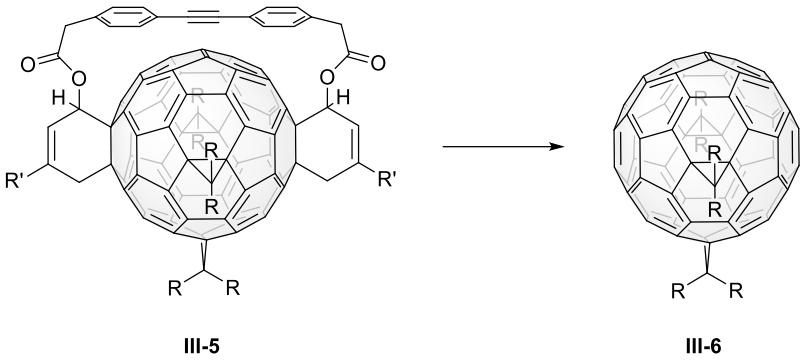


Figure III-6 : Formation of tris-adducts with a removable tether as double bonds activator.

With a similar approach, Rubin's group have synthesized regioselectively a *trans-4,trans-4,trans-4* tris-adduct.[16] First, they synthesized a cis-1 C_{60} bis-adducts with a removable tether. This intermediate had three activated double bonds in a *trans-4* positional relationships. Secondly, functionalization of these activated double bonds and subsequent removal of the tether afforded the *all-trans-4* tris-adducts (Figure III-7).

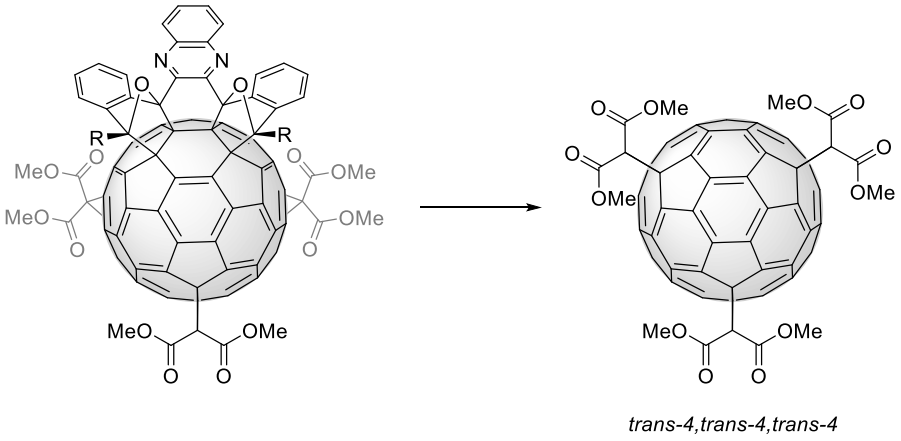


Figure III-7 : Formation of the all-trans-4 tris-adducts by temporary saturation of the cis-1 positions.

In the reported methodologies, either the starting tris-malonates precursors are rather difficult to synthesize or the bridging subunits allowing the control of the addition pattern are difficult to remove upon reaction with the fullerene, thus limiting the accessibility of fullerene tris-adducts building blocks. In this context, our group became interested in the development of a quite simple tether-directed methodology for the formation of C_{60} *e,e,e* tris-adducts. In this effect, the two important criteria were an efficient synthesis with a low number of steps for the formation of the tris-malonates tether and an easily deprotectable tether. Based on a silyl tether linked to the malonates by ethyl spacers, the *e,e,e* tris-adducts was regioselectively obtained in three steps from commercial starting materials.[17] The *e,e,e* addition pattern was

confirmed by spectroscopic data and by a X-Ray crystal structure. The silyl tether was easily removed to afford the corresponding tris-adducts triol.

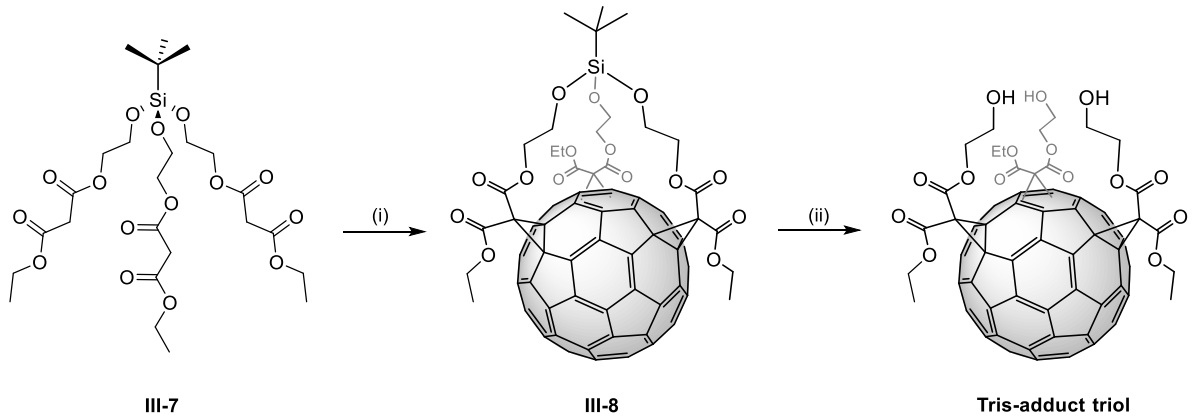


Figure III-8 : Preliminary results for the regioselective functionalization of C_{60} based on a trialkoxysilane tether.

However, the 8% yield for the threefold Bingel reaction of the tris-malonates tether with C_{60} is not satisfying and prevents a large scale synthesis. In this chapter, the preparation of *e,e,e* tris-adducts with different spacers between the silyl tether and the malonates will be presented. Our aim being to optimize the yield for the preparation of fullerene *e,e,e* tris-adducts.

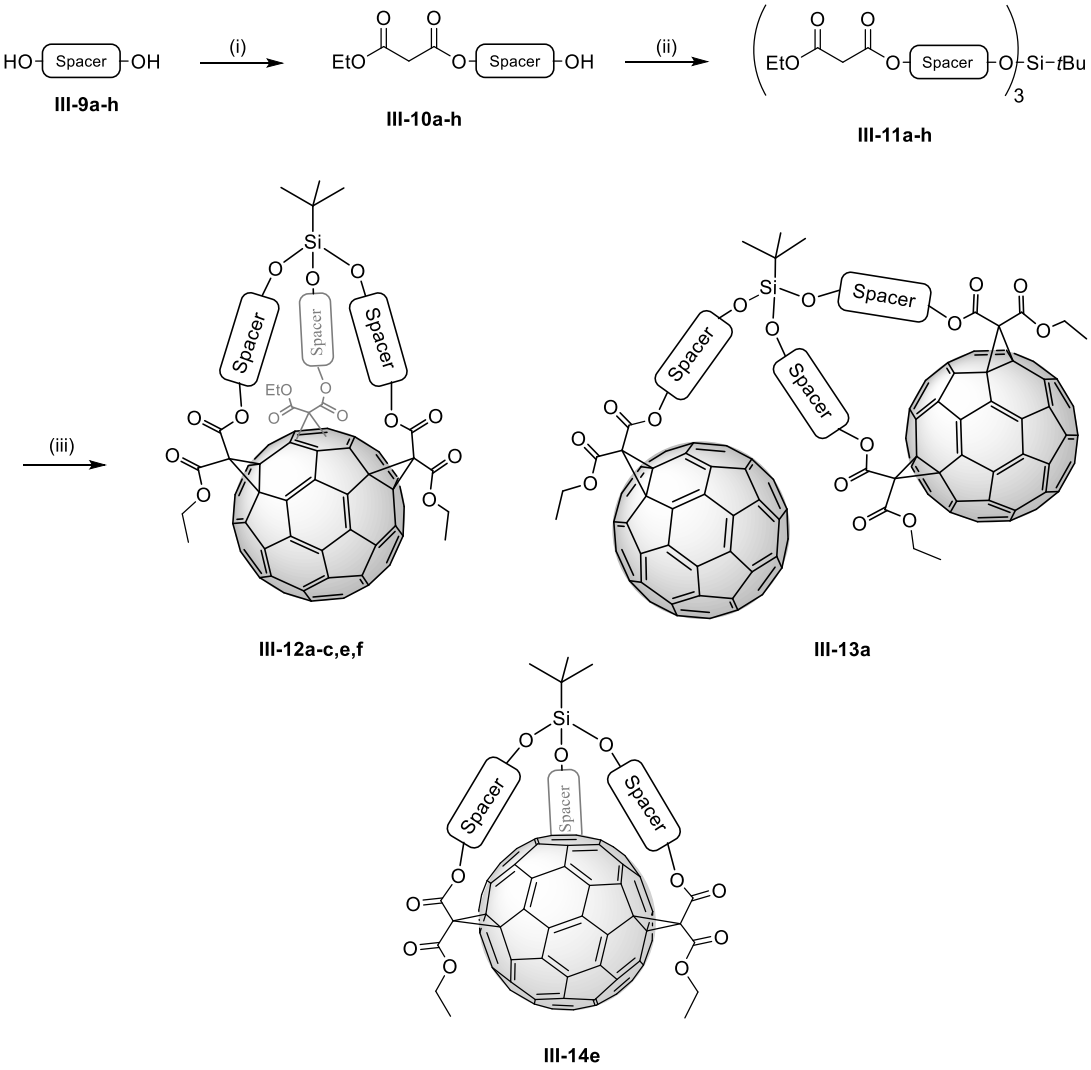
2. Regioselective syntheses of C_{60} Tris-adducts.

2.1 Syntheses.

As shown in the literature, the tether/spacer that link the malonates determine the regioselectivity. The silane tether developed in the group has shown promising results for the regioselective functionalization of C_{60}. In order to increase the yield of the formation of the C_{60} *e,e,e* tris-adducts, 8 different spacers were tested (Table III-*1*).

The preparation of the tris-malonate precursors and their subsequent reactions with C_{60} are depicted in **Scheme III-1**. Esterification of ethyl malonyl chloride with diols **III-9a-h** gave malonates **III-10a-h**. By using a large excess of diol, the formation of the corresponding bis-malonates are largely prevented and compounds **III-10a-h** were thus obtained in moderate to good yields. Treatment of **III-10a-h** with tert-butyl(trichloro)silane (*t*-BuSiCl$_3$) in dry DMF in the presence of imidazole gave the tris-malonates **III-11a-h**. Compounds **III-11a-h** were found to be only moderately stable but their purifications by column chromatography on SiO_2 were possible. Rapid decomposition was however observed upon storage even at low temperature. Compounds **III-11a-h** should be used for the next step within the next 12 h following their purifications.

The reactions of **III-11** with C_{60} were performed under the conditions developed in our laboratory for the preparation of fullerene *e,e,e* tris-adducts **III-8** from *t*-butyl(trialkoxy)silane derivative **III-7**. Specifically, DBU was added to a solution of **III-11**, C_{60} and iodine in toluene at -15°C. A key feature of these conditions is a strict control of the temperature. Indeed, fast decomposition of the *t*-butyl(trialkoxy)silane precursor was observed when the reaction was performed at a temperature higher than 0°C. Results of the threefold Bingel reactions of compound **III-11a-h** with C_{60} are shown in Table III-1. In all the cases except for **III-11e**, the fullerene tris-adduct with an *e,e,e* addition pattern was the only isolable regioisomer. The *e,e,e* addition pattern being chiral, the tris-adducts **III-12** were obtained as a racemic.



Scheme III-1. Reagents and conditions: (i) Ethyl malonyl chloride, pyridine, THF, rt, 2 h; (ii) *t*BuSiCl$_3$, imidazole, DMF, rt, 12 h; (iii) C_{60}, I_2, DBU, toluene, -15°C, 1 h.

In the case of **III-11a**, the reaction was highly regioselective and no regioisomeric tris-adduct of **III-12a** could be obtained. The by-product of the reaction, compound **III-13a** was identified by MALDI-TOF mass spectrometry as a bis-fullerene derivative resulting from the reaction of **III-11a** with two molecules of C_{60}. The formation of the bis-fullerene **III-13** resulted

from the possibility of the tris-malonate **III-11** to functionalize several molecules of C_{60} but also from a stereochemical problem attributable to the tether. In fact, after the second malonate addition, chirality is introduced by the formation of a macrocycle on the C_{60} core and thus a stereogenic center is generated on the silicium atom. Four stereoisomers are possible based on the generated chirality (Figure III-9). In the upper cases, the third malonate is directed toward the C_{60} core and the intramolecular reactions furnished racemic *e,e,e* tris-adducts. In the lower cases, the third malonate is directed toward the outside. The intramolecular reaction is no longer possible and the intermolecular reaction afforded the bis-fullerene derivatives.

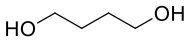
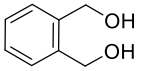
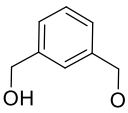
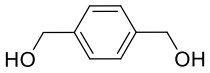
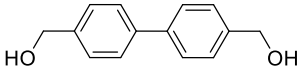
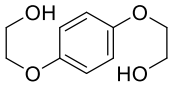
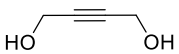
Spacer		Tris-adduit (%)
III-9a		**III-12a 26% *e,e,e*** **III-13a 11%**
III-9b		**III-12b 14% *e,e,e***
III-9c		**III-12c 23% *e,e,e***
III-9d		**Mixture**
III-9e		**III-12e 10% *e,e,e*** **III-14e 1% *all-trans-3***
III-9f		**III-12f 3% *e,e,e***
III-9g		**Mixture**
III-9h		**Degradation**

Table III-1: Results of the threefold Bingel reactions of the tris-malonates **III-11a-h** with C_{60}.

The bis-fullerenes derivatives **III-13** were also formed with the other tris-malonates derivatives **III-11b-g** but were not isolated. For **III-11d** and **III-11g**, no regioselectivity was observed and inseparable mixtures of regioisomers were obtained. In the case of **III-11h**, the silyl tether was too unstable even at -15°C and only degradation products were obtained.

The reactions using compounds with aromatic spacers (**III-11c-e**) showed that the *ortho*, *meta* and *para* orientations have an impact on the outcome of the threefold Bingel reactions with C_{60}. The ortho derivative **III-11c** furnished the better yield of C_{60} *e,e,e* tris-

adducts with a rigid spacer. The meta derivative **III-11d** showed no regioselectivity. On the other hand, the para compound **III-11e** is the only tris-malonate derivative where another regioisomer of C_{60} tris-adduct (**III-14e**) was also isolated.

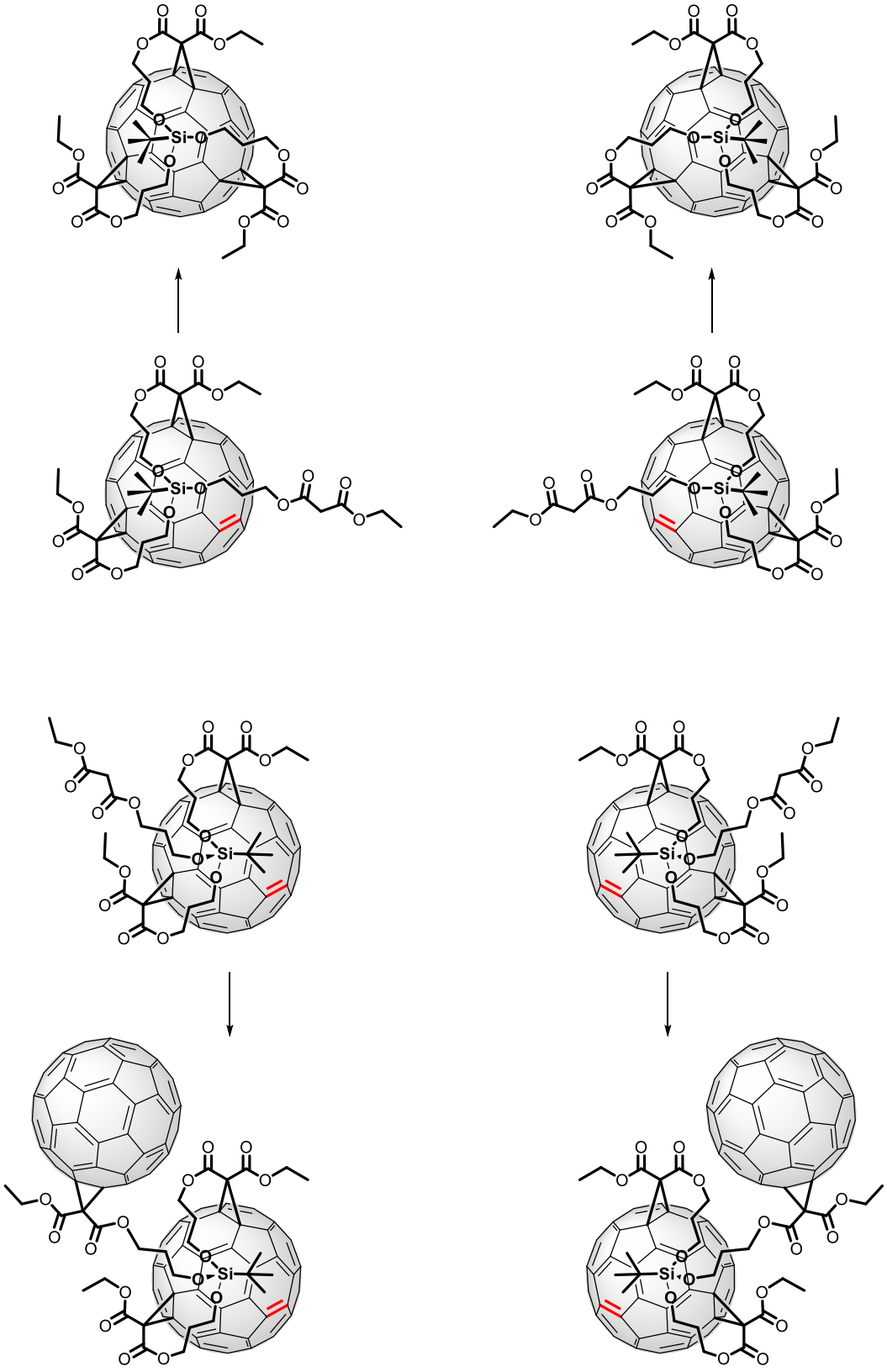


Figure III-9 : Illustration of the four possible stereoisomers of the intermediary bis-adducts and theirs resulting products.

All these experiments show that the spacer between the malonate subunits and the central t-butylsilane group plays an important role in the outcome of the reaction as it acts as a directing tether. 1,3-Propane is the most appropriate spacer. Indeed, the best yields in fullerene tris-adducts were obtained when the reaction was performed from **III-11a**.

Compounds **III-12a-c,e,f**, **III-13a** and **III-14d** have been characterized by ^{1}H and ^{13}C NMR, UV-vis and IR spectroscopies and MALDI-TOF mass spectrometry. The relative position of the three cyclopropane rings on the C_{60} core in **III-12** has been determined based on the C_3 molecular symmetry deduced from the ^{1}H and ^{13}C NMR spectra. As a typical example, the ^{13}C NMR spectrum of **III-12a** recorded in $CDCl_3$ is shown in Figure III-10. The expected fullerene resonances are clearly observed: two at δ = 70.2 and 70.9 ppm for the two different sp^3 C atoms, 17 between δ = 140 and 148 ppm for the different sp^2 C atoms. All the resonances seen in the sp^2 region show the same intensity except one signal corresponding to two C atoms having fortuitously the same chemical shift. This is in perfect agreement with the C_3 symmetry of an *e,e,e* fullerene tris-adducts. This is further supported by the 10 expected non-fullerenic signals seen for **III-12a**. The cherry-red color and the UV/vis spectrum of **III-12** (Figure III-11) are also fully consistent with those of previously prepared compound **III-8**.

For **III-13a**, no addition pattern of the bis-adduct part could be assigned based on the ^{1}H and ^{13}C NMR spectra and the UV/vis absorption spectrum.

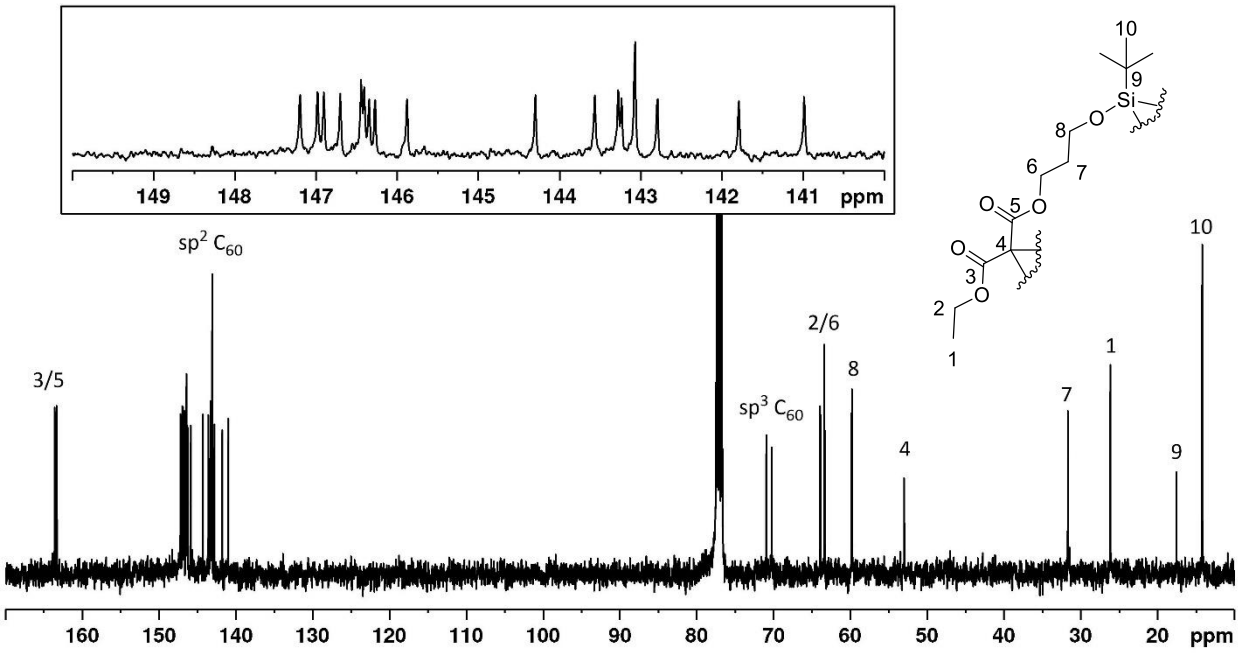


*Figure III-10 : ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **III-12** showing its threefold symmetry. Inset: detailed view showing the resonances of the fullerene sp^2 C atoms.*

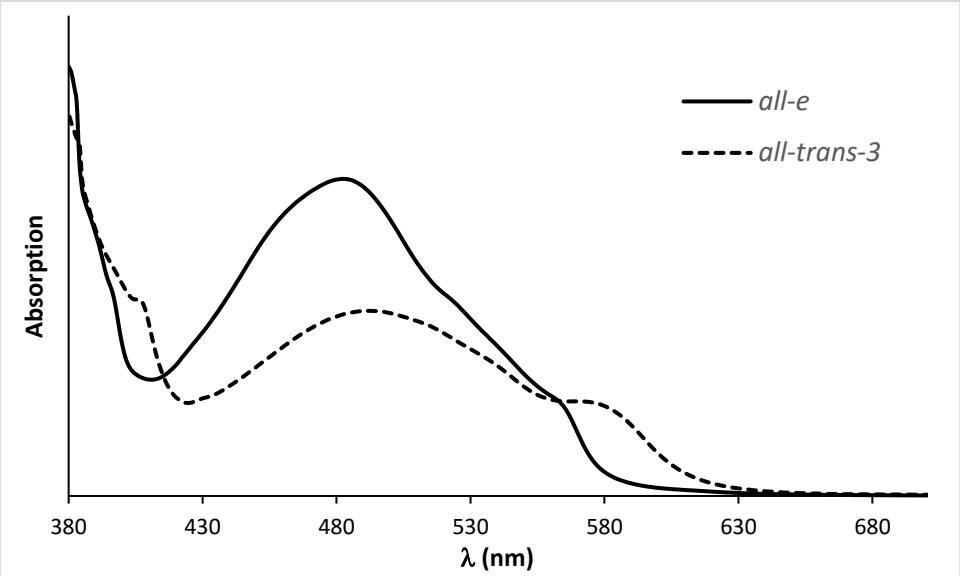
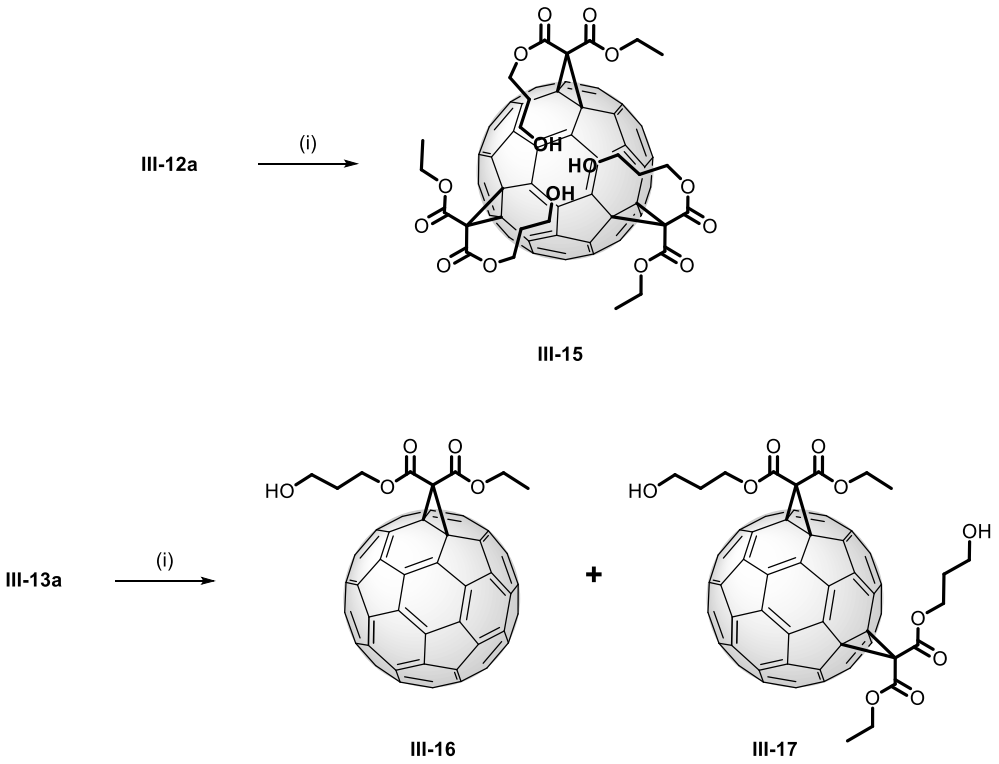


*Figure III-11 : UV/vis spectrum of **III-12** (—) characteristic of the e,e,e addition pattern and UV/vis spectrum of **III-14d** (- - -) characteristic of the all-trans-3 addition pattern .*

The *all-trans-3* tris-adduct **III-14d** is also obtained as a racemic. The *trans-3,trans-3,trans-3* addition pattern was determined based on the C_3 molecular symmetry deduced from the ^{1}H and ^{13}C NMR spectra. It's to note that the D_3 symmetry of the *all-trans-3* addition pattern is reduced by the tether and thus the *all-trans-3* tris-adducts is the only other possible C_3-symmetrical regioisomer. The UV/vis absorption spectrum, being highly dependent on the addition pattern, was also recorded (Figure III-11). Indeed the UV/vis spectrum of **III-14d** was fully consistent with those previously reported for analogous *all-trans-3* C_{60} tris-adducts.[18]

Finally, the removal of the silyl tether has been performed. Basic deprotection conditions are excluded to preserve the ester functions. Our first attempts were then with acidic conditions. The use of trifluoroacetic acid (TFA) or HBr (aq) were inefficient for the deprotection of the silyl tether. It was finally found that the treatment of the silylated fullerene derivatives with an excess of $BF_3.Et_2O$ (20 equiv) in CH_2Cl_2/CH_3CN was the most efficient route for the removal of the tether. Reaction of **III-12a** in this optimized conditions led to the triol building block **III-15** in an excellent yield of 99%. The removal of the tether in the bis-fullerene derivative **III-13a** gave two products, the mono-adduct derivative **III-16** and the bis-adduct derivative **III-17**.



Scheme III-2. Reagents and conditions: (i) $BF_3.Et_2O$, CH_2Cl_2/MeCN 2:1, rt, 12 h (**III-15**: 99%; **III-16**: 77% and **III-17**: 62%).

As for compound **III-12a**, the Bingel reactions were highly regioselective and an equatorial addition pattern was assigned for the bis-adduct **III-17**. In reason of the in/out stereoisomerism, the unambiguous assignation of the addition pattern was not possible based on the C_1 molecular symmetry deduced from the NMR spectra. The UV/vis spectrum of **III-17** was then recorded and clearly revealed the diagnostic features previously reported for analogous *equatorial* C_{60} bis-adducts.

In this work, we have shown that the spacer between the malonate subunits and the central *t*-butylsilane group plays an important role in the outcome of the reaction as it acts as a part of the directing tether. The removal of the silyl group in the *e,e,e* tris-adduct **III-12a** and its by-products **III-13a** gave access to racemic polyols derivatives **III-15** and **III-17** with *e* addition patterns. Based on the reactivity of the alcohol functions and on the *e* addition pattern, **III-15** and **III-17** are ideal building blocks for the preparation of mixed C_{60} hexa-adducts with an octahedral addition pattern.

It should be noted that this work has been done before the publication of a similar work of Hirsch and coworkers in which they used a phosphate tether.[19]

3. Synthesis of optically pure [60]fullerene *e,e,e*-tris-adducts.

3.1 Introduction.

Fullerene chemistry has quickly generated unprecedented stereochemical problems and the covalent functionalization of fullerenes has produced a plethora of chiral compounds.[20] Among them, derivatives with inherently chiral addition pattern, i.e. derivatives of an achiral parent fullerene in which the derivatization creates a chiral functionalization pattern on the fullerene scaffold irrespective of the nature of the addends, are fascinating molecules.[21] C_{60} multi-adducts with rotational symmetry are typical examples of this family of compounds. A specific nomenclature has been set to describe this type of chirality (**Chapter I-2.3.1**).[22]

The *C_3*-symmetrical addition pattern *e,e,e* is inherently chiral. As shown in Figure III-12, the achiral parent bis-adduct *e* presents two possible bonds with *e* relationship toward the two already bond addends. Functionalization of the "^{f}Re" face leads to the ^{f}A-tris-adduct *e,e,e*. In opposition, functionalization of the "^{f}Si" face leads to ^{f}C-tris-adducts *e,e,e*. There is no energetic difference between the two double bonds and thus an enantiomeric pair of the ^{f}A (50%) and ^{f}C (50%) *e,e,e* tris-adducts is obtained.

Separation of this two enantiomers requires preparative chromatography (HPLC) with a chiral stationary phase.[23] An alternative of chiral HPLC is to use chiral addends in order to generate diastereoisomeric compounds. Stepwise additions of chiral addends also required preparative HPLC but with achiral stationary phase.[24,25] However separation of the enantiomeric *e,e,e* addition pattern was achieved as diastereoisomeric *e,e,e* tris-adducts.[24,25]

Since then, a few strategies allowing the regioselective preparation of racemic fullerene tris(malonates) have been reported but only one example of tris-cyclopropanation of C_{60} has been applied in the preparation of enantiomerically pure tris-adducts of C_{60} with an *e,e,e* addition pattern.[26] In this particular case, the reaction of C_{60} with an optically pure macrocyclic tris-malonate derivative provided two separable diastereoisomers with opposite inherently chiral *e,e,e* addition patterns. The formation of the tris-adducts was diastereoselective and a diastereoisomeric excess (de value) of 55% was measured. A major drawback of this strategy is related to the particularly difficult synthesis of the cyclo-tris(malonate) precursor.

An efficient synthetic approach for the preparation of optically pure *C_3*-symmetrical tris-adducts still remains an important challenge in fullerene chemistry. In particular, an easy access to the water-soluble tris(malonic acid) derivative of C_{60} with an *e,e,e* addition pattern is highly desirable in the context of its remarkable biological activity.[27] In this context, we now show that our methodology for the regioselective formation of *e,e,e* tris-adducts of C_{60} is perfectly suited for an expeditious synthesis and separation of both ^{f}A and ^{f}C enantiomers.

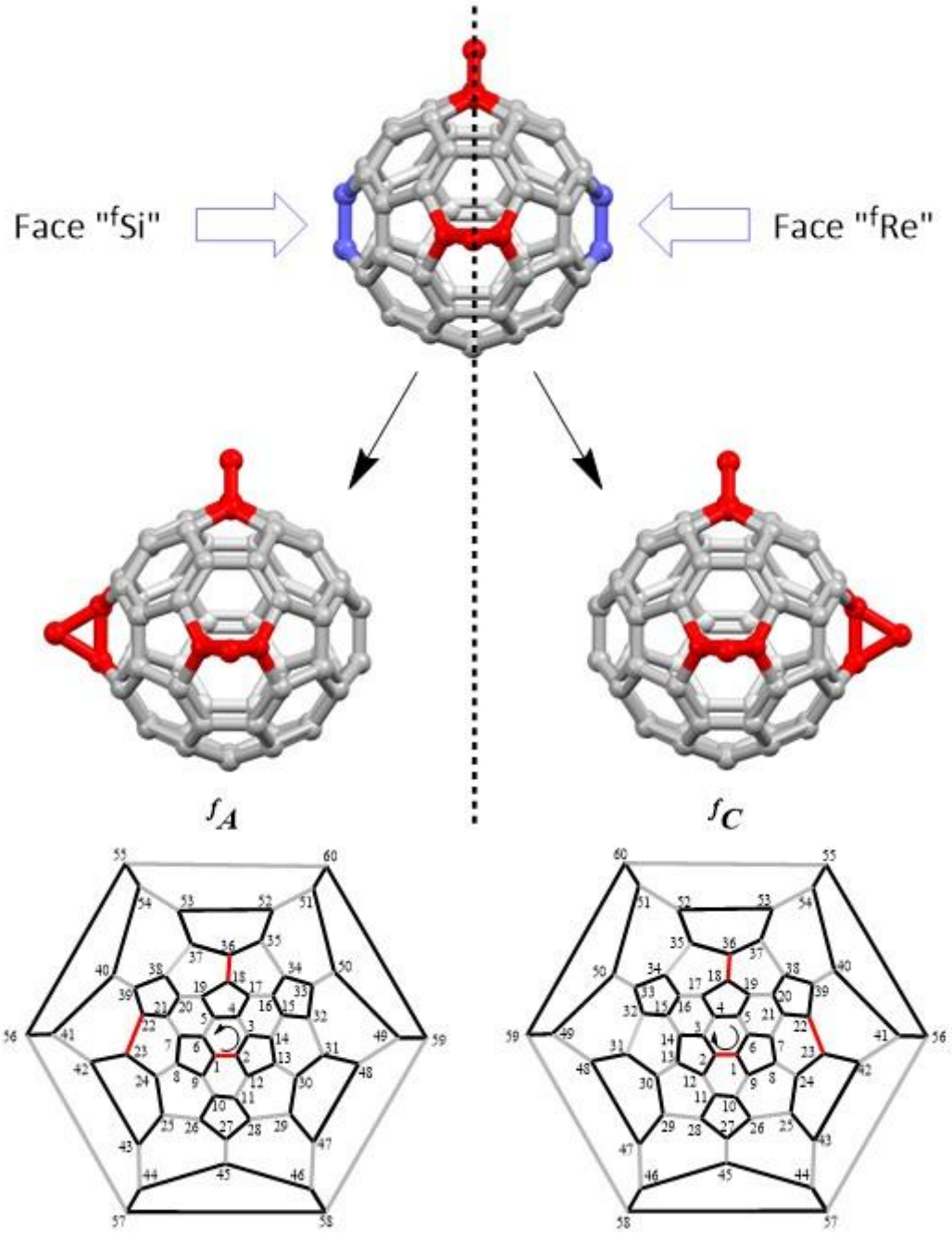
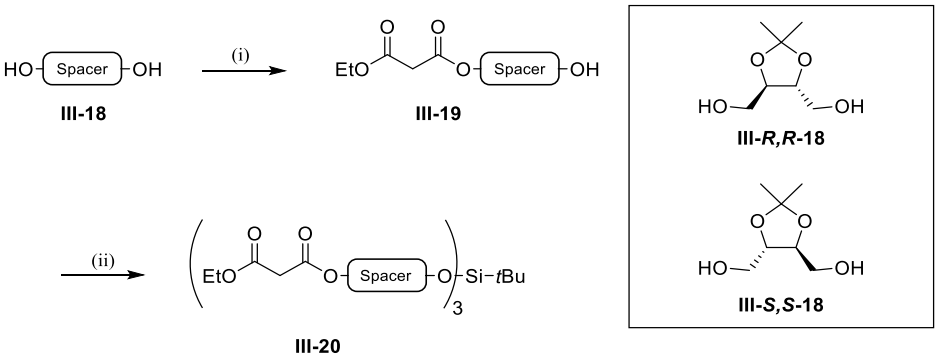


Figure III-12 : Illustration of the chirality of the e,e,e addition pattern.

3.2 Syntheses.

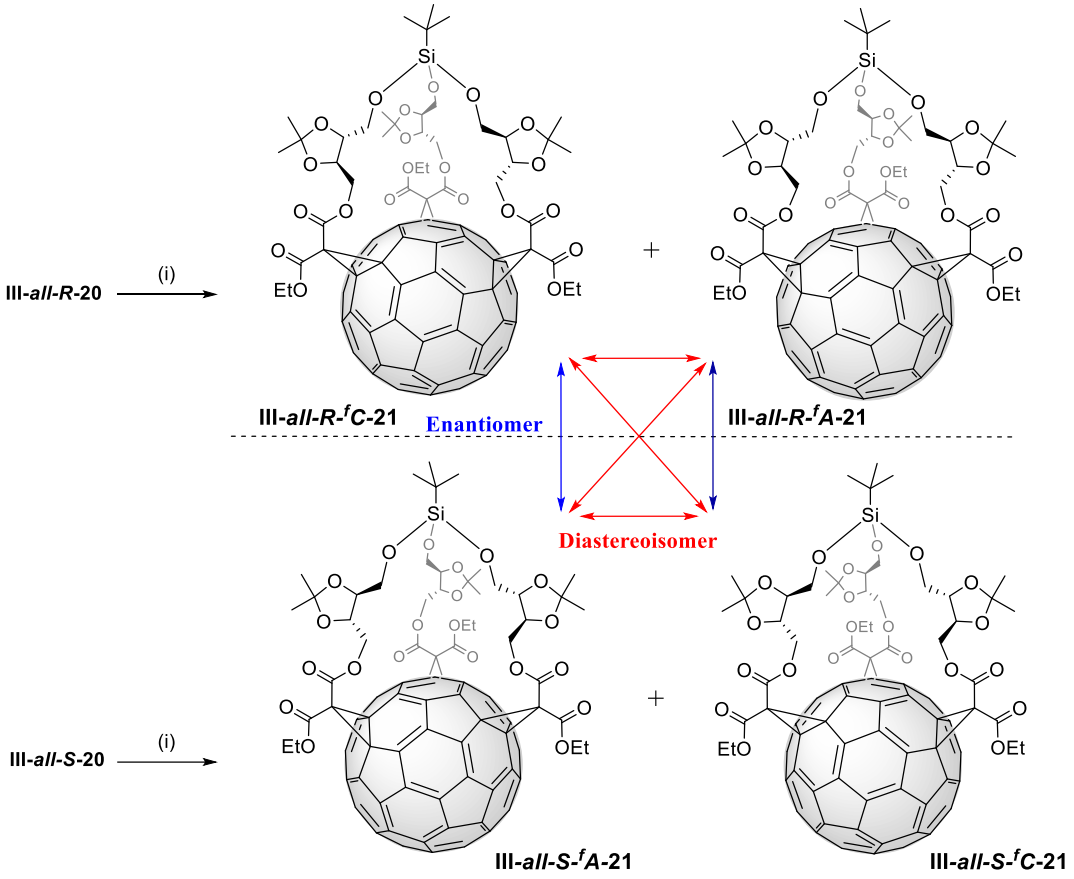
This work has been done in collaboration with Dr. Sebastiano Guerra.

The optically pure Si-tethered tris(malonate) precursors **III-*all*-*R*-20** and **III-*all*-*S*-20** were prepared from the commercially available C_2-symmetrical diols **III-*R,R*-18** and **III-*S,S*-18**, respectively (**Scheme III-3**). Mono-esterification of diols **III-*R,R*-18** and **III-*S,S*-18** with ethyl malonyl chloride followed by reaction of the resulting alcohol with *t*BuSiCl$_3$ in the presence of imidazole gave tris-malonates **III-*all*-*R*-20** and **III-*all*-*S*-20**, respectively.



Scheme III-3. Reagents and conditions: (i) Ethyl malonyl chloride, pyridine, THF, rt, 2 h; (ii) *t*BuSiCl$_3$, imidazole, DMF, rt, 12 h.

The reaction of both enantiomers of **III-20** with C_{60} was then performed under the conditions developed for preparation of fullerene *e,e,e* tris-adducts from *t*-butyl(trialkoxy)silane derivatives (**Scheme III-4**). Specifically, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added to a solution of **III-*all*-*R*-20** or **III-*all*-*S*-20**, C_{60} and iodine in toluene at -15°C. Starting from **III-*all*-*R*-20**, diastereoisomeric *e,e,e* fullerene tris-adducts **III-*all*-*R*-^{f}*C*-21** and **III-*all*-*R*-^{f}*A*-21** were obtained. Importantly, a significant difference in polarity between the two diastereoisomers allowed for an easy separation using classical silica column chromatography. The two compounds differ by the absolute configuration of the inherently chiral addition pattern on the fullerene core (^{f}*C* or ^{f}*A*, *f* = fullerene, *C* = clockwise and *A* = anticlockwise). The corresponding enantiomers, **III-*all*-*S*-^{f}*A*-21** and **III-*all*-*S*-^{f}*C*-21**, were prepared from **III-*all*-*S*-20**. The addition of the Si-tethered tris(malonate) proceeded with complete regioselectivity, giving rise to products with the *e,e,e* fullerene addition pattern exclusively. On the other hand, no significant diastereoselectivity was evidenced as the two possible diastereoisomers were thus obtained in an almost 1:1 ratio. Diastereoselectivity was not particularly expected due to the rather flexible structures of the starting *t*-butyl(trialkoxy)silane precursors. Similar observations have been also reported by Diederich and co-workers for the addition of optically pure cyclotriveratrylene-tethered tris(malonate) to C_{60} leading to almost equal amounts of the two possible diastereoisomeric *trans-3,trans-3,trans-3* tris-adducts.[10]



Scheme III-4. Reagents and conditions: (i) C_{60}, I_2, DBU, PhMe, -15°C, 1 h (**III-all-R-^{f}C-21**: 9% and **III-all-R-^{f}A-21**: 9%; **III-all-S-^{f}A-21**: 7% and **III-all-S-^{f}C-21**: 5%).

For each pair of enantiomers of **III-21**, the relative position of the three addends on the C_{60} core was determined based on the C_3-symmetry deduced from their ^{1}H- and ^{13}C-NMR spectra. Furthermore, the four compounds exhibit the classical cherry-red colour of *e,e,e* fullerene tris-adducts in solution. Hence, their UV/vis spectra present effectively the characteristic features reported for related fullerene *e,e,e* tris-adducts. A tentative assignment of the absolute configuration of the *e,e,e* addition pattern on the fullerene sphere in **III-*all-R-^{f}C*-21**, **III-*all-R-^{f}A*-21**, **III-*all-S-^{f}A*-21** and **III-*all-S-^{f}C*-21** was based on the comparison of their circular dichroism (CD) spectra with known literature data. For related *e,e,e* tris-adducts, the determination of the absolute configuration was achieved by the comparison of experimental CD spectra with calculated ones for specific optical isomers.[24] As shown in Figure III-13, the CD spectra of each pair of enantiomers (**III-*all-R-^{f}C*-21** and **III-*all-S-^{f}A*-21**; **III-*all-R-^{f}A*-21** and **III-*all-S-^{f}C*-21**) display the expected mirror-image shapes with band positions in full agreement with those reported by Hirsch and co-workers for *e,e,e* tris-adducts.[24] The pronounced Cotton effects observed for these compounds result essentially from the strong chiroptical contributions of the chirally functionalized fullerene chromophore and influence of the chiral tether are minor.[24,28–31] Indeed, the CD spectra recorded for compounds **III-*all-R-^{f}C*-21**, **III-*all-R-^{f}A*-21**, **III-*all-S-^{f}A*-21** and **III-*all-S-^{f}C*-21** were not only clear fingerprints allowing the

assignment of their absolute configurations, they also confirmed the *e,e,e* addition pattern on the fullerene sphere.

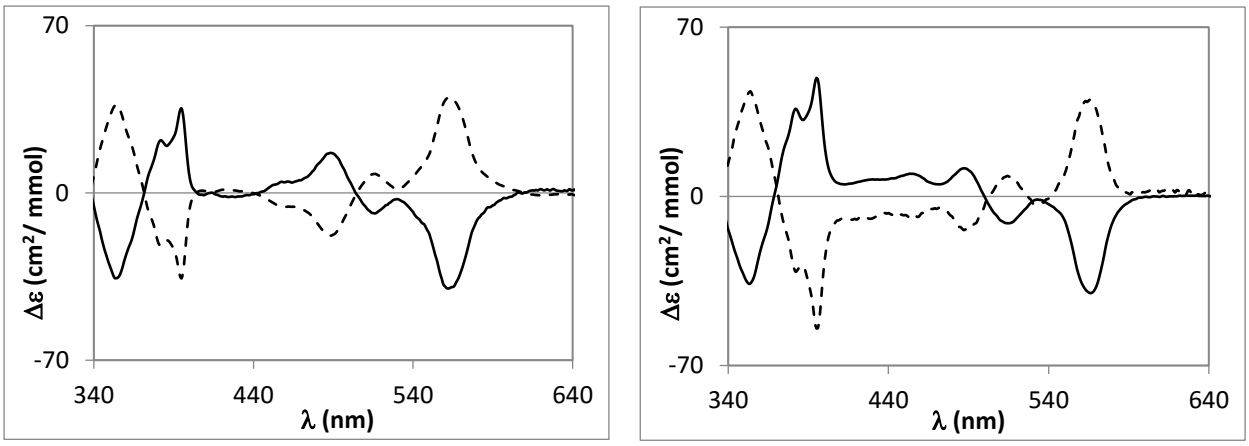


Figure III-13 : Left: CD spectra (CH_2Cl_2) of ***III-all-R-^{f}C-21*** *(—) and* ***III-all-S-^{f}A-21*** *(- - -); Right: CD spectra (CH_2Cl_2) of* ***III-all-R-^{f}A-21*** *(- - -) and* ***III-all-S-^{f}C-21*** *(—).*

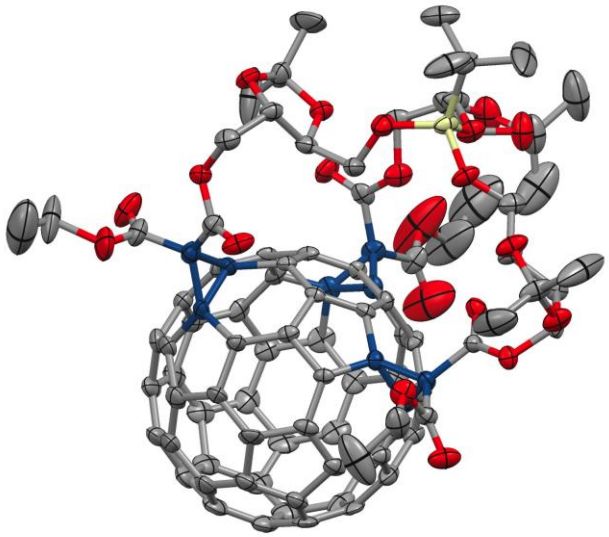
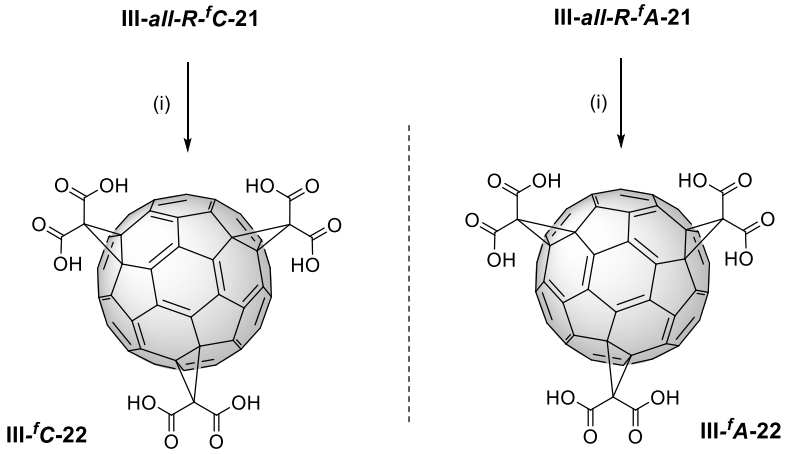


Figure III-14 : ORTEP plot of the structure of ***III-all-S-^{f}A-21***.*$(CH_2Cl_2)_3$ (thermal ellipsoids are shown at 50% probability level; for clarity, the co-crystallized solvent molecules are not shown; C: gray; O: red, Si: yellow; H: white). To highlight the chiral e,e,e-^{f}A addition pattern on the fullerene scaffold, the C atoms of the three cyclopropane rings are shown in dark blue.*

For compound **III-*all-S-^{f}A*-21**, crystals suitable for X-ray crystal structure analysis were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of **III-*all-S-^{f}A*-21** (Figure III-14). Importantly, the X-ray crystal analysis of **III-*all-S-^{f}A*-21** unambiguously confirmed the structural assignment based on the CD data, the addition pattern on the fullerene sphere being effectively *e,e,e* with an absolute ^{f}*A* configuration.

Finally, treatment of diastereoisomers **III-*all*-R-^{f}*C*-21** and **III-*all*-R-^{f}*A*-21** with NaH/MeOH/PhMe afforded the optically pure tris(malonic acid) derivatives of C_{60}, **III-^{f}*C*-22** and **III-^{f}*A*-22** (Fig. 3). The CD spectra of **III-^{f}*C*-22** and **III-^{f}*A*-22** recorded in MeOH are depicted in Figure III-15.



Scheme III-5. Reagents and conditions: (i) PhMe, MeOH, NaH, 60 °C (**III-^{f}C-22**: 77%; **III-^{f}A-22**: 87%).

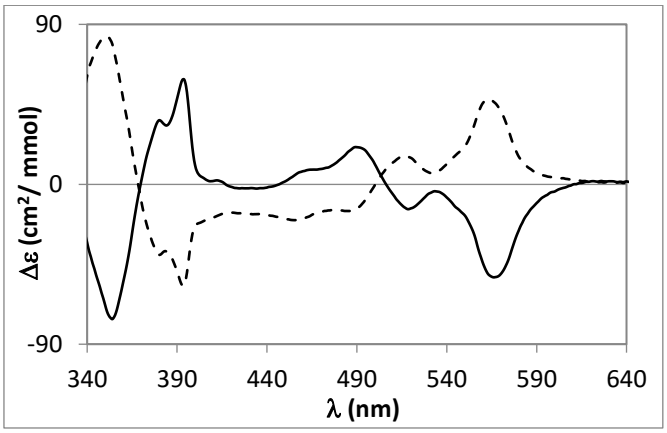


Figure III-15 : CD spectra (MeOH) of **III-^{f}C-22** *(—) and* **III-^{f}A-22** *(- - -).*

4. Conclusion.

The expeditious preparation of e,e,e tris-adducts of C_{60} has been achieved. The key step is a threefold Bingel reaction between C_{60} and t-butyl(trialkoxy)silane derivatives bearing three malonate substituents. The *t*-BuSi group connecting the three reactive malonates acts as a directing unit and the tris-addition is highly regioselective. A major advantage of using a silane-based connecting moiety is related to the easy cleavage of Si-O bonds upon the cyclisation step. The resulting polyols derivatives are valuable building blocks for further chemical transformation based on the reactivity of the alcohol functions. Furthermore, with

their e or e,e,e fullerene addition pattern, these compounds are also perfectly suited for the preparation of fullerene hexa-adducts with an octahedral addition pattern.

Our methodology was also perfectly suited for the preparation of optically pure *e,e,e* tris-adducts. The reaction of readily available optically active Si-tethered tris(malonates) with C_{60} gave easily separable diastereoisomers differing by the absolute configuration of the inherently chiral addition pattern on the fullerene core. Importantly, the absolute configuration of the inherently chiral *e,e,e* addition pattern has been unambiguously determined using X-ray crystal structure analysis for the first time. Finally, ester hydrolysis of the diastereoisomeric cyclic fullerene derivatives gave easy access to optically pure tris(malonic acid) derivatives of C_{60}.

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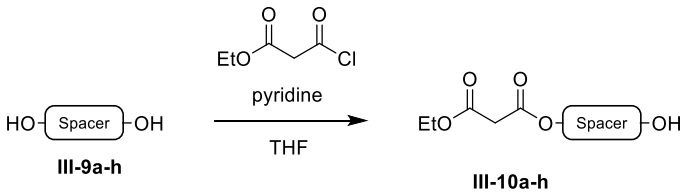
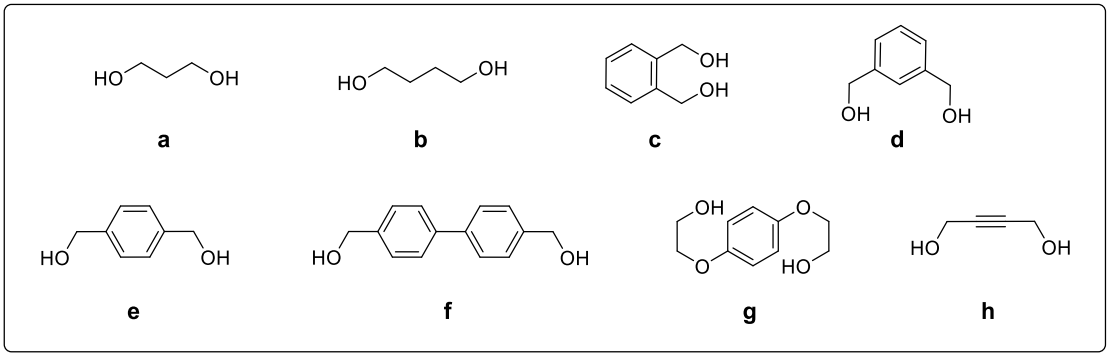
6. Experimental part.

General: Reagents and solvents were purchased as reagent grade and used without further purification. All reactions were performed in standard glassware under an inert Ar atmosphere. Evaporation and concentration were done at water aspirator pressure and drying in vacuo at 10^{-2} Torr. Column chromatography: silica gel 60 (230-400 mesh, 0.040-0.063 mm) was purchased from E. Merck. Thin Layer Chromatography (TLC) was performed on aluminum sheets coated with silica gel 60 F_{254} purchased from E. Merck. IR spectra (cm^{-1}) were recorded on a Perkin–Elmer Spectrum One Spectrophotometer. UV/Visible spectra were recorded on a Perkin-Elmer Lamda 35 UV/Vis Spectrometer. NMR spectra were recorded on a Bruker AC 300 or AC 400 with solvent peaks as reference at 25°C. MALDI-TOF-MS were obtained on a Bruker ULTRAFLEX TOF/TOF mass spectrometer with a dithranol matrix.

Synthesis.





General Procedures. Preparation of III-10a-h (GP I): A solution of ethyl malonyl chloride (1 equiv.) in anhydrous THF was added dropwise within 30 min. to a solution of appropriate diol (**III-9a-h**, 2-4 equiv.) and pyridine (2 equiv.) in anhydrous THF at 0 °C. The mixture was then stirred at room temperature overnight. The resulting mixture was filtered on SiO_2 and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2 to CH_2Cl_2/EtOAc, 97:3) gave **III-10a-h**.

Compound III-10a: III-10a was synthetized according to **GP I** from diol **III-9a** (1.1 mL, 15 mmol), ethyl malonyl chloride (1.0 mL, 7.5 mmol) and pyridine (1.1 mL, 15 mmol) in anhydrous THF (75 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2 to CH_2Cl_2/EtOAc, 97:3) yielded **III-10a** (1.07 g, 5.6 mmol, 74 %) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.36 (t, ^3J = 7 Hz, 2 H, CH_2CH_2OOC), 4.23 (q, ^3J = 7 Hz, 2 H, CH_3CH_2), 3.75 (q, ^3J = 6 Hz, 2 H, $HOCH_2CH_2$), 3.41 (s, 2 H, $OOCCH_2COO$), 1.92 (quint., ^3J = 6 Hz, 2 H, $CH_2CH_2CH_2$), 1.87 (t, ^3J = 6 Hz, 1 H, $HOCH_2$), 1.31 (t, ^3J = 7 Hz, 3 H, CH_3CH_2) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.9, 166.7, 62.7, 61.7, 59.2, 41.6, 31.5, 14.1 ppm.

Compound III-10b: III-10b was synthetized according to **GP I** from diol **III-9b** (5.4 mL, 60 mmol), ethyl malonyl chloride (1.9 mL, 15 mmol) and pyridine (2.3 mL, 30 mmol) in anhydrous THF (130 mL). Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/EtOAc, 97:3) yielded **III-10b** (2.52 g, 12.3 mmol, 82 %) as a colorless oil. IR (neat): υ = 3442 (br, OH), 1728 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.23 (q, ^3J = 7 Hz, 2 H, CH_3CH_2), 4.22 (t, ^3J = 6 Hz, 2 H, CH_2CH_2OOC), 3.70 (q, ^3J = 6 Hz, 2 H, $HOCH_2CH_2$), 3.39 (s, 2 H, $OOCCH_2COO$), 1.83-1.65 (m, 4 H, $CH_2CH_2CH_2CH_2$), 1.45 (m, 1 H, $HOCH_2$), 1.30 (t, ^3J = 7 Hz, 3 H, CH_3CH_2) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.6, 65.3, 62.3, 61.6, 41.7, 29.0, 24.9, 14.1 ppm.

Compound III-10c: III-10c was synthetized according to **GP I** from diol **III-9c** (3.0 g, 21.7 mmol), ethyl malonyl chloride (1.4 mL, 10.8 mmol) and pyridine (1.7 mL, 21.7 mmol) in anhydrous THF (100 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2 to CH_2Cl_2/EtOAc, 97:3) yielded **III-10c** (1.30 g, 5.1 mmol, 47 %) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.48-7.28 (m, 4 H, Ar*H*), 5.33 (s, 2 H, ArC*H*$_2$OOC), 4.78 (s, 2 H, ArC*H*$_2$OH), 4.20 (q, ^3J = 7 Hz, 2 H, CH_3CH_2), 3.43 (s, 2 H, OOCC*H*$_2$COO), 2.18 (br s, 1 H, *H*OCH$_2$), 1.26 (t, ^3J = 7 Hz, 3 H, C*H*$_3$CH$_2$) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.6, 166.3, 139.5, 133.1, 130.1, 129.2, 129.1, 128.2, 65.2, 62.9, 61.8, 41.6, 14.0 ppm.

Compound III-10d: III-10d was synthetized according to **GP I** from diol **III-9d** (3.0 g, 21.7 mmol), ethyl malonyl chloride (1.8 mL, 14 mmol) and pyridine (2.3 mL, 28.5 mmol) in anhydrous THF (100 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2 to CH_2Cl_2) yielded **III-10d** (1.03 g, 4.1 mmol, 28 %) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.36 (m, 4 H, Ar*H*), 5.19 (s, 2 H, ArC*H*$_2$OOC), 4.71 (s, 2 H, ArC*H*$_2$OH), 4.20 (q, ^3J = 7 Hz, 2 H, CH_3CH_2), 3.42 (s, 2 H, OOCC*H*$_2$COO), 1.64 (br s, 1H, *H*OCH$_2$), 1.25 (t, ^3J = 7 Hz, 3 H, C*H*$_3$CH$_2$) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.5, 141.8, 135.6, 128.8, 127.4, 127.0, 126.7, 67.1, 64.9, 61.7, 41.6, 14.0 ppm.

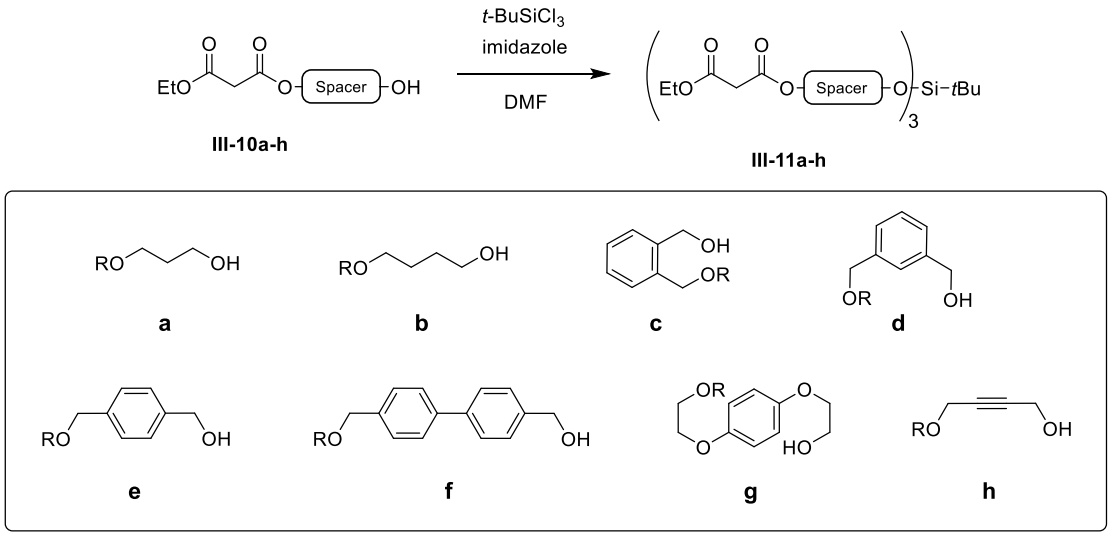
Compound III-10e: III-10e was synthetized according to **GP I** from diol **III-9e** (5.0 g, 36.2 mmol), ethyl malonyl chloride (2.3 mL, 18.1 mmol) and pyridine (2.8 mL, 34.6 mmol) in anhydrous THF (300 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2 to CH_2Cl_2) yielded **III-10e** (2.08 g, 8.2 mmol, 45 %) as a colorless oil. IR(neat): υ = 3442 (br, OH), 1727 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.38 (m, 4 H, Ar*H*), 5.20 (s, 2 H, ArC*H*$_2$OOC), 4.72 (d, ^3J = 5 Hz, 2 H, ArC*H*$_2$OH), 4.21 (q, ^3J = 7 Hz, 2H, CH_3CH_2), 3.43 (s, 2H, OOCC*H*$_2$COO), 1.76 (br s, 1H, *H*OCH$_2$), 1.27 (t, ^3J = 7 Hz, 3H, C*H*$_3$CH$_2$) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.5, 166.4, 141.2, 134.7, 128.6, 127.1, 66.9, 65.0, 61.6, 41.6, 14.0 ppm.

Compound III-10f: III-10f was synthetized according to **GP I** from diol **III-9f** (2.5 g, 11.6 mmol), ethyl malonyl chloride (0.8 mL, 5.8 mmol) and imidazole (0.79 g, 11.6 mmol) in anhydrous THF (150 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2 to CH_2Cl_2) yielded **III-10f** (0.82 g, 2.5 mmol, 43 %) as a colorless oil. IR(neat): υ = 3454 (br, OH), 1732 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.59 (2d, ^3J = 8 Hz, 2 H, Ar*H*), 7.58 (2d, ^3J = 8 Hz, 2 H, Ar*H*), 7.45 (2d, ^3J = 8 Hz, 2 H, Ar*H*), 7.44 (2d, ^3J = 8 Hz, 2 H, Ar*H*), 5.23 (s, 2 H, ArC*H*$_2$OOC), 4.75 (s, 2 H, ArC*H*$_2$OH), 4.20 (q, ^3J = 7 Hz, 2 H, CH_3CH_2), 3.44 (s, 2 H, OOCC*H*$_2$COO), 1.26 (t, ^3J = 7 Hz, 3 H, C*H*$_3$CH$_2$) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.5, 166.4, 141.0, 140.2, 140.0, 134.4, 128.9, 127.5, 127.3, 127.2, 66.9, 65.1, 61.6, 41.7, 14.1 ppm.

Compound III-10g: III-10g was synthetized according to **GP I** from diol **III-9g** (2.5 g, 12.6 mmol), ethyl malonyl chloride (.74 mL, 4.2 mmol) and imidazole (0.57 g, 8.4 mmol) in anhydrous THF (110 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2 to CH_2Cl_2) yielded **III-10g** (2.35 g, 7.5 mmol, 65 %) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.85 (s, 4 H, Ar*H*),

4.48 (t, ^3J = 5 Hz, 2 H, CH_2CH_2OOC), 4.19 (q, ^3J = 7 Hz, 2 H, $COOCH_2CH_3$), 4.14 (t, ^3J = 5 Hz, 2 H, OCH_2CH_2OOC), 4.03 (t, ^3J = 5 Hz, 2 H, CH_2CH_2OH), 3.93 (t, ^3J = 5 Hz, 2 H, CH_2CH_2OH), 3.41 (s, 2 H, $OOCCH_2COO$), 1.26 (t, ^3J = 7 Hz, 3 H, CH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.6, 166.4, 153.2, 152.9, 115.8, 115.6, 69.8, 66.4, 63.8, 61.6 (two peaks), 41.5, 14.0 ppm.

Compound III-10h: III-10h was synthetized according to **GP I** from diol **III-9h** (3.8 g, 43.9 mmol), ethyl malonyl chloride (2.9 mL, 22.6 mmol) and pyridine (3.4 mL, 43.9 mmol) in anhydrous THF (130 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2 to CH_2Cl_2) yielded **III-10h** (2.71 g, 13.5 mmol, 59 %) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.78 (t, ^4J = 2 Hz, 2 H, $COOCH_2C{\equiv}CCH_2$), 4.30 (t, ^4J = 2 Hz, 2 H, $CH_2C{\equiv}CCH_2OH$), 4.21 (q, ^3J = 7 Hz, 2 H, CH_3CH_2), 3.41 (s, 2 H, $OOCCH_2COO$), 1.81 (s, 1 H, O*H*), 1.28 (t, ^3J = 7 Hz, 3 H, CH_3CH_2) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.1, 165.9, 85.5, 79.1, 61.7, 53.2, 51.0, 41.3, 14.0 ppm.



General Procedures. Preparation of III-11a-h (GP II): A mixture of *t*$BuSiCl_3$ (1 equiv.), the appropriate alcohol (**III-10a-h**; 3.2 equiv.) and imidazole (3.5 equiv.) in anhydrous DMF was stirred at room temperature overnight. Then, water was added and the aqueous layer extracted with Et_2O. The organic layer was washed, dried ($MgSO_4$) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/EtOAc, 97:3) gave **III-11a-h**.

Compound III-11a: III-11a was synthetized according to **GP II** from **III-10a** (1.06 g, 5.6 mmol), t$BuSiCl_3$ (0.34 g, 1.8 mmol) and imidazole (0.43 g, 6.3 mmol) in anhydrous DMF (11 mL). Column chromatography on SiO2 (CH_2Cl_2 to CH_2Cl_2/EtOAc, 97:3) yielded **III-11a** (0.76 g, 1.2 mmol, 66 %) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.28 (t, ^3J = 7 Hz, 6 H, CH_2CH_2OOC), 4.20 (q, ^3J = 7 Hz, 6 H, CH_3CH_2), 3.89 (t, ^3J = 6 Hz, 6 H, $SiOCH_2CH_2$), 3.38 (s, 6 H, $OOCCH_2COO$), 1.92 (quint., ^3J = 6 Hz, 6 H, $CH_2CH_2CH_2$), 1.29 (t, ^3J = 7 Hz, 9 H, CH_3CH_2), 0.98 (s, 9 H, $SiC(CH_3)_3$)

ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.6, 166.5, 62.4, 61.5, 59.5, 41.6, 31.5, 26.3, 17.7, 14.1 ppm.

Compound III-11b: III-11b was synthetized according to **GP II** from **III-10b** (1.00 g, 4.9 mmol), *t*BuSiCl_3 (0.29 g, 1.5 mmol) and imidazole (0.36 g, 5.3 mmol) in anhydrous DMF (10 mL). Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/EtOAc, 97:3) yielded **III-11b** (0.66 g, 1.0 mmol, 63 %) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.22 (t, ^3J = 7 Hz, 6 H, CH_2CH_2OOC), 4.20 (q, ^3J = 7 Hz, 6 H, CH_3CH_2), 3.81 (t, ^3J = 6 Hz, 6 H, $SiOCH_2CH_2$), 3.39 (s, 6 H, $OOCCH_2COO$), 1.62-1.59 (m, 12 H, $CH_2CH_2CH_2CH_2$), 1.30 (t, ^3J = 7 Hz, 9 H, CH_3CH_2), 0.96 (s, 9 H, $SiC(CH_3)_3$) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.7, 166.6 (6 C, $OOCCH_2COO$), 65.3, 62.5, 61.5, 41.6, 28.8, 26.4, 25.0, 17.7, 14.1 ppm.

Compound III-11c: III-11c was synthetized according to **GP II** from **III-10c** (1.00 g, 4.0 mmol), *t*BuSiCl_3 (0.24 g, 1.2 mmol) and imidazole (0.30 g, 4.3 mmol) in anhydrous DMF (15 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2 to CH_2Cl_2) yielded **III-11c** (1.04 g, 1.2 mmol, 51 %) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.30 (m, 12 H, Ar*H*), 5.15 (s, 6 H, $ArCH_2OOC$), 4.87 (s, 6 H, $ArCH_2OSi$), 4.15 (q, ^3J = 7 Hz, 6 H, CH_3CH_2), 3.35 (s, 6 H, $OOCCH_2COO$), 1.22 (t, ^3J = 7 Hz, 9 H, CH_3CH_2), 1.02 (s, 9 H, $SiC(CH_3)_3$) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.4, 166.3, 138.6, 132.7, 129.1, 128.6, 127.6, 127.4, 64.5, 62.9, 61.6, 41.5, 26.9, 26.3, 17.9, 14.0 ppm.

Compound III-11d: III-11d was synthetized according to **GP II** from **III-10d** (1.0 g, 4 mmol), *t*BuSiCl_3 (0.17 g, 0.9 mmol) and imidazole (0.21 g, 3.1 mmol) in anhydrous DMF (15 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2 to CH_2Cl_2) yielded **III-11d** (0.47 g, 0.6 mmol, 44 %) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.28 (m, 12 H, Ar*H*), 5.14 (s, 6 H, $ArCH_2OOC$), 4.87 (s, 6 H, $ArCH_2OSi$), 4.17 (q, ^3J = 7 Hz, 6 H, CH_3CH_2), 3.38 (s, 6 H, $OOCCH_2COO$), 1.23 (t, ^3J = 7 Hz, 9 H, CH_3CH_2), 1.06 (s, 9 H, $SiC(CH_3)_3$) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.5, 165.4, 140.9, 135.4, 128.3, 127.1, 126.6, 126.3, 67.1, 64.8, 61.6, 41.6, 18.0, 14.0 ppm.

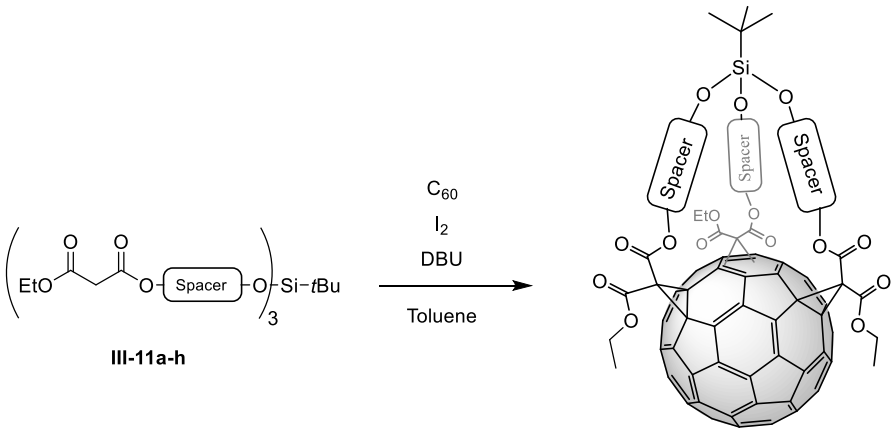
Compound III-11e: III-11e was synthetized according to **GP II** from **III-10e** (1.5 g, 5.9 mmol), *t*BuSiCl_3 (0.36 g, 1.9 mmol) and imidazole (0.44 g, 6.5 mmol) in anhydrous DMF (12 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2 to CH_2Cl_2) yielded **III-11e** (0.97 g, 1.2 mmol, 62 %) as a colorless oil. IR(neat): υ = 1730 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.33 (m, 12 H, Ar*H*), 5.20 (s, 6 H, $ArCH_2OOC$), 4.88 (s, 6 H, $ArCH_2OSi$), 4.21 (q, ^3J = 7 Hz, 6 H, CH_3CH_2), 3.44 (s, 6 H, $OOCCH_2COO$), 1.27 (t, ^3J = 7 Hz, 9 H, CH_3CH_2), 1.07 (s, 9 H, $SiC(CH_3)_3$) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.5, 166.4, 140.1, 134.2, 128.3, 126.4, 67.0, 64.8, 61.6, 41.6, 26.4, 18.0, 14.0 ppm.

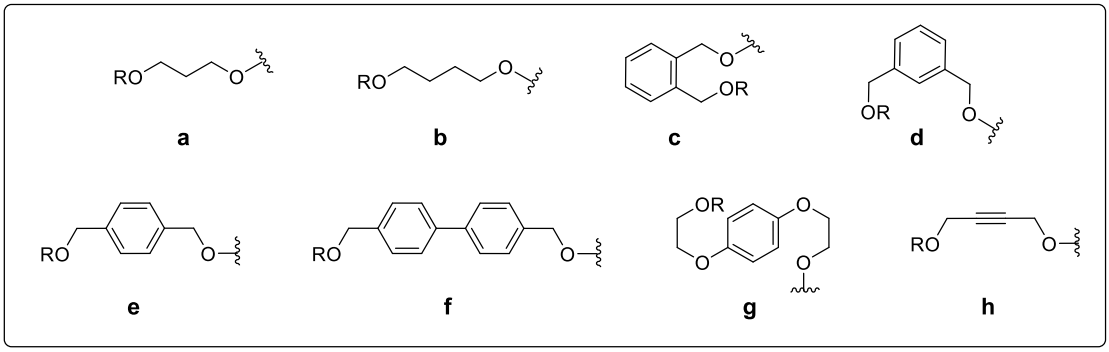
Compound III-11f: III-11f was synthetized according to **GP II** from **III-10f** (0.82 g, 2.5 mmol), *t*BuSiCl_3 (0.15 g, 0.8 mmol) and imidazole (0.19 g, 2.8 mmol) in anhydrous DMF (10 mL).

Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2 to CH_2Cl_2) yielded **III-11f** (0.48 g, 0.45 mmol, 56 %) as a colorless oil. IR(neat): υ = 1733 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.57 (d, ^3J = 8 Hz, 6 H, Ar*H*), 7.53 (d, ^3J = 8 Hz, 6 H, Ar*H*), 7.42 (d, ^3J = 8 Hz, 6 H, Ar*H*), 7.39 (d, ^3J = 8 Hz, 6 H, Ar*H*), 5.23 (s, 6 H, ArCH_2OOC), 4.95 (s, 6 H, ArCH_2OSi), 4.20 (q, ^3J = 7 Hz, 6 H, CH_3CH_2), 3.44 (s, 6 H, OOCCH_2COO), 1.26 (t, ^3J = 7 Hz, 9 H, CH_3CH_2), 1.12 (s, 9 H, SiC(CH_3)$_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.5, 166.4, 141.2, 139.9, 139.5, 134.3, 128.8, 127.2, 127.0, 126.8, 67.0, 64.9, 61.6, 41.7, 26.5, 18.1, 14.1 ppm.

Compound III-11g: III-11g was synthetized according to **GP II** from **III-10g** (1.74 g, 5.5 mmol), *t*BuSiCl_3 (0.34 g, 1.8 mmol) and imidazole (0.43 g, 6.3 mmol) in anhydrous DMF (10 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2 to CH_2Cl_2) yielded **III-11g** (0.67 g, 0.65 mmol, 37 %) as a colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ = 6.80 (s, 12 H, Ar*H*), 4.47 (t, ^3J = 5 Hz, 6 H, CH_2CH_2OOC), 4.19 (q, ^3J = 7 Hz, 6 H, $COOCH_2CH_3$), 4.15 (t, ^3J = 5 Hz, 6 H, OCH_2CH_2OOC), 4.12 (t, ^3J = 5 Hz, 2 H, CH_2CH_2OSi), 4.01 (t, ^3J = 5 Hz, 2 H, CH_2CH_2OSi), 3.42 (s, 6 H, OOCCH_2COO), 1.26 (t, ^3J = 7 Hz, 9 H, CH_2CH_3), 1.00 (s, 9 H, SiC(CH_3)$_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.6, 166.4, 153.5, 152.6, 115.7, 115.6, 69.6, 66.4, 63.8, 62.1, 61.6, 41.5, 26.2, 17.8, 14.0 ppm.

Compound III-11h: III-11h was synthetized according to **GP II** from **III-10h** (1.72 g, 8.6 mmol), *t*BuSiCl_3 (0.52 g, 2.7 mmol) and imidazole (0.64 g, 9.3 mmol) in anhydrous DMF (20 mL). Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/EtOAc, 97:3) yielded **III-11h** (0.79 g, 1.2 mmol, 43 %) as a colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 4.79 (t, ^4J = 2 Hz, 6 H, COOCH_2C≡CCH_2), 4.52 (t, ^4J = 2 Hz, 6 H, CH_2C≡CCH_2OSi), 4.20 (q, ^3J = 7 Hz, 6 H, CH_3CH_2), 3.41 (s, 6 H, OOCCH_2COO), 1.28 (t, ^3J = 7 Hz, 3 H, CH_3CH_2), 0.97 (s, 9 H, SiC(CH_3)$_3$) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.1, 165.9, 85.1, 78.6, 61.7, 53.2, 51.9, 41.2, 25.8, 17.5, 14.0 ppm.





General Procedures. Preparation of *e,e,e*-Trisadducts III-12a-h (GP III): DBU (7.5 equiv.) was added to a solution of C_{60} (1.5 equiv.), the appropriate tris-malonate **III-11a-h** (1 equiv.) and I_2 (3.5 equiv.) in toluene (2 mL / mg of C_{60}) at -15°C. The resulting mixture was stirred for 1 h at -15 °C, then filtered on SiO_2 (cyclohexane to CH_2Cl_2) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 1:1) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) or by recrystallization by slow diffusion in THF/cyclohexane if necessary gave **III-12a-c,e,f**.

Compound III-12a & III-13a: III-12a & III-13a were synthetized according to **GP III** from **III-11a** (153 mg, 0.23 mmol), C_{60} (250 mg, 0.35 mmol), I_2 (213 mg, 0.84 mmol) and DBU (0.26 mL, 1.7 mmol) in toluene (500 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 5:5) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) afforded **III-12a** (86 mg, 0.06 mmol, 26 %) as a cherry-red glassy solid and **III-13a** (53 mg, 0.03 mmol, 11%) as a brown glassy solid. **III-12a**: IR(neat): $\upsilon = 1740$ (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 230 (102500), 251 (102000), 280 (67000), 302 (sh, 54100), 381 (sh, 6100), 484 (4500), 566 (sh, 1200) nm. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.54 (m, 3 H), 4.41 (m, 6 H, CH_3CH_2), 4.22 (m, 3 H), 3.59 (t, ^3J = 6 Hz, 6 H, $SiOCH_2CH_2$), 1.93 (m, 6 H, $CH_2CH_2CH_2$), 1.38 (t, ^3J = 7 Hz, 9 H, CH_3CH_2), 0.89 (s, 9 H, $SiC(CH_3)_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.6, 163.3, 147.2, 147.0, 146.9, 146.7, 146.5, 146.4 (two peaks), 146.3, 145.9, 144.3, 143.6, 143.3, 143.2, 143.1 (two peaks), 142.8, 141.8, 141.0, 70.9, 70.2, 63.9, 63.4, 59.8, 31.7, 26.1, 17.5, 14.2 ppm. MALDI-TOF-MS: 1366.2 ($[M]^+$, calcd. for $C_{88}H_{42}O_{15}Si$: 1366.2). **III-13a**: IR(neat): $\upsilon = 1740$ (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 392

(sh, 11100), 408 (sh, 6900), 426 (5600), 481 (5300), 547 (sh, 3000), 612 (sh, 1200), 689 (300) nm. ^{1}H NMR ($CDCl_3$, 300 MHz): 4.89-4.81 (m, 1H), 4.77-4.70 (m, 1H), 4.65 (t, ^3J = 6 Hz, 2H), 4.59 (q, ^3J = 7 Hz, 2H), 4.56-4.48 (m, 4H), 4.46-4.38 (m, 1H), 4.33-4.26 (m, 1H), 4.07 (t, ^3J = 6 Hz, 2H), 3.91-3.73 (m, 4H), 2.16 (quint., ^3J = 6 Hz, 2H), 2.08-1.97 (m, 4H), 1.51 (t, ^3J = 7 Hz, 3H), 1.45 (m, 6H), 0.93 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): 163.6 (two peaks), 163.5, 163.4, 163.1, 148.6, 147.3, 147.2, 146.8, 146.6, 146.5, 146.4, 146.3, 146.1, 146.0, 145.7, 145.5, 145.3 (two peaks), 145.2 (two peaks), 145.1, 145.0, 144.9 (two peaks), 144.8, 144.7 (two peaks), 144.6 (two peaks), 144.5, 144.3, 144.1, 144.0, 143.9, 143.8, 143.7 (two peaks), 143.6 (two peaks), 143.5, 143.4, 143.3, 143.1, 143.0, 142.9, 142.5, 142.4, 142.2, 142.0, 141.9, 141.8, 141.7, 141.6, 141.5, 141.3, 141.0, 140.6, 139.8, 139.7, 139.0, 138.9, 138.6, 71.8, 71.7 (two peaks), 71.6, 70.5, 64.4, 63.6, 63.5, 63.4, 63.1, 60.0, 59.7, 58.6, 53.9, 52.3, 51.6, 32.1, 31.7, 31.5, 26.3, 17.6, 14.3, 14.2 ppm. MALDI-TOF-MS: 2087.2 ([M]$^+$, calcd for $C_{148}H_{42}O_{15}Si$: 2087.2).

Compound III-12b: III-12b was synthetized according to **GP III** from **III-11b** (159 mg, 0.23 mmol), C_{60} (250 mg, 0.35 mmol), I_2 (213 mg, 0.84 mmol) and DBU (0.26 mL, 1.7 mmol) in toluene (500 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 5:5) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) afforded **III-12b** (44 mg, 0.03 mmol, 14%) as a cherry-red glassy solid. IR(neat): $\upsilon = 1747$ (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 252 (74900), 281 (50600), 305 (sh, 38600), 380 (3900), 484 (3300), 564 (sh, 960) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.53 (m, 3 H), 4.43 (m, 6 H, CH_3CH_2), 4.09 (m, 3 H), 3.64 (m, 6 H, $SiOCH_2CH_2$), 1.73 (quint., ^3J = 7 Hz, 6 H), 1.51 (m, 6 H), 1.39 (t, ^3J = 8 Hz, 9 H, CH_3CH_2), 0.93 (s, 9 H, $SiC(CH_3)_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.4, 163.2, 146.9 (two peaks), 146.8, 146.7 (two peaks), 146.5, 146.3 (two peaks), 145.8, 144.2 (two peaks), 143.7, 143.3, 143.0, 142.6, 142.3, 142.1, 141.0, 71.0, 70.1, 66.4, 63.3, 62.2, 43.5, 30.2, 28.2, 27.0, 26.4, 25.2, 17.9, 14.2 ppm. MALDI-TOF-MS: 1408.2 ([M]$^+$, calcd. for $C_{91}H_{48}O_{15}Si$: 1408.3).

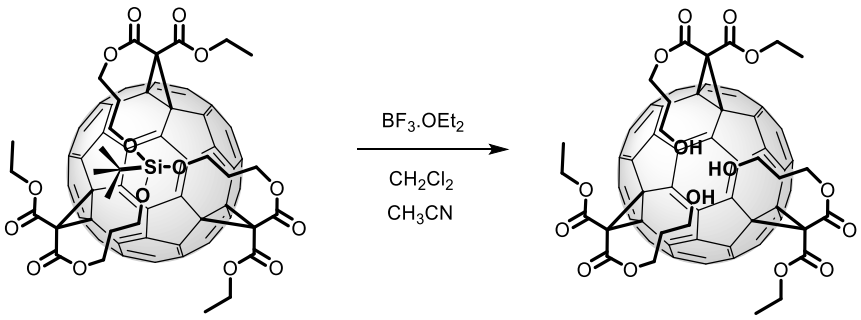
Compound III-12c: III-12c was synthetized according to **GP III** from **III-11c** (388 mg, 0.46 mmol), C_{60} (500 mg, 0.69 mmol), I_2 (408 mg, 1.6 mmol) and DBU (0.54 mL, 3.4 mmol) in toluene (1 L). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 1:1) followed by recrystallization by slow diffusion in THF/cyclohexane afforded **III-12c** (165 mg, 0.11 mmol, 23%) as a cherry-red glassy solid. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 374 (11800), 468 (5700), 557 (sh, 1600) nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34-7.22 (m, 12 H, Ar*H*), 5.42 (d, 3*J* = 11 Hz, 3 H), 5.26 (d, 3*J* = 11 Hz, 3 H), 4.78 (d, 3*J* = 11 Hz, 3 H), 4.60 (d, *J* = 11 Hz, 3 H), 4.36 (m, 6 H), 1.33 (t, ^3J = 7 Hz, 9 H, CH_3CH_2), 0.86 (s, 9 H, $SiC(CH_3)_3$) ppm.^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.3, 163.2, 147.2, 146.8, 146.5 (two peaks), 146.3, 146.2 (two peaks) ,145.7, 145.6, 144.4, 144.2, 144.1, 143.2, 142.3, 141.8, 141.0, 140.7, 139.4, 132.0 ,130.8, 130.1, 127.9, 127.8, 70.3, 69.7, 66.3, 63.2, 62.5, 52.4, 26.1, 17.6, 14.3 ppm. MALDI-TOF-MS: 1554.3 ([M+H]$^+$, calcd for $C_{103}H_{49}O_{15}Si$: 1554.3).

Compound III-12e: III-12e was synthetized according to **GP III** from **III-11e** (262 mg, 0.31 mmol), C_{60} (340 mg, 0.47 mmol), I_2 (279 mg, 1.1 mmol) and DBU (0.35 mL, 2.3 mmol) in toluene (675 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 1:1) followed by

recrystallization by slow diffusion in THF/cyclohexane afforded **III-12e** (48 mg, 0.03 mmol, 10%) as a cherry-red glassy solid. IR(neat): υ = 1746 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 230 (236200), 249 (229700), 283 (153200), 305 (sh, 120600), 383 (2700), 479 (1500), 563 (sh, 500) nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.03 (d, ^3J = 8 Hz, 6 H, Ar*H*), 6.81 (d, ^3J = 8 Hz, 6 H, Ar*H*), 5.44 (d, *J* = 13 Hz, 3 H), 5.06 (d, *J* = 13 Hz, 3 H), 4.42 (d, *J* = 12 Hz, 3 H), 4.35 (q, ^3J = 7 Hz, 6 H), 4.16 (d, *J* = 12 Hz, 3 H), 1.30 (t, ^3J = 7 Hz, 9 H, C*H*$_3$CH$_2$), 0.98 (s, 9 H, SiC(C*H*$_3$)$_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.6, 163.3, 146.9, 146.8, 146.7, 146.5 (two peaks), 146.4, 146.3, 145.8, 144.5, 144.4, 144.1, 143.3, 143.0, 142.4, 142.3, 142.2, 141.0, 140.7 (two peaks), 133.9, 128.1, 126.5, 70.8, 70.1, 68.2, 65.3, 63.4, 53.0, 26.9, 26.2, 18.1, 14.2 ppm. MALDI-TOF-MS: 1553.3 ([M]$^+$, calcd for $C_{103}H_{48}O_{15}Si$: 1553.3).

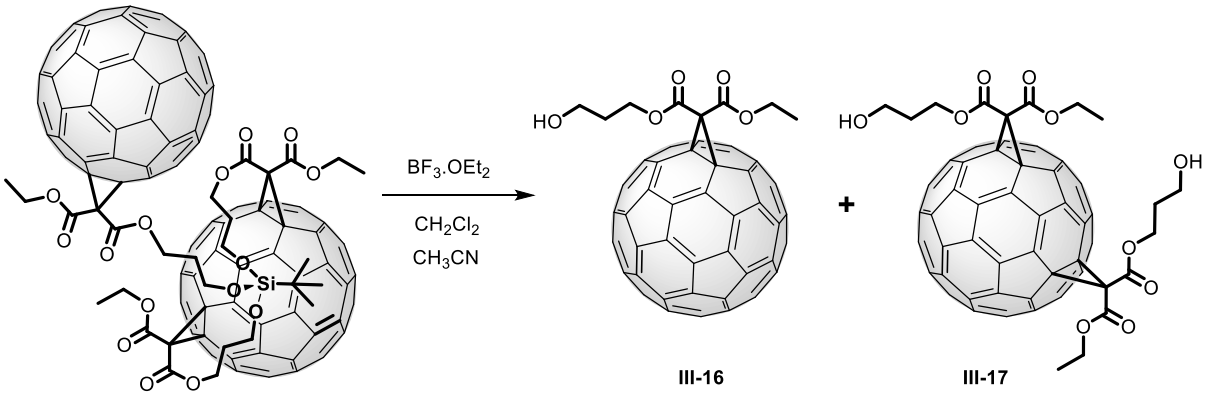
Compound III-14e (all-*trans 3*): III-14e (all-*trans 3*) was synthetized according to **GP III** from **III-11e** (1.59 g, 1.89 mmol), C_{60} (1.50 g, 2.07 mmol), I_2 (1.68 g, 6.6 mmol) and DBU (2.22 mL, 14.1 mmol) in toluene (3 L). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 1:1) afforded **III-14e (all-*trans 3*)** (30 mg, 0.02 mmol, 1%) as a purple-red glassy solid. IR(neat): υ = 1745 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 246 (42200), 302 (19300), 407 (sh, 1600), 493 (1500), 574 (sh, 760) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, ^3J = 8 Hz, 6 H, Ar*H*), 7.10 (d, ^3J = 8 Hz, 6 H, Ar*H*), 5.88 (d, *J* = 11 Hz, 3 H), 4.94 (q, ^3J = 7 Hz, 6 H), 4.91 (d, *J* = 11 Hz, 3 H), 4.40 (m, 6 H), 1.37 (t, ^3J = 7 Hz, 9 H, C*H*$_3$CH$_2$), 1.04 (s, 9 H, SiC(C*H*$_3$)$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.6, 148.3, 147.6, 147.1, 146.2, 146.0, 145.5, 145.4, 145.1, 145.0, 143..7, 143.0, 142.9, 142.7, 142.0, 141.8, 141.6, 141.2, 138.8, 133.5, 131.2, 124.7, 71.2, 70.9, 68.8, 64.6, 63.4, 53.4, 50.4, 26.4, 19.3, 14.2 ppm. MALDI-TOF-MS: 1553.3 ([M]$^+$, calcd for $C_{103}H_{48}O_{15}Si$: 1553.3).

Compound III-12f: III-12f was synthetized according to **GP III** from **III-11f** (480 mg, 0.45 mmol), C_{60} (357 mg, 0.49 mmol), I_2 (399 mg, 1.6 mmol) and DBU (0.51 mL, 3.4 mmol) in toluene (720 mL). Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 5:5) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) afforded **III-12f** (25 mg, 0.01 mmol, 3%) as a cherry-red glassy solid. IR(neat): υ = 1739 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 253 (67800), 279 (sh, 39900), 304 (sh, 22600), 483 (1900), 565 (sh, 600) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, ^3J = 8 Hz, 6 H, Ar*H*), 7.28 (d, ^3J = 8 Hz, 6 H, Ar*H*), 7.24 (d, ^3J = 8 Hz, 6 H, Ar*H*), 6.86 (d, ^3J = 8 Hz, 6 H, Ar*H*), 5.53 (d, *J* = 12 Hz, 3 H), 5.05 (d, *J* = 12 Hz, 3 H), 4.63 (d, *J* = 12 Hz, 3 H), 4.51 (d, *J* = 12 Hz, 3 H), 4.39 (m, 6 H), 1.33 (t, ^3J = 7 Hz, 9 H, C*H*$_3$CH$_2$), 1.06 (s, 9 H, SiC(C*H*$_3$)$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.1, 163.4, 148.0, 146.9, 146.7 (two peaks), 146.6, 146.5 (two peaks), 146.3, 145.9, 145.6, 145.1, 144.3, 143.5, 143.3, 141.7, 141.3, 141.1, 141.0, 140.7, 139.9, 139.6, 133.8, 128.5, 127.9, 127.7, 127.0, 70.9, 69.9, 68.9, 65.6, 63.2, 52.7, 26.9, 18.6, 14.2 ppm. MALDI-TOF-MS: 1781.5 (100%, [M]$^+$, calcd for $C_{121}H_{60}O_{15}Si$: 1781.3), 1736.5 (7%, [M-OEt]$^+$, calcd for $C_{119}H_{55}O_{14}Si$: 1736.3).



III-12a III-15

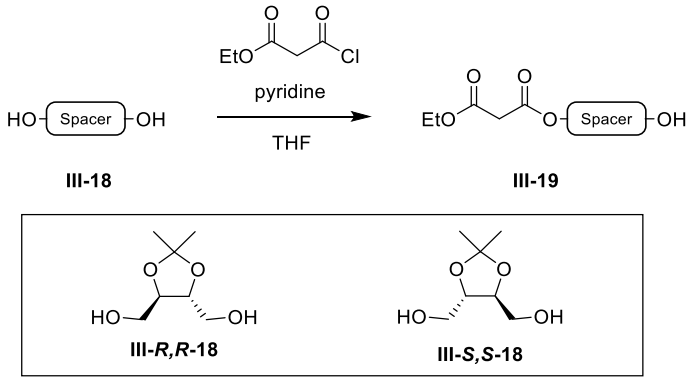
Compound III-15: $BF_3{\cdot}Et_2O$ (0.32 mL, 1.8 mmol) was added to a solution of **III-12a** (252 mg, 0.18 mmol) in CH_2Cl_2/CH_3CN (4:2 mL) at room temperature. The resulting mixture was stirred overnight at room temperature. A saturated $NaHCO_3$ aqueous solution was added and the aqueous layer extracted with CH_2Cl_2. The organic layer was washed with water, dried ($MgSO_4$) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/MeOH 96:4) afforded **III-15** (229 mg, 0.18 mmol, 99%) as a cherry-red glassy solid. IR(neat): υ = 3377 (br, OH), 1737 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 251 (115000), 282 (80000), 304 (sh, 60600), 353 (sh, 16400), 379 (sh, 7000), 485 (5100), 564 (sh, 1500) nm. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.51-4.35 (m, 12 H), 3.68 (t, ^3J = 6 Hz, 6 H, CH_2CH_2OH), 2.23 (br s, 3 H, $HOCH_2$), 1.94 (quint., ^3J = 6 Hz, 6 H, $CH_2CH_2CH_2$),1.38 (t, ^3J = 7 Hz, 9 H, CH_3CH_2) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 163.6, 163.4, 147.1, 146.9, 146.7, 146.6, 146.5, 146.4, 146.3, 145.8, 145.7, 144.8, 144.6, 144.3, 143.4, 142.7, 142.6, 141.9, 141.8, 141.0, 70.8, 70.1, 64.0, 63.3, 59.0, 31.3, 14.2 ppm. MALDI-TOF-MS: 1284.1 ($[M]^+$, calcd for $C_{84}H_{36}O_{15}$: 1284.2).



III-13a III-16 III-17

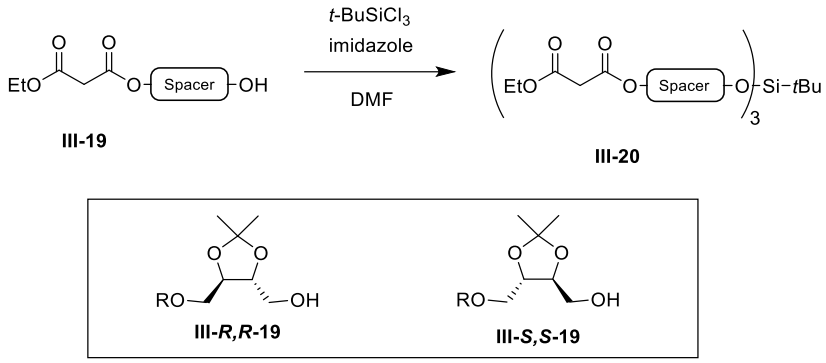
Compound III-16 & III-17: $BF_3{\cdot}Et_2O$ (0.32 mL, 2.60 mmol) was added to a solution of **III-13a** (274 mg, 0.13 mmol) in CH_2Cl_2/CH_3CN (4:2 mL). The resulting mixture was stirred overnight at room temperature. A saturated $NaHCO_3$ aqueous solution was added and the aqueous layer extracted with CH_2Cl_2. The organic layer was washed with water, dried ($MgSO_4$) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/MeOH 96 : 4) yielded **III-16** (90 mg, 0.10 mmol, 77%) as a brown glassy solid and **III-17** (86 mg, 0.08 mmol, 62%) as red-brown

glassy solid. **III-16:** IR(neat): $\upsilon = 3370$ (OH), 1743 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 257 (106000), 326 (33600), 394 (sh, 4000), 400 (sh, 2900), 414 (sh, 2100), 426 (2200), 488 (1300), 551 (sh, 860), 605 (sh, 470), 688 (180) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.59 (t, ^3J = 6 Hz, 2 H, COOC*H*$_2$CH$_2$), 4.50 (q, ^3J = 7 Hz, 2 H, COOC*H*$_2$CH$_3$), 3.79 (t, ^3J = 6 Hz, 2 H, CH$_2$C*H*$_2$OH), 2.04 (quint., ^3J = 6 Hz, 2 H, CH$_2$C*H*$_2$CH$_2$), 1.42 (t, ^3J = 7 Hz, 3 H,CH$_2$C*H*$_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.9, 163.6, 145.3 (two peaks), 145.2 (two peaks), 145.1, 144.9, 144.7, 144.6, 143.9, 143.6, 143.1, 143.0 (three peaks), 142.2, 141.9, 141.0 (two peaks), 139.1, 138.9, 71.6, 64.3, 63.6, 63.4, 59.1, 52.2, 34.2, 31.6, 30.3, 29.7, 29.5, 14.3, 14.2 ppm. MALDI-TOF-MS: 908.0 ($[M]^+$, calcd for $C_{68}H_{12}O_5$: 908.1). **III-17:** IR(neat): $\upsilon = 3450$ (br, OH), 1740 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 306 (sh, 21900), 331 (sh, 7400), 397 (sh, 2400), 409 (sh, 1600), 421 (1400), 478 (sh, 1600) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.61-4.48 (m, 8 H), 3.80 (m, 4 H), 2.04 (m, 4 H), 1.94 (br s, 2 H, O*H*), 1.46 (t, ^3J = 7 Hz, 3 H, CH$_2$C*H*$_3$), 1.45 (t, ^3J = 7 Hz, 3 H, CH$_2$C*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.9, 163.7, 163.6, 163.5, 147.7, 147.5, 147.3 (two peaks), 146.5 (two peaks), 146.2, 146.1, 146.0 (two peaks), 145.6 (two peaks), 145.4 (two peaks), 145.2 (two peaks), 145.1, 144.8 (two peaks), 144.7 (two peaks), 144.6 (two peaks), 144.4 (two peaks), 144.3 (two peaks), 144.2 (two peaks), 144.1 (two peaks), 143.8 (two peaks), 143.7 (two peaks), 143.5 (two peaks), 143.2, 143.0 (four peaks), 142.6, 142.2, 142.0, 141.9, 141.8, 141.6 (two peaks), 141.5, 138.9 (two peaks), 138.7 (two peaks), 71.6, 70.3, 64.2 (two peaks), 63.5, 63.4, 59.1, 53.5 (two peaks), 51.3, 31.5 (two peaks), 14.2 ppm. MALDI-TOF-MS: 1096.1 ($[M]^+$, calcd for $C_{76}H_{24}O_{10}$: 1096.1).



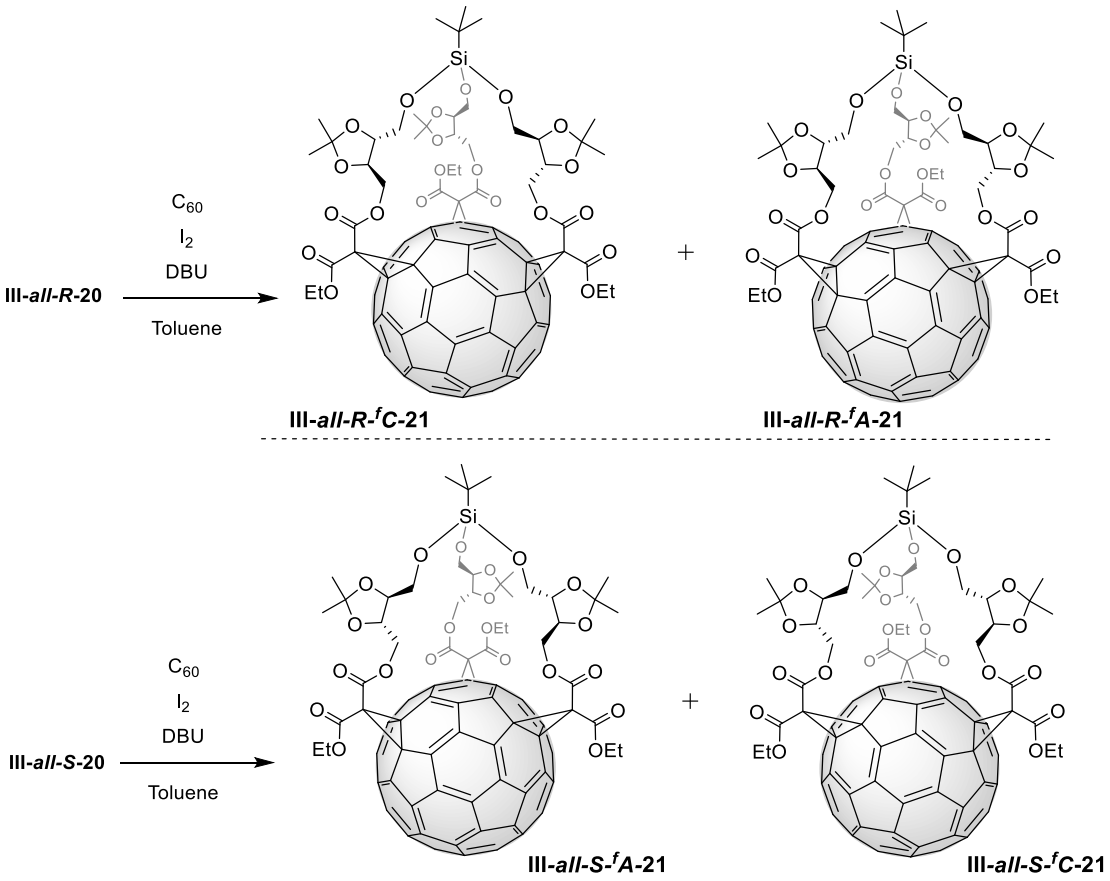
Compound III-*S,S*-19: A solution of ethyl malonyle chloride (0.80 mL, 6.25 mmol) in anhydrous THF (60 mL) was added dropwise over 1 h to a stirred solution of (*4S,5S*)-2,2-dimethyl-1,3-dioxolane-4,5-dimethanol (**III-*S,S*-18**) (2.03 g, 12.50 mmol) and pyridine (0.95 mL, 11.75 mmol) in anhydrous THF (20 mL) at 0°C. The mixture was then stirred at room temperature overnight. The resulting mixture was filtered to remove the salts and concentrated. Column chromatography (SiO_2, CH_2Cl_2) gave **III-*S,S*-19** (1.21 g, 70%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): 4.40-4.15 (m, 5H), 3.98 (m, 1H), 3.86 (m, 1H), 3.67 (m, 1H), 3.45 (s, 2H), 1.93 (m, 1H), 1.45 (s, 3H), 1.44 (s, 3H), 1.31 (t, *J* = 7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): 166.35, 166.3, 109.9, 78.3, 74.8, 64.9, 61.8, 61.7, 41.4, 27.0, 26.9, 14.0.

Compound III-*R,R*-19: As described for **III-*S,S*-19** starting from (4R,5R)-2,2-dimethyl-1,3-dioxolane-4,5-dimethanol (**III-*R,R*-18**) (2.00 g, 12.33 mmol), pyridine (1.00 mL, 12.33 mmol) and ethyl malonyle chloride (0.79 mL, 6.17 mmol). Column chromatography (SiO2, CH2Cl2) gave **III-*R,R*-19** (1.31 g, 77%) as a colorless oil. ^{1}H and ^{13}C-NMR data are rigorously identical to those described for the corresponding enantiomer **III-*S,S*-19**.



Compound III-*all*-*S*-20: A mixture of **III-*S,S*-19** (1.14 g, 4.10 mmol), imidazole (262 mg, 3.85 mmol) and *t*BuSiCl$_3$ (248 mg, 1.30 mmol) in anhydrous DMF (10 mL) was stirred at 0°C for 1 h. The mixture was then allowed to warm slowly to room temperature and stirred for 12 h at this temperature, then H_2O (50 mL) was added. The aqueous layer was extracted with Et_2O (3 x). The combined organic layers were washed with water, dried over $MgSO_4$, filtered and concentrated. Column chromatography (SiO_2, CH_2Cl_2) gave **III-*all*-*S*-20** (460 mg, 39%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): 4.49-4.42 (m, 3H), 4.27-4.15 (m, 12H), 4.05-3.92 (m, 9H), 3.45 (s, 6H), 1.43 (s, 18H), 1.30 (t, *J* = 7 Hz, 9H), 1.00 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): 166.4, 166.2, 109.9, 65.2, 63.3, 61.6, 41.3, 27.1, 26.9, 26.2, 17.8, 14.0.

Compound III-*all*-*R*-20: As described for **III-*all*-*S*-20** starting from **III-*R,R*-19** (1.00 g, 3.62 mmol), imidazole (269 mg, 3.96 mmol) and *t*BuSiCl$_3$ (217 mg, 1.13 mmol). Column chromatography (SiO_2, CH_2Cl_2) gave **III-*all*-*R*-20** (538 mg, 52 %) as a colorless oil. ^{1}H and ^{13}C NMR data rigorously identical to those described for the corresponding enantiomer **III-*all*-*S*-20**.

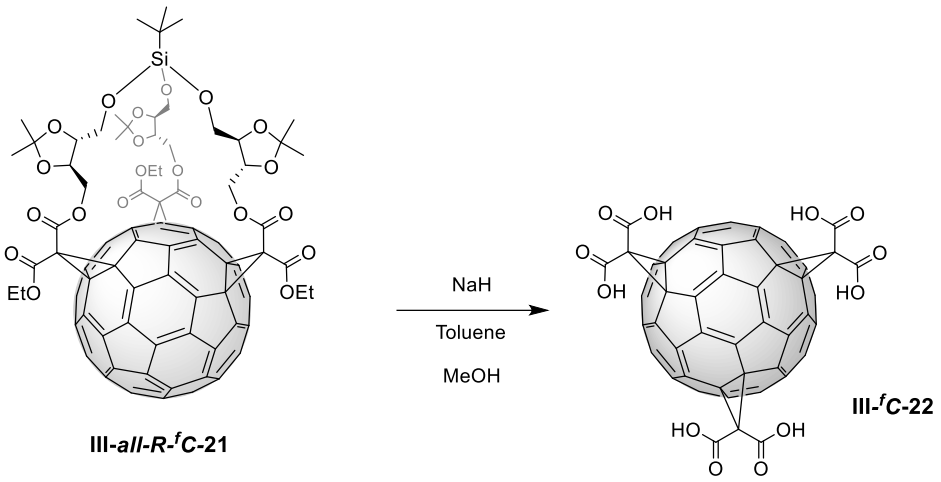


Compound III-*all-S-^{f}A*-21 & III-*all-S-^{f}C*-21: DBU (0.56 mL, 3.75 mmol) was added to a stirred solution of C_{60} (536 mg, 0.75 mmol), **III-*all-S*-20** (460 mg, 0.50 mmol) and I_2 (444 mg, 1.75 mmol) in toluene (1.2 L) at -15 °C. After 1 h, the mixture was filtered through a short plug of SiO_2, eluting first with toluene (to remove unreacted C_{60}), then with CH_2Cl_2. Gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) followed by column chromatography (SiO_2, cyclohexane/EtOAc 80:20) gave **III-*all-S-^{f}A*-21** (59.4 mg, 7%) and **III-*all-S-^{f}C*-21** (41.4 mg, 5%). **III-*all-S-^{f}A*-21**: Red solid. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.00 (s, 9H), 1.41 (t, *J* = 7 Hz, 9H), 1.415 (br s, 9H), 1.49 (br s, 9H), 3.69 (d, *J* = 5 Hz, 6H), 3.92 (td, *J* = 8 Hz and 5 Hz, 3H), 4.09 (br d, *J* = 8 Hz, 3H), 4.35-4.51 (m, 9H), 4.57 (dd, *J* = 13 Hz and 2 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 14.1, 18.0, 26.5, 26.7, 27.2, 52.8, 62.2, 63.4, 63.8, 70.1, 70.8, 75.5, 75.7, 109.7, 141.7, 141.7, 142.0, 142.6, 143.0, 143.3, 143.5, 144.1, 144.2, 145.8, 146.2, 146.25, 146.3, 146.4, 146.8, 146.9, 146.9, 147.0, 162.6, 162.7. IR (neat): 1750 (C=O). MALDI-TOF-MS: 1647.31 ([M+Na]$^+$, calcd for $C_{100}H_{60}O_{21}SiNa$: 1647.33), 1624.33 ([M]$^+$, calcd for $C_{100}H_{60}O_{21}Si$: 1624.34).**III-*all-S-^{f}C*-21:** Red solid. IR (neat): 1749 (C=O). ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.05 (s, 9H), 1.40 (t, *J* = 7 Hz, 9H), 1.42 (s, 18H), 3.69 (dd, *J* = 11 Hz and 2 Hz, 3H), 3.81-3.90 (m, 6H), 4.30-4.50 (m, 15H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 14.0, 18.4, 26.8, 26.9, 27.3, 52.8, 62.5, 63.3, 68.2, 70.0, 70.7, 75.3, 78.1, 110.1, 141.0, 141.8, 142.2, 142.8, 143.3 (2C), 143.4, 143.7, 144.3, 145.7, 146.3, 146.4 (2C), 146.5, 146.7, 146.85 (2C), 146.9, 163.0, 163.6. MALDI-TOF-MS: 1647.3 ([M+Na]$^+$, calcd for $C_{100}H_{60}O_{21}SiNa$: 1647.33), 1624.3 ([M]$^+$, calcd for $C_{100}H_{60}O_{21}Si$: 1624.34).

Compound III-*all-R-^{f}A*-21 & III-*all-R-^{f}C*-21: As described for **III-*all-S-^{f}A*-21** and **III-*all-S-^{f}C*-21** starting from C_{60} (468 mg, 0.65 mmol), **III-*all-R*-20** (538 mg, 0.59 mmol) and I_2 (524 mg, 2.07 mmol). Gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) followed by column chromatography (SiO_2, cyclohexane/EtOAc 80:20) gave **III-*all-R-^{f}C*-21** (80.1 mg, 9%) and **III-*all-R-^{f}A*-21** (81.6 mg, 9%).

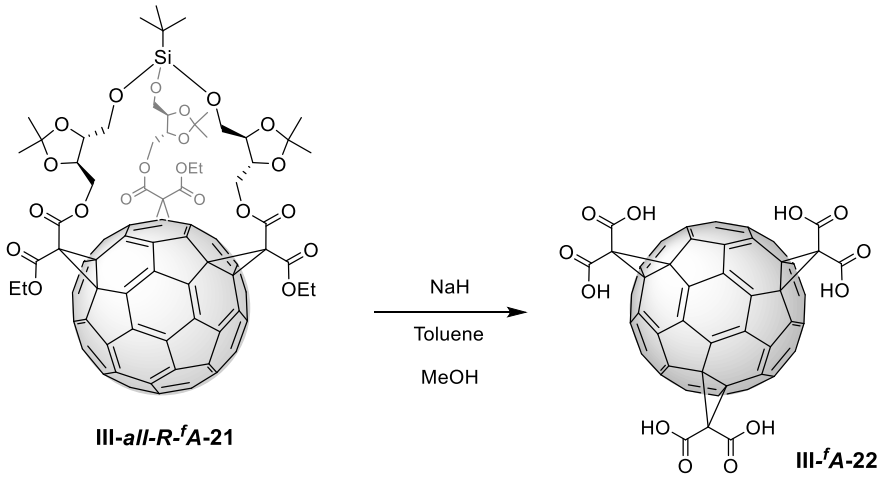
Data for **III-*all-R-^{f}C*-21**. Red solid. ^{1}H and ^{13}C NMR, IR, MS and UV/vis data rigorously identical to those described for the corresponding enantiomer **III-*all-S-^{f}A*-21**.

Data for **III-*all-R-^{f}A*-21**. Red solid. ^{1}H and ^{13}C NMR, IR, MS and UV/vis data rigorously identical to those described for the corresponding enantiomer **III-*all-S-^{f}C*-21**.



III-*all-R-^{f}C*-21 **III-^{f}C-22**

Compound III-^{f}C-22: A solution of **III-*all-R-^{f}C*-21** (70.3 mg, 0.04 mmol) and NaH (60% dispersion in mineral oil, 19.2 mg, 0.80 mmol) in toluene (10 mL) was stirred at 60°C for 3 h. Then, MeOH (1 mL) was added. After 1 h, the resulting precipitate was collected by centrifugation, washed with toluene, an aqueous 2M H_2SO_4 solution and water. Finally, drying *in vacuo* at 60°C overnight gave **III-^{f}C-22** (31.5 mg, 77 %) as a red solid. The analytical data of **III-^{f}C-22** were in complete agreement with literature data.[32]



III-*all-R-^{f}A*-21 **III-^{f}A-22**

Compound III-^{f}*A*-22: A solution of **III-*all*-*R*-^{f}*A*-21** (75.3 mg, 0.046 mmol) and NaH (60% dispersion in mineral oil, 22.2 mg, 0.93 mmol) in toluene (10 mL) was stirred at 60°C for 3 h. Then, MeOH (1 mL) was added. After 1 h, the resulting precipitate was collected by centrifugation, washed with toluene, an aqueous 2M H_2SO_4 solution and water. Finally, drying *in vacuo* at 60°C overnight gave **III-^{f}*A*-22** (39.3 mg, 87%) as a red solid. The analytical data of **III-^{f}*A*-22** were in complete agreement with literature data.[32]

Chapter IV : Syntheses of multi-functionalized hexa-adducts by sequential “click” reactions.

1. Introduction.

The geometry of T_h-symmetrical C_{60} hexa-adducts with an octahedral addition pattern is unique in organic chemistry (Figure IV-1). Each addend has four *e* neighbors and a fifth addend in a *trans-1* relationship. This addition pattern can also be compared to an octahedral motif.

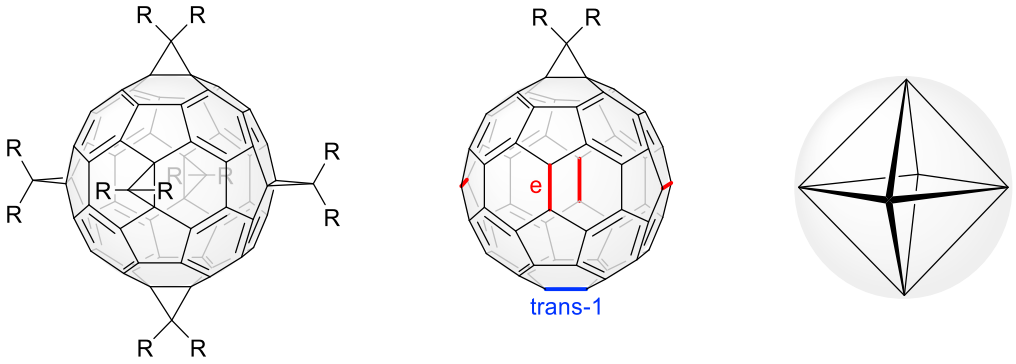


Figure IV-1 : Representation of the T_h-symmetrical hexa-adducts of C_{60}.

Hexa-adducts [6:0] and [1:5] are the easiest to prepare (Figure IV-2). The number in the bracket correspond to the different addends bond on C_{60} (e.g. [1:5] means that five malonates are identical and one malonate is different). Hexa-adducts [6:0] are directly prepared from C_{60} and hexa-adducts [1:5] from easily available C_{60} mono-adducts. In contrast, the preparation of more elaborated mixed hexa-adducts with different ratios of addends is more difficult. The preparation of fullerene bis- or tris-adduct precursors with a controlled regiochemistry is the key to have access to hexa-adducts with different ratio (e.g. [2:4] and [3:3])(Figure IV-2). Type I mixed hexa-adducts are obtained from lower multi-adducts with only *e* relationships. Type II mixed hexa-adducts are obtained from lower multi-adducts with *trans-1* and *e* relationships.[1]

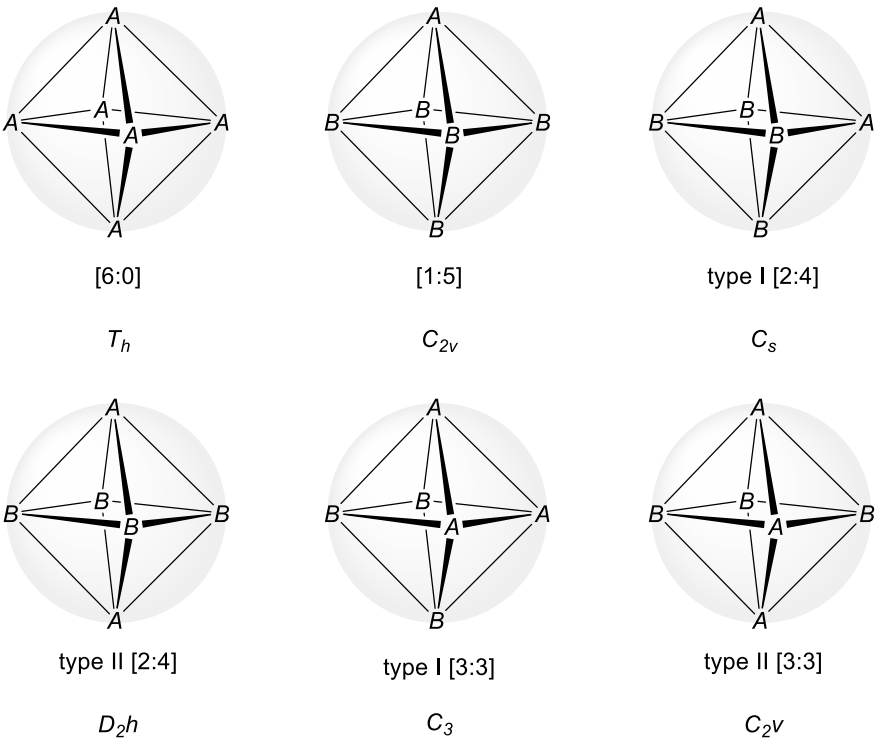


Figure IV-2 : Schematic representation of some mixed hexa-adducts of C_{60}.

Different strategies have been reported in the literature for the elaboration of mixed hexa-adducts and can be sorted in five different approaches.

The stepwise approach:

This approach is based on the reactivity of the *e* double bonds and no regioselective method is employed. Precursors were synthesized by stepwise procedures and required fastidious purifications of the *e* regioisomers. Mixed hexa-adducts could be obtained from the classical modified Bingel conditions.[2] This strategy is limited to symmetrical addends and to type I mixed hexa-adducts. Several mixed hexa-adducts prepared by stepwise approach have been described in the literature[1,3,4].

The template approach:

This second approach is based on the addition reversibility of the Diels-Alder reaction and the reactivity of *e* double bonds. The regiochemistry is induced by the removable Diels-Alder adducts bond on the C_{60}.

Kräutler and coworkers have developed a method to prepare a *trans-1* bis-adducts with removable anthracene addends.[5] This *trans-1* bisanthracene adduct can be used for the formation of type II [4:2] hexa-adducts with excellent yields (Figure IV-3). The two anthracene adducts were removed by heating the hexa-adducts in the solid state. The resulting tetra-adducts with an equatorial belt of addends could be then re-functionalized to afford type II fullerene [4:2] hexa-adducts.[6]

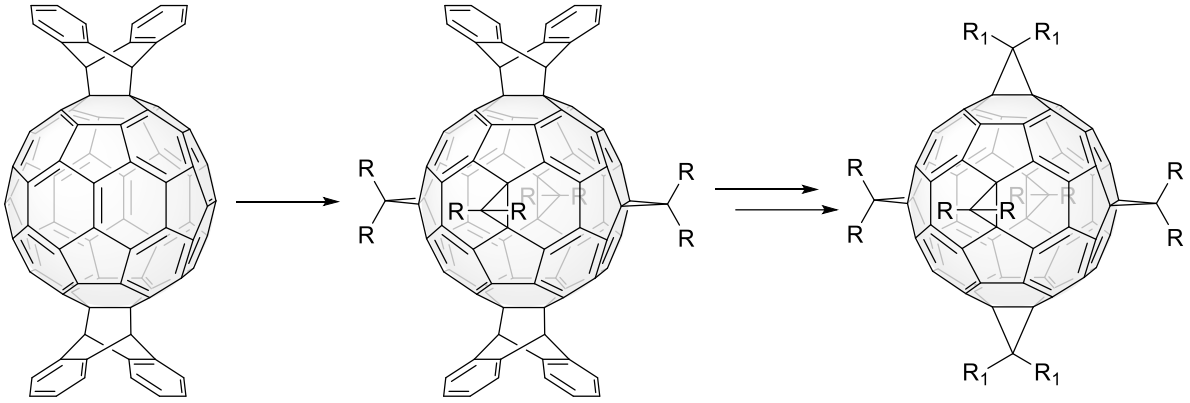


Figure IV-3 : Template strategy for the formation of type II [4:2] hexa-adducts.

The macrocyclic approach:

By a macrocyclic approach, multi-adducts of C_{60} can be formed with high regioselectivity. Using this strategy, only type I [3:3] hexa-adducts are reported in the literature.[7–9]. The tris-adducts bearing a cyclo-[3]-octyl malonate have been used for the preparation of type I [3:3] hexa-adducts (Figure IV-4). The disadvantage of those compounds is that the cyclo-[3]-octyl malonate part cannot be subjected to further post-functionalization. This aspects limits considerably the scope of the functionalization of the carbon sphere.

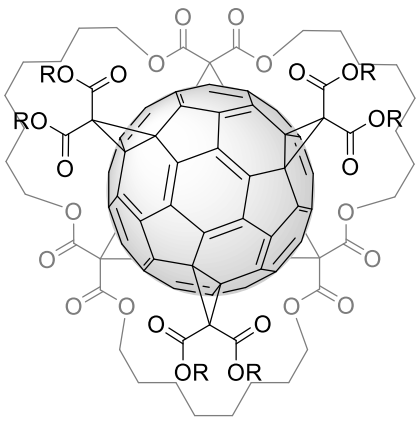


Figure IV-4 : Example of mixed C60 hexa-adduct obtained by the macrocyclic approach.

The tether-directed approach:

Currently, this is certainly the most efficient method to control the regio- and the stereo-chemistry of the addends around the C_{60}. The design of the tether is an important matter. Indeed, removable of the tether would allow post-functionalization of the addends and thus afford building blocks for the preparation of new compounds with specific properties.

Hirsch and coworkers have developed three different tripodal malonate tethers for the regioselective preparation of tris-adducts of C_{60} in order to have access to mixed [3:3] hexa-

adducts of C_{60} with four spherically defined addend zones (Figure IV-5).[10,11] The removal of two of the three tethers afforded carboxylic acid, alcohol or bromide functions depending on the used tether. Different reactions can be envisaged based on the reactivity of the released functions for the post-functionalization of the hexa-adducts.

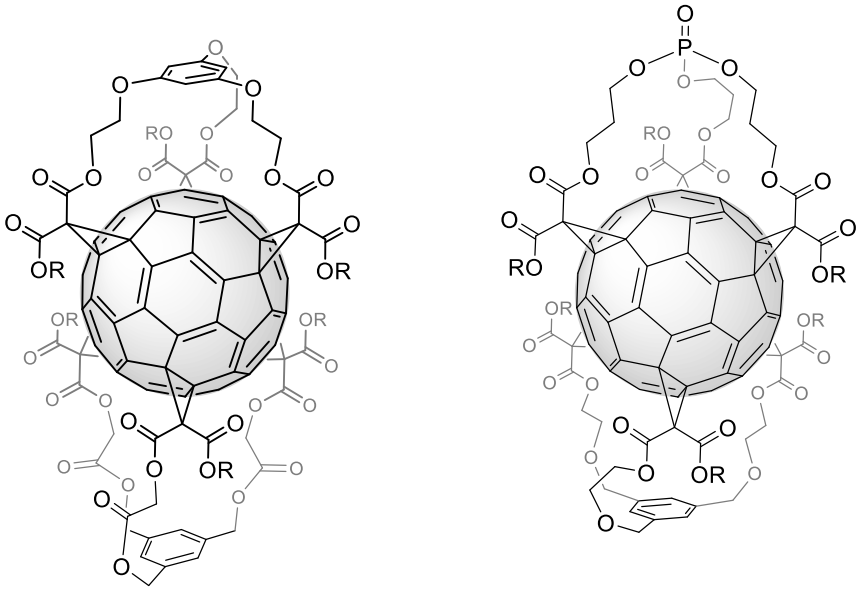


Figure IV-5 : The three tethers developed by Hirsch and coworkers for the preparation of mixed [3:3] hexa-adducts of C_{60}.

Mixed approach:

This category regroups the mixed hexa-adducts formed by the union of the tether-directed, template and stepwise approaches.

Diederich and coworkers have developed a malonate tether bearing two "Diels-Alder addends". Reaction of this tether with C_{60} gave only one regioisomer of tris-adducts with a C_{2v} symmetry which was assigned to an *e,e,trans-1* tris-adducts of C_{60}. The two Diels-Alder adducts have been removed by retro-Diels-Alder reactions after the formation of the C_{60} hexa-adducts (Figure IV-6). Following different paths, they were able to synthesize mixed hexa-adducts with different ratio bearing up to four different addends (e.g. type II [4:2], [1:2:3] and [1:1:2:2]).[12–16]

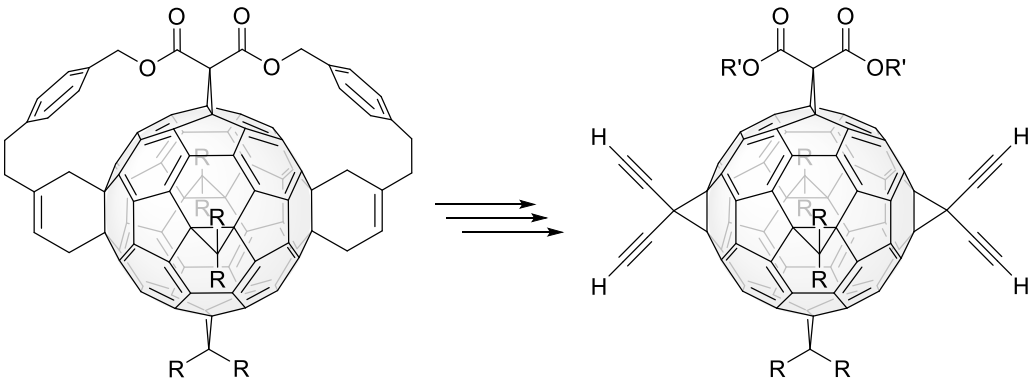


Figure IV-6 : Strategy employed by Diederich and coworkers for the preparation of mixed hexa-adducts of C_{60}.

Rubin and coworkers used a tether with two "Diels-Alder addends" at both ends. They obtained a trans-1 bis-adducts with a masked *e* position by the tether. The complete functionalization of the carbon sphere led only to the penta-adducts with an incomplete octahedral addition pattern (Figure IV-7). Mixed [3:3] hexa-adducts were obtained by the removal of the tether and the subsequent three-fold additions. It was also observed that the remaining *e* positions could be exclusively functionalized in a sequential manner (*e-face*, *e-edge* and finally *e'-face*).[17] In the continuity of this work, they succeeded to synthesize seven mixed [2:2:2] C_{60} hexa-adducts out of the eight possible regioisomers.[18]

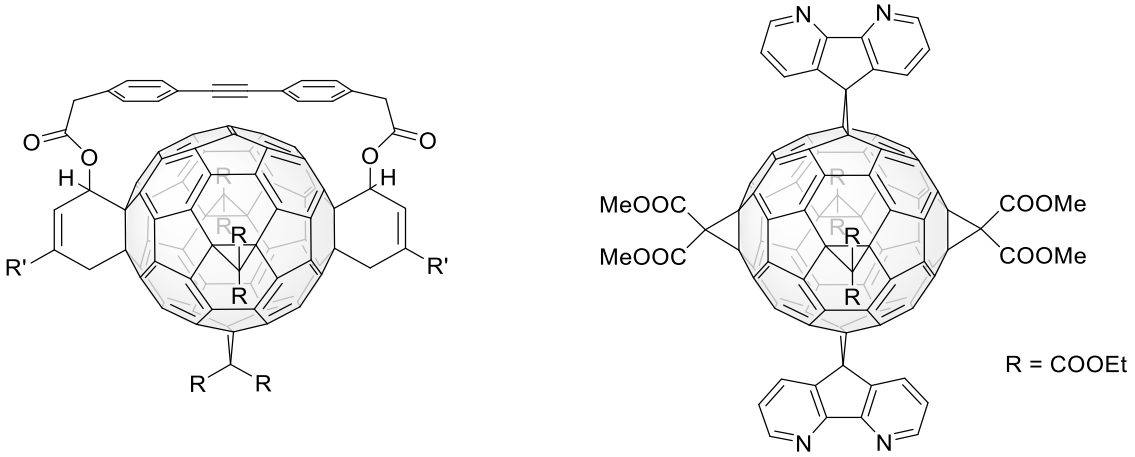


Figure IV-7 : left: Penta-adduct with an incomplete octahedral addition pattern; right: Example of one of the seven mixed [2:2:2] hexa-adducts obtained.

In the reported methodologies, the lack of post-functionalization possibilities, low yields or fastidious syntheses limited the preparation of highly functionalized mixed hexa-adducts of C_{60}. In this chapter, we will exploit the synthetic strategies described in the previous chapters in order to synthesize mixed C_{60} hexa-adducts. These compounds will be furthermore post-functionalized by sequential "click" reactions in order to obtain multi-functionalized C_{60} hexa-adducts.

2. Synthesis of mixed C_{60} hexa-adducts by "click" reactions.

2.1 Preparation of mixed C_{60} hexa-adducts building blocks.

Based on our efficient and regioselective methodology for the preparation of *e,e,e* tris-adducts, we have now easy access to the triol building block **III-14** in a relatively good yield (13% over 4 steps). With its *e,e,e* addition pattern, compound **III-14** is perfectly suited for the preparation of mixed hexa-adducts with an octahedral addition pattern. In order to have access to more functionalized hexa-adducts, the ethyl esters of **III-14** must be modified to allow the post-functionalization of these side chains. For this reason, malonate **IV-2** was prepared from 3-bromo-1-propanol (Scheme IV-1) in order to obtain two more building blocks: the *e,e,e* C_{60} tris-adduct **IV-6** and the *e* C_{60} bis-adduct **IV -9** (Figure IV-8).

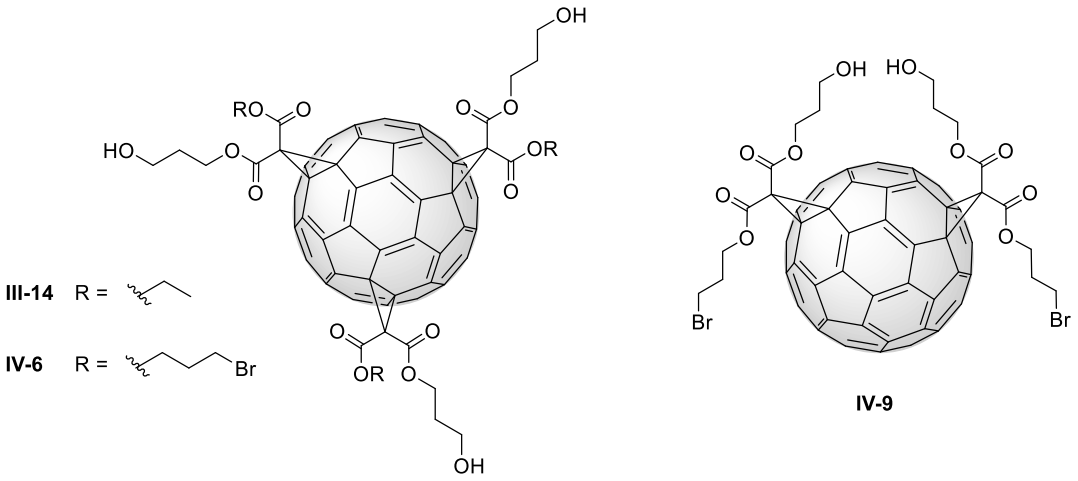
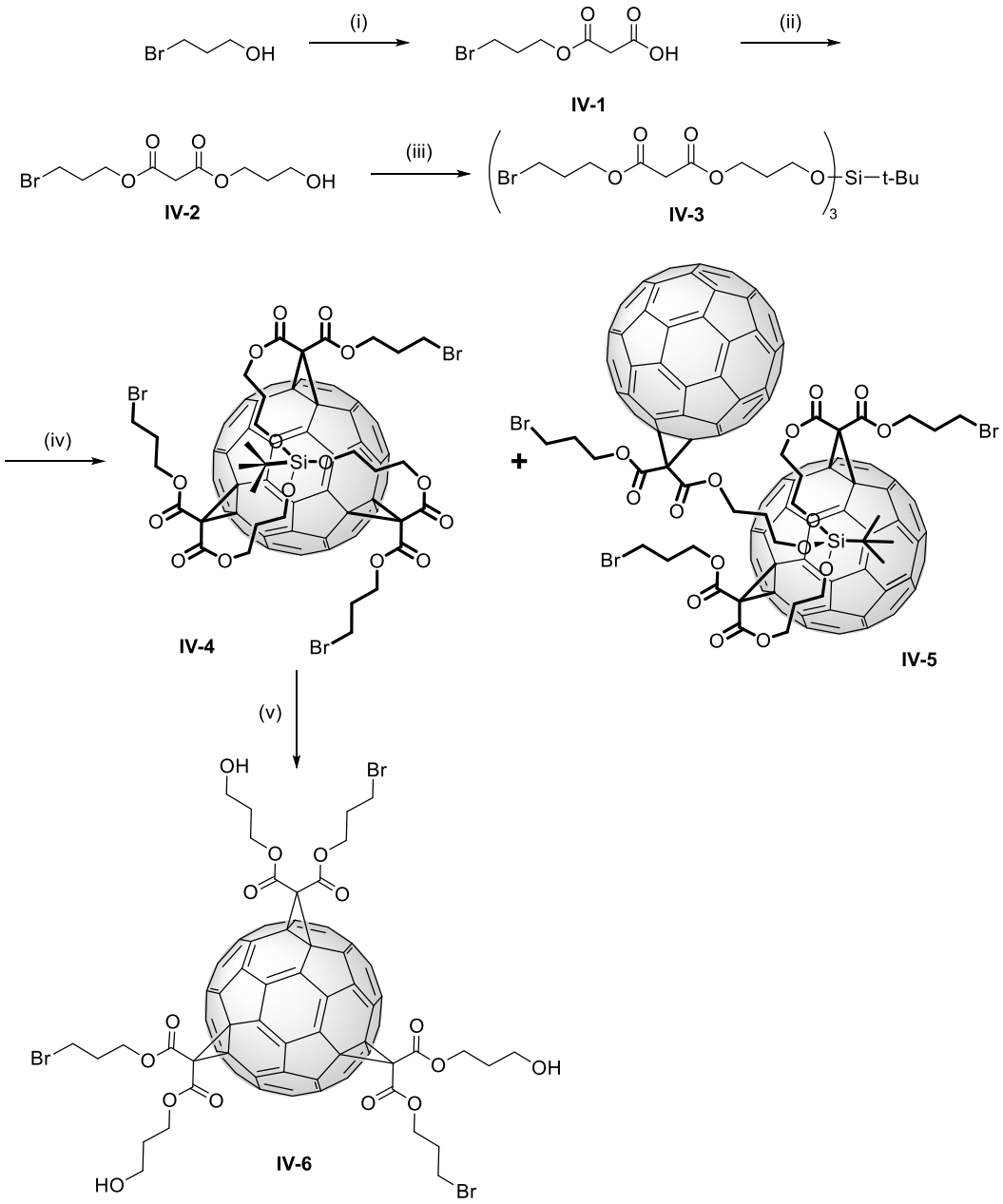


Figure IV-8 : The three building blocks used for the preparation of mixed C_{60} hexa-adducts.

Reaction of 3-bromo-1-propanol with Meldrum acid at 80 °C afforded the malonic acid derivative **IV-1** (**Scheme IV-*1***). Subsequent esterification reaction of **IV-1** with an excess of 1,3-propanediol in the presence of DCC and DMAP gave the malonate **IV-2** in 46% yield over two steps. The tris-malonate derivative **IV-3** was then prepared by treatment of **IV-2** with *t*-$BuSiCl_3$ in the presence of pyridine in CH_2Cl_2 at 0 °C. The key conditions of this reaction were the use of an apolar solvent and a low temperature to avoid bromide to chloride substitution side reactions. Reaction of **IV-3** with C_{60}, under the conditions developed for preparation of fullerene *e,e,e* tris-adducts from *t*-butyl(trialkoxy)silane derivatives, afforded tris-adduct **IV-4** and bis-fullerene derivative **IV-5**. The side chains of the tris-malonate **IV-3** do not affect the regioselectivity of the reaction and the *e,e,e* addition pattern was confirmed by NMR and UV/vis spectroscopies. The structure of **IV-4** was further confirmed by mass spectrometry. Finally, treatment of **IV-4** with $BF_3.Et_2O$ (20 equiv) in CH_2Cl_2/CH_3CN afforded the triol derivative **IV-6** in a good yield. The protons of the alkyl chains are diastereotopic as observed on the ^1H

NMR spectrum of **IV-6.** That can be rationalized by intramolecular hydrogen-bonding between the released alcohol functions (Figure IV-9).[19]



Scheme IV-1. Reagents and conditions: (i) Meldrum acid, 80 °C; (ii) 1,3-propanediol, DCC, DMAP, CH_2Cl_2, 0 °C to rt, 12 h (46% over two steps); (iii) *t*BuSiCl$_3$, pyridine, CH_2Cl_2, rt, 12 h (66%); (iv) C_{60}, I_2, DBU, PhMe, -15 °C, 1 h (**IV-4**: 13% and **IV-5**: 3%); (v) $BF_3.Et_2O$, CH_2Cl_2/MeCN 2:1, rt, 12 h (86%).

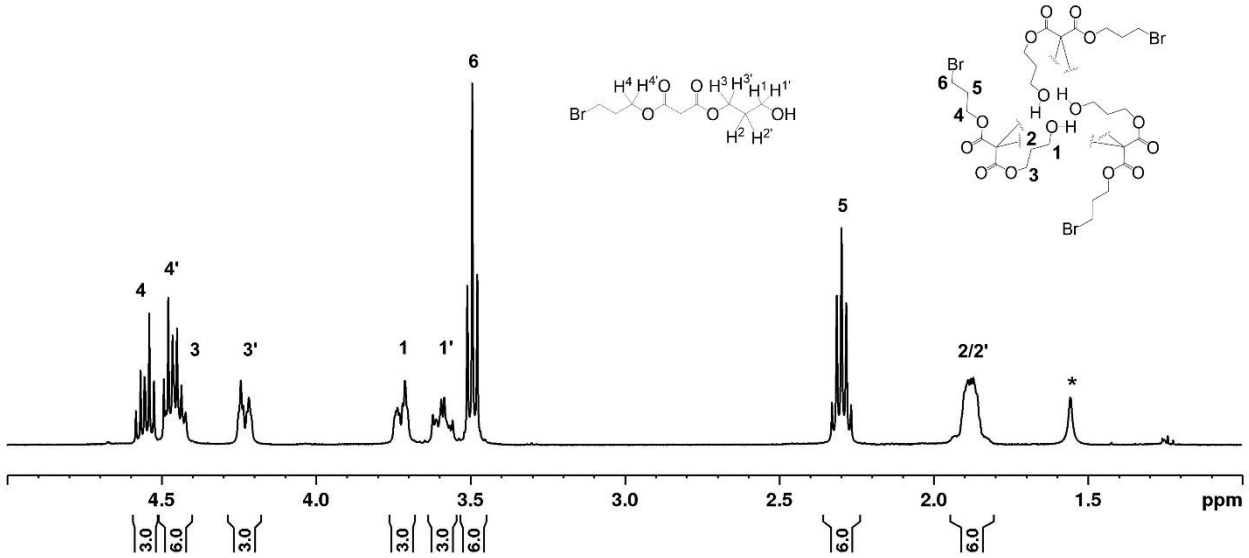
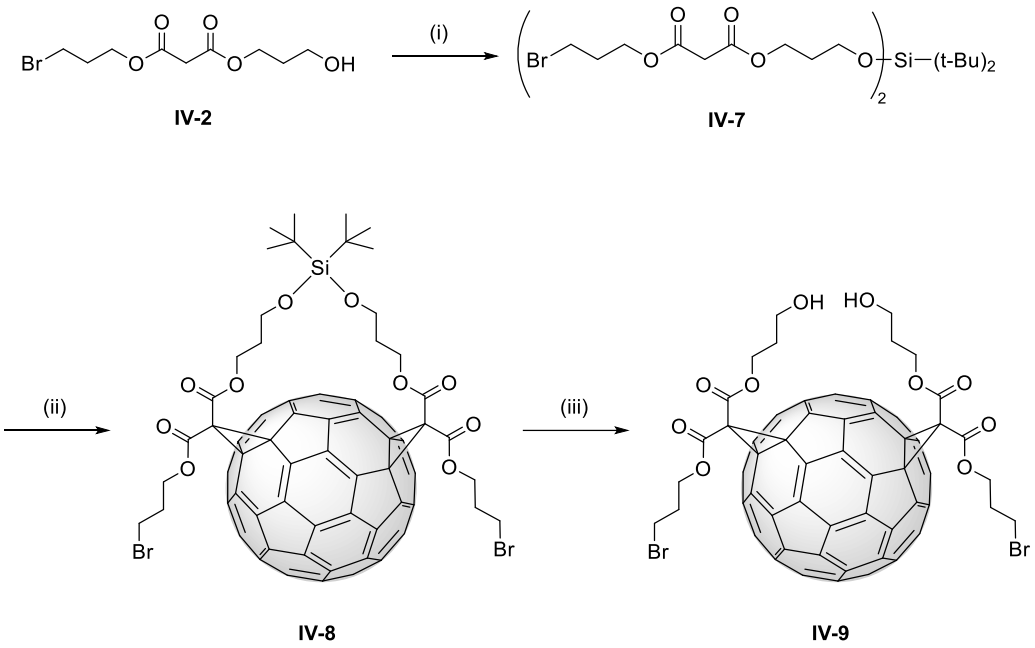


*Figure IV-9 : ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **IV-6**. (*) water.*

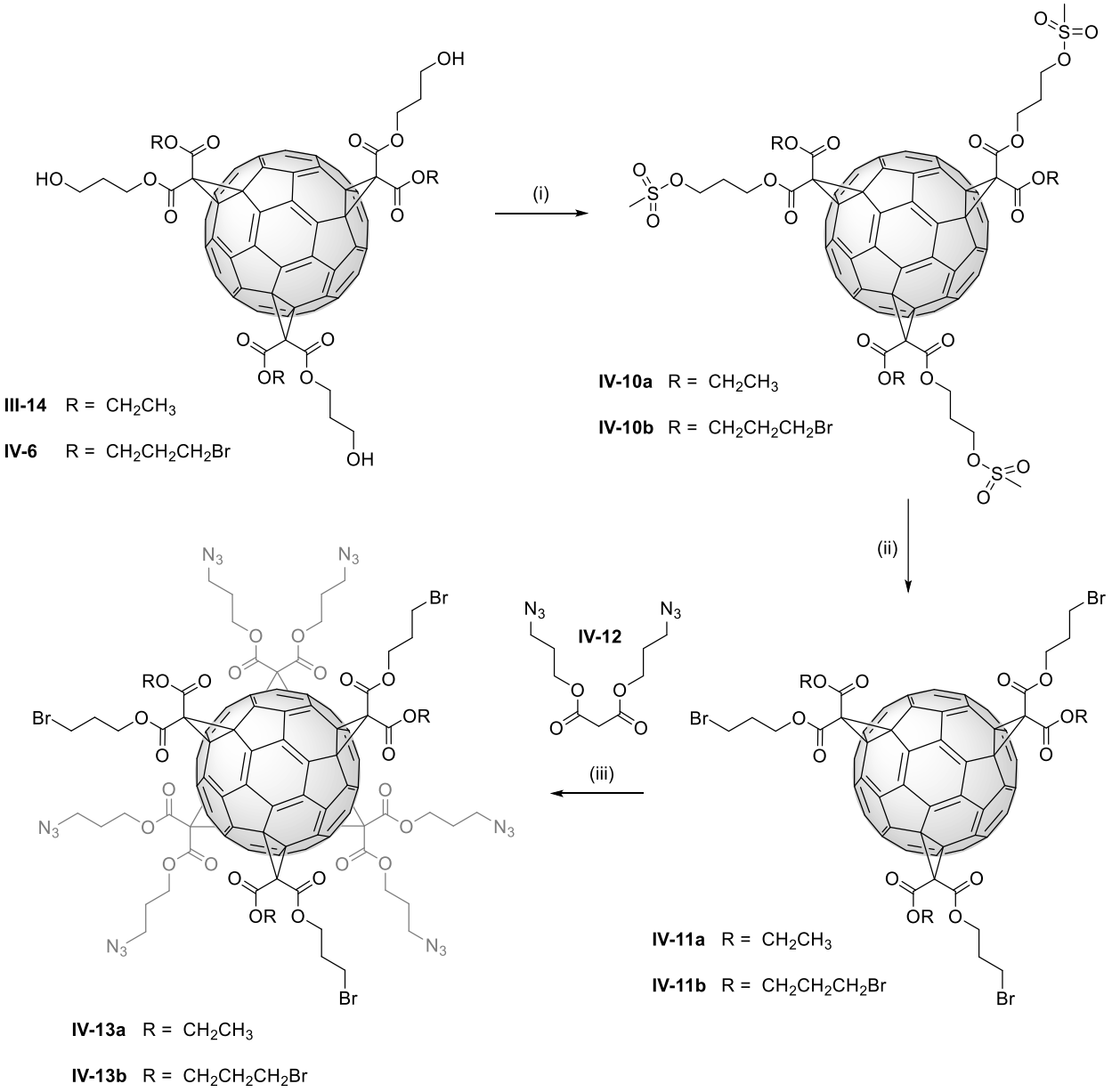
The synthesis of compound **IV-9** is depicted in **Scheme IV-*2***. Treatment of compound **IV-2** (2 equiv.) with di-*t*-butylsilyl bis(trifluoromethanesulfonate) (tBu$_2$Si(OTf)$_2$, 1 equiv.) in DMF in the presence of pyridine gave the bis-malonate **IV-7**. Reaction of **IV-7** with C_{60}, I_2 and DBU in toluene afforded the corresponding cyclization product **IV-8** in 48% yield. Fullerene bis-adduct **IV-8** was characterized by ^{1}H and ^{13}C NMR, UV/vis and IR spectroscopies. In addition, its structure was confirmed by MALDI-TOF mass spectrometry showing the expected pseudo-molecular ion peaks at *m/z* = 1423.0 ($[M+H]^+$, calcd for $C_{86}H_{43}O_{10}Br_2Si$: 1423.1). The C_1 molecular symmetry deduced from the ^{1}H and ^{13}C NMR spectra suggests an *equatorial* addition pattern. This was further confirmed by the UV/vis spectrum revealing the diagnostic features previously reported for analogous *equatorial* C_{60} bis-adducts. Finally, desilylation of **IV-8** with $BF_3.Et_2O$ provided *e* bis-adduct **IV-9**.



Scheme IV-2. Reagents and conditions: (i) $(t\text{Bu})_2\text{Si(OTf)}_2$, pyridine, DMF, rt, 12 h (68%); (ii) C_{60}, I_2, DBU, PhMe, rt, 1 h (48%); (iii) $BF_3.Et_2O$, CH_2Cl_2/MeCN 2:1, rt, 12 h (91%).

The post-functionalization of C_{60} hexa-adducts by copper-catalyzed alkyne-azide 1,3-dipolar cycloaddition (CuAAC) reactions has shown its efficiency[20] and thus, we oriented the synthesis of the mixed hexa-adducts building blocks in this direction.

As shown in **Scheme IV-*3***, the preparation of tris-adduct **IV-11** was first achieved. Treatment of **III-14** and **IV-6** with methanesulfonyl chloride ($MeSO_2Cl$) in CH_2Cl_2 in the presence of triethylamine at 0 °C gave compounds **IV-10a,b**. As for the preparation of compound **IV-3**, the low temperature was the key condition to avoid the substitution of the bromide by a chloride. Subsequent bromination of **IV-10** with LiBr in THF afforded **IV-11** in good yields. Reaction of **IV-11a-b** with **IV-12** (5 equiv.) were then performed in the presence of CBr_4 (100 equiv.) and DBU (18 equiv.) in toluene at room temperature.[2] The *C_3*-molecular symmetry deduced from the ^{1}H NMR spectrum (Figure IV-10) is in agreement with the octahedral addition pattern of C_{60} hexa-adducts **IV-13.** In the case of **IV-13**, the reactivity of azides towards the C_{60} core is considerably reduced but reactions can still occur. [11,21,22] Typically, C_{60} hexa-adducts bearing azides are rapidly used after purification.



Scheme IV-3. Reagents and conditions: (i) $MeSO_2Cl$, Et_3N, CH_2Cl_2, 0 °C, 2 h (**IV-10a**: 86%; **IV-10b**: 94%); (ii) LiBr, THF, 60 °C, 12 h (**IV-11a**: 83%; **IV-11b**: 98%); (iii) **IV-12**, CBr_4, DBU, PhMe, rt, 12 h (**IV-13a**: 42%; **IV-13b**: 63%).

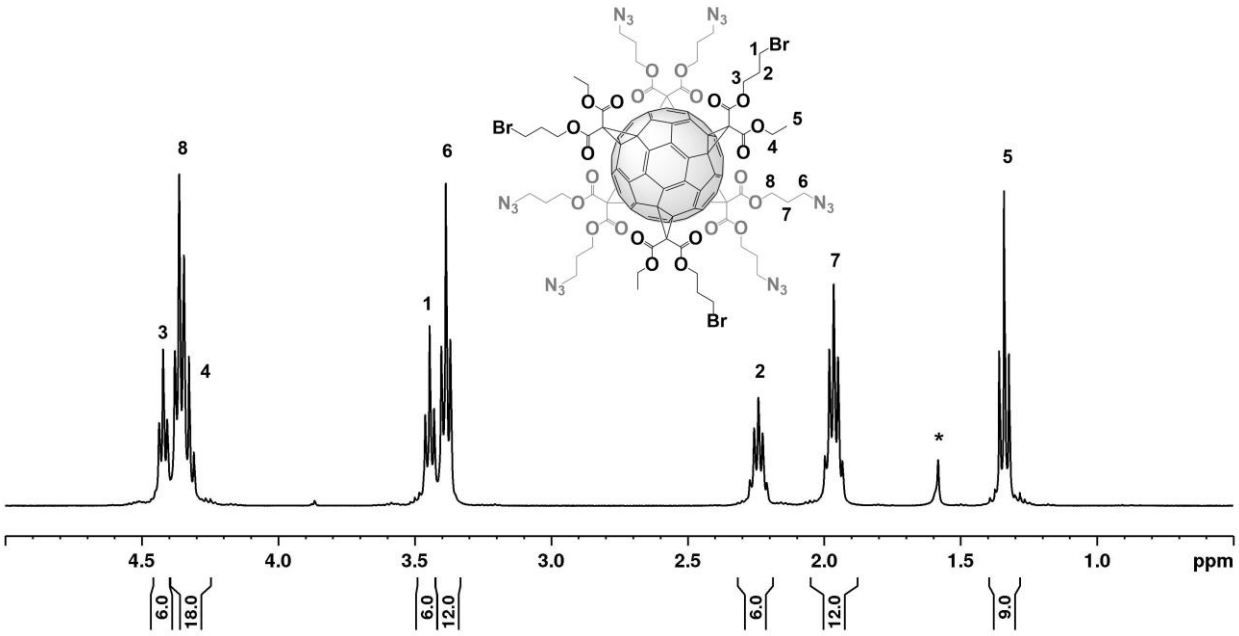
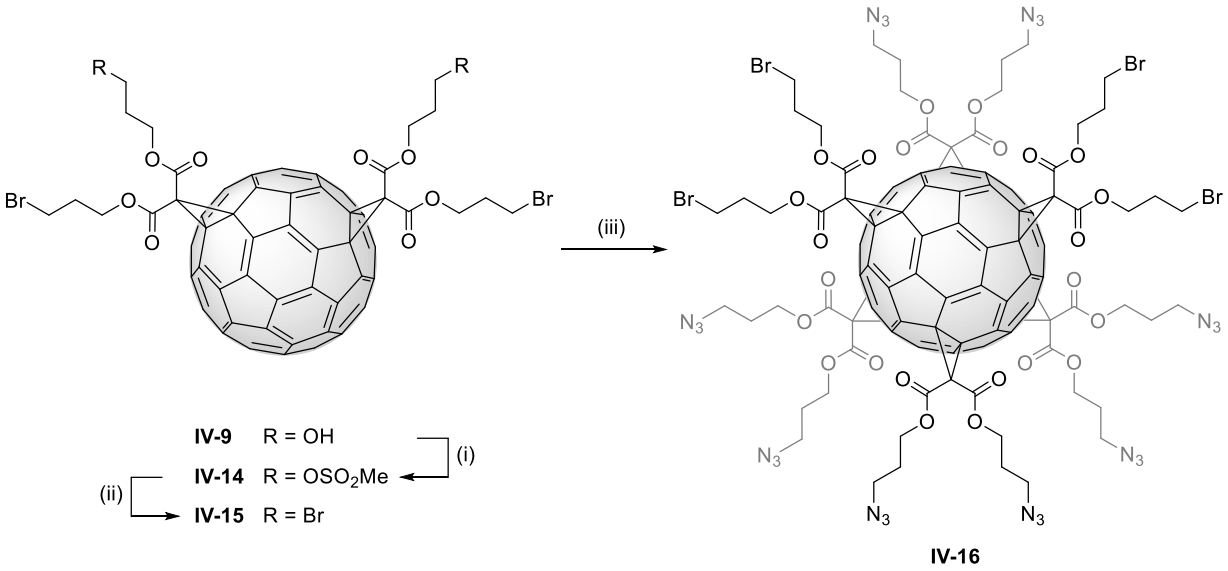


*Figure IV-10 : ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **IV-13a** showing the C_3 molecular symmetry. (*) water.*

Following the same synthetic route, the preparation of the mixed [2:4] C_{60} hexa-adduct **IV-16** was achieved (**Scheme IV-*4***). Mesylation of **IV-9** followed by bromination afforded the tetrabrominated bis-adduct **IV-15**. Whereas derivatives **IV-8**, **IV-9** and **IV-14** bearing unsymmetrically substituted malonate addends are all C_1-symmetrical compounds, C_{60} bis-adduct **IV-15** with its two identical malonate subunits is C_s symmetric as deduced from a careful analysis of its ^{13}C NMR spectrum (Figure IV-11). Out of the 32 expected fullerene resonances, three are observed at δ = 70.1, 71.3 and 71.4 ppm (sp^3 C atoms) and 29 between δ = 138.7 and 147.4 ppm (sp^2 C atoms). It is also worth noting that two of the resonances seen in the sp^2 region show half intensity as well as two of the three resonances observed for the fullerene sp^3 C atoms. Actually, the latter observation are unambiguous proofs for the C_s symmetry of compound **IV-15**. Furthermore, out of the three possible C_s-symmetrical addition patterns (cis-2, e and trans-4), the only one for which 3 resonances are expected for the sp^3 fullerene C atoms is the *equatorial* bis-adduct. This is further confirmed by the observation of three resonances for the carbonyl C atoms (δ = 163.2, 163.29 and 163.32 ppm). Finally, formation of the hexa-adduct **IV-16** was achieved in 56% yield.



Scheme IV-4. Reagents and conditions: (i) $MeSO_2Cl$, Et_3N, CH_2Cl_2, 0 °C, 15 min (93%); (ii) LiBr, THF, 60 °C, 12 h (96%); (iii) **IV-12**, CBr_4, DBU, PhMe, rt, 12 h (56%).

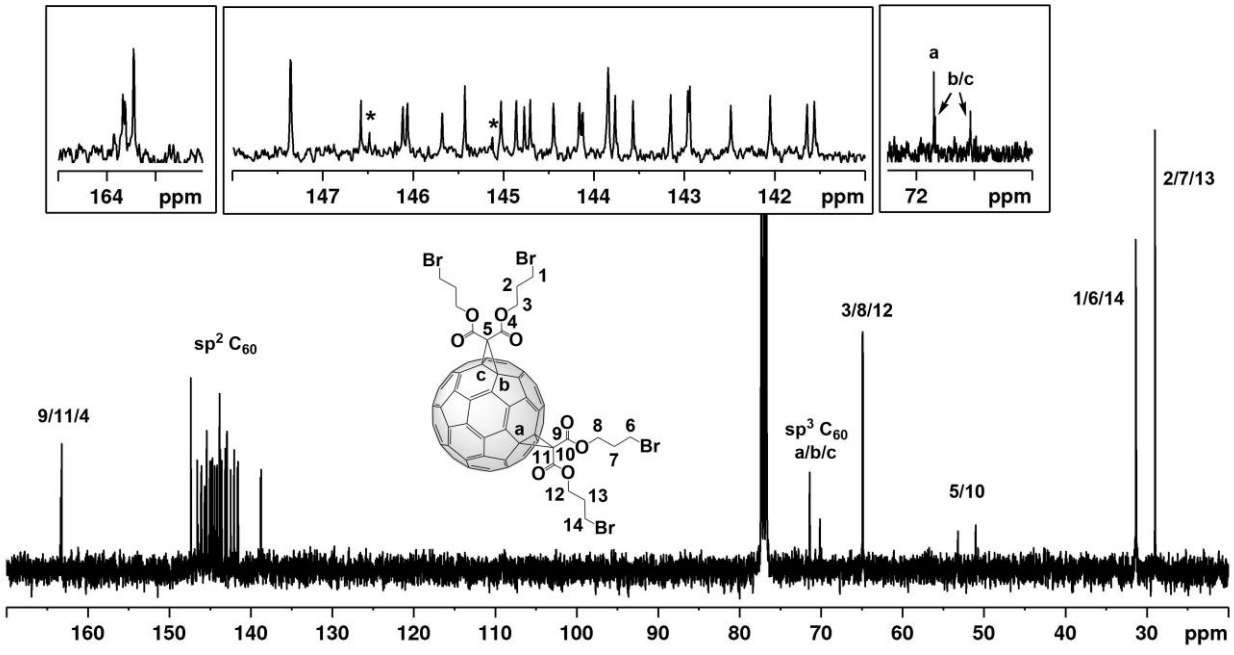


*Figure IV-11 : ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **IV-15** showing the C_s-symmetry; Inset: detailed views showing the resonances of the carbonyl and the fullerene sp^2 and sp^3 C atoms; * indicates the sp^2 fullerene C atoms showing half intensity signals.*

2.2 Post-functionalization of the mixed C_{60} hexa-adducts by CuAAC reactions.

Based on the three developed hexa-adducts building blocks **IV-13a,b** and **IV-16**, two different addend zones on the C_{60} can be functionalized by sequential CuAAC reactions.

The synthesis of the mixed [3:3] C_{60} hexa-adduct **IV-19** was performed first (**Scheme IV-*5***). Reaction of **IV-13a** with phenylacetylene under typical conditions of CuAAC reactions ($CuSO_4.5H_2O$, sodium ascorbate and CH_2Cl_2/H_2O) gave the first "click" compound **IV-17** in 94% yield (**Scheme IV-*5***). Compound **IV-17** has been characterized by ^1H and ^{13}C NMR, UV/vis and IR spectroscopies. The absence of azide residues was confirmed by the IR data (2099 cm^{-1}) and by the disappearance of the CH_2-N_3 signal at δ = 3.39 ppm on the ^1H NMR spectrum (Figure IV-12). The ^1H NMR spectrum of **IV-17** confirmed also the formation of the triazoles with the presence of the characteristic singlets of the 1,2,3-triazole units at δ = 7.82 and 7.86 ppm as well as the signal of the CH_2-triazole protons at δ = 4.4 ppm (Figure IV-12). In addition, the MALDI-TOF mass spectrum shows the expected pseudo-molecular ion peak at *m/z* = 2892.8 ($[M+H]^+$, calcd for $C_{159}H_{106}O_{24}N_{18}Br_3$: 2892.5).

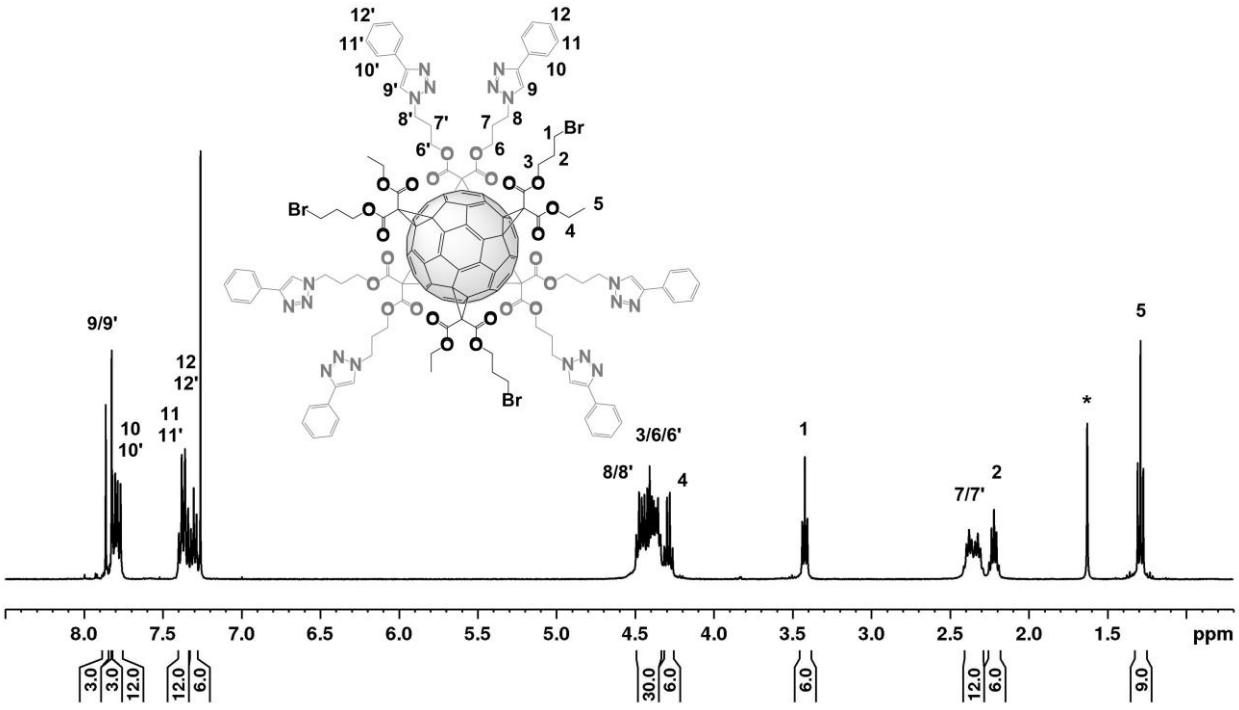
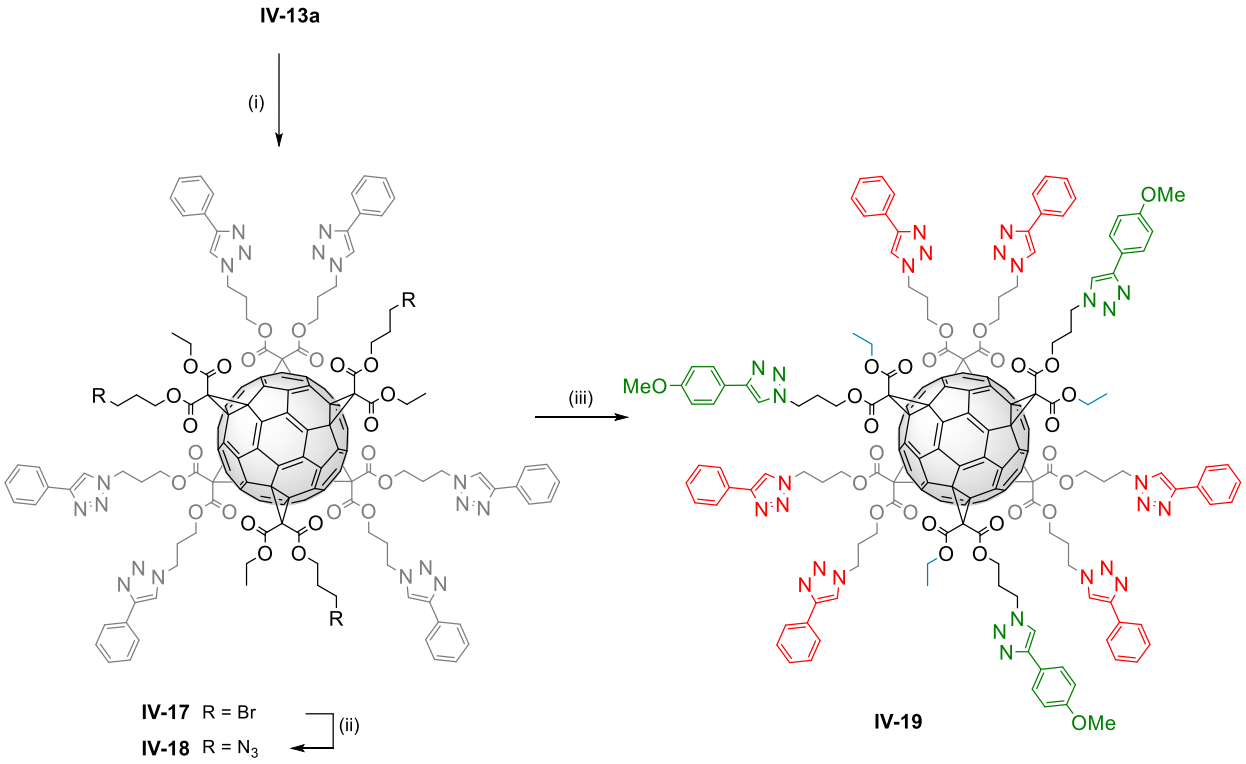


*Figure IV-12 : ^1H NMR spectrum (400 MHz, $CDCl_3$) of **IV-17**. (*) water.*



Scheme IV-5. Reagents and conditions: (i) Phenylacetylene, $CuSO_4.5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, 30 °C, 12 h (94%); (ii) NaN_3, DMF, rt, 12 h (96%); (iii) 4-ethynylanisole, $CuSO_4.5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, 30 °C, 19 h (97%).

Subsequent conversion of the bromide functions in **IV-17** by treatment with sodium azide in DMF afforded tris-azide **IV-18**. Finally, CuAAC reaction of **IV-18** with 4-ethynylanisole gave mixed hexa-adduct **IV-19** in an excellent yield (97%). The chemical structure of **IV-19** was confirmed by ^{1}H and ^{13}C NMR, UV/vis and IR spectroscopies, mass spectrometry and elemental analysis. The mixed [3:3] hexa-adducts **IV-19** with a function ratio of (6:3) was obtained in 10 steps from 1,3-propanediol in an overall yield of 3%. Three different addend zones can be defined in the mixed hexa-adducts **IV-19** by the control of the regio- and the stereochemistry of our methodology (Figure IV-13).

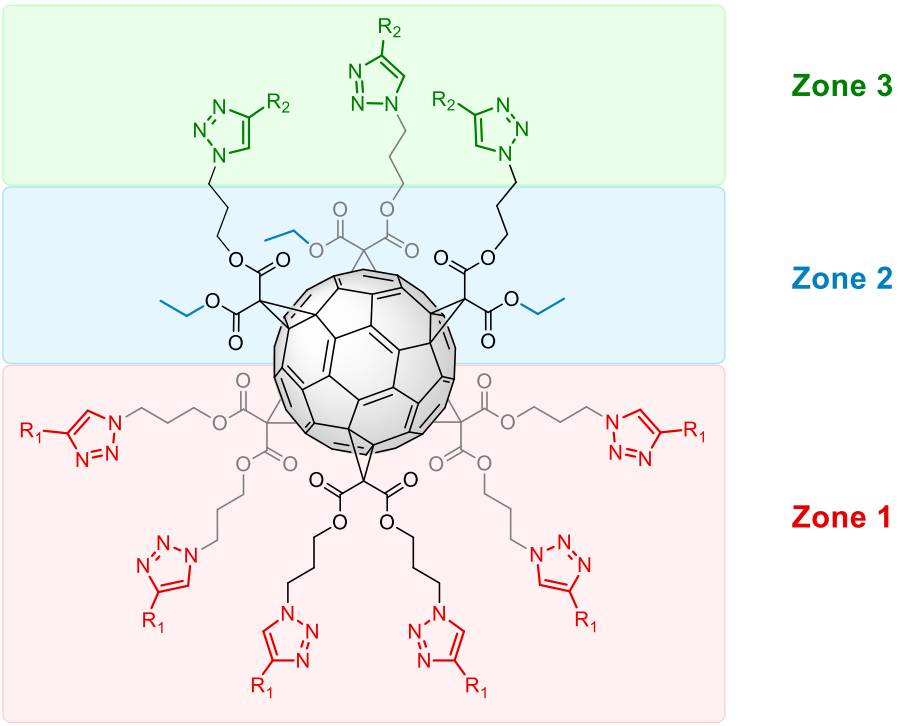
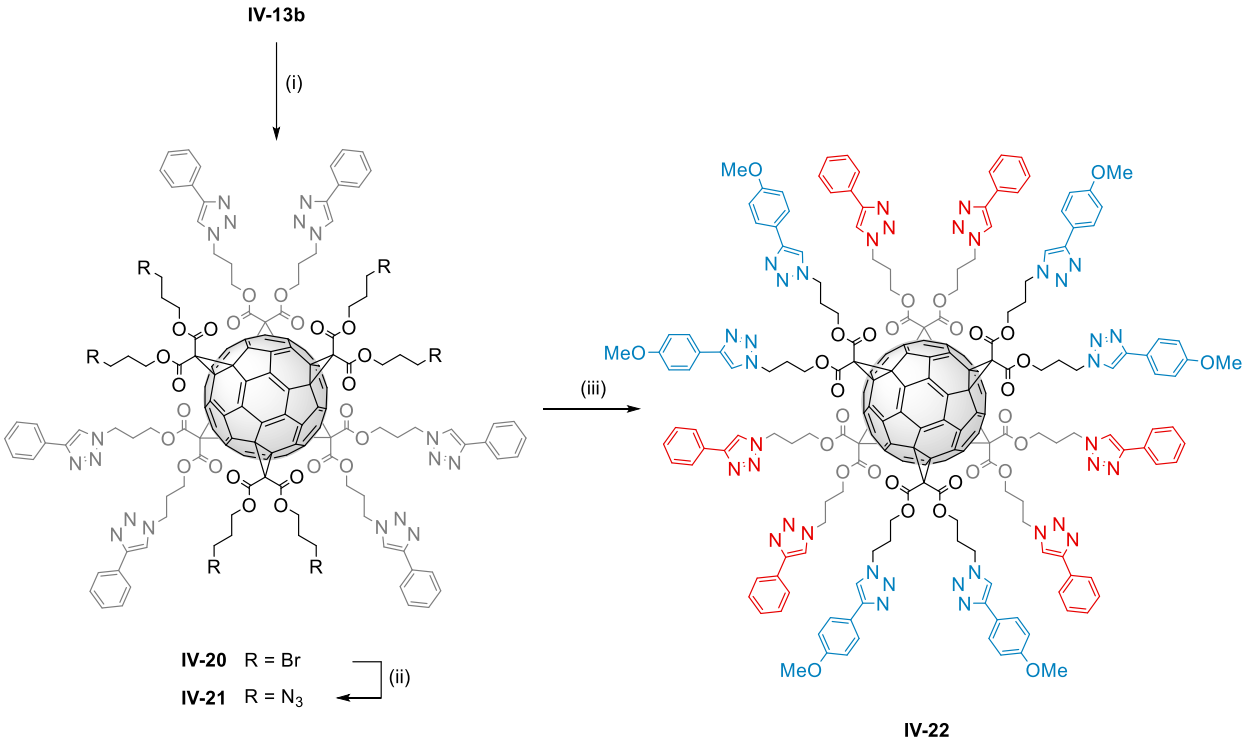


*Figure IV-13 : Illustration of the three different addend zones of the mixed hexa-adduct **IV-19**.*

Following the successful preparation of hexa-adducts **IV-19** from the triol **III-14**, the same synthetic route was used for the preparation of an additional mixed [3:3] hexa-adduct **IV-22** with a (6:6) function ratio (**Scheme IV-*6***). The final hexa-adduct **IV-22** was synthesized from compound **IV-13b** by two sequential CuAAC reactions. The chemical structure of **IV-22** was confirmed by ^{1}H and ^{13}C NMR, UV/vis and IR spectroscopies, mass spectrometry and elemental analysis. As shown in Figure IV-14, the ^{13}C NMR spectrum of **IV-22** exhibits a high local symmetry with only three fullerene resonances at δ = 145.9 and 141.3 ppm for the sp^2 C atoms and at δ = 69.2 ppm for the sp^3 C atoms which is in full agreement with an octahedral addition pattern. No influence of the C_3 overall symmetry of **IV-22** can be deduced for the C_{60} core. Similar observations have been reported by Hirsch and coworkers for mixed hexa-adducts of C_{60}.[1] The particularity of this mixed [3:3] hexa-adduct **IV-22** is the localization of the two different functions in two defined hemispheres (Figure IV-15).



Scheme IV-6. Reagents and conditions: (i) Phenylacetylene, $CuSO_4.5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, 30 °C, 12 h (99%); (ii) NaN_3, DMF, rt, 12 h (98%); (iii) 4-ethynylanisole, $CuSO_4.5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, 30 °C, 12 h (88%).

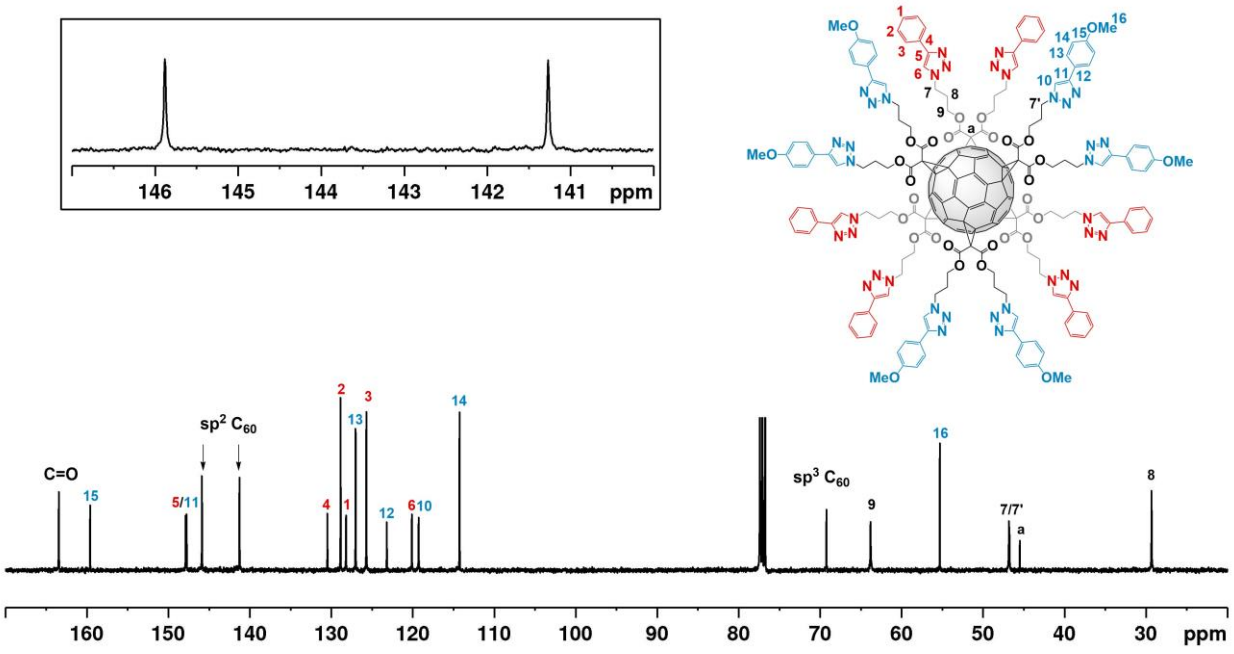


*Figure IV-14 : ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **IV-22** showing the high local symmetry. Inset: detailed view showing the resonances of the fullerene sp^2 C atoms.*

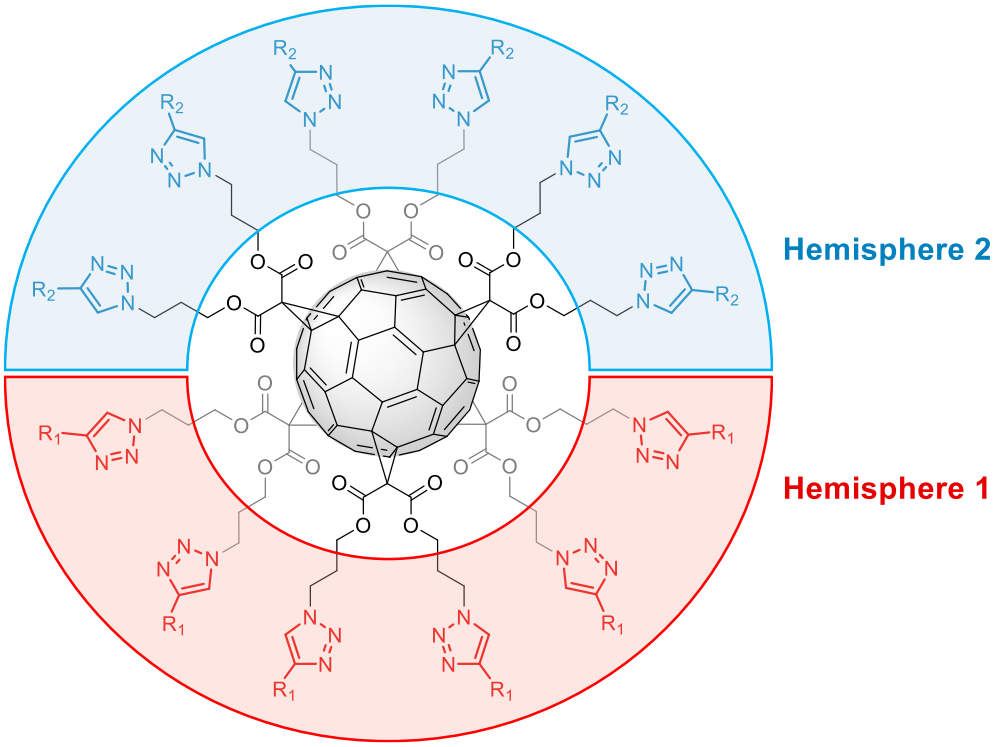
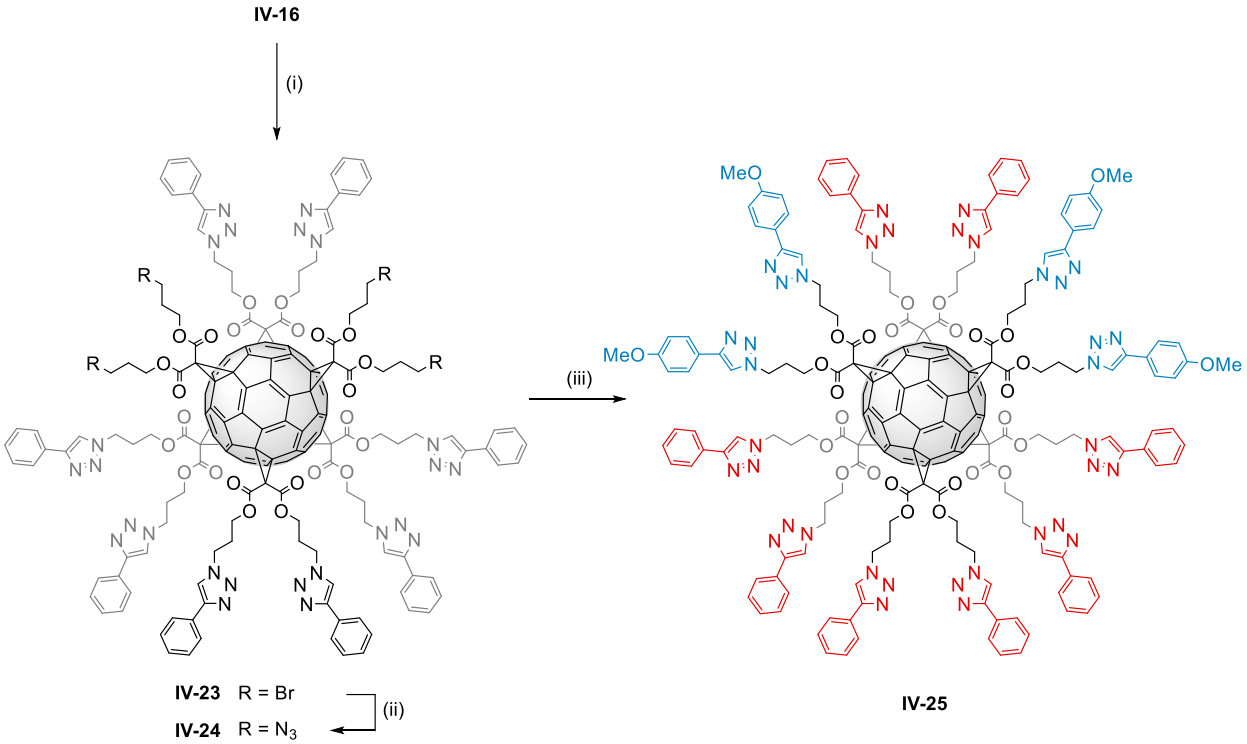


*Figure IV-15 : Illustration of the two hemisphere of the mixed C_{60} hexa-adduct **IV-22**.*

Finally, the [2:4] hexa-adduct **IV-25** was also synthesized by two sequential CuAAC reactions (**Scheme IV-*7***). The chemical structure of **IV-25** was confirmed by ^{1}H and ^{13}C NMR, UV/vis and IR spectroscopies, mass spectrometry and elemental analysis. As for compound **IV-22**, the octahedral addition pattern was unambiguously confirmed by the high local symmetry of the C_{60} core observed on the ^{13}C NMR spectrum of **IV-25**. The mixed [2:4] hexa-adducts **IV-25** with two defined addend zones (Figure IV-16) was obtained in 11 steps from 3-bromo-1-propanol in an overall yield of 5%.

Our methodology relies on the selective functionalization of two different reactive sites. By sequential CuAAC reactions, the post-functionalization of three different mixed C_{60} hexa-adducts was performed in very good yields (75-99%).



Scheme IV-7. Reagents and conditions: (i) Phenylacetylene, $CuSO_4.5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, 30 °C, 12 h (91%); (ii) NaN_3, DMF, rt, 12 h (98%); (iii) 4-ethynylanisole, $CuSO_4.5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, 30 °C, 12 h (75%).

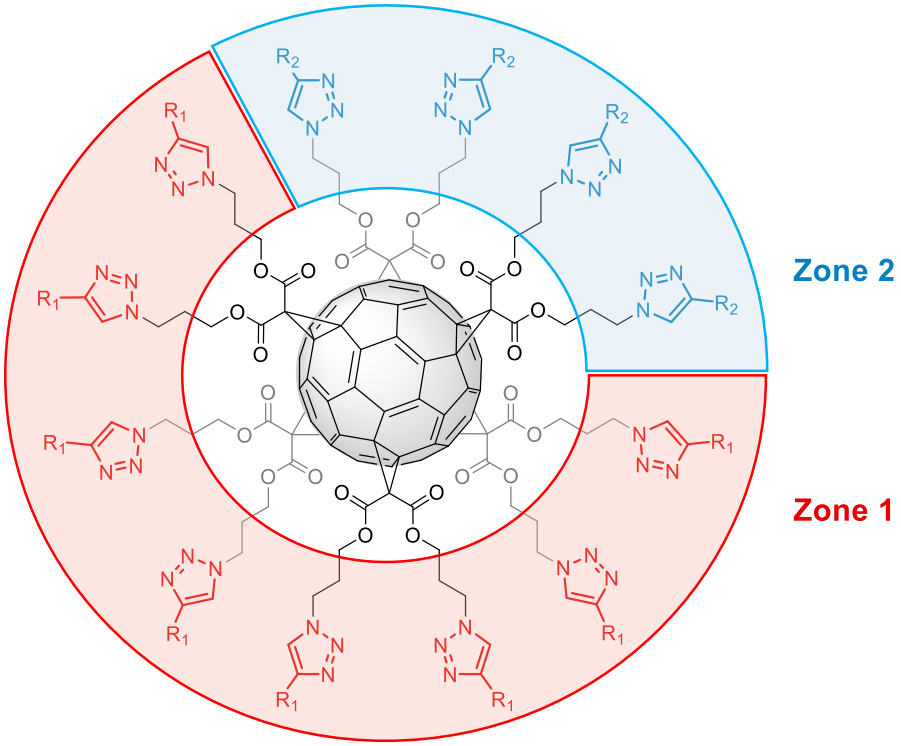


*Figure IV-16 : Illustration of the two different addend zones of the mixed C_{60} hexa-adduct **IV-25**.*

3. Synthesis of mixed C_{60} hexa-adducts by esterification and "click" reactions.

Based on the chemical reactivity of the alcohol function, tris-adduct triol **IV-13** can be post-functionalized first by an esterification reaction (Scheme IV-8). Treatment of **IV-13b** with acetyl chloride in the presence of pyridine gave tri-ester **IV-26** in 79% yield. As shown in Figure IV-18, the ^{1}H NMR spectrum of **IV-26** reveals the disappearance of the C*H*$_2$OH signals at δ = 3.6-3.7 ppm and the formation of the acetyl esters (at δ = 4.15 ppm for the C*H*$_2$OOC signal and δ = 2.07 ppm for the OOCC*H*$_3$ signal). Reaction of **IV-26** with malonate **IV-27** (6 equiv.), CBr_4 (50 equiv.) and DBU (16 equiv.) in toluene at room temperature afforded hexa-adduct **IV-28**. Subsequent conversion of the bromide functions in azide by treatment with sodium azide followed by a CuAAC reaction with phenylacetylene gave the final mixed [3:3] hexa-adducts **IV-30**. Compound **IV-30** has been characterized by ^{1}H and ^{13}C NMR, UV/vis and IR spectroscopies, mass spectrometry and elemental analysis. As in the case of hexa-adducts **IV-22** and **IV-25**, the molecular symmetry (*C*$_3$) of **IV-30** is deduced from the ^{1}H and ^{13}C NMR spectra and confirmed the octahedral addition pattern. As proof of the *C*$_3$-symmetry, the ^{13}C NMR spectrum shows only one resonance for each C atoms of the side chains bearing the terminal acetyl group, as shown in Figure IV-19. IV-30 has a 3:9 function ratio regioselectively distributed (Figure IV-17).

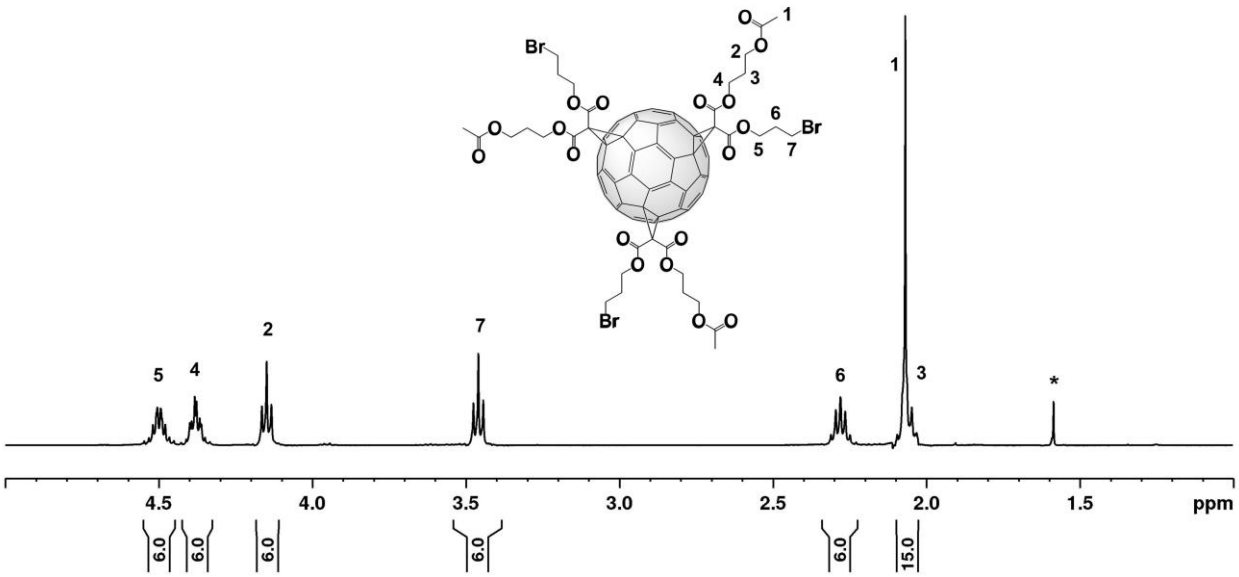
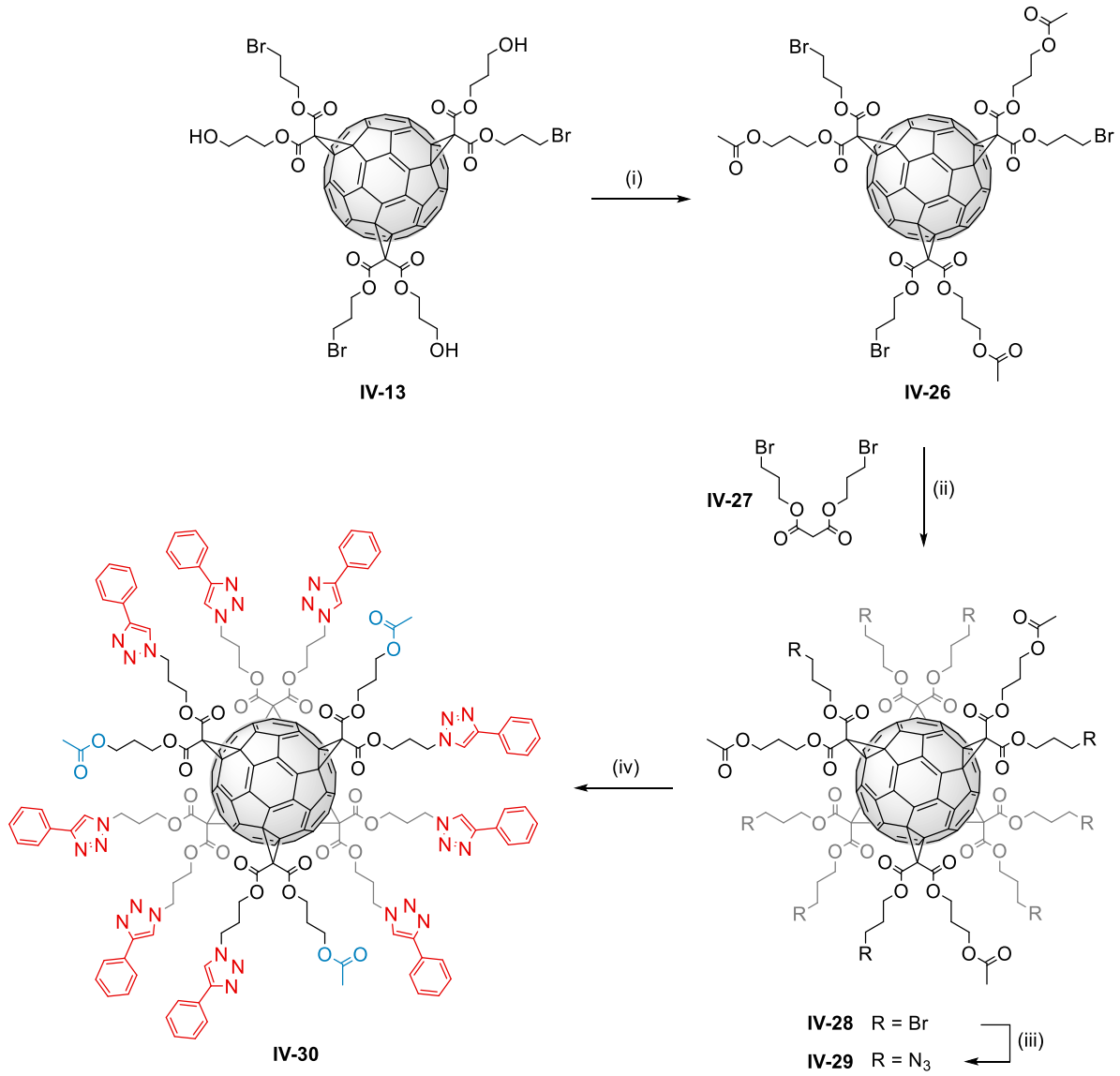


*Figure IV-18 : ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **IV-26**. (*) water.*



Scheme IV-8. Reagents and conditions: (i) Acetyl chloride, pyridine, THF, 0 °C (79%); (ii) **IV-32**, CBr_4, DBU, PhMe, rt, 2 h (67%); (iii) NaN_3, DMF, rt, 12 h (97%); (iv) Phenylacetylene, $CuSO_4.5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, 30 °C, 12 h (94%).

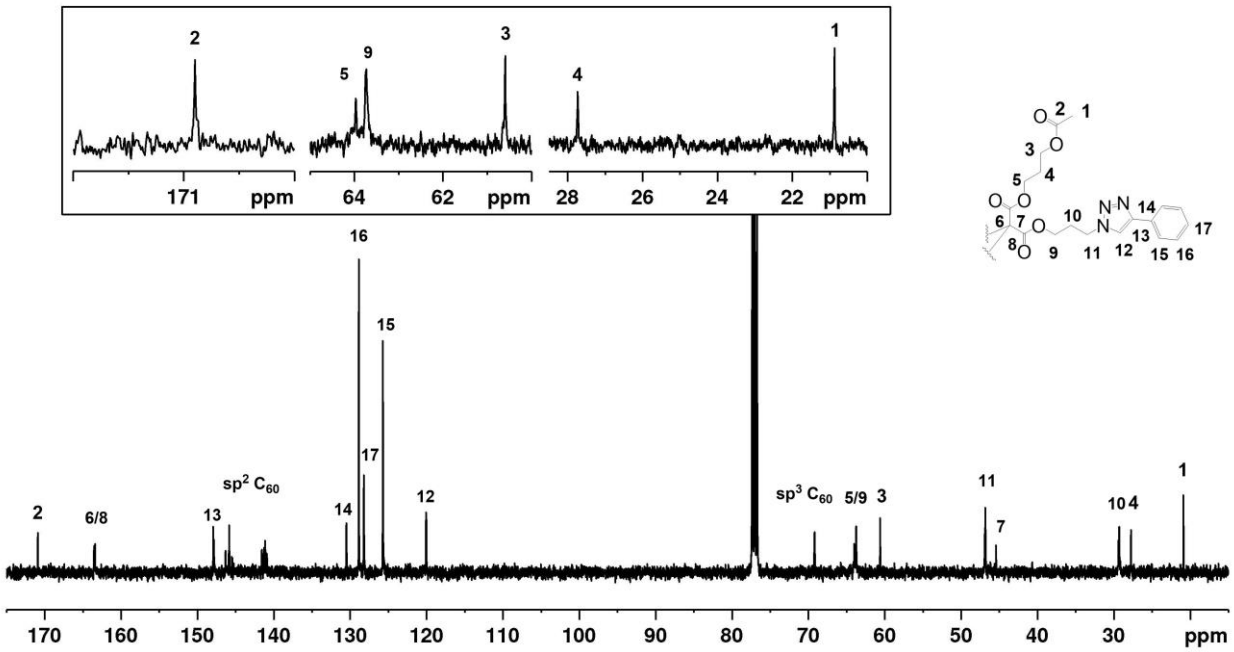


*Figure IV-19 : ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **IV-30** showing its threefold symmetry. Inset: detailed view showing one resonance for each C atoms of the side chains bearing the acetyl.*

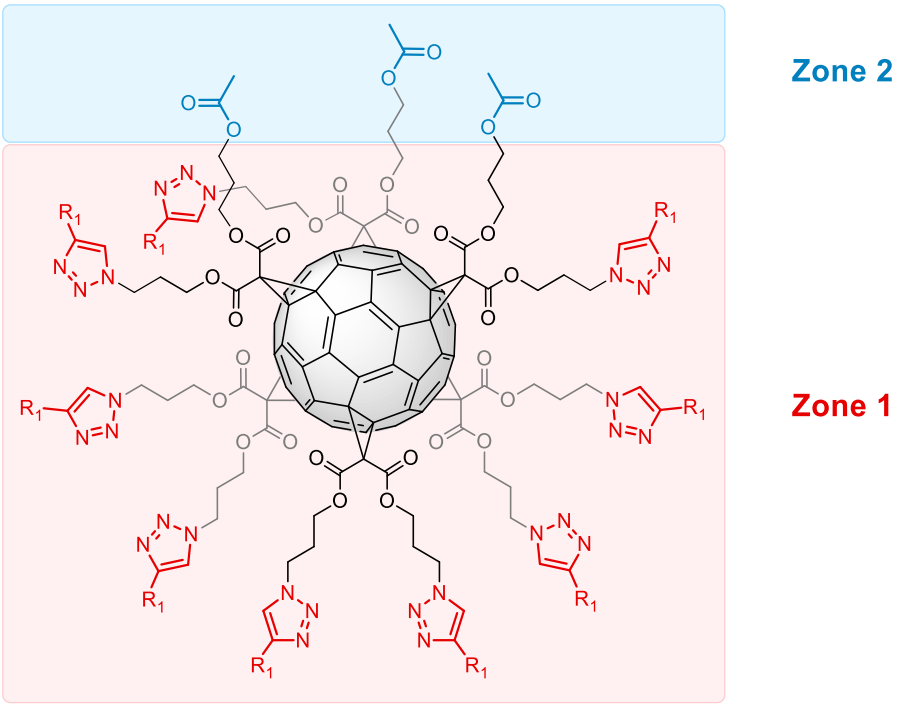
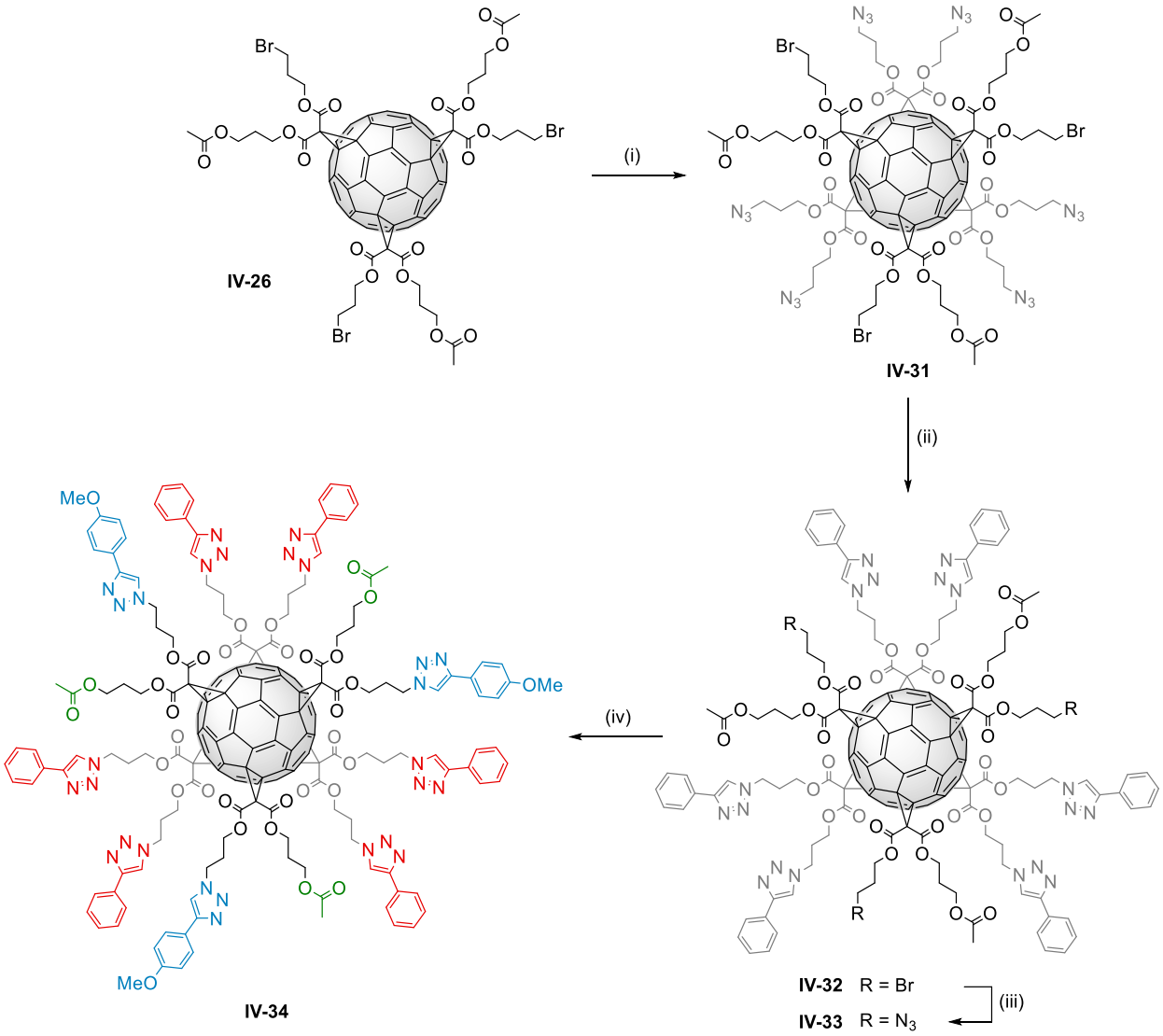


*Figure IV-20 : Illustration of the two different addend zones of the mixed C_{60} hexa-adduct **IV-30**.*

As shown in **Scheme IV-*9***, the preparation of the mixed [3:3] hexa-adduct **IV-34** was performed from the tri-ester **IV-26**. The use of malonate **IV-12** instead of the malonate **IV-27** provided a third different reactive site. Treatment of **IV-26** with **IV-12** under modified Bingel conditions afforded hexa-adduct **IV-31** in 73% yield. Subsequent CuAAC reaction with phenylacetylene gave the first "clicked" derivative (**IV-32**) in an excellent yield (99%). Finally,

conversion of the bromide functions into azides followed by a second CuAAC reaction with 4-ethynylanisole gave the final mixed [3:3] C_{60} hexa-adducts **IV-34** with a (3:3:6) function ratio. As for compound **IV-30**, the chemical structure of **IV-34** was confirmed by ^{1}H and ^{13}C NMR, UV/vis and IR spectroscopies, mass spectrometry and elemental analysis. In the case of **IV-34**, the three different addends zones have been selectively post-functionalized (Figure IV-21).



Scheme IV-9. Reagents and conditions: (i) **IV-12**, CBr_4, DBU, PhMe, rt, 2 h (73%); (ii) Phenylacetylene, $CuSO_4.5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, 30 °C, 12 h (99%); (iii) NaN_3, DMF, rt, 12 h (94%); (iv) 4-ethynylanisole, $CuSO_4.5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, 30 °C, 12 h (90%).

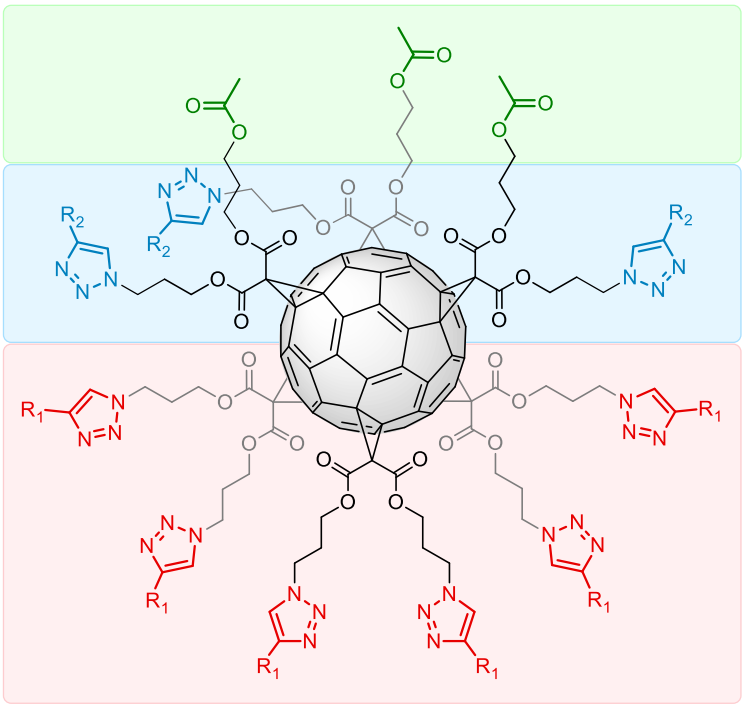


Figure IV-21 : Illustration of the three different addend zones of the mixed hexa-adduct ***IV-34****.*

4. Conclusion.

Based on our efficient methodologies for the preparation of *e,e,e* C_{60} tris-adducts and *e* C_{60} bis-adducts, an easy access to mixed C_{60} hexa-adducts building blocks was possible. The modification of the side chains of the malonate addends has provided various functionalized mixed C_{60} hexa-adducts. The sequential CuAAC reactions has been efficient for the post-functionalization of the C_{60} hexa-adducts. Moreover, the utilization of an esterification reaction has diversified the scope of the post-functionalization possibilities and two more mixed hexa-adducts were obtained.

With the control of the regiochemistry and the stereochemistry of our methodology, up to three different addend zones can be defined according to the mixed C_{60} hexa-adduct. These different addend zones have been selectively post-functionalized. The high tolerance of the CuAAC reactions to a wide variety of functions will thus provide a possible access to unprecedented globular multifunctional nanomaterials with a controlled distribution of functional groups on the spherical framework.

5. Bibliography.

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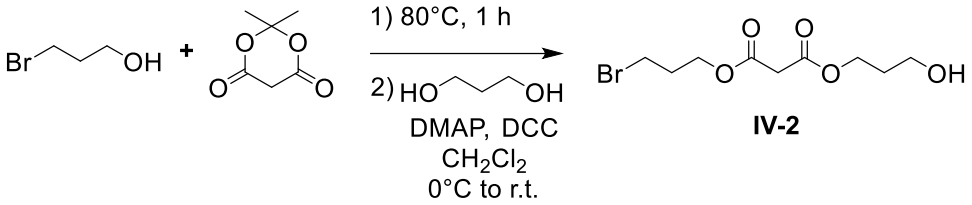
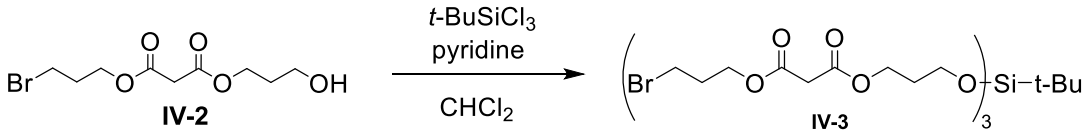
6. Experimental part.

General: Reagents and solvents were purchased as reagent grade and used without further purification. All reactions were performed in standard glassware under an inert Ar atmosphere. Evaporation and concentration were done at water aspirator pressure and drying in vacuo at 10^{-2} Torr. Column chromatography: silica gel 60 (230-400 mesh, 0.040-0.063 mm) was purchased from E. Merck. Thin Layer Chromatography (TLC) was performed on aluminum sheets coated with silica gel 60 F_{254} purchased from E. Merck. IR spectra (cm^{-1}) were recorded on a Perkin–Elmer Spectrum One Spectrophotometer. UV/Visible spectra were recorded on a Perkin-Elmer Lamda 35 UV/Vis Spectrometer. NMR spectra were recorded on a Bruker AC 300 or AC 400 with solvent peaks as reference at 25°C. MALDI-TOF-MS were obtained on a Bruker ULTRAFLEX TOF/TOF mass spectrometer with a dithranol matrix.

Synthesis.

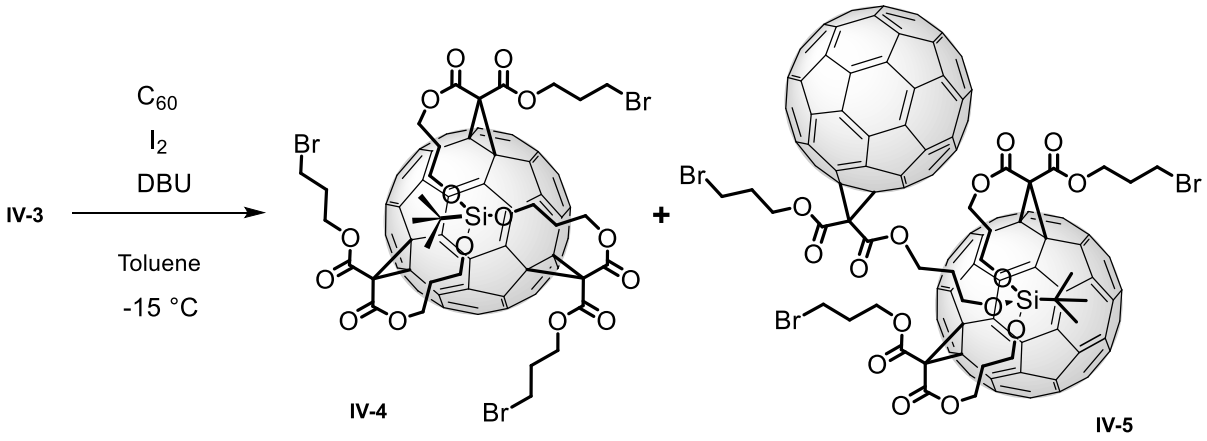


Compound IV-2: 3-Bromopropanol (4.16 mL, 46 mmol) and 2,2-dimethyl-1,3-dioxane-4,6-dione (6.63 g, 46 mmol) were stirred at 80°C. After 1 h the mixture was dried under reduced pressure and used in the next step without further purification. DCC (10.9 g, 53 mmol) was added to a solution of the crude, 3-propanediol (10.0 mL, 138 mmol) and DMAP (1.12 g, 9.2 mmol) in CH_2Cl_2 (110 mL) at 0°C. The resulting mixture was stirred overnight at room temperature, then filtered on SiO_2 (CH_2Cl_2/EtOAc, 8:2) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/EtOAc, 9:1) yielded **IV-2** (6.08 g, 21.5 mmol, 46%) as a colroless oil. IR (neat): $\upsilon = 3451$ (br, OH), 1731 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ= 4.33 (t, ^3J = 6 Hz, 2 H, CH_2CH_2OOC), 4.31 (t, ^3J = 6 Hz, 2 H, CH_2CH_2OOC), 3.73 (t, ^3J = 6 Hz, 2 H, CH_2CH_2OH), 3.47 (t, ^3J = 6 Hz, 2 H, CH_2CH_2Br), 3.41 (s, 2 H, $OOCCH_2COO$), 2.21 (quint., ^3J = 6 Hz, 2 H, $COOCH_2CH_2CH_2Br$), 1.91 (quint., ^3J = 6 Hz, 2 H, $COOCH_2CH_2CH_2OH$) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ= 166.7, 166.4, 63.3, 62.7, 59.2, 41.4, 31.5, 31.4, 29.1 ppm.



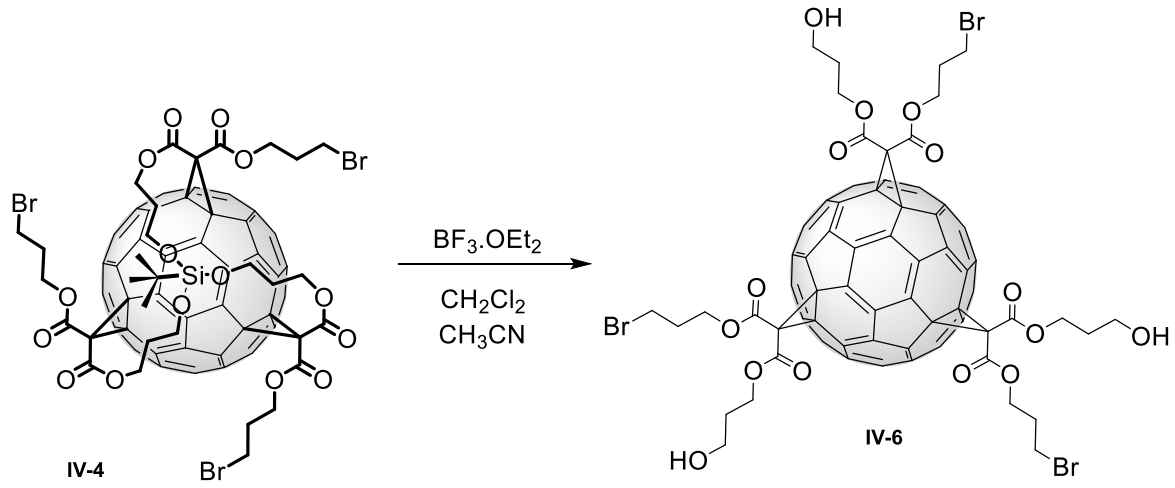
Compound IV-3: *t*-$BuSiCl_3$ (47 mg, 0.25 mmol) was added to a solution of **IV-2** (210 mg, 0.74 mmol) and pyridine (0.07 mL, 0.8 mmol) in CH_2Cl_2 (4 mL). After 18 h, the reaction mixture was filtered on SiO_2 (CH_2Cl_2/MeOH, 97:3) and concentrated. Column chromatography on SiO_2

(CH_2Cl_2 to CH_2Cl_2/MeOH, 99:1) yielded **IV-3** (151 mg, 0.16 mmol, 66%) as a colorless oil. IR (neat): υ = 1732 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.29 (t, ^3J = 6 Hz, 6 H, CH_2CH_2OOC), 4.27 (t, ^3J = 6 Hz, 6 H, CH_2CH_2OOC), 3.85 (t, ^3J = 6 Hz, 6 H, CH_2CH_2OSi), 3.46 (t, ^3J = 6 Hz, 6 H, CH_2CH_2Br), 3.39 (s, 6 H, $OOCCH_2COO$), 2.19 (quint., ^3J = 6Hz, 6 H, $CH_2CH_2CH_2OSi$), 1.90 (quint., ^3J = 6 Hz, 6 H, $CH_2CH_2CH_2Br$), 0.94 (s, 9 H, *t*-BuSi) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.4, 166.3, 63.1, 62.5, 59.5, 41.4, 31.5, 29.1, 26.3, 17.7 ppm.

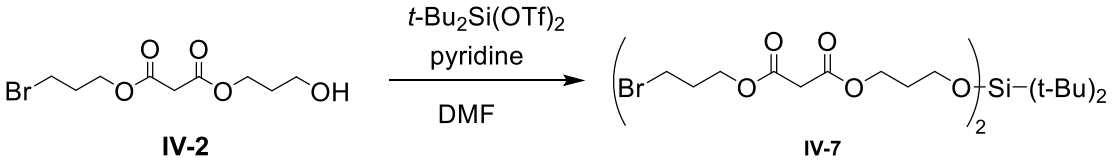


Compound IV-4 & IV-5: DBU (0.81 mL, 5.3 mmol) was added to a solution of C_{60} (550 mg, 0.76 mmol), **IV-3** (710 mg, 0.76 mmol) and I_2 (639 mg, 2.5 mmol) in toluene (1.1 L) at -15°C. The resulting mixture was stirred for 1 h at -15°C, filtered on SiO_2 (cyclohexane to CH_2Cl_2) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 5:5 to 8:2) yielded **IV-4** (150 mg, 91 μmol, 12%) as a red glassy solid and **IV-5** (53 mg, 22 μmol, 3%) as a brown glassy solid. **IV-4:** IR (neat): υ = 1740 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 233 ($1.3x10^5$), 251 ($1.3x10^5$), 283 ($9x10^4$), 302 (sh, $7x10^4$), 483 ($8x10^3$), 563 (sh, $2x10^3$) nm. ^1H NMR ($CDCl_3$, 300 MHz): δ = 4.56 (m, 3 H, CHH'C*H*H'OOC), 4.51 (m, 6 H, CH_2CH_2OOC), 4.24 (m, 3 H, CHH'CH*H*'OOC), 3.60 (m, 6 H, CHH'CH_2OSi), 3.49 (t, ^3J = 6 Hz, 6 H, CH_2CH_2Br), 2.30 (quint., ^3J = 6 Hz, 6 H, $CH_2CH_2CH_2Br$), 1.94 (m, 6 H, CHH'C*HH*'CH_2OSi), 0.89 (s, 9 H, *t*-BuSi) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 163.3, 163.0, 147.0, 146.9, 146.8, 146.7, 146.4 (two peaks), 146.3, 146.1, 145.9, 144.4, 143.5, 143.4, 143.2, 143.1, 142.9, 142.5, 141.6, 141.0, 70.8, 70.1, 64.7, 64.0, 59.7, 52.7, 31.6, 31.2, 28.9, 26.1, 17.6 ppm. MS-MALDI-TOF : 1646.0 ($[M]^+$, calcd for $C_{91}H_{45}O_{15}Br_3Si$: 1646.0). **IV-5:** IR (neat): υ = 1745 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon$ = 256 ($1.5x10^5$), 325 (sh, $5x10^4$), 422 ($3x10^3$), 425 ($3x10^3$), 480 ($3x10^3$), 553 (sh, $2x10^3$) nm. ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.84 (m, 1 H, CHH'C*H*H'OOC), 4.73 (m, 1 H, CHH'C*H*H'OOC), 4.68-4.55 (m, 8 H, CH_2CH_2OOC), 4.40 (m, 1 H, CHH'CH*H'*OOC), 4.30 (m, 1 H, CHH'CH*H'*OOC), 4.06 (m, 2 H, CH_2CH_2OSi), 3.88-3.74 (m, 4 H, CHH'C*HH'*OSi), 3.58 (t, ^3J = 6 Hz, 2 H, CH_2CH_2Br), 3.55 (t, ^3J = 6 Hz, 2 H, CH_2CH_2Br), 3.53 (t, ^3J = 6 Hz, 2 H, CH_2CH_2Br), 2.40 (quint., ^3J = 6 Hz, 2 H, $CH_2CH_2CH_2Br$), 2.34 (m, 4 H, $CH_2CH_2CH_2Br$), 2,15 (quint., ^3J = 6 Hz, 2 H, $CH_2CH_2CH_2OSi$), 1.99 (m, 4 H, $CH_2CH_2CH_2OSi$), 0.91 (s, 9 H, *t*-BuSi) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.5 (two peaks), 163.4, 163.2, 162,9, 148.3, 147.4, 147.3, 146.7, 146.6, 146.5, 146.4, 146.2, 146.1, 146.0, 145.7, 145.6, 145.3 (two peaks), 145.2 (three peaks), 145.1 (three peaks), 145.0 (two peaks), 144.9 (two peaks), 144.8,

144.7 (four peaks), 144.6 (two peaks), 144,5, 144.3, 144.2, 144.1, 143.9 (two peaks), 143.8, 143.7 (two peaks), 143.6 (two peaks), 143.5 (two peaks), 143.1 (four peaks), 143.0 (two peaks), 142.3 (two peaks), 142.2, 142.1, 141.9 (three peaks), 141.7 (two peaks), 141.5, 141.0 (two peaks), 140.7, 139.6, 139.5, 139.3, 138.9, 138.8, 138.7, 71.7, 71.5 (three peaks), 70.4, 64.9 (two peaks), 64.8, 64.6, 63.8, 63.3, 60.0, 59.6, 58.6, 53.7, 52.1, 51.3, 32.1, 31.8, 31.5, 31.3, 29.1, 29.0 (two peaks), 26.3, 17.6 ppm. MS-MALDI-TOF : 2367.0 ($[M+H]^+$, calcd for $C_{151}H_{46}O_{15}Br_3Si$: 2367.0).

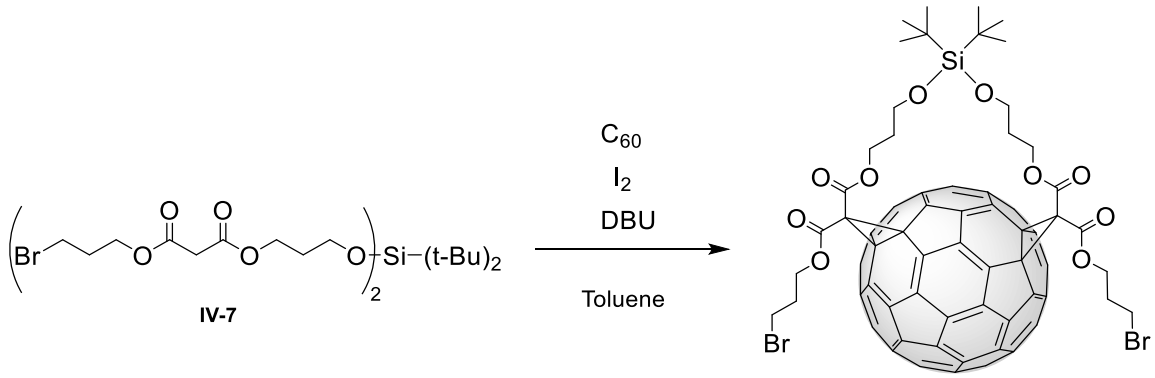


Compound IV-6: $BF_3.OEt_2$ (40 μL, 267 μmol) was added to a solution of **IV-4** (44 mg, 27 μmol) in CH_2Cl_2/MeCN (9/4 mL). The solution was stirred overnight at room temperature, then filtered on SiO_2 (THF) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 97:3) yielded **IV-6** (36 mg, 23 μmol, 86%) as a red glassy solid. IR (neat): υ= 3208 (br, OH), 1742 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 235 ($8x10^4$), 251 ($9x10^4$), 283 ($6x10^4$), 305 (sh, $4x10^4$), 396 (sh, $2x10^3$), 483 ($4x10^3$), 523 (sh, $3x10^3$), 562 (sh, $1x10^3$) nm. ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.58-4.52 (m, 3 H, $CH_2CHH'OOOC$), 4.49-4.42 (m, 6 H, $CHH'CHH'OOC$), 4.25-4.21 (m, 3 H, $CHH'CHH'OOC$), 3.74-3.70 (m, 3 H, $CHH'CHH'OH$), 3.62-3.56 (m, 3 H, $CHH'CHH'OH$), 3.49 (t, ^3J = 6 Hz, 6 H, CH_2CH_2Br), 2.30 (quint., ^3J = 6 Hz, $CH_2CH_2CH_2Br$), 1.88 (m, 6 H, $CHH'CHH'CHH'$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.1, 163.0, 147.2, 147.0, 146.9, 146.8, 146.4, 146.3, 146.1, 145.9, 145.8, 144.3, 143.5, 143.3, 143.2, 143.1, 142.7, 141.3, 140.9, 70.9, 70.0, 64.6, 62.6, 57.8, 52.6, 31.2, 28.9, 28.7 ppm. MS-MALDI-TOF : 1564.0 ($[M]^+$, calcd for $C_{87}H_{39}O_{15}Br_3$: 1564.0).



IV-2 **IV-7**

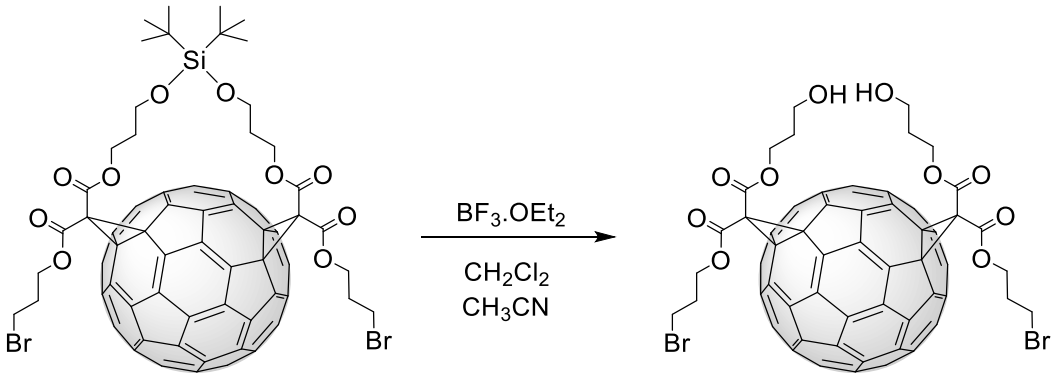
Compound IV-7: A solution of **IV-2** (3.53 g, 12.46 mmol), pyridine (1.26 mL, 15.5 mmol) and (*t*-Bu)$_2$Si(OTf)$_2$ (2.02 mL, 6.22 mmol) in anhydrous DMF (20 mL) was stirred at room temperature overnight. Then, H_2O was added and the aqueous layer extracted with Et_2O. The organic layer was washed with H_2O and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2 to CH_2Cl_2) yielded **IV-7** (3.00 g, 4.22 mmol, 68%) as a colorless oil. IR (neat): υ = 1735 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 4.30 (t, ^3J = 6 Hz, 8 H, CH_2CH_2OOC), 3.91 (t, ^3J = 6 Hz, 4 H, CH_2CH_2OSi), 3.46 (t, ^3J = 6 Hz, 4 H, CH_2CH_2Br), 3.39 (s, 4 H, $OOCCH_2COO$), 2.20 (quint., ^3J = 6 Hz, 4 H, $COOCH_2CH_2CH_2Br$), 1.91 (quint., ^3J = 6 Hz, 4 H, $COOCH_2CH_2CH_2OSi$), 1.00 (s, 18 H, Si(*t*-Bu)$_2$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 166.4, 166.3, 63.1, 62.7, 60.1, 41.4, 31.7, 31.5, 29.1, 27.8, 21.2 ppm.



IV-7 **IV-8**

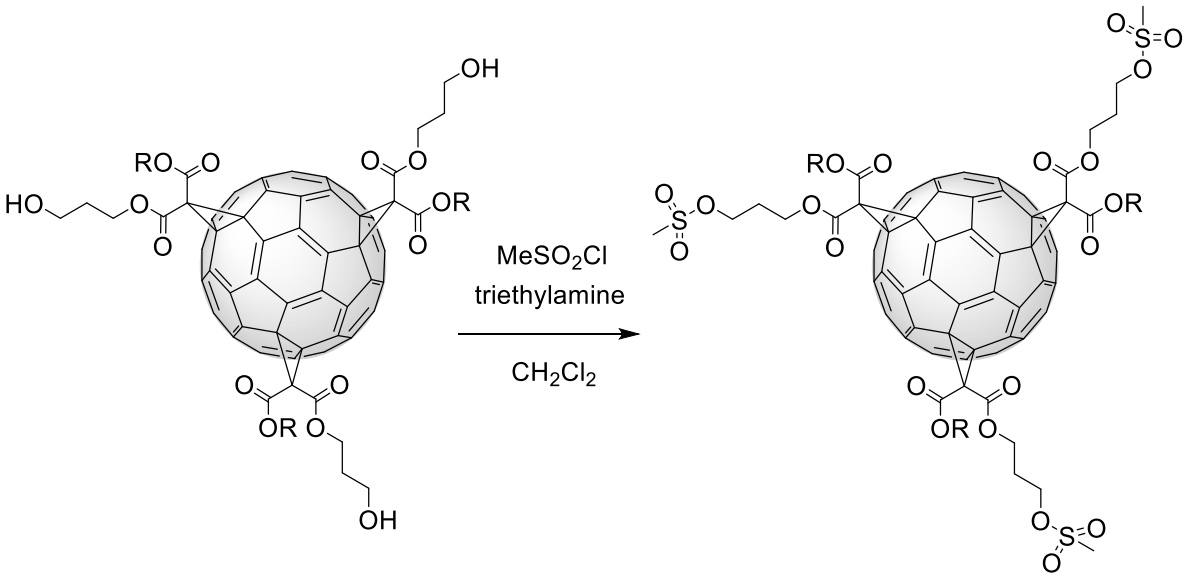
Compound IV-8: DBU (0.73 mL, 4.9 mmol) was added to a solution of C_{60} (700 mg, 0.97 mmol), **IV-7** (690 mg, 0.97 mmol) and I_2 (616 mg, 2.4 mmol) in toluene (1.4 L) at room temperature. The resulting mixture was stirred for 1 h, directly filtered on SiO_2 (cyclohexane then CH_2Cl_2) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 5:5) yielded **IV-8** (660 mg, 0.46 mmol, 48%) as a brown glassy solid. IR (neat): υ = 1747 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 252 (1.4x10^5), 313 (sh, 5x10^4), 397 (5x10^3), 409 (sh, 3x10^3), 421 (3x10^3), 477 (4x10^3) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 4.75 (m, 2 H), 4.60 (m, 4 H), 4.41 (m, 2 H), 3.89 (m, 2 H), 3.81 (m, 2 H), 3.54 (t, ^3J = 6 Hz, 2 H, CH_2CH_2Br), 3.53 (t, ^3J = 6 Hz, 2 H, CH_2CH_2Br), 2.35 (m, 4 H), 1.99 (m, 4H), 1.02 (s, 9H, *t*-BuSi), 0.90 (s, 9H, *t*-BuSi) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 164.1, 163.4, 163.2, 163.1, 148.5, 147.4, 147.3, 146.8, 146.6, 146.5 (two peaks), 146.3, 146.2 (two peaks), 146.1, 145.8, 145.6, 145.3, 145.2, 145.1, 145.0, 144.9, 144.8, 144.7 (three peaks), 144.6, 144.5, 144.4, 144.2, 144.1, 144.0, 143.9, 143.8, 143.7 (two peaks), 143.6, 143.5 (two peaks), 143.2, 143.1 (two peaks), 142.3, 142.1, 142.0 (three peaks), 141.7, 141.5, 141.4, 140.6, 139.4 (two peaks), 138.8, 138.7, 71.6, 71.5 (two peaks), 70.3, 64.8, 64.4, 63.5, 60.3, 59.7, 53.9,

51.3, 32.2, 31.7, 31.4, 31.3, 29.0, 28.8, 27.8, 21.3 ppm. MS-MALDI-TOF: 1423.0 ($[M+H]^+$, calcd for $C_{86}H_{43}O_{10}Br_2Si$: 1423.1).



IV-8 **IV-9**

Compound IV-9: A solution of **IV-8** (1.32 g, 0.93 mmol) and $BF_3.OEt_2$ (1.53 mL, 12.0 mmol) in CH_2Cl_2/CH_3CN (40/25 mL) was stirred overnight at room temperature, then filtered on SiO_2 (CH_2Cl_2/MeOH, 95 :5) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 97:3) yielded **IV-9** (1.08 g, 0.85 mmol, 91%) as a brown glassy solid. IR (neat): $\upsilon = 3405$ (br, OH), 1742 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 252 ($1x10^5$), 313 (sh, $5x10^4$), 397 ($6x10^3$), 409 (sh, $4x10^3$), 421 ($4x10^3$), 481 ($5x10^3$) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.58 (m, 8 H, CH_2CH_2OOC), 3.77 (t, ^3J = 6 Hz, 2 H, CH_2CH_2OH), 3.76 (t, ^3J = 6 Hz, 2 H, CH_2CH_2OH), 3.52 (t, ^3J = 6 Hz, 4 H, CH_2CH_2Br), 2.34 (m, 4 H, $CH_2CH_2CH_2OH$), 2.03 (m, 4 H, $CH_2CH_2CH_2Br$), 1.95 (br s, 2 H, O*H*) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.7, 163.5, 163.4, 163.3, 147.4 (two peaks), 147.3 (two peaks), 146.6, 146.5 (two peaks), 146.1, 146.0, 145.7, 145.6, 145.4, 145.1, 145.0, 144.8 (two peaks), 144.7 (three peaks), 144.4, 144.3, 144.1, 143.9 (two peaks), 143.8, 143.7, 143.5 (two peaks), 143.2 (two peaks), 142.9, 142.8, 142.5, 142.3, 142.0 (two peaks), 141.7, 141.6, 141.5, 138.8, 138.7, 138.6, 71.5, 71.4 (two peaks), 70.2, 64.9, 64.8, 64.4 (two peaks), 59.0, 53.4, 51.2, 31.5, 31.4 (three peaks), 29.1 ppm. MS-MALDI-TOF: 1281.9 ($[M]^+$, calcd for $C_{78}H_{26}O_{10}Br_2$: 1281.9).



III-14 R = CH_2CH_3

IV-6 R = $CH_2CH_2CH_2Br$

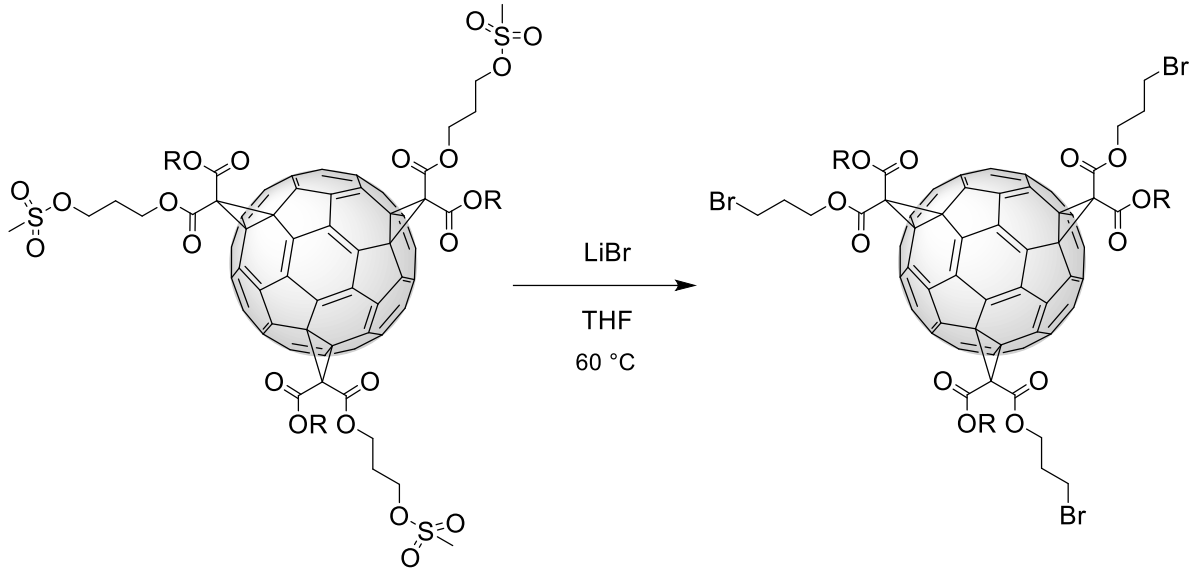
IV-10a R = CH_2CH_3

IV-10b R = $CH_2CH_2CH_2Br$

Compound IV-10a: $MeSO_2Cl$ (0.11 mL, 1.44 mmol) was added to a solution of **III-14** (311 mg, 0.24 mmol) and triethylamine (0.2 mL, 1.44 mmol) in CH_2Cl_2 (40 mL) at 0°C. After 2 h, the mixture was filtered on SiO_2 (CH_2Cl_2/MeOH, 95:5) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 99:1) yielded **IV-10a** (316 mg, 0.21 mmol, 86%) as a red glassy solid. IR (neat): υ = 1740 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 237 ($1.2x10^5$), 251 ($1.3x10^5$), 282 ($9x10^4$), 305 (sh, $6x10^4$), 484 ($7x10^3$), 524 (sh, $4x10^3$), 565 (sh, $2x10^3$) nm. ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.43 (m, 12 H, CH_2OOC), 4.30 (t, ^3J = 6 Hz, 6 H, $CH_2CH_2OSO_2CH_3$), 3.03 (s, 9 H, OSO_2CH_3), 2.17 (quint., ^3J = 6 Hz, 6 H, $CH_2CH_2CH_2$), 1.37 (t, ^3J = 7Hz, 9 H, CH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.2, 147.0, 146.8, 146.7, 146.6, 146.5, 146.4, 146.3, 145.7, 145.6, 144.9, 144.6, 144.4, 143.4, 142.7, 142.6, 141.8, 141.6, 141.0, 70.7, 69.9, 65.8, 63.4, 62.6, 52.6, 37.4, 28.4, 14.2 ppm. MS-MALDI-TOF: 1518.2 ($[M]^+$, calcd for $C_{87}H_{42}O_{21}S_3$: 1518.1).

Compound IV-10b: $MeSO_2Cl$ (16 μL, 207 μmol) was added to a solution of **IV-6** (36 mg, 23 μmol) and triethylamine (29 μL, 207 μmol) in CH_2Cl_2 (3 mL) at 0°C. After 30 min, the mixture was filtered on SiO_2 (CH_2Cl_2/MeOH, 97:3) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 99:1) yielded **IV-10b** (39 mg, 22 μmol, 94%) as a red glassy solid. IR (neat): υ = 1740 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 234 ($1x10^5$), 251 ($1x10^5$), 283 ($7x10^4$), 304 (sh, $5x10^4$), 483 ($7x10^3$), 523 (sh, $4x10^3$), 564 (sh, $2x10^3$) nm. ^1H NMR ($CDCl_3$, 300 MHz): δ = 4.52 (dt, ^2J = 1.5 Hz & ^3J = 6 Hz, 6 H, CH_2CH_2OOC), 4.43 (t, ^3J = 6 Hz, 6 H, CH_2CH_2OOC), 4.30 (t, ^3J = 6 Hz, 6 H, $CH_2CH_2OSO_2CH_3$), 3.47 (t, ^3J = 6 Hz, 6 H, CH_2CH_2Br), 3.03 (s, 9 H, OSO_2CH_3), 2.29 (quint., ^3J = 6 Hz, 6 H, $CH_2CH_2CH_2Br$), 2.18 (quint., ^3J = 6 Hz, 6 H, $CH_2CH_2CH_2OSO_2CH_3$) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 163.1 (two peaks), 147.0, 146.9, 146.7, 146.6, 146.5, 146.4, 145.7, 145.4, 145.3, 144.8, 144.5, 143.5, 142.7, 142.3, 141.5, 141.4, 141.1, 70.6, 69.8, 65.7,

64.8, 62.8, 52.6, 37.5, 31.2, 29.1, 28.4 ppm. MS-MALDI-TOF: 1797.9 (100%, $[M]^+$, calcd for $C_{90}H_{45}O_{21}S_3Br_3$: 1797.9), 1702.9 (12%, $[M\text{-}CH_2Br]^+$, calcd for $C_{89}H_{43}O_{21}S_3Br_2$: 1703.0).



IV-10a R = CH_2CH_3

IV-10b R = $CH_2CH_2CH_2Br$

IV-11a R = CH_2CH_3

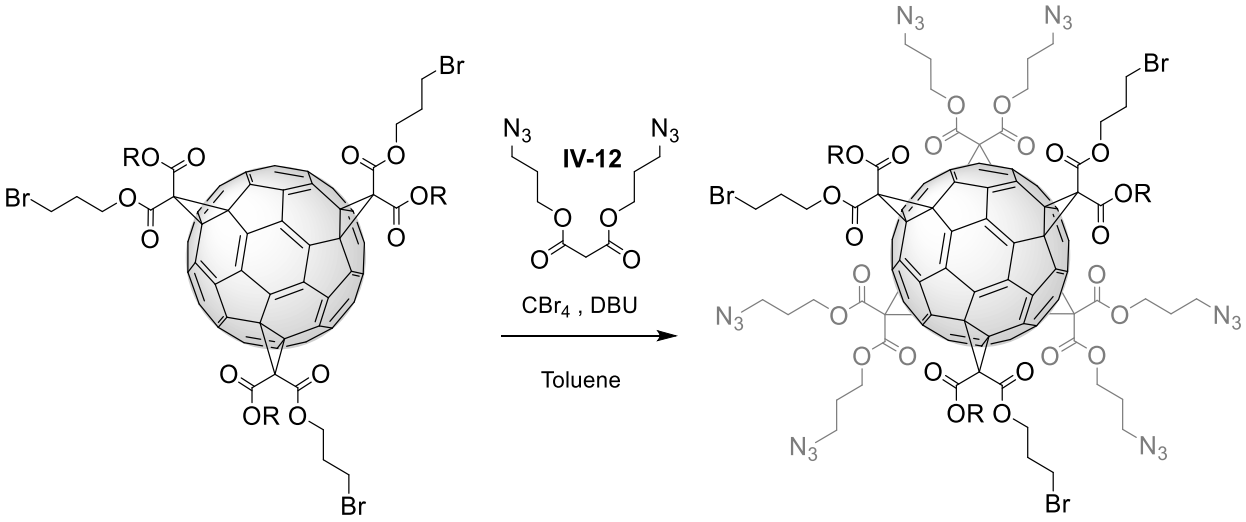
IV-11b R = $CH_2CH_2CH_2Br$

Compound IV-11a: A solution of **IV-10a** (304 mg, 0.20 mmol) and LiBr (104 mg, 1.2 mmol) was stirred overnight at 60°C, then filtered on SiO_2 (CH_2Cl_2) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 6:4) yielded **IV-11a** (244 mg, 0.16 mmol, 83%) as a red glassy solid. IR (neat): υ = 1743 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 235 ($1.1x10^5$), 251 ($1.1x10^5$), 282 ($8x10^4$), 303 (sh, $6x10^4$), 484 ($7x10^3$), 525 (sh, $4x10^3$), 564 (sh, $2x10^3$) nm. ^1H NMR ($CDCl_3$, 400 MHz):δ = 4.42 (m, 12 H, CH_2OOC), 3.46 (t, ^3J = 6 Hz, 6 H, CH_2CH_2Br), 2.25 (quint., ^3J = 6 Hz, 6 H, $CH_2CH_2CH_2$), 1.38 (t, ^3J = 7 Hz, 9 H, CH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.3, 163.2, 147.1, 146.8, 146.7, 146.6, 146.5 (two peaks), 146.3, 145.7, 145.5, 144.9, 144.8, 144.3, 143.4, 142.7, 142.5, 141.9, 141.7, 141.0, 70.8, 70.0, 64.5, 63.3, 52.6, 31.3, 28.9, 14.2 ppm. MS-MALDI-TOF: 1474.0 ($[M]^+$, calcd for $C_{84}H_{33}O_{12}Br_3$: 1474.0).

Compound IV-11b: A solution of **IV-10b** (192 mg, 107 μmol) and LiBr (56 mg, 640 μmol) in THF (10 mL) was stirred overnight at 60°C, then filtered on SiO_2 (CH_2Cl_2) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2) yielded **IV-11b** (184 mg, 105 μmol, 98%) as a red glassy solid. IR (neat): υ = 1741 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 235 ($1.1x10^5$), 251 ($1.1x10^5$), 282 ($8x10^4$), 305 (sh, $6x10^4$), 484 ($6x10^3$), 524 (sh, $4x10^3$), 565 (sh, $2x10^3$) nm. ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.50 (m, 6 H, CH_2CH_2OOC), 4.45 (m, 6 H, CH_2CH_2OOC), 3.47 (t, ^3J = 6 Hz, 6 H, CH_2CH_2Br), 3.45 (t, ^3J = 6 Hz, 6 H, CH_2CH_2Br), 2.29 (quint., ^3J = 6 Hz, 6 H, $CH_2CH_2CH_2Br$), 2.26 (quint., ^3J = 6 Hz, 6 H, $CH_2CH_2CH_2Br$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.1 (two peaks), 147.1, 146.9, 146.7, 146.6 (two peaks), 146.5, 146.3, 145.7, 145.3, 145.2, 144.9, 144.5, 143.5, 142.7, 142.3, 141.6, 141.3, 141.0, 70.7, 69.8, 64.7 (two peaks), 52.6, 31.3, 31.2, 29.0 ppm. MS-

MALDI-TOF: 1751.8 (100%, $[M]^+$, calcd for $C_{87}H_{36}O_{12}Br_6$: 1751.7), 1614.8 (16%, $[M-(OCH_2CH_2CH_2Br)]^+$, calcd for $C_{84}H_{30}O_{11}Br_5$: 1614.8).

Compound IV-12: IV-12 was prepared as described in *Chem. Commun.* **2008**, 2450–2452.

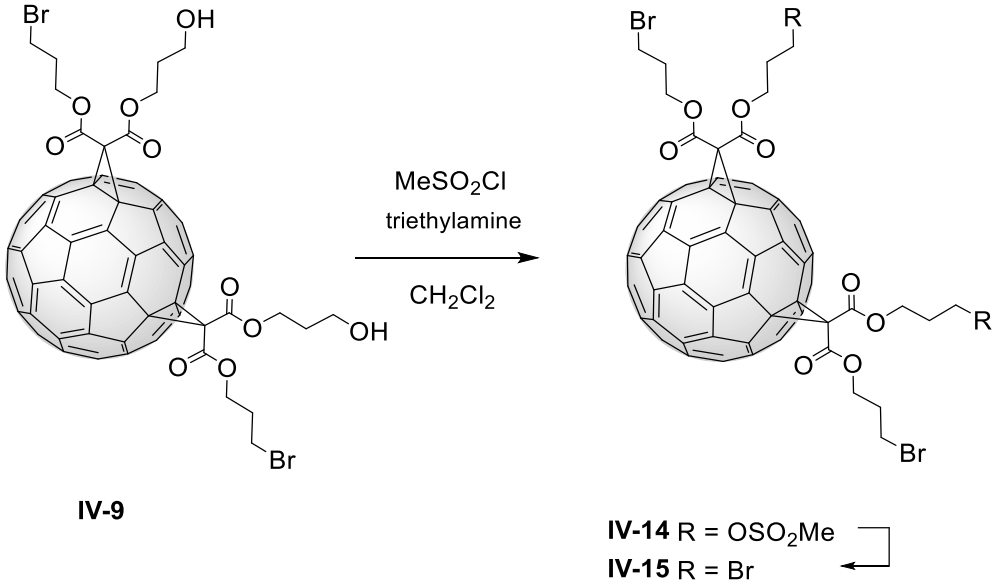


IV-11a R = CH_2CH_3
IV-11b R = $CH_2CH_2CH_2Br$

IV-13a R = CH_2CH_3
IV-13b R = $CH_2CH_2CH_2Br$

Compound IV-13a: DBU (0.43 mL, 2.9 mmol) was added to a solution of **IV-2** (240 mg, 0.16 mmol), **IV-3** (220 mg, 0.81 mmol) and CBr_4 (2.12 g, 6.4 mmol) in toluene (35 mL). The mixture was stirred overnight at room temperature, then filtered on SiO_2 (CH_2Cl_2/MeOH, 98:2) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/EtOAc, 96:4) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) yielded **IV-4** (155 mg, 68 μmol, 42%) as an orange glassy solid. IR (neat): υ = 2099 (N_3), 1742 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.42 (t, ^3J = 6 Hz, 6 H, $COOCH_2CH_2CH_2Br$), 4.36 (t, ^3J = 6 Hz, 12 H, $COOCH_2CH_2CH_2N_3$), 4.34 (q, ^3J = 7 Hz, 6 H, $COOCH_2CH_3$), 3.44 (t, ^3J = 6 Hz, 6 H, CH_2CH_2Br), 3.39 (t, ^3J = 6 Hz, 12 H, $CH_2CH_2N_3$), 2.24 (quint., ^3J = 6 Hz, 6 H, $CH_2CH_2CH_2Br$), 1.96 (quint., ^3J = 6 Hz, 12 H, $CH_2CH_2CH_2N_3$), 1.34 (t, ^3J = 7 Hz, 9 H, CH_2CH_3) ppm.

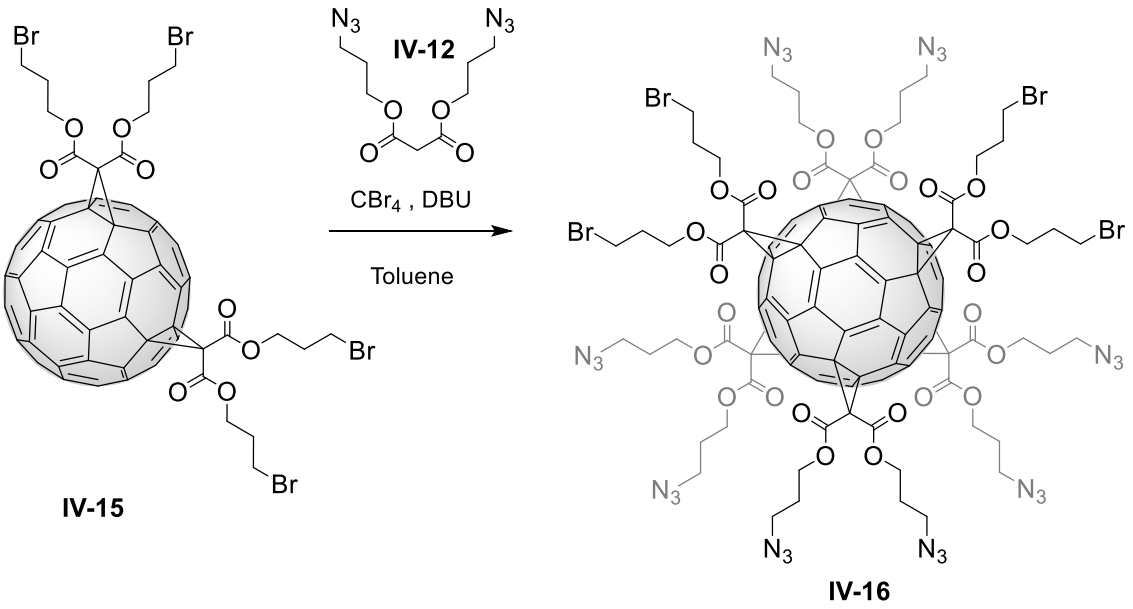
Compound IV-13b: DBU (0.14 mL, 0.9 mmol) was added to a solution of **IV-11b** (102 mg, 58 μmol), **IV-12** (94 mg, 0.35 mmol) and CBr_4 (965 mg, 2.9 mmol) in toluene (20 mL). The resulting mixture was stirred overnight at room temperature, then filtered on SiO_2 (CH_2Cl_2/MeOH, 98:2) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/EtOAc, 98:2) yielded **IV-13b** (94 mg, 37 μmol, 63%) as an orange glassy solid. IR (neat): υ = 2097 (N_3), 1741 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 4.43 (t, ^3J = 6 Hz, 12 H, CH_2CH_2OOC), 4.37 (t, ^3J = 6 Hz, 12 H, CH_2CH_2OOC), 3.44 (t, ^3J = 6 Hz, 12 H, $CH_2CH_2N_3$), 3.40 (t, ^3J = 6 Hz, 12 H, CH_2CH_2Br), 2.25 (quint., ^3J = 6 Hz, 12 H, $CH_2CH_2CH_2Br$), 1.97 (quint., ^3J = 6 Hz, 12 H, $CH_2CH_2CH_2N_3$) ppm.



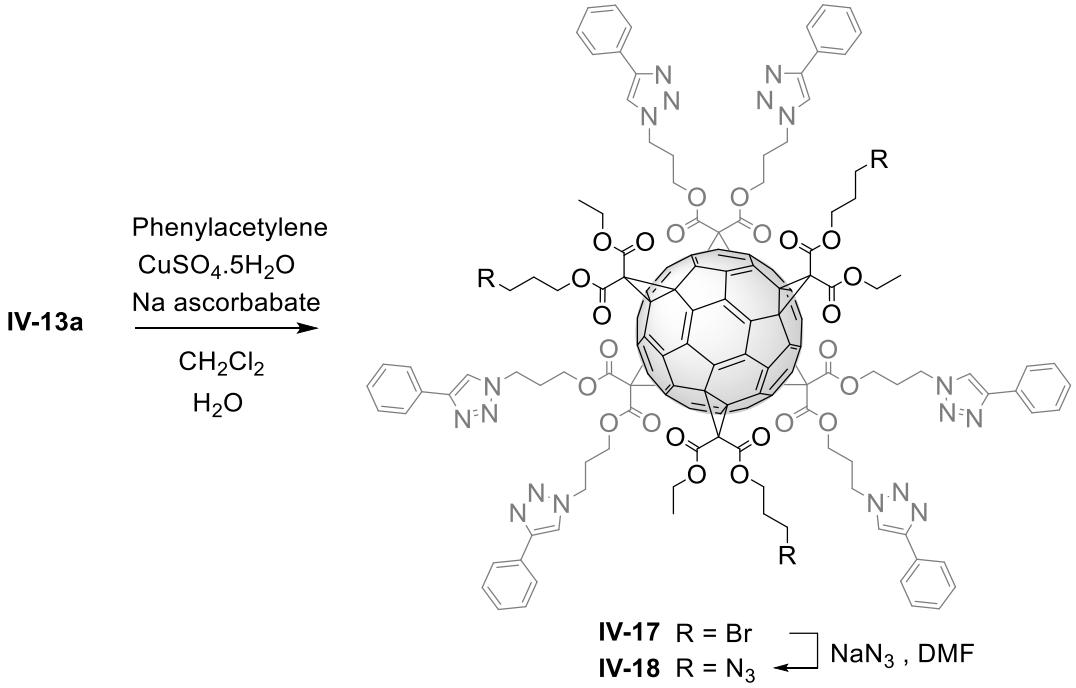
Compound IV-14: Methane sulfonyl chloride (0.27 mL, 3.5 mmol) in CH_2Cl_2 (2 mL) was added slowly to a solution of **IV-9** (1.30 g, 1.0 mmol) and triethylamine (0.56 mL, 4.0 mmol) in CH_2Cl_2 (145 mL) at 0°C. The mixture was stirred at 0°C for 15 min, then filtered on SiO_2 (CH_2Cl_2/EtOAc, 9:1) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/EtOAc, 97:3) yielded **IV-14** (1.37 g, 0.95 mmol, 93%) as a brown glassy solid. IR (neat): $\upsilon = 1739$ (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 252 (1.4x10^5), 312 (sh, 5x10^4), 397 (5x10^3), 408 (sh, 3x10^3), 421 (3x10^3), 480 (4x10^3) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.58 (m, 8 H, CH_2CH_2OOC), 4.37 (t, ^3J = 6 Hz, 2 H, CH_2CH_2OS), 4.35 (t, ^3J = 6 Hz, 2 H, CH_2CH_2OS), 3.51 (t, ^3J = 6 Hz, 4 H, CH_2CH_2Br), 3.06 (s, 3 H, $OOSCH_3$), 3.05 (s, 3 H, $OOSCH_3$), 2.34 (m, 4 H), 2.25 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.3 (two peaks), 163.2 (two peaks), 147.4, 147.2, 146.6 (two peaks), 146.5, 146.1 (two peaks), 146.0, 145.7, 145.5, 145.4, 145.1, 145.0, 144.9, 144.8 (two peaks), 144.7, 144.4, 144.1 (two peaks), 143.8 (two peaks), 143.7 (two peaks), 143.6 (two peaks), 143.2, 143.1, 143.0 (two peaks), 142.8, 142.5, 142.4, 142.1, 141.7, 141.5 (two peaks), 138.8, 138.7 (two peaks), 71.4, 71.3, 70.1, 65.7 (two peaks), 65.0, 64.9, 63.0, 53.2, 51.0, 37.5, 31.3, 29.1, 28.5 (two peaks) ppm. MS-MALDI-TOF: 1437.9 ([M]$^+$, calcd for $C_{80}H_{30}O_{14}S_2Br_2$: 1437.9).

Compound IV-15: A solution of **IV-25** (1.29 g, 0.89 mmol) and LiBr (0.31 g, 3.6 mmol) in THF (40 mL) was stirred at 60°C for 21 h. Then the mixture was filtered on SiO_2 (CH_2Cl_2) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 6:4) yielded **IV-15** (1.21 g, 0.86 mmol, 96%) as a brown glassy solid. IR (neat): $\upsilon = 1745$ (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 252 (2x10^5), 313 (sh, 5x10^4), 397 (9x10^3), 409 (sh, 6x10^3), 421 (5x10^3), 482 (6x10^3) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.57 (m, 8 H, CH_2CH_2OOC), 3.52 (t, ^3J = 6 Hz, 6 H, CH_2CH_2Br), 3.50 (t, ^3J = 6 Hz, 2 H, CH_2CH_2Br), 2.34 (m, 8 H, $CH_2CH_2CH_2Br$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.3 (two peaks), 163.2, 147.4, 146.6, 146.5, 146.1 (two peaks), 145.7, 145.4, 145.1, 145.0, 144.9, 144.8, 144.7, 144.5, 144.2, 144.1, 143.8 (two peaks), 143.6, 143.2, 143.0, 142.5,

142.1, 141.6 (two peaks), 138.8, 138.7, 71.4 (two peaks), 70.1, 64.9 (two peaks), 53.2, 51.0, 31.4, 31.3, 29.0 ppm. MS-MALDI-TOF: 1408.2 ([M]$^+$, calcd for $C_{78}H_{24}O_8Br_4$: 1407.8).



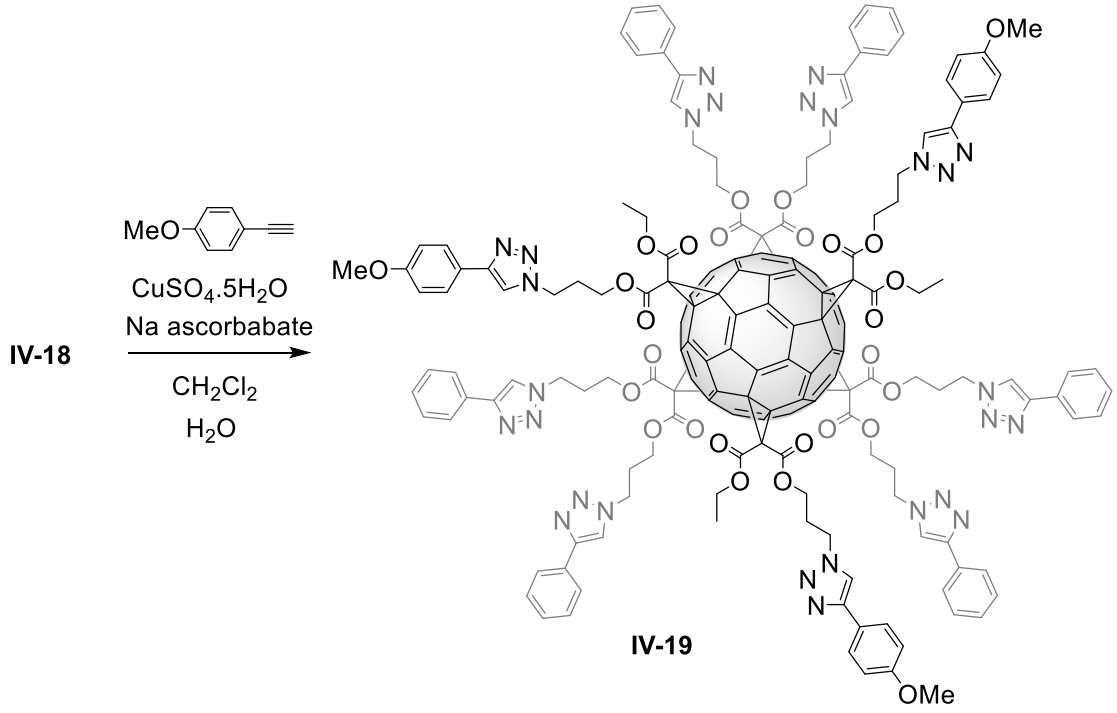
Compound IV-16: DBU (0.57 mL, 3.8 mmol) was added to a solution of **IV-15** (270 mg, 0.19 mmol), **IV-12** (311 mg, 1.15 mmol) and CBr_4 (3.18 g, 9.6 mmol) in toluene (45 mL). After 22 h, the mixture was filtered on SiO_2 (CH_2Cl_2/EtOAc, 95:5) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 8:2 to CH_2Cl_2/EtOAc, 96:4) yielded **IV-16** (267 mg, 0.11 mmol, 56%) as an orange glassy solid. IR (neat): υ = 2097 (N_3), 1742 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.42 (t, ^3J = 6 Hz, 8 H, CH_2CH_2OOC), 4.35 (t, ^3J = 6 Hz, 16 H, CH_2CH_2OOC), 3.43 (t, ^3J = 6 Hz, 8 H, CH_2CH_2Br), 3.38 (t, ^3J = 6 Hz, 16 H, $CH_2CH_2N_3$), 2.23 (m, 8 H, $CH_2CH_2CH_2Br$), 1.96 (m, 16 H, $CH_2CH_2CH_2N_3$) ppm.



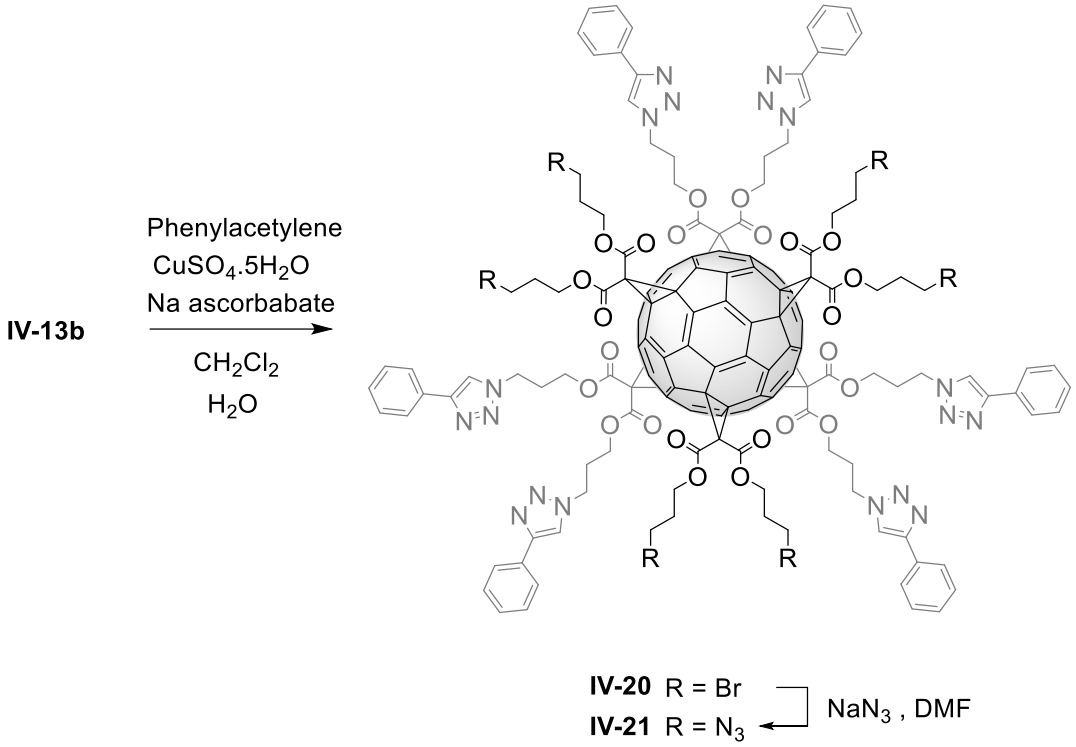
Compound IV-17: A solution of **IV-13a** (150 mg, 66 μmol), phenylacetylene (0.08 mL, 0.76 mmol), $CuSO_4.5H_2O$ (5 mg, 19 μmol) and sodium ascorbate (10 mg, 50 μmol) in CH_2Cl_2/H_2O (2 : 1 mL) was stirred at 30°C for 15 h, then CH_2Cl_2 was added, the organic layer washed with H_2O and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 98:2) yielded **IV-17** (179 mg, 62 μmol, 94%) as an orange glassy solid. IR (neat): υ = 1741 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 246 ($1.5x10^5$), 266 (sh, $8x10^4$), 282 ($7x10^4$), 317 ($4x10^4$), 336 ($3x10^4$) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.86 (s, 3 H, $H_{triazole}$), 7.82 (s, 3 H, $H_{triazole}$), 7.79 (m, 12 H, ArH_o), 7.36 (m, 12 H, ArH_m), 7.30 (m, 6 H, ArH_p), 4.40 (m, 30 H, CH_2CH_2OOC and $CH_2CH_2N_{triazole}$), 4.28 (q, ^3J = 7 Hz, 6 H, $COOCH_2CH_3$), 3.42 (t, ^3J = 6 Hz, 6 H, CH_2CH_2Br), 2.34 (m, 12 H, $CH_2CH_2CH_2N_{triazole}$), 2.21 (quint., ^3J = 6 Hz, 6 H, $CH_2CH_2CH_2Br$), 1.28 (t, ^3J = 7 Hz, 9 H, CH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 163.6, 163.5 (two peaks), 163.4, 147.9 (two peaks), 146.2, 146.0 (two peaks), 145.7 (two peaks), 145.4, 141.4 (two peaks), 141.2, 141.1 (two peaks), 141.0, 130.5 (two peaks), 128.8 (two peaks), 128.2, 125.8, 125.7, 120.1 (two peaks), 69.3, 69.2, 69.1, 69.0, 64.6, 63.7, 63.4, 46.8, 45.4, 45.3, 31.3, 29.3, 29.0, 14.1 ppm. MS-MALDI-TOF: 2892.8 ($[M+H]^+$, calcd for $C_{159}H_{106}O_{24}N_{18}Br_3$: 2892.5).

Compound IV-18: IV-17 (79 mg, 27 μmol) and NaN_3 (10 mg, 150 μmol) in DMF (2 mL) were stirred at room temperature. After 17 h, the product was precipitated with H_2O/Et_2O and resolubilized in CH_2Cl_2, the organic layer washed with H_2O and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/MeOH, 98:2) yielded **IV-18** (73 mg, 26 μmol, 96%) as an orange glassy solid. IR (neat): υ = 2099 (N_3), 1741 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.86 (s, 3 H, $H_{triazole}$), 7.83 (s, 3 H, $H_{triazole}$), 7.81 (d, ^3J = 8 Hz, 6 H, ArH_o), 7.78 (d, ^3J = 8 Hz, 6 H, ArH_o), 7.38 (t, ^3J = 8 Hz, 6 H, ArH_m), 7.36 (t, ^3J = 8 Hz, 6 H, ArH_m), 7.30 (t, ^3J = 8 Hz, 6 H, ArH_p), 4.47 (t, ^3J = 6 Hz, 12 H, $CH_2CH_2N_{triazole}$), 4.44 (t, ^3J = 6 Hz, 12 H, $CH_2CH_2N_{triazole}$), 4.36 (m, 18 H,

CH_2CH_2OOC), 4.28 (q, ^3J = 7 Hz, 6 H, $COOCH_2CH_3$), 3.37 (t, ^3J= 6 Hz, $CH_2CH_2N_3$), 2.37 (m, 6 H, $CH_2CH_2CH_2N_{triazole}$), 2.32 (m, 6 H, $CH_2CH_2CH_2N_{triazole}$), 1.94 (quint., ^3J = 6 Hz, 6 H, $CH_2CH_2CH_2Br$), 1.28 (t, ^3J = 7 Hz, 9 H, CH_2CH_3) ppm.



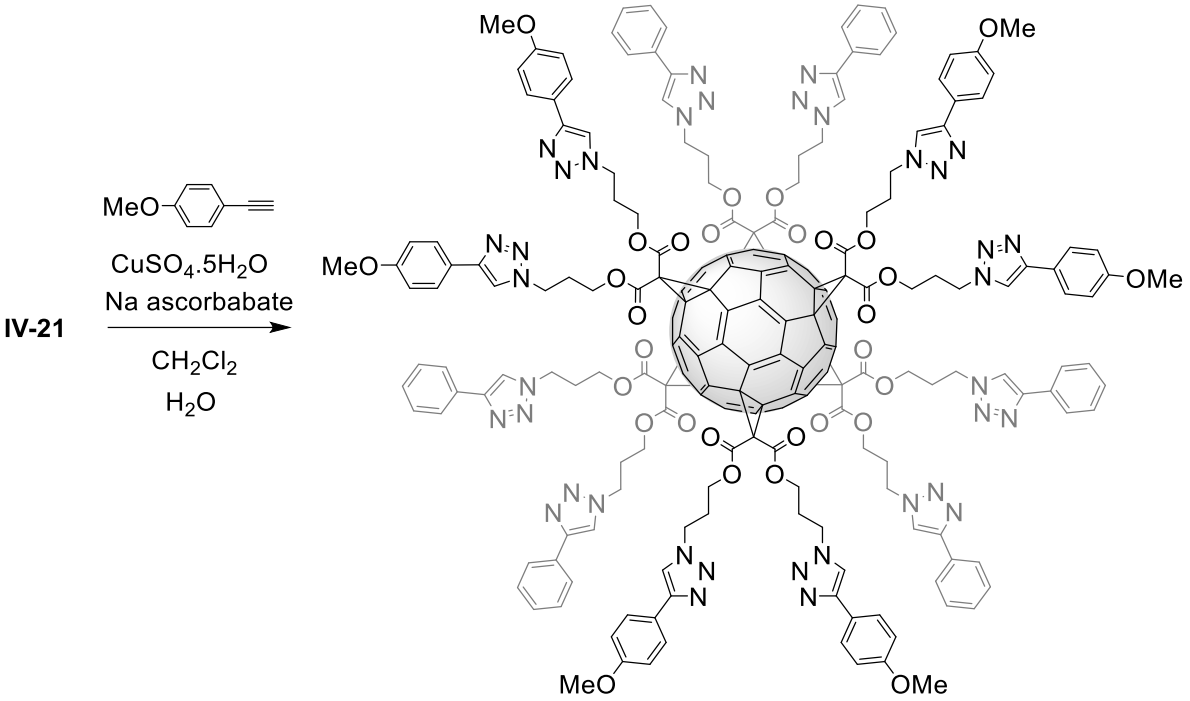
Compound IV-19: IV-18 (73 mg, 26 μmol) was added to a solution of 4-ethynylanisole (20 mg, 155 μmol), $CuSO_4.5H_2O$ (1 mg, 5 μmol) and sodium ascorbate (3 mg, 15 μmol) in CH_2Cl_2/H_2O (2/1 mL). The resulting mixture was stirred at 30°C for 15 h, then a small amount of reactant and catalyst were added. After 4 h, CH_2Cl_2 was added to the mixture, the organic layer washed with H_2O and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 97:3) yielded **IV-19** (80 mg, 25 μmol, 92 %) as an orange glassy solid. IR (neat): υ = 1741 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 247 ($2x10^5$), 266 (sh, $1x10^5$), 282 (sh, $8x10^4$), 317 ($4x10^4$), 336 ($3x10^4$) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.85 (s, 3 H, $H_{triazole\text{-}Ph}$), 7.83 (s, 3 H, $H_{triazole\text{-}Ph}$), 7.79 (m, 12 H, ArH_o), 7.78 (d, ^3J = 8 Hz, 6 H, MeOArH_o), 7.65 (s, 3 H, $H_{triazole\text{-}PhOMe}$), 7.36 (m, 12 H, Ar$H_m$), 7.29 (m, 6 H, Ar$H_p$), 6.92 (d, ^3J = 8 Hz, 6 H, MeOArH_m), 4.45 (m, 12 H, $CH_2CH_2N_{triazole}$), 4.37 (m, 18 H, $COOCH_2CH_2$ and $CH_2CH_2N_{triazole}$), 4.29 (m, 12 H, $COOCH_2$), 3.80 (s, 9 H, $ArOCH_3$), 2.34 (m, 12 H,$CH_2CH_2CH_2$), 2.27 (m, 6 H, $CH_2CH_2CH_2$), 1.25 (t, ^3J = 7 Hz, CH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 163.5 (two peaks), 163.4 (two peaks), 159.6, 147.9 (two peaks), 147.7, 146.3 (two peaks), 146.0, 145.9, 145.8 (two peaks), 145.5, 145.4, 141.6, 141.5, 141.2, 141.1 (two peaks), 141.0, 134.5, 130.5 (two peaks), 128.8, 128.2, 127.0, 125.7 (two peaks), 124.3, 123.2, 122.0, 120.1, 119.2, 114.3, 69.3, 69.2, 69.1 (two peaks), 63.8, 63.7, 63.5, 63.4, 55.3, 46.8, 46.7, 45.5, 45.4, 29.3, 14.1 ppm. MS-MALDI-TOF: 3176.3 ($[M+2H]^+$, calcd for $C_{186}H_{131}O_{27}N_{27}$: 3176.0). Anal. $C_{214}H_{152}O_{28}N_{36}$•1/2$CHCl_3$•1/2$CH_2Cl_2$ (3276.34): calcd. C 68.55, H 4.01, N 11.54 ; found C 68.66, H 3.62, N 11.54.



Compound IV-20: A solution of **IV-13b** (94 mg, 37 μmol), phenylacetylene (0.05 mL, 0.47 mmol), $CuSO_4.5H_2O$ (3 mg, 11 μmol) and sodium ascorbate (4 mg, 22 μmol) in CH_2Cl_2/H_2O (2/1 mL) was stirred at 30°C for 15 h, then CH_2Cl_2 was added, the organic layer washed with H_2O and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 98:2) yielded **IV-20** (116 mg, 36 μmol, 99%) as an orange glassy solid. IR (neat): υ = 1743 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 246 (2.5x105), 267 (sh, 1.3x105), 281 (sh, 1.1x105), 318 (sh, 6x104), 336 (sh, 5x104) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.86 (s, 3 H, $H_{triazole\text{-}Ph}$), 7.83 (s, 3 H, $H_{triazole\text{-}Ph}$), 7.79 (m, 12 H, ArH_o), 7.37 (m, 12 H, ArH_m), 7.30 (m, 6 H, ArH_p), 4.49-4.34 (m, 36 H, CH_2CH_2OOC & $CH_2CH_2N_{triazole}$), 3.41 (t, ^3J = 6 Hz, 6 H, CH_2CH_2Br), 3.39 (t, ^3J = 6 Hz, 6 H, CH_2CH_2Br), 2.38 (quint., ^3J = 6 Hz, 6 H, $CH_2CH_2CH_2N_{triazole}$), 2.32 (quint., ^3J = 6 Hz, 6 H, $CH_2CH_2CH_2N_{triazole}$), 2.22 (quint., ^3J = 6 Hz, 6 H, $CH_2CH_2CH_2Br$), 2.19 (quint., ^3J = 6 Hz, 6 H, $CH_2CH_2CH_2Br$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.5, 163.4 (three peaks), 147.9 (two peaks), 145.9 (two peaks), 145.8 (two peaks), 145.7, 141.3, 141.2 (three peaks), 141.1, 141.0, 130.5 (two peaks), 128.8, 128.2, 125.7 (two peaks), 120.1 (two peaks), 69.2, 69.1 (three peaks), 64.8, 63.7 (two peaks), 46.8, 45.4, 45.3, 31.2 (two peaks), 29.3, 29.1 (two peaks) ppm. MS-MALDI-TOF: 3171.1 ($[M+H]^+$, calcd for $C_{162}H_{109}O_{24}N_{18}Br_6$: 3171.3).

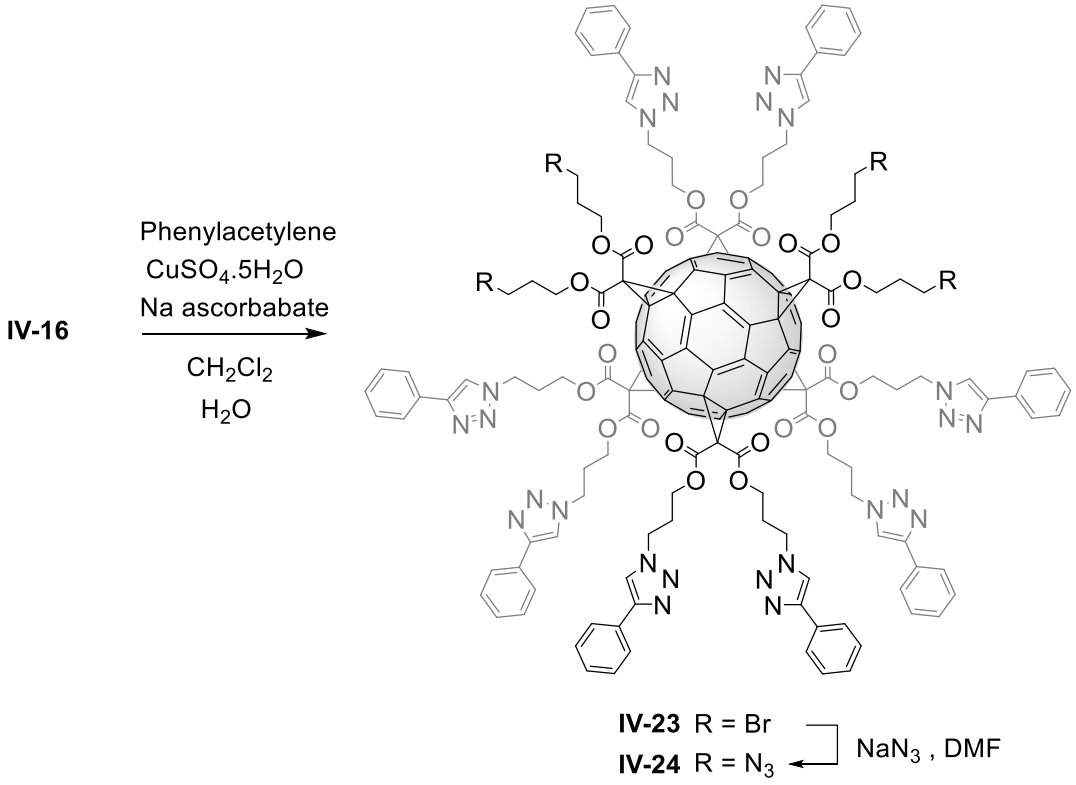
Compound IV-21: A solution of **IV-20** (113 mg, 35 μmol) and NaN_3 (23 mg, 356 μmol) in DMF (2 mL) was stirred at room temperature. After 17 h, the product was precipitated with H_2O/Et_2O and resolubilized in CH_2Cl_2, the organic layer washed with H_2O and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 98:2) yielded **IV-21** (103 mg, 35 μmol, 98%) as an orange glassy solid. IR (neat): υ = 2098 (N_3), 1742 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz):δ = 7.86 (s, 3 H, $H_{triazole}$), 7.83 (s, 3 H, $H_{triazole}$), 7.79 (m, 12 H, ArH_o), 7.35 (m, 12 H,

ArH_m), 7.30 (m, 6 H, ArH_p), 4.45 (m, 12 H, $CH_2CH_2N_{triazole}$), 4.34 (m, 24 H, CH_2CH_2OOC), 3.36 (t, ^3J = 6 Hz, 6 H, $CH_2CH_2N_3$), 3.33 (t, ^3J = 6 Hz, 6 H, $CH_2CH_2N_3$), 2.34 (m, 12 H, $CH_2CH_2CH_2N_{triazole}$), 1.94 (quint., ^3J = 6 Hz, 6 H, $CH_2CH_2CH_2N_3$), 1.90 (quint., ^3J = 6 Hz, 6 H, $CH_2CH_2CH_2N_3$) ppm.



IV-22

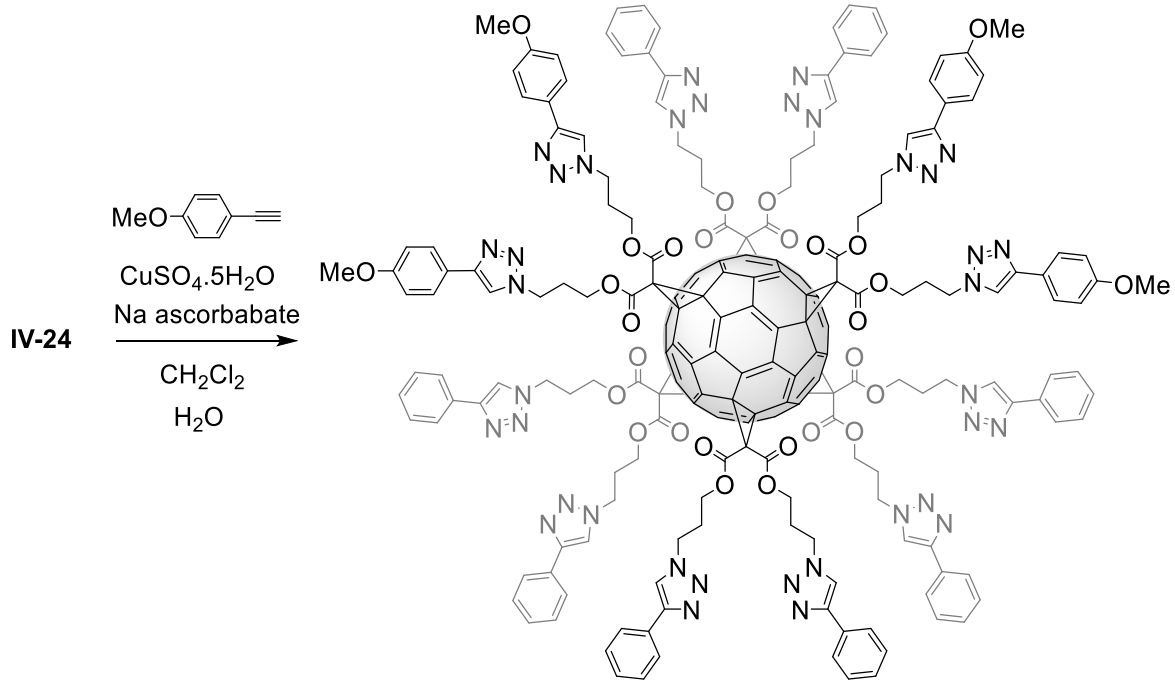
Compound IV-22: IV-21 (103 mg, 35 μmol) was added to a solution of 4-ethynylanisole (57 mg, 428 μmol), $CuSO_4.5H_2O$ (3 mg, 11 μmol) and sodium ascorbate (4 mg, 22 μmol) in CH_2Cl_2/H_2O (2/1 mL). The resulting mixture was stirred at 30°C for 15 h, then CH_2Cl_2 was added to the mixture, the organic layer washed with H_2O and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 97:3) yielded **IV-22** (117 mg, 31 μmol, 88%) as an orange glassy solid. IR (neat): υ = 1742 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 248 ($2.5x10^5$), 318 (sh, $5x10^4$), 335 (sh, $4x10^4$) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.82 (s, 6 H, $H_{triazole\text{-}Ph}$), 7.76 (d, ^3J = 7 Hz, 12 H, ArH_o), 7.71 (s, 6 H, $H_{triazole\text{-}PhOMe}$), 7.67 (d, ^3J = 9 Hz, 12 H, MeOArH_o), 7.34 (t, ^3J = 7 Hz, 12 H, ArH_m), 7.28 (d, ^3J = 7 Hz, 6 H, ArH_p), 6.87 (d, ^3J = 9 Hz, 12 H, MeOArH_m), 4.41 (t, ^3J = 7 Hz, 12 H, $CH_2CH_2N_{triazole}$), 4.39 (t, ^3J = 7 Hz, 12 H, $CH_2CH_2N_{triazole}$), 4.33 (t, ^3J = 6 Hz, 24 H, CH_2CH_2OOC), 3.77 (s, 18 H, $ArOCH_3$), 2.29 (m, 24 H, $CH_2CH_2CH_2N_{triazole}$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.4, 159.6, 147.9, 147.8, 145.9, 141.3, 130.5, 128.9, 128.2, 127.0, 125.7, 123.2, 120.1, 119.3, 114.3, 69.2, 63.8, 55.3, 46.8 (two peaks), 45.5, 29.3 ppm. MS-MALDI-TOF: 3735.8 ($[M+H]^+$, calcd for $C_{216}H_{156}O_{30}N_{36}$: 3736.2). Anal. $C_{216}H_{156}O_{30}N_{36}$•0.8$CHCl_3$ (3831.28): calcd. C 67.96 H 4.12 N 13.16 ; found C 68.00 H 4.00 N 13.07.



Compound IV-23: A solution of **IV-16** (265 mg, 107 μmol), phenylacetylene (0.19 mL, 1.7 mmol), $CuSO_4.5H_2O$ (10 mg, 42 μmol) and sodium ascorbate (17 mg, 85 μmol) in CH_2Cl_2/H_2O (2/1 mL) was stirred at 30°C for 15 h, then CH_2Cl_2 was added, washed with H_2O and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 98:2) yielded **IV-23** (322 mg, 98 μmol, 91%) as an orange glassy solid. IR (neat): $\upsilon = 1742$ (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 246 (2.4x10^5), 284 (sh, 9x10^4), 322 (sh, 5x10^4), 338 (sh, 4x10^4) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.79 (m, 24 H), 7.34 (m, 24 H), 4.44 (m, 16 H, $CH_2CH_2N_{triazole}$), 4.36 (m, 24 H, CH_2CH_2OOC), 3.39 (m, 8 H, CH_2CH_2Br), 2.23 (m, 16 H, $CH_2CH_2CH_2N_{triazole}$), 2.18 (m, 8 H, $CH_2CH_2CH_2Br$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.5 (two peaks), 163.4 (two peaks), 163.3, 147.9 (three peaks), 145.9 (three peaks), 145.8 (two peaks), 145.7, 141.3 (two peaks), 141.2 (three peaks), 141.1 (three peaks), 130.5 (two peaks), 128.8, 128.2, 125.7 (two peaks), 120.1 (two peaks), 69.2, 69.1 (two peaks), 64.8, 63.7 (two peaks), 46.8, 45.4 (three peaks), 45.3, 31.2 (two peaks), 29.3, 29.1 ppm. MS-MALDI-TOF: 3300.1 ([M+H]$^+$, calcd for $C_{178}H_{121}O_{24}N_{24}Br_4$: 3299.6).

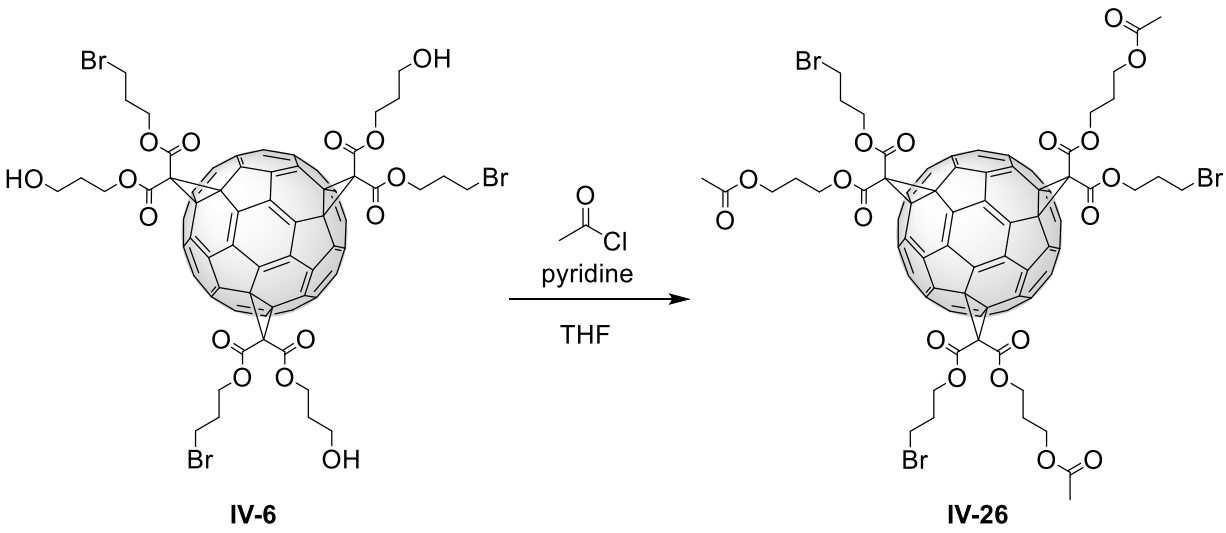
Compound IV-24: A solution of **IV-23** (149 mg, 45 μmol) and NaN_3 (18 mg, 271 μmol) in DMF (2 mL) was stirred at room temperature. After 17 h, the product was precipitated with H_2O/Et_2O and resolubilized in CH_2Cl_2, washed with H_2O and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 98:2) yielded **IV-24** (139 mg, 44 μmol, 98%) as an orange glassy solid. IR (neat): $\upsilon = 2098$ (N_3), 1741 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.86-7.81 (4s, 8 H, $H_{triazole}$), 7.75 (m, 16 H, ArH_o), 7.30 (m, 24 H, Ar$H_{m,p}$), 4.41 (m, 16 H,

$CH_2CH_2N_{triazole}$), 4.31 (m, 24 H, CH_2CH_2OOC), 3.30 (t, ^3J = 7 Hz, 8 H, $CH_2CH_2N_3$), 2.30 (m, 16 H, $CH_2CH_2CH_2N_{triazole}$), 1.87 (m, 8 H, $CH_2CH_2CH_2N_3$) ppm.



IV-25

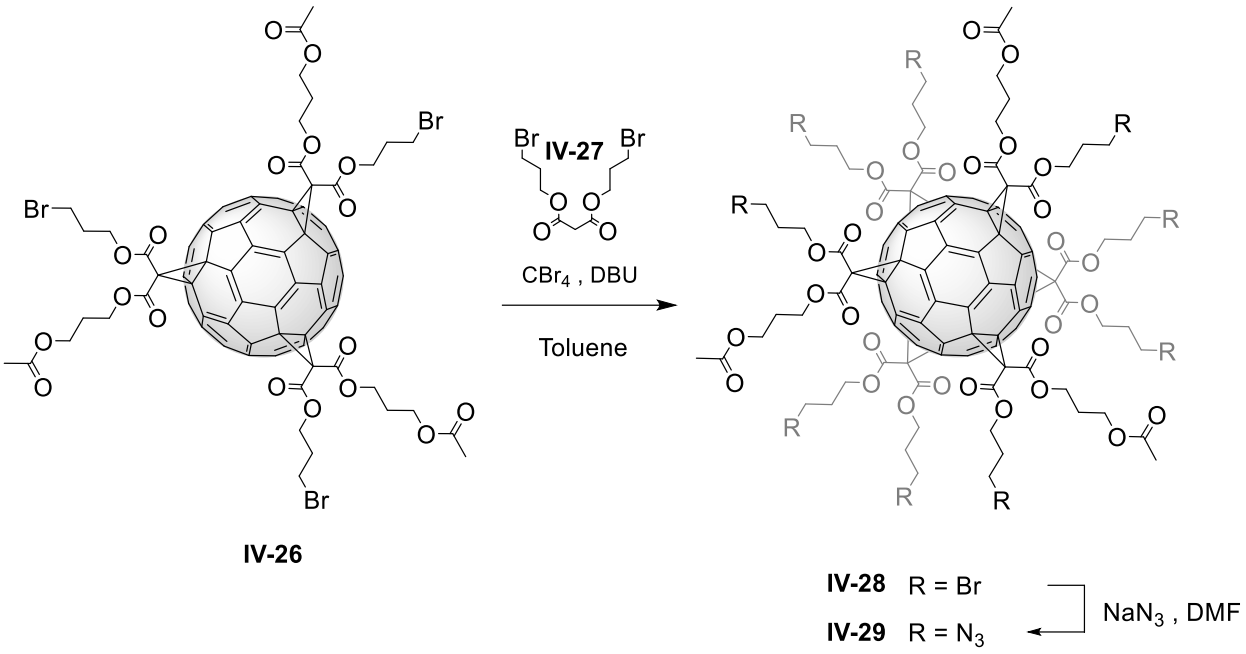
Compound IV-25: IV-24 (139 mg, 44 μmol) was added to a solution of 4-ethynylanisole (0.06 mL, 0.5 mmol), $CuSO_4.5H_2O$ (2 mg, 9 μmol) and sodium ascorbate (3 mg, 18 μmol) in CH_2Cl_2/H_2O (2/1 mL). The resulting mixture was stirred at 30°C for 24 h, then a small amount of reactant and catalyst were added. After 18 h, CH_2Cl_2 was added to the mixture, the organic layer washed with H_2O and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 97:3) yielded **IV-25** (122 mg, 33 μmol, 75%) as an orange glassy solid. IR (neat): $\upsilon = 1742$ (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 247 ($2.2x10^5$), 284 (sh, $7x10^4$), 321 (sh, $4x10^4$), 336 (sh, $3x10^4$) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.82 (s, 8 H, $H_{Triazole\ Ph}$), 7.76 (d, ^3J = 7 Hz, 16 H, ArH_o), 7.72 (s, 4 H, $H_{Triazole\ PhOMe}$), 7.67 (d, ^3J = 9 Hz, 8 H, $H_3COAr H_o$), 7.34 (t, ^3J = 7 Hz, 8 H, ArH_m), 7.28 (d, ^3J = 7 Hz, 16 H, ArH_p), 6.87 (d, ^3J = 9 Hz, 8 H, $H_3COAr H_m$), 4.41 (t, ^3J = 7 Hz, 16 H, $CH_2CH_2N_{triazole}$), 4.39 (t, ^3J = 7 Hz, 8 H, $CH_2CH_2N_{triazole}$), 4.33 (t, ^3J = 6 Hz, 24 H, CH_2CH_2OOC), 3.77 (s, 12 H, OCH_3), 2.29 (m, 24 H, $CH_2CH_2CH_2$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.4, 159.6, 147.9, 147.8, 145.9, 141.3, 130.5, 128.9, 128.2, 127.0, 125.7, 123.2, 120.1, 119.3, 114.3, 69.2, 63.8, 55.3, 46.8 (two peaks), 45.5, 29.3 ppm. MS-MALDI-TOF : 3676.7 ($[M+H]^+$, calcd for $C_{214}H_{153}N_{36}O_{28}$: 3676.2). Anal. $C_{214}H_{152}O_{28}N_{36}\bullet CHCl_3$ (3795.11) : calcd. C 68.04, H 4.06, N 13.29 ; found C 68.05, H 3.87, N 13.38.



IV-6 **IV-26**

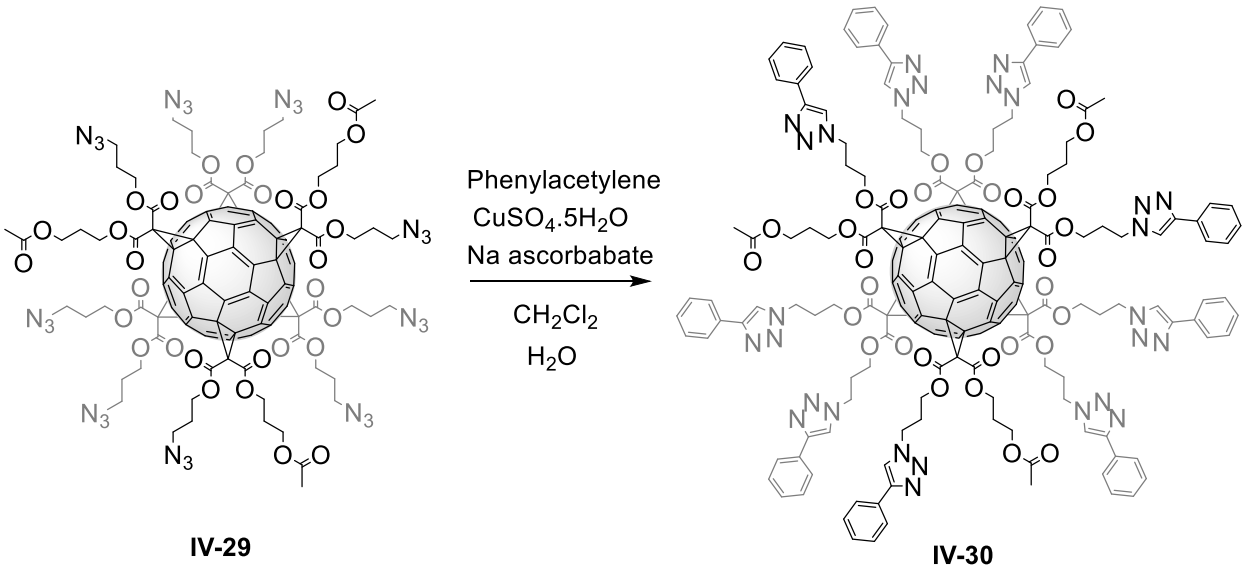
Compound IV-26: Acetyl chloride (20 μL, 253 μmol) was added to a solution of **IV-6** (66 mg, 42 μmol) and pyridine (20 μL, 253 μmol) in THF (5 mL) at 0°C. After 1.5 h, the mixture was filtered on SiO_2 (CH_2Cl_2/EtOAc, 97:5) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/EtOAc, 98:2) yielded **IV-26** (56 mg, 33 μmol, 79%) as a red glassy solid. IR (neat): υ = 1738 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 233 ($1.4x10^5$), 252 ($1.4x10^5$), 282 ($1.0x10^5$), 305 (sh, $7.5x10^4$), 380 ($8x10^3$), 484 ($7x10^3$), 523 (sh, $4x10^3$), 565 (sh, $2x10^3$) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.50 (m, 6 H, COOCH_2CH$_2$), 4.38 (m, 6 H, COOCH_2CH$_2$), 4.15 (t, ^3J = 6 Hz, 6 H, CH$_2$CH_2OOCCH$_3$), 3.46 (t, ^3J = 6 Hz, 6 H, CH$_2$CH_2Br), 2.28 (quint., ^3J = 6 Hz, 6 H, CH$_2$CH_2CH$_2$), 2.07 (m, 15 H, CH$_2$CH_2CH$_2$OOCCH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.9, 163.2, 163.1, 147.2, 146.9, 146.7, 146.6 (two peaks), 146.5, 146.3, 145.6, 145.5, 145.2, 145.1, 144.5, 143.5, 142.8, 142.2, 141.4, 141.3, 141.0, 70.7, 69.9, 64.7, 63.8, 60.6, 52.6, 31.3, 29.0, 27.8, 20.9 ppm. MALDI-TOF-MS: 1712.7 (27%, $[M+Na]^+$, calcd for $C_{93}H_{45}O_{18}Br_3Na$: 1713.0), 1689.6 (100%, $[M]^+$, calcd for $C_{93}H_{45}O_{18}Br_3$: 1690.0), 1572.6 (19%, $[M-(OCH_2CH_2CH_2OOCCH_3)]^+$, calcd for $C_{88}H_{36}O_{15}Br_3$: 1572.9).

Compound IV-27: IV-27 was prepared as described in *Chem. Commun.* **2008**, 2450–2452.



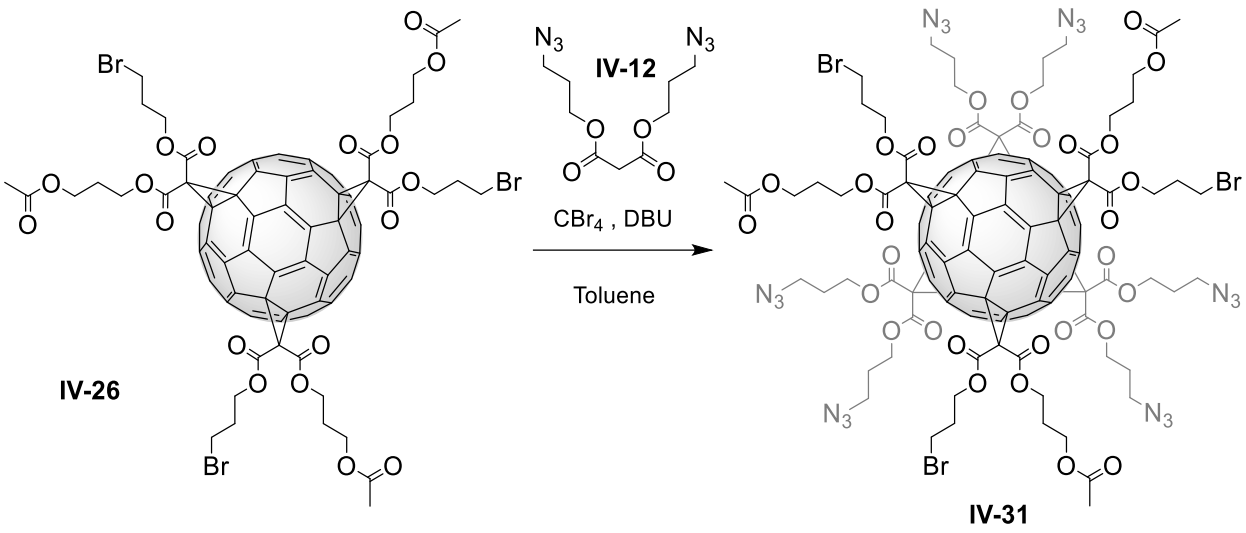
Compound IV-28: DBU (0.11 mL, 0.76 mmol) was added to a solution of **IV-26** (80 mg, 47 μmol), **IV-27** (98 mg, 284 μmol) and CBr_4 (784 mg, 2.4 mmol) in toluene (25 mL). The resulting mixture was stirred at room temperature for 2 h, then filtered on SiO_2 (CH_2Cl_2/Et_2O, 95:5) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/Et_2O, 98:2) yielded **IV-28** (86 mg, 31.6 μmol, 67%) as an orange glassy solid. IR (neat): υ = 1735 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 245 ($1.2x10^5$), 270 (sh, $8.6x10^4$), 281 ($9.0x10^4$), 317 (sh, $5.6x10^4$), 336 (sh, $4.6x10^4$) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.43 (t, ^3J = 6 Hz, 18 H, $COOCH_2CH_2CH_2Br$), 4.37 (t, ^3J = 6 Hz, 6 H, $COOCH_2CH_2CH_2OOCCH_3$), 4.14 (t, ^3J = 6 Hz, 6 H, $CH_2CH_2OOCCH_3$), 3.44 (m, 18 H, CH_2CH_2Br), 2.25 (m, 18 H, $CH_2CH_2CH_2Br$), 2.06 (m, 15 H, $CH_2CH_2CH_2OOCCH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.9, 163.5, 146.0, 145.9, 145.8, 145.7 (two peaks), 145.6, 141.2, 141.1 (two peaks), 140.0, 69.1 (two peaks), 64.7, 63.8, 60.6, 45.2, 31.3, 29.1, 27.8, 20.9 ppm. MALDI-TOF-MS: 2721.5 (100%, $[M]^+$, calcd for $C_{120}H_{81}O_{30}Br_9$: 2721.7), 2585.6 (39%, $[M+H-(OCH_2CH_2CH_2Br)]^+$, calcd for $C_{117}H_{76}O_{29}Br_8$: 2585.8), 2377.7 (28%, $[M-(malonate-Br)]^+$, calcd for $C_{111}H_{69}O_{26}Br_7$: 2377.8).

Compound IV-29: A solution of **IV-28** (66 mg, 24.2 μmol) and NaN_3 (28 mg, 436 μmol) in DMF (2 mL) was stirred at room temperature for 16 h. Then filtered on SiO_2 (CH_2Cl_2/Et_2O, 92:8) and concentrated. Gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) yielded **IV-29** (56 mg, 23.5 μmol, 97%) as an orange glassy solid. IR (neat): υ = 2097 (N_3), 1740 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.37 (t, ^3J = 6 Hz, 24 H, $COOCH_2CH_2$), 4.14 (t, ^3J = 6 Hz, 6 H, $CH_2CH_2OOCCH_3$), 3.39 (m, 18 H, CH_2CH_2Br), 2.07 (m, 15 H, $CH_2CH_2CH_2OOCCH_3$), 1.97 (quint., ^3J = 6 Hz, 18 H, $CH_2CH_2CH_2N_3$) ppm.

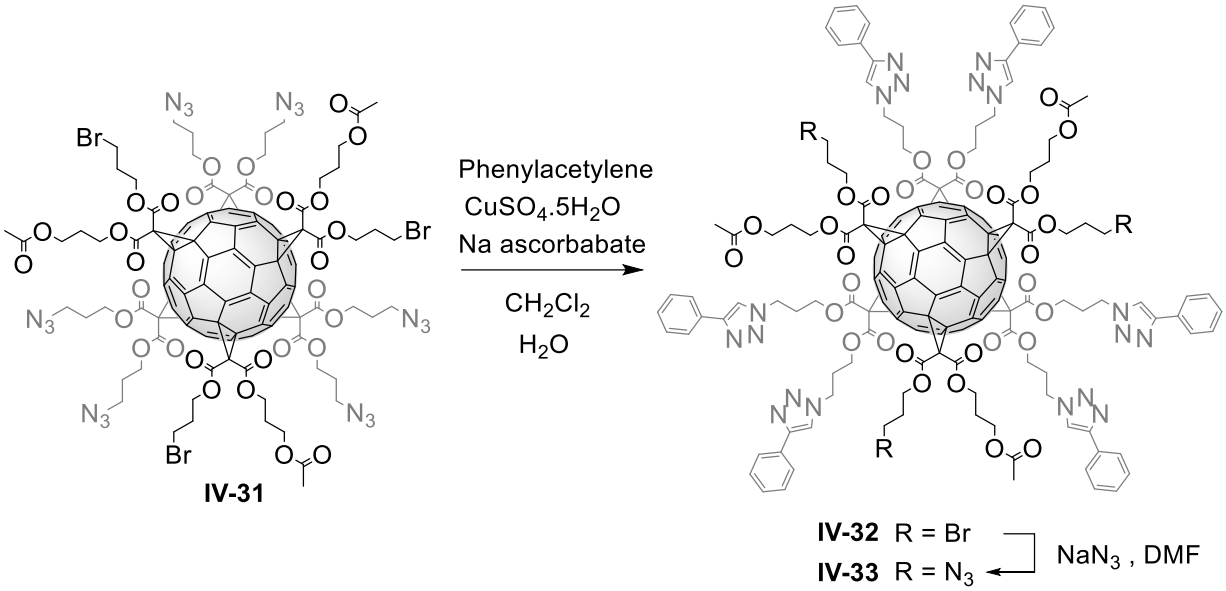


IV-29 **IV-30**

Compound IV-30: A solution of **IV-29** (55 mg, 23.1 μmol), phenylacetylene (0.04 mL, 323 μmol), $CuSO_4.5H_2O$ (3 mg, 11 μmol) and sodium ascorbate (4 mg, 22 μmol) in CH_2Cl_2/H_2O (3/1 mL) was stirred at 30°C for 4 days, then CH_2Cl_2 was added, the organic layer washed with H_2O and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 → CH_2Cl_2/MeOH, 96:4) yielded **IV-30** (72 mg, 21.8 μmol, 94%) as an orange glassy solid. IR (neat): υ = 1740 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 246 ($2.2x10^5$), 263 (sh, $1.3x10^5$), 282 (sh, $8x10^4$), 318 (sh, $5x10^4$), 337 (sh, $4x10^4$) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.82 (s, 3 H, $H_{triazole}$), 7.80-7.75 (m, 24 H, $H_{triazole}$ & ArH_o) 7.36 (m, 18 H, ArH_m), 7.29 (m, 9 H, ArH_p), 4.44-4.30 (m, 42 H, $CH_2CH_2N_{triazole}$ & $COOCH_2CH_2$), 4.10 (t, ^3J = 6 Hz, 6 H, $CH_2CH_2OOCCH_3$), 2.29 (m, 18 H, $CH_2CH_2CH_2N_{triazole}$), 2.01 (m, 15 H, $CH_2CH_2CH_2OOCCH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.9, 163.5, 163.4 (three peaks), 147.9, 147.8, 146.3 (two peaks), 145.9, 145.8, 145.5, 145.4, 141.6, 141.5, 141.3, 141.2, 141.1 (two peaks), 141.0, 140.9, 130.5 (two peaks), 130.4, 128.8, 128.2, 125.7, 120.0 (two peaks), 69.2 (two peaks), 69.1, 64.0, 63.7 (br), 60.6, 46.9, 46.8, 45.4 (two peaks), 29.4, 29.3, 27.7, 20.9 ppm. MALDI-TOF-MS: 3301.2 ($[M+H]^+$, calcd for $C_{192}H_{136}O_{30}N_{27}$: 3301.0). Anal. $C_{192}H_{135}O_{30}N_{27}\bullet CH_2Cl_2$ (3385.23): calcd. C 68.48 H 4.08 N 11.17; found C 68.66 H 4.03 N 11.07.



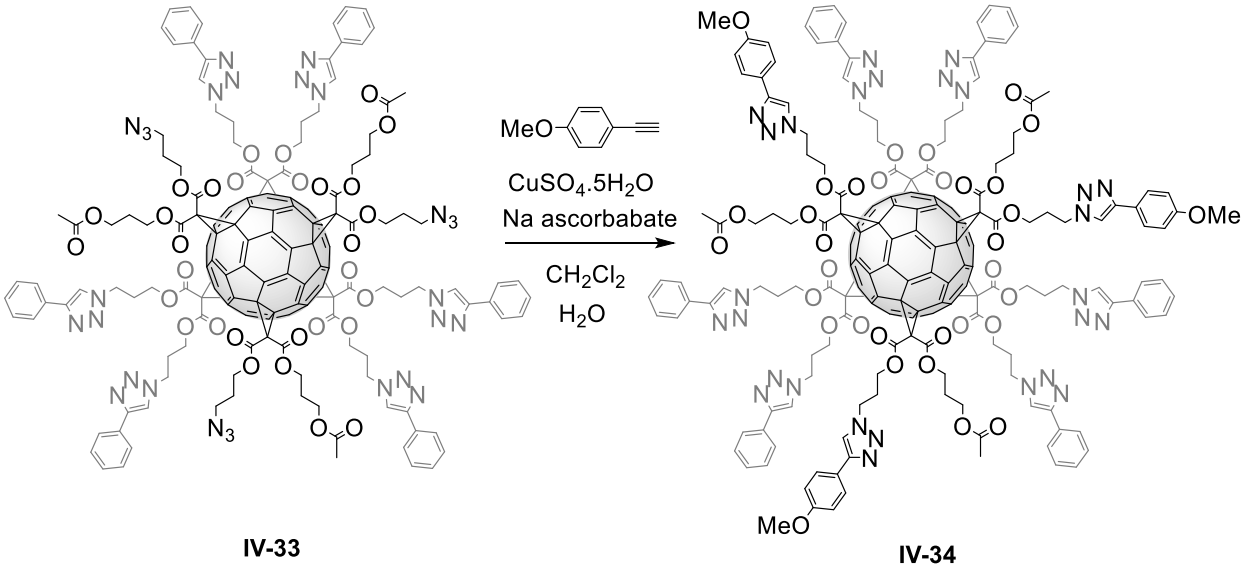
Compound IV-31: DBU (0.08 mL, 0.5 mmol) was added to a solution of **IV-26** (55 mg, 32.5 μmol), **IV-3** (53 mg, 195 μmol) and CBr_4 (540 mg, 1.6 mmol) in toluene (15 mL). The resulting mixture was stirred at room temperature for 4 h, then filtered on SiO_2 (CH_2Cl_2/Et_2O, 9:1) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/Et_2O, 95:5) yielded **IV-31** (59 mg, 23.6 μmol, 73%) as an orange glassy solid. IR (neat): υ = 2098 (N_3), 1739 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 4.43 (t, ^3J = 6 Hz, 6 H, $COOCH_2CH_2CH_2Br$), 4.38 (t, ^3J = 6 Hz, 18 H, $COOCH_2CH_2$), 4.15 (t, ^3J = 6 Hz, 6 H, $CH_2CH_2OOCCH_3$), 3.43 (t, ^3J = 6 Hz, 6 H, CH_2CH_2Br), 3.40 (t, ^3J = 6 Hz, 12 H, $CH_2CH_2N_3$), 2.25 (quint., ^3J = 6 Hz, 6 H, $CH_2CH_2CH_2Br$), 2.07 (m, 15 H,), 1.97 (quint., ^3J = 6 Hz, 12 H, $CH_2CH_2CH_2N_3$) ppm.



Compound IV-32: A solution of **IV-31** (59 mg, 23.6 μmol), phenylacetylene (0.03 mL, 238 μmol), $CuSO_4.5H_2O$ (3 mg, 11 μmol) and sodium ascorbate (4 mg, 22 μmol) in CH_2Cl_2/H_2O (2 : 1 mL) was stirred at 30°C for 16 h, then CH_2Cl_2 was added, the organic layer washed with H_2O and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 98:2) yielded **IV-**

32 (73 mg, 23.5 μmol, 99%) as an orange glassy solid. IR (neat): υ = 1740 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 246 ($1.4x10^5$), 266 (sh, $8x10^4$), 282 (sh, $6x10^4$), 319 (sh, $4x10^4$), 336 (sh, $3x10^4$) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.87 (s, 3 H, $H_{triazole}$), 7.83 (s, 3 H, $H_{triazole}$), 7.81 (d, ^3J = 8 Hz, 6 H, ArH_o), 7.78 (d, ^3J = 8 Hz, 6 H, ArH_o), 7.38 (t, ^3J = 8 Hz, 6 H, ArH_m), 7.36 (t, ^3J = 8 Hz, 6 H, ArH_m), 7.30 (t, ^3J = 8 Hz, 6 H, ArH_p), 4.48 (t, ^3J = 6 Hz, 6 H, $CH_2CH_2N_{triazole}$), 4.44 (t, ^3J = 6 Hz, 6 H, $CH_2CH_2N_{triazole}$), 4.37 (m, 24 H, $COOCH_2CH_2$), 4.12 (t, ^3J = 6 Hz, 6 H, $CH_2CH_2OOCCH_3$), 3.38 (t, ^3J = 6 Hz, CH_2CH_2Br), 2.38 (m, 6 H, $CH_2CH_2CH_2N_{triazole}$), 2.32 (m, 6 H, $CH_2CH_2CH_2N_{triazole}$), 2.18 (quint., ^3J = 6 Hz, 6 H, $CH_2CH_2CH_2Br$), 2.06 (m, 15 H, $CH_2CH_2CH_2OOCH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.9, 163.5, 163.5, 163.4, 147.9 (two peaks), 146.0 (two peaks), 145.9, 145.8 (four peaks), 145.7, 145.6, 141.4 (two peaks), 141.2, 141.1, 141.0 (two peaks), 130.5, 130.4, 128.8, 128.2 (two peaks), 125.7 (two peaks), 120.1 (two peaks), 69.2, 69.1, 69.0, 64.8, 63.9, 63.7 (br), 60.6, 46.8 (br), 45.3 (two peaks), 31.2, 29.3, 29.1, 27.7, 20.9 ppm. MALDI-TOF-MS: 3108.6 ($[M]^+$, calcd for $C_{168}H_{118}O_{30}N_{18}Br_3$: 3108.6).

Compound IV-33: A solution of **IV-32** (72 mg, 23.2 μmol) and NaN_3 (14 mg, 208 μmol) in DMF (2 mL) was stirred at room temperature. After 16 h, the product was precipitated with H_2O/Et_2O and resolubilized in CH_2Cl_2, the organic layer washed with H_2O and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 96:4) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) yielded **IV-33** (65 mg, 21.7 μmol, 94%) as an orange glassy solid. IR (neat): υ = 2098 (N_3), 1736 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.86 (s, 3 H, $H_{triazole}$), 7.83 (s, 3 H, $H_{triazole}$), 7.79 (m, 12 H, ArH_o), 7.37 (m, 12 H, ArH_m), 7.30 (m, 6 H, ArH_p), 4.48 (t, ^3J = 6 Hz, 6 H, $CH_2CH_2N_{triazole}$), 4.44 (t, ^3J = 6 Hz, 6 H, $CH_2CH_2N_{triazole}$), 4.37 (m, 24 H, $COOCH_2CH_2$), 4.12 (t, ^3J = 6 Hz, 6 H, $CH_2CH_2OOCCH_3$), 3.33 (t, ^3J = 6 Hz, $CH_2CH_2N_3$), 2.38 (m, 6 H, $CH_2CH_2CH_2N_{triazole}$), 2.32 (m, 6 H, $CH_2CH_2CH_2N_{triazole}$), 2.05 (m, 15 H, $CH_2CH_2CH_2OOCH_3$), 1.91 (quint., ^3J = 6 Hz, 6 H, $CH_2CH_2CH_2N_3$), ppm.



IV-33 **IV-34**

Compound IV-34: A solution of **IV-33** (65 mg, 21.7 μmol), 4-ethynylanisole (26 mg, 195 μmol), $CuSO_4.5H_2O$ (3 mg, 11 μmol) and sodium ascorbate (4 mg, 22 μmol) in CH_2Cl_2/H_2O (3/1 mL) was stirred at 30°C for 3.5 days, then CH_2Cl_2 was added, the organic layer washed with H_2O and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 96:4) yielded **IV-34** (66 mg, 19.5 μmol, 90%) as an orange glassy solid. IR (neat): υ = 1738 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 247 ($1.9x10^5$), 265 (sh, $1.2x10^5$), 282 (sh, $7x10^4$), 319 (sh, $4x10^4$), 337 (sh, $3x10^4$) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.82 (s, 3 H, $H_{triazole\text{-}Ph}$), 7.80 (s, 3 H, $H_{triazole\text{-}Ph}$), 7.77 (d, ^3J = 8 Hz, 6 H, ArH_o), 7.75 (d, ^3J = 8 Hz, 6 H, ArH_o), 7.71 (d, ^3J = 8 Hz, 6 H, ArH_oOMe), 7.70 (s, 3 H, $H_{triazole\text{-}PhOMe}$), 7.36 (t, ^3J = 8 Hz, 6 H, ArH_m), 7.34 (t, ^3J = 8 Hz, 6 H, ArH_m), 7.29 (m, 6 H, ArH_p), 6.91 (d, ^3J = 8 Hz, 6 H, ArH_mOMe), 4.42-4.30 (m, 42 H, $CH_2CH_2N_{triazole}$ & $COOCH_2CH_2$), 4.10 (t, ^3J = 6 Hz, 6 H, $CH_2CH_2OOCCH_3$), 3.79 (s, 9 H, $ArOCH_3$), 2.30 (m, 18 H, $CH_2CH_2CH_2N_{triazole}$), 2.02 (m, 15 H, $CH_2CH_2CH_2OOCCH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.9, 163.5, 163.4 (three peaks), 159.6, 147.9, 147.7, 146.3 (two peaks), 145.9, 145.8, 145.5, 145.4, 141.6, 141.5, 141.3, 141.2, 141.1 (two peaks), 141.0, 140.9, 130.5, 130.4, 128.8, 128.2, 127.0, 125.7 (two peaks), 125.6, 123.2, 120.0 (two peaks), 119.2, 114.3, 69.2 (two peaks), 69.1, 64.0, 63.7 (two peaks), 60.6, 55.3, 46.8, 45.4 (two peaks), 29.4, 29.3, 27.7, 20.9 ppm. MALDI-TOF-MS: 3391.1 ($[M+H]^+$, calcd for $C_{195}H_{142}O_{33}N_{27}$: 3391.0). Anal. $C_{195}H_{141}O_{33}N_{27}\bullet CH_2Cl_2$ (3475.31): calcd. C 67.74 H 4.15 N 11.88; found C 67.77 H 4.15 N 10.78.

Chapter V : Elaboration of dendrimers based on C_{60} hexa-adducts.

1. Introduction.

Dendrimers are remarkable polyfunctional molecular structures. Due to their branched architecture, dendrimers are able to generate specific properties.[1,2] Furthermore, the high number of functional groups at the periphery of the dendrimer is very attractive for the tuning of potential properties.

Since the first reported C_{60} derivative functionalized with a dendritic macromolecule,[3] the field of fullerodendrimers has developed concurrently with the fullerene chemistry allowing the formation of more and more elaborated dendritic structures.[4–7] The spherical shape of C_{60} has proven to be an efficient scaffold for the elaboration of globular dendrimers even with low generation dendrons. T_h-symmetrical hexa-adducts of C_{60} are particularly interesting in this field with their multiplicity of 12 and their 3D architectures. Formation of T_h-hexa-adducts of C_{60} are sensitive to steric hindrances and when malonates are bearing bulky substituents yields are low or the hexa-adducts are not formed. Only few examples of C_{60} hexa-adducts dendrimers have been reported in the literature, among them C_{60} hexa-adducts bearing two different type of addends (Figure V-1).[5] In this last case, the regiochemistry of multiple additions on C_{60} is an additional problem.

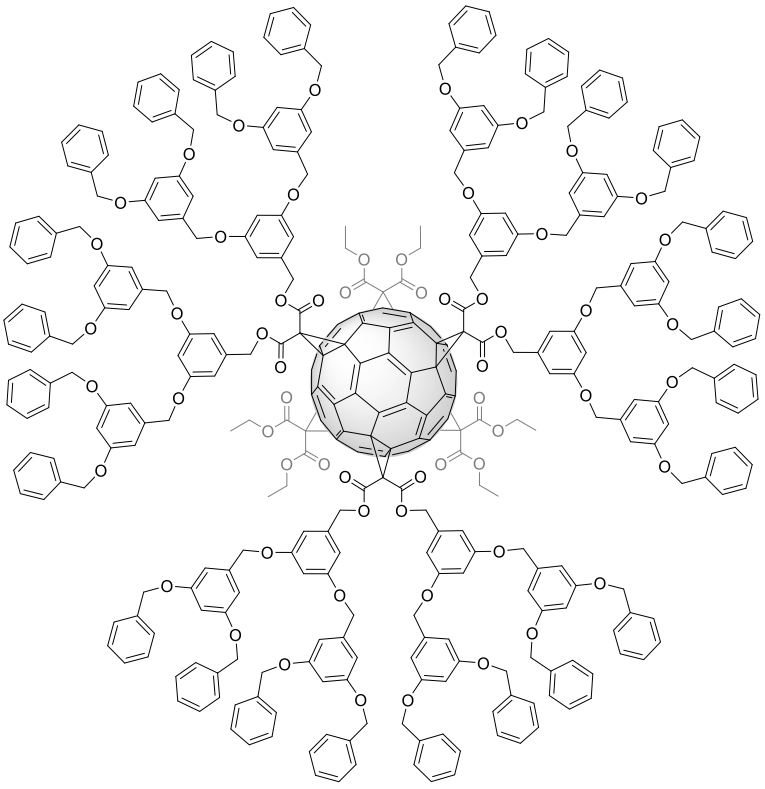


Figure V-1 : Example of fullerodendrimer of C_{60} hexa-adduct bearing two different type of addends.

The problem of accessibility of bulky hexa-adducts of C_{60} has been resolved by Nierengarten's group.[8] Easily accessible C_{60} hexa-adducts bearing 12 terminal alkyne or azide groups have been synthesized. Post-functionalization of these building blocks by copper-

catalyzed alkyne-azide 1,3-dipolar cycloaddition (CuAAC) reactions has allowed the formation of C_{60} hexa-adducts dendrimers in good yields.[9–13]

Among the fullerodendrimers, fullerene rich dendrimers have generated a particular interest.[6,7] The fullerene rich dendrimers reported in the literature are mainly focused on mono- or bis-functionalized C_{60} at the periphery of the dendrimer limiting their applications to material science. The principal interest of such type of dendrimers is based on the physico-chemical properties of the C_{60} sphere (the properties of pristine C_{60} are kept in mono- and bis-functionalized C_{60}). On the other hand, there are only few examples of fullerodendrimers with a C_{60} core surrounded by multi-substituted C_{60}. The synthesis of the heptafullerene **V-1** is the first example and was reported in 2009 by Hirsch and coworkers (Figure V-2).[14] The synthesis of this compound **V-1** was based on a [5:1] hexa-adduct of C_{60} and on macrocyclic linkers. However, each step of the synthesis suffers of low yield and fastidious purification by the means of preparative HPLC is required.

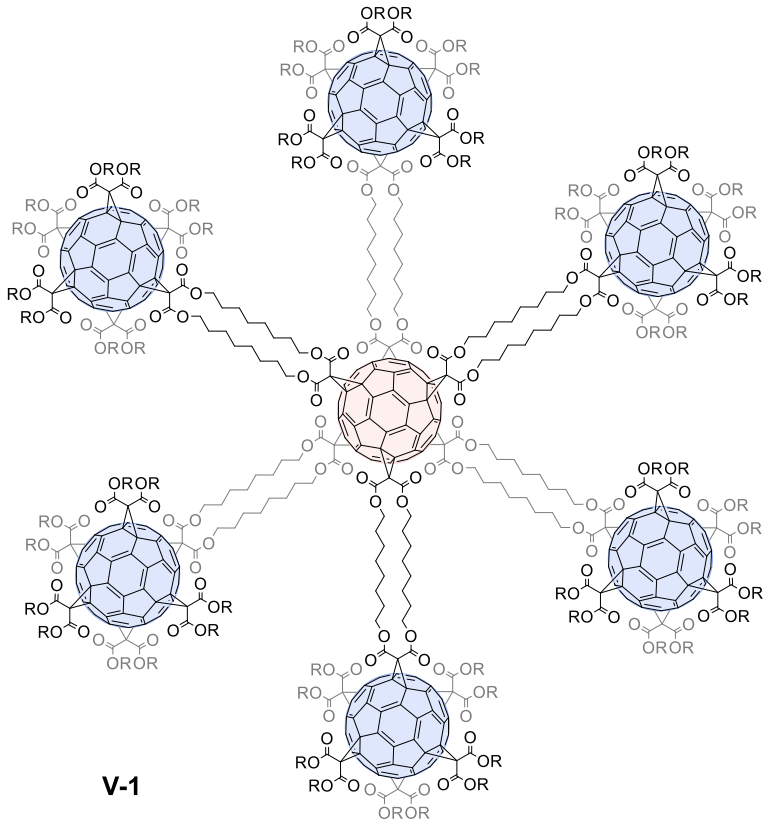


Figure V-2 : First example of fullerodendrimer with a C_{60} core surrounded by multi-substituted C_{60}.

Later, Hirsch and coworker reported also the syntheses of tetra- and hexafullerenes with a precisely defined structure (Figure V-3).[15] In this case, a different approach was used for the synthesis of the key intermediate [5:1] hexa-adducts of C_{60} which was isolated in much better yields. Furthermore, two other central building blocks were used. Nonetheless, the syntheses of the tetra- and hexafullerenes were subjected to the same synthetic difficulty as for the preparation of **V-1**.

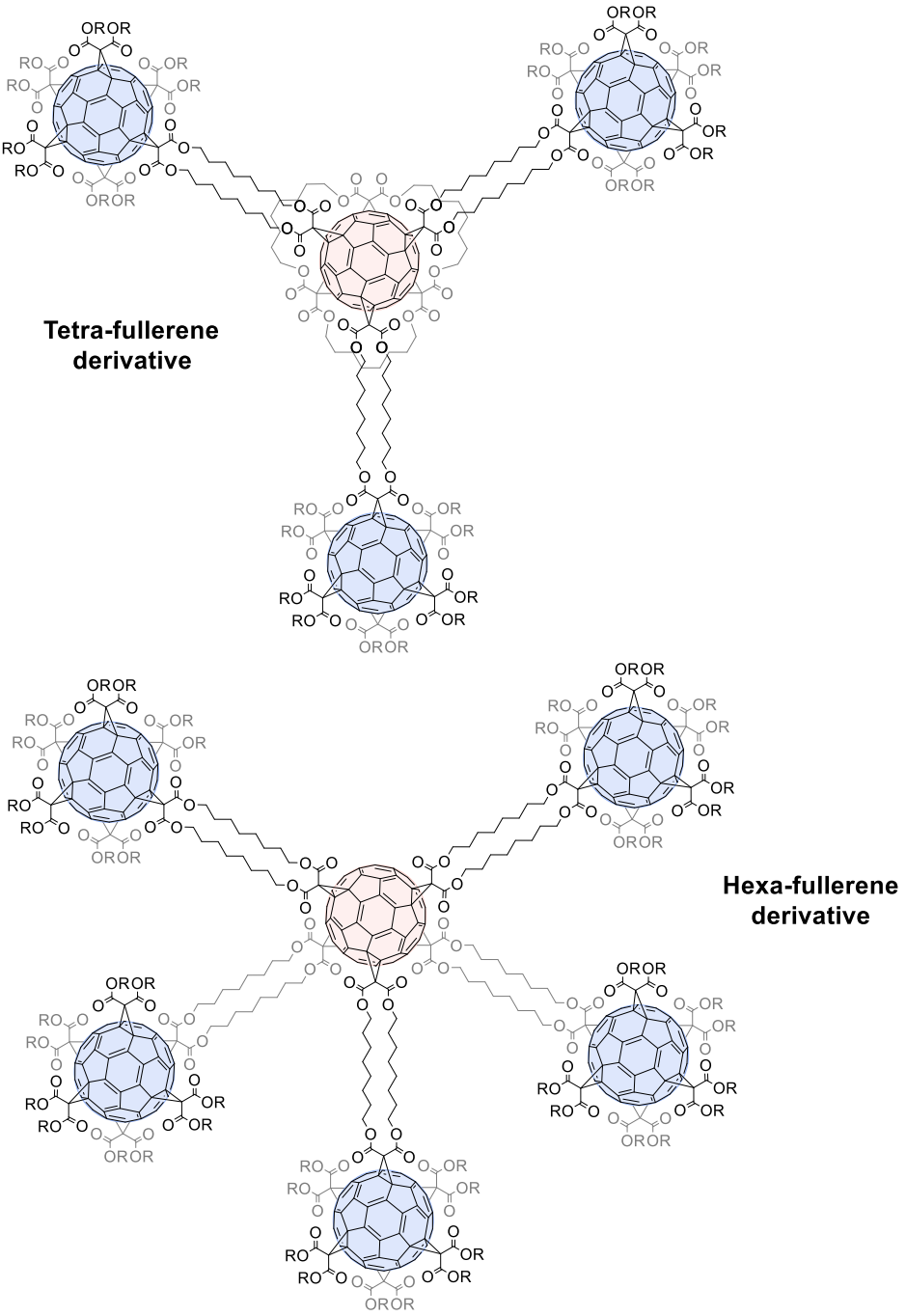


Figure V-3 : Structures of the tetrafullerene and hexafullerene derivatives.

Recently, Nierengarten's group has reported the syntheses of dendritic tridecafullerene derivatives (Figure V-4).[16,17] The tridecafullerene derivatives were obtained by the grafting of [5:1] hexa-adducts of C_{60} onto a central C_{60} hexa-adduct bearing 12 alkyne functions under copper catalyzed azide-alkyne cycloaddition conditions. These fullerodendrimers of first generation are surrounded by 120 or 132 peripheral functions. This synthetic strategy provides an efficient access to giant functional macromolecules in a minimum of synthetic steps.

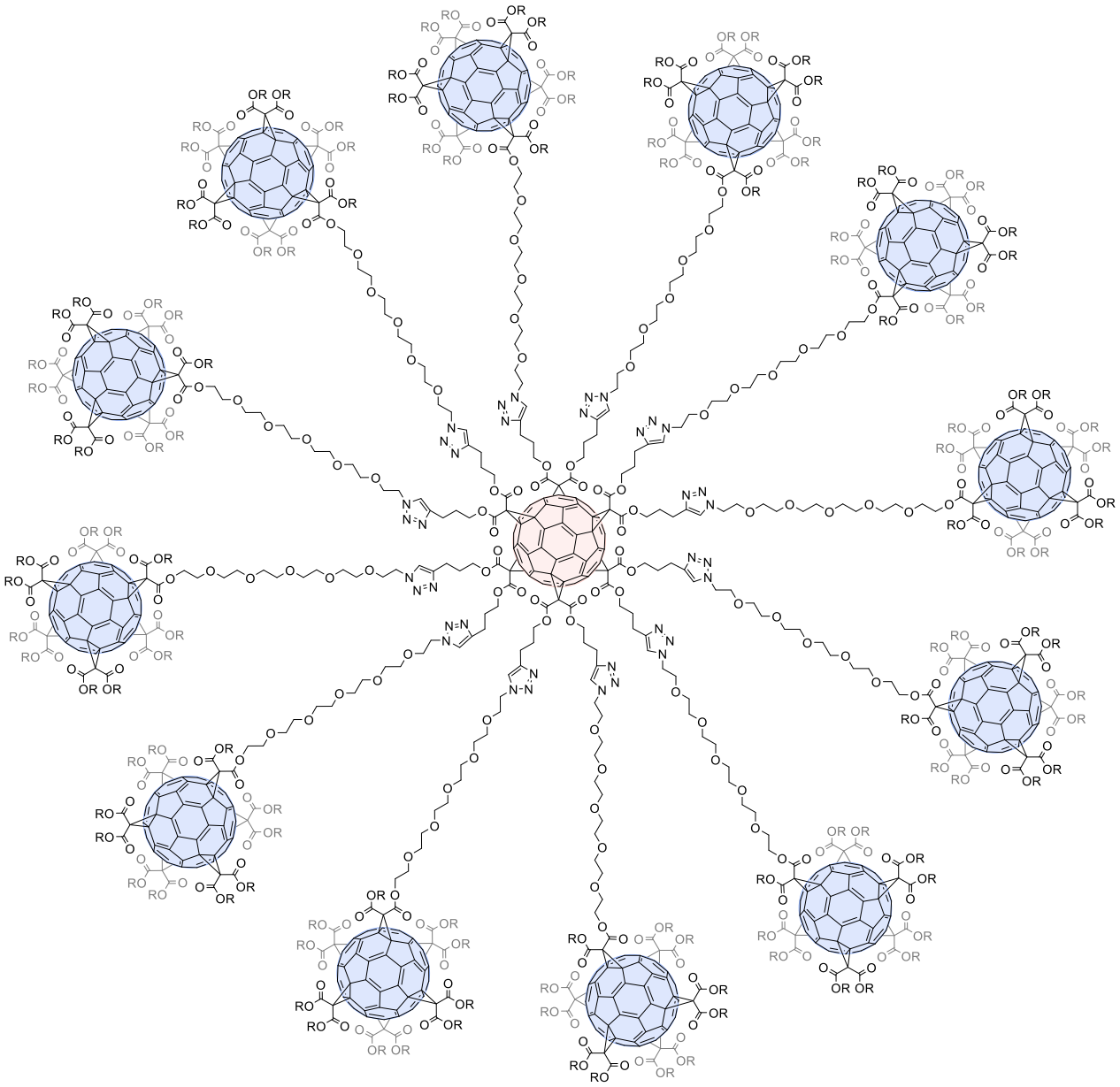


Figure V-4 : Dendritic tridecafullerene derivative synthesized by "click" reaction.

The synthesis of fullerodendrimers with different types of functions disposed in a precisely defined structure at the periphery is still a challenging task. The regio- and stereoselective functionalization of C_{60} and the subsequent post-functionalization of the fullerene derivatives are the main difficulties in order to have access to such type of fullerodendrimers.

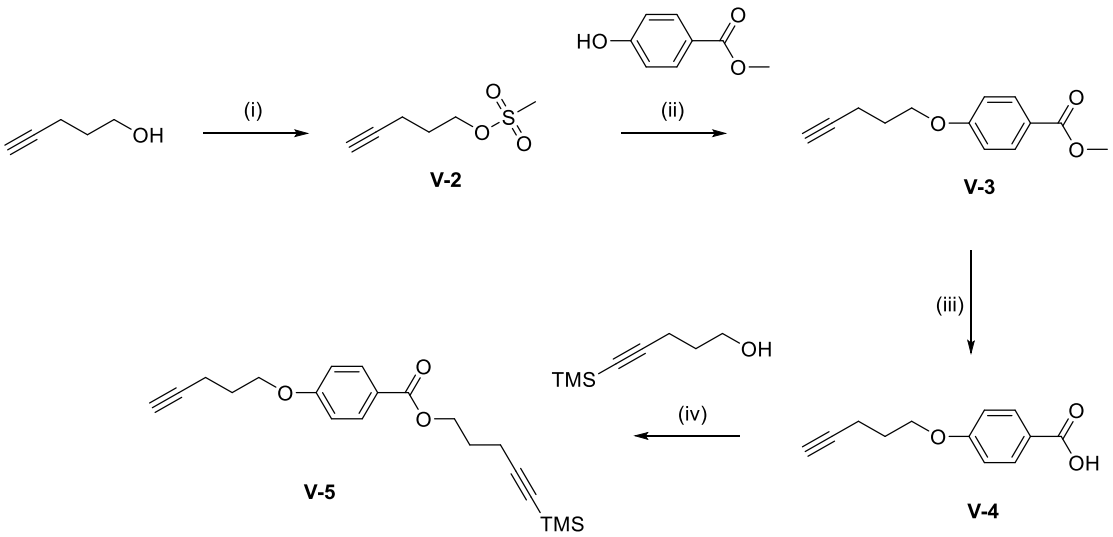
Based on the mixed C_{60} hexa-adducts building blocks developed in the **Chapter IV**, the synthesis of 4 structurally new fullerodendrimers with two different types of functions at the periphery are presented in this chapter.

2. Preparation of tri-, tetra- and pentafullerene derivatives.

The synthesis of the tri-, tetra and pentafullerene derivatives **V-20-22** relies on the grafting of peripheral C_{60} [5:1] hexa-adducts **V-15** onto the central mixed C_{60} hexa-adducts building blocks **V-19**, **IV-18** and **IV-24** (Figure V-5). For synthetic reasons, the peripheral and the central C_{60} hexa-adducts are both bearing azide functions. In order to allow the grafting of the peripheral hexa-adducts onto the central core, the synthesis of a dialkyne linker is therefore also required.

2.1 Preparation of the building blocks.

The synthesis of the dialkyne linker **V-5** is depicted in **Scheme V-*1***. Treatment of 4-pentyn-1-ol with methanesulfonyl chloride ($MeSO_2Cl$) in CH_2Cl_2 in the presence of triethylamine gave compound **V-2**. Subsequent Williamson reaction of methyl 4-hydroxybenzoate with **V-2** afforded compound **V-3** in good yield (83%). Saponification of the methyl ester of **V-3** gave the corresponding carboxylic acid **V-4**. The key derivative **V-5** was then obtained by an esterification reaction of **V-4** with 5-(trimethylsilyl)-4-pentyn-1-ol under Steglich conditions.[18] A key feature of **V-5** is the protection of one alkyne function by a trimethylsilane group. The protected alkyne is inert under CuAAC reaction conditions and allows the functionalization of only one side of the linker **V-5**.



Scheme V-1. Reagents and conditions: (i) $MeSO_2Cl$, trimethylamine, CH_2Cl_2, rt, 1 h (96%); (ii) K_2CO_3, crown 18C6 (cat.), acetone, reflux, 1.5 d (83%); (iii) KOH, THF/EtOH, reflux, 2.5 h (96%); (iv) DCC, DMAP, CH_2Cl_2, 0 °C to rt, 12 h (65%).

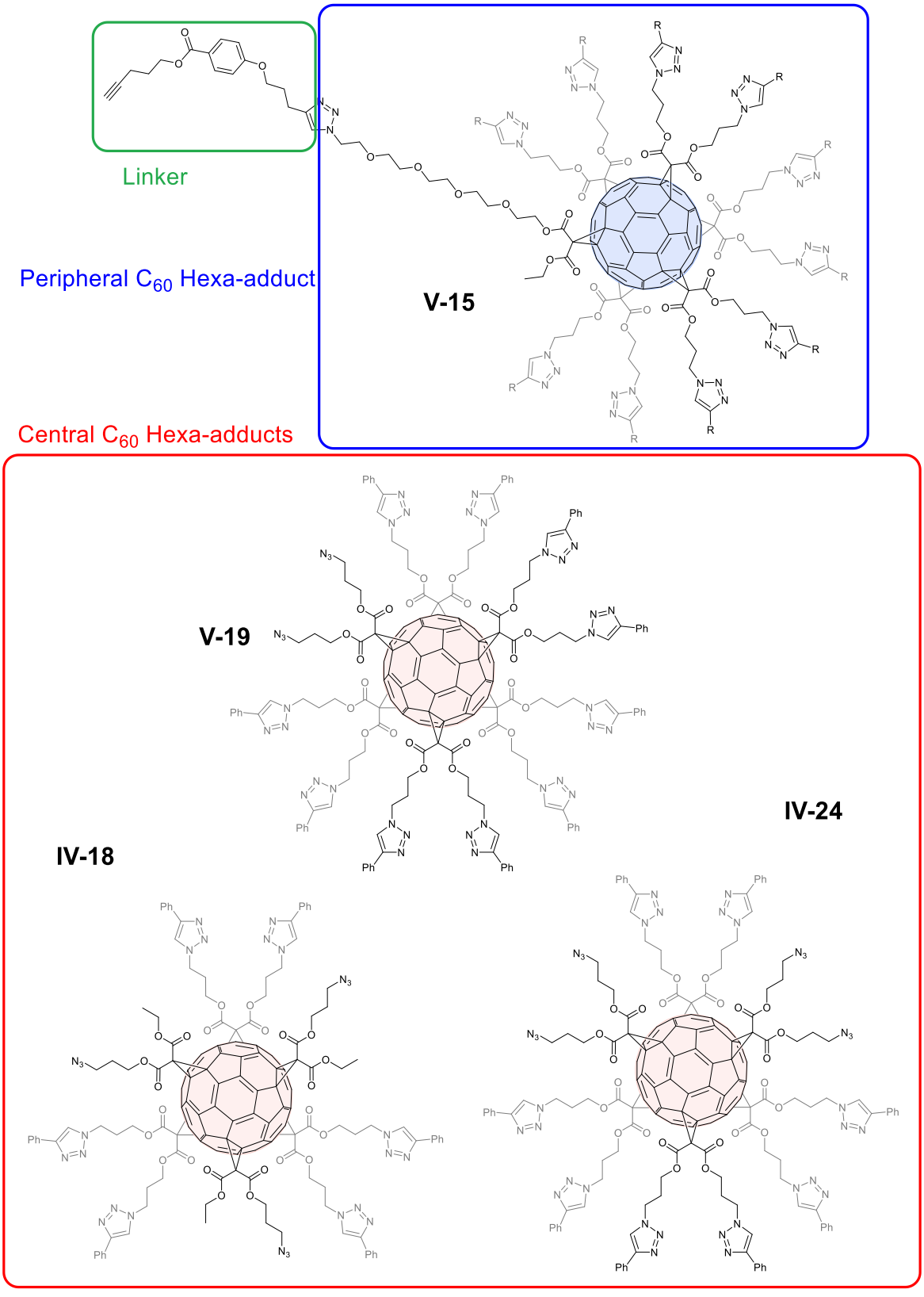
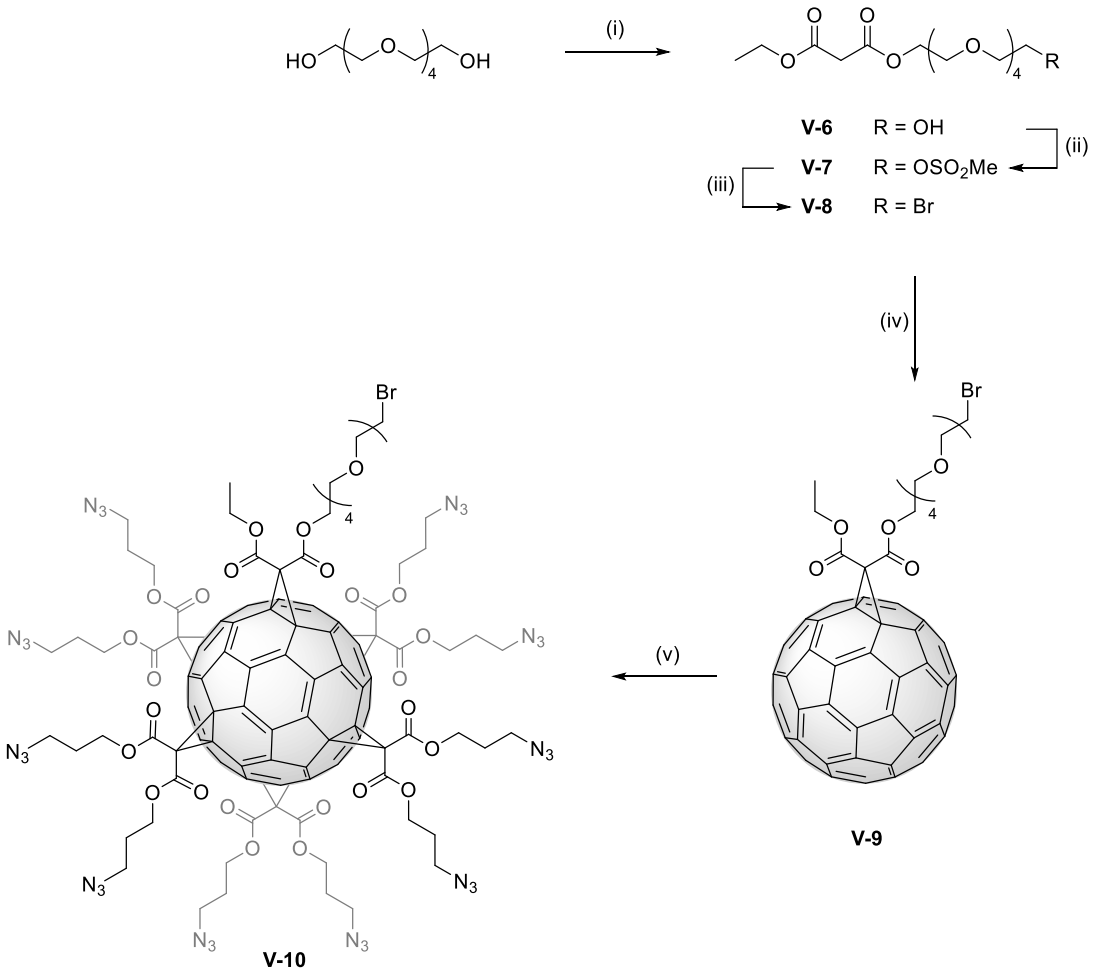


Figure V-5 : C_{60} hexa-adducts building blocks for the preparation the tri-, tetra and pentafullerene derivatives ***V-20-22.***

The preparation of the peripheral C_{60} [5:1] hexa-adduct **V-14** is depicted in **Scheme V-*2***. Reaction of an excess of pentaethylene glycol with ethyl malonyl chloride in the presence of pyridine gave malonate **V-6** in 65% yield. Mesylation of **V-6** by treatment with $MeSO_2Cl/Et_3N$ followed by a bromination reaction with LiBr afforded malonate **V-8**. Reaction of malonate **V-8** with C_{60} in the presence of I_2 and DBU gave the mono-adduct **V-9** in 51% yield. Subsequent reaction of **V-9** with malonate **IV-12** (6.5 equiv.), CBr_4 (65 equiv.) and DBU (16 equiv.) in toluene gave hexa-adduct **V-10**. The "clicked" compounds **V-12a-b** were then prepared from **V-10** under typical CuAAC reaction conditions (**Scheme V-*3***). Compounds **V-12a-b** have been characterized by NMR, UV-vis and IR spectroscopies and mass spectrometry. As previously reported for [5:1] C_{60} hexa-adducts,[9,19,20] the ^{13}C NMR spectra of **V-12a-b** reveal the influence of the high local symmetry. Only one set of signals is observed for the five pseudoequivalent "clicked" malonates (Figure V-6). The signals of the unique malonate are also clearly distinguishable.



Scheme V-2. Reagents and conditions: (i) Ethyl malonyl chloride, pyridine, CH_2Cl_2, rt, 2 h (65%); (ii) $MeSO_2Cl$, trimethylamine, CH_2Cl_2, rt, 1 h (91%); (iii) LiBr, THF, 60 °C, 4 h (87%); (iv) C_{60}, I_2, DBU, PhMe, rt, 1 h (51%); (v) **IV-12**, CBr_4, DBU, PhMe, rt, 12 h (38%).

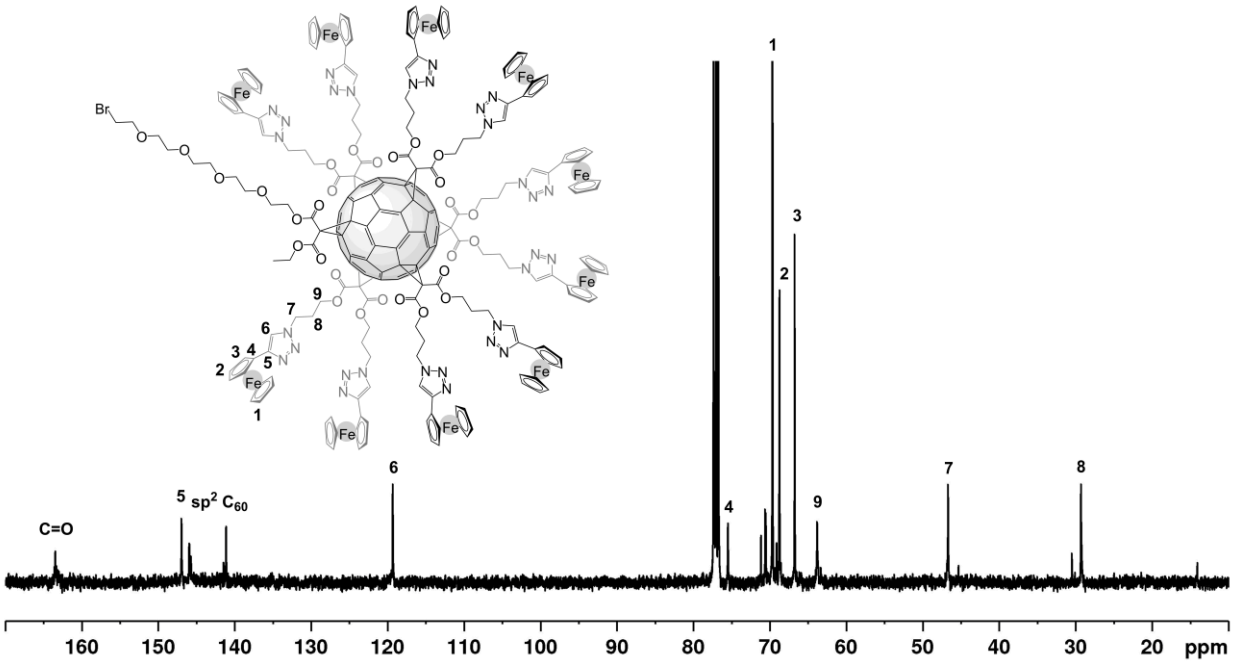
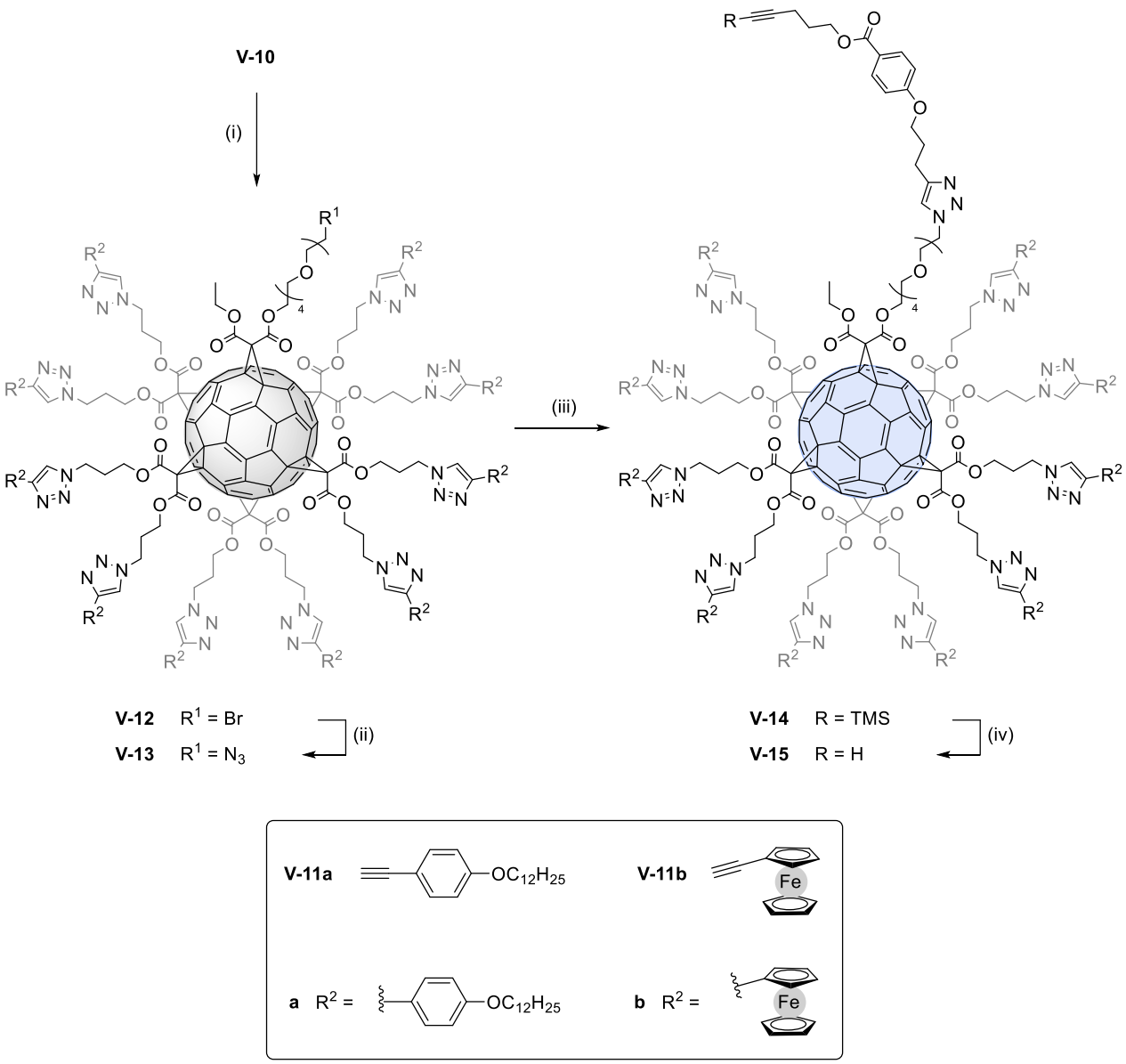


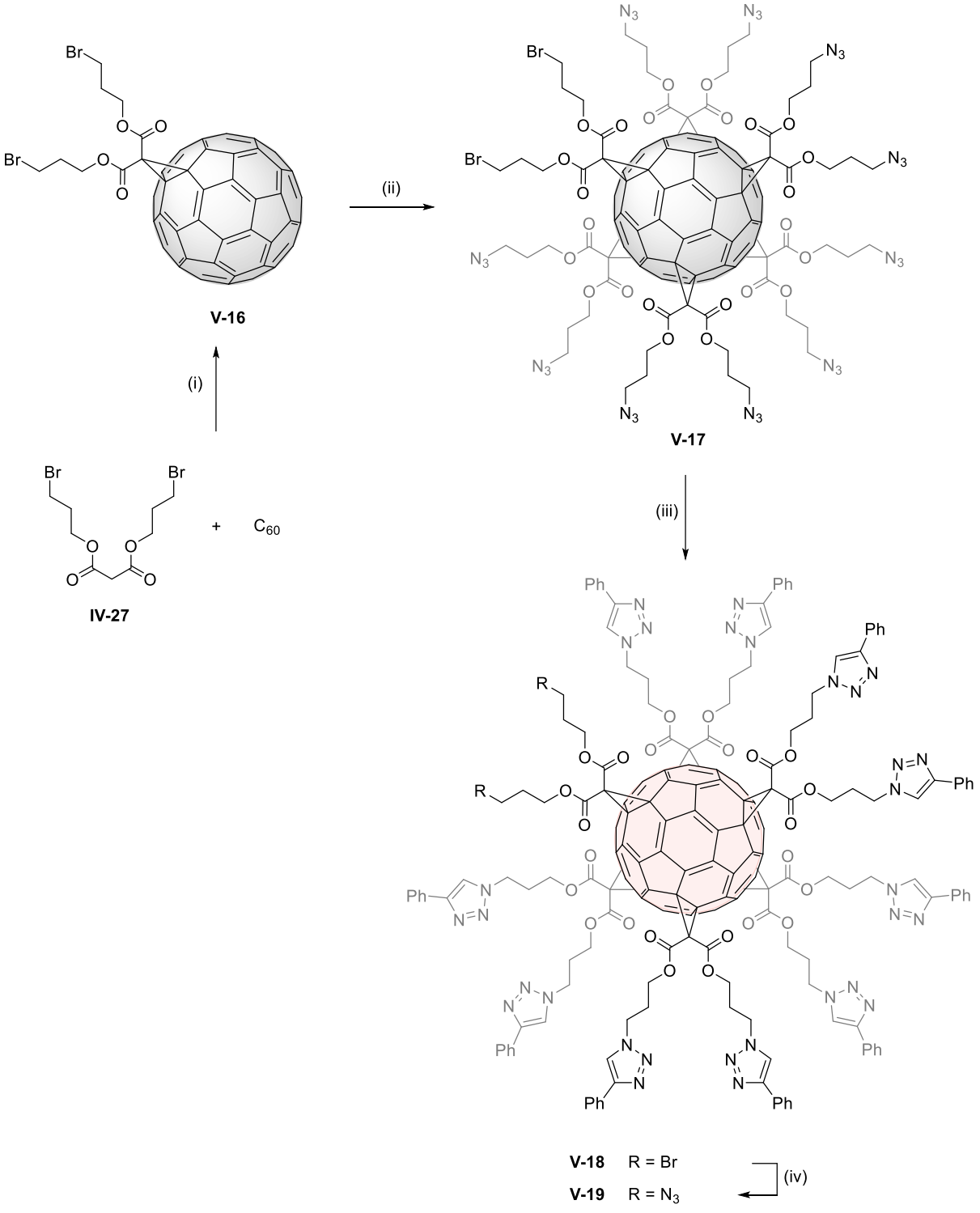
*Figure V-6 : ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **V-12b** showing the influence of the high local symmetry.*

The key derivatives **V-15a-b** were obtained in 3 steps from compound **V-12a-b** (**Scheme V-*3***). Conversion of the bromides was carried out by treatment of **V-12a-b** with sodium azide in DMF to afford the corresponding azides (**V-13a-b**). Reaction of **V-13a-b** with the dialkyne linker **V-5** under CuAAC reaction conditions gave compounds **V-14a-b** in very good yields (99% and 88%, respectively). Finally, the deprotection of the trimethylsilyl group (TMS) was performed by treatment of **V-14a-b** with tetrabutylammonium fluoride (TBAF) in THF at 0 °C to afford the key derivatives **V-15a-b**. In both cases, the removal of the TMS group was confirmed by NMR and IR spectroscopies as well as by mass spectrometry.



Scheme V-3. Reagents and conditions: (i) **V-11a or b**, $CuSO_4.5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, 30 °C, 12 h (**V-12a**: 97%, **V-12b**: 87%; (ii) NaN_3, DMF, rt, 12 h (**V-13a**: 93%, **V-13b**: 94%); (iii) **V-5**, $CuSO_4.5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, 30 °C, 2.5 h (**V-14a**: 99%, **V-14b**: 88%); (iv) TBAF, THF, 0 °C, 20 min (**V-15a**: 99%, **V-15b**: 92%).

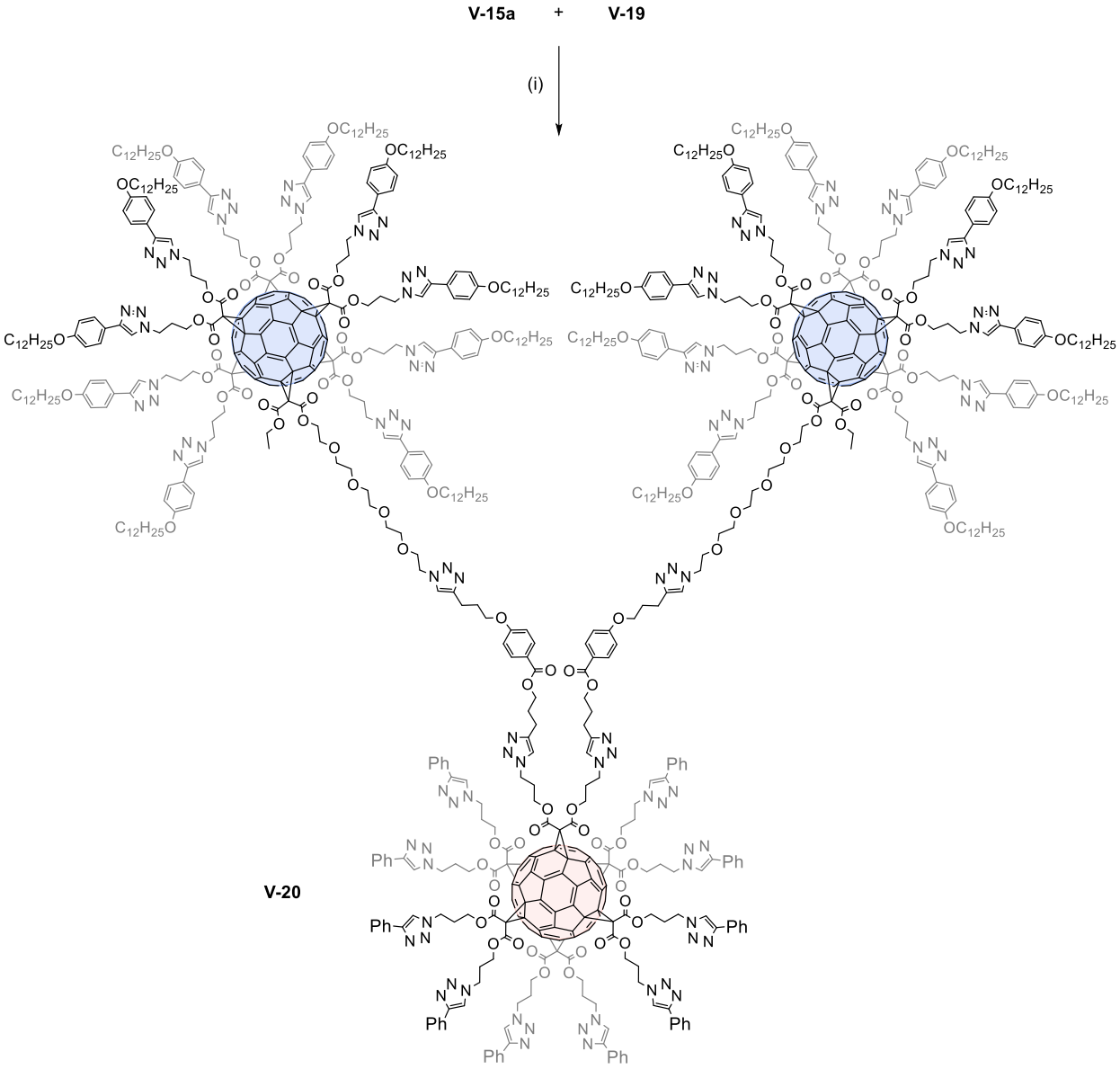
The synthesis of **V-19** is depicted in **Scheme V-*4***. Reaction of the malonate **IV-27** with C_{60} in the presence of I_2 and DBU afforded the mono-adduct **V-16** in 51% yield. Subsequent reaction of **V-16** with the malonate **IV-12** (7 equiv.), CBr_4 (70 equiv.) and DBU (17 equiv.) in toluene at room temperature gave the hexa-adduct **V-17**. Reaction of **V-17** with phenylacetylene under typical conditions of CuAAC reactions gave the "click" compound **V-18** in a good yield (79%). Compound **V-18** has been characterized by NMR, UV-vis and IR spectroscopies. In addition, the MALDI-TOF mass spectrum was also consistent with the proposed structure. Finally, the bromide functions in **V-18** were converted into azides to afford the mixed C_{60} hexa-adduct building blocks **V-19.**



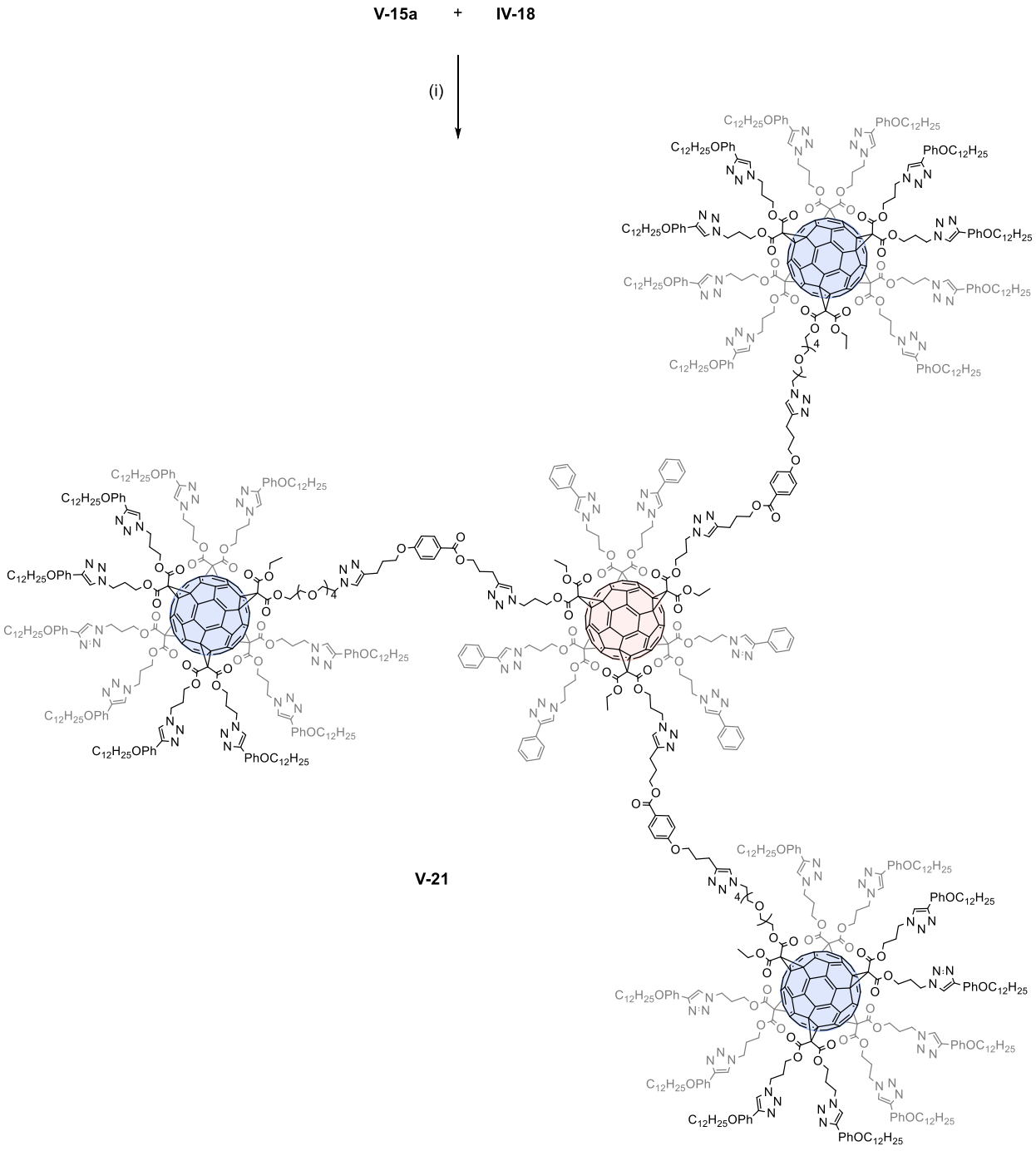
Scheme V-4. Reagents and conditions: (i) I_2, DBU, PhMe, rt, 1 h (51%); (ii) **IV-12**, CBr_4, DBU, PhMe, 12 h (55%); (iii) Phenylacetylene, $CuSO_4.5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, 30 °C, 12 h (79%); (iv) NaN_3, DMF, rt, 12 h (93%).

2.2 Synthesis of tris-, tetra- and pentafullerene derivatives.

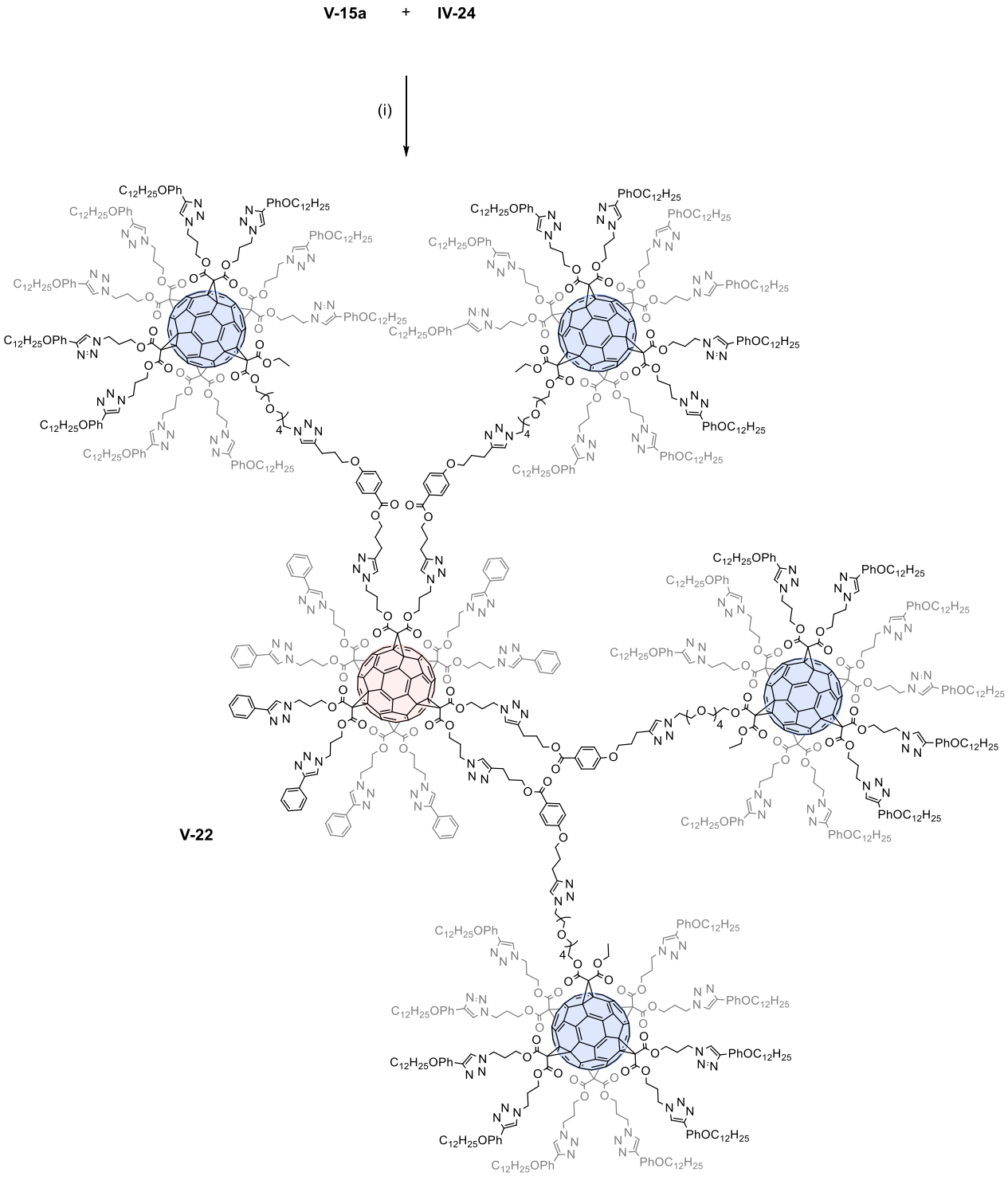
Based on the previously prepared building blocks, the syntheses of the trifullerene derivative **V-20** (**Scheme V-*5***), the tetrafullerene derivative **V-21** (**Scheme V-*6***) and the pentafullerene derivative **V-22** (**Scheme V-*7***) were achieved. Reaction of the peripheral C_{60} [5:1] hexa-adducts **V-15a** with the appropriated mixed C_{60} hexa-adduct building block (**V-19**, **IV-18** or **IV-24**) under CuAAC reaction conditions afforded the compounds **V-20-22**. Purification of **V-20-22** were achieved by column chromatography on silica gel followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2).



Scheme V-5. Reagents and conditions: (i) $CuSO_4.5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, 30 °C, 12 h (56%).



Scheme V-6. Reagents and conditions: (i) $CuSO_4.5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, 30 °C, 12 h (62%).



Scheme V-7. Reagents and conditions: (i) $CuSO_4.5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, 30 °C, 12 h (68%).

Compounds **V-20-22** have been characterized by NMR, UV-vis and IR spectroscopies and mass spectrometry. The ^{1}H NMR spectrum of **V-22** is showed in Figure V-7 as typical example. The appearance of a second resonance between δ =2.8-2.9 ppm relative to the $CH_2C_{triazole}$ signal indicates that compound **V-22** is "clicked" on compound **IV-24**. The integration ratio of the signals of each different protons is also compatible with the proposed structure. Furthermore, the ^{1}H NMR spectrum reveals the absence of resonance at δ = 1.9 and 3.3 ppm relative to the $CH_2CH_2N_3$ parts of **IV-24** and at δ = 2.0 ppm relative to the $CH_2CH_2C{\equiv}CH$ parts of **V-15a**. These latter observations are also confirmed by the IR data with the absence of signal for the azide (2098 cm^{-1}) and for the alkyne (3315 cm^{-1}).

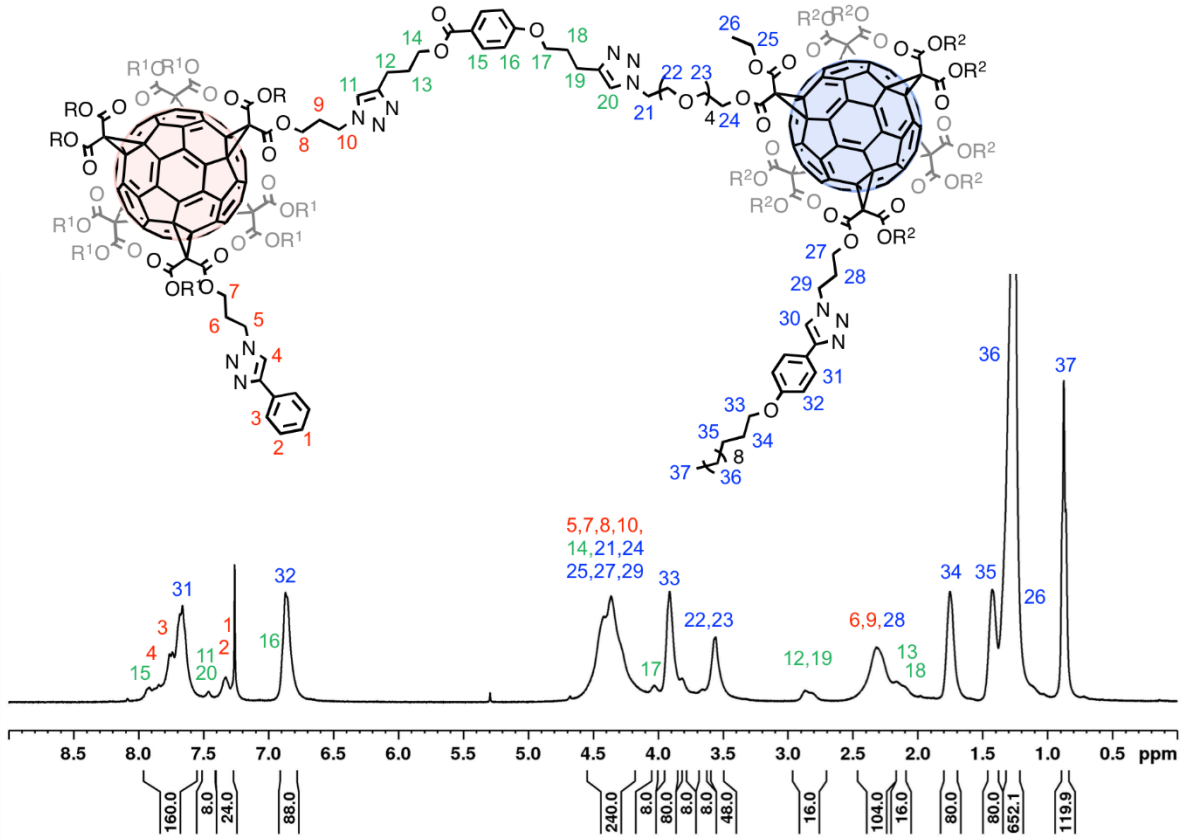


*Figure V-7 : ^{1}H NMR spectrum (400MHz, $CDCl_3$) of **V-22**.*

In addition, the MALDI-TOF mass spectra were consistent with the proposed structures. Due to the high molecular weight, the signals are broad and thus the resolution of the spectra are not optimum. Furthermore, high level of fragmentation is also observed. In the case of compounds **V-20 and V-22**, the molecular ion peak could not be measured precisely (**V-20**: *m/z* = 14489 ([M]$^+$, calcd for $C_{868}H_{938}O_{106}N_{102}$: 14495); **V-22**: *m/z* ≈ 25440 ([M]$^+$, calcd for $C_{1526}H_{1732}O_{188}N_{168}$: 25434)). For compound **V-21**, the molecular ion peak is not detected. Nonetheless, characteristic fragmentation resulting from ester hydrolysis followed by decarboxylation and retro-Bingel reactions on the peripheral C_{60} hexa-adducts are observed on the three mass spectra (Figure V-8).[21,22] All these observations are proofs of the formation of compounds **V-20-22**.

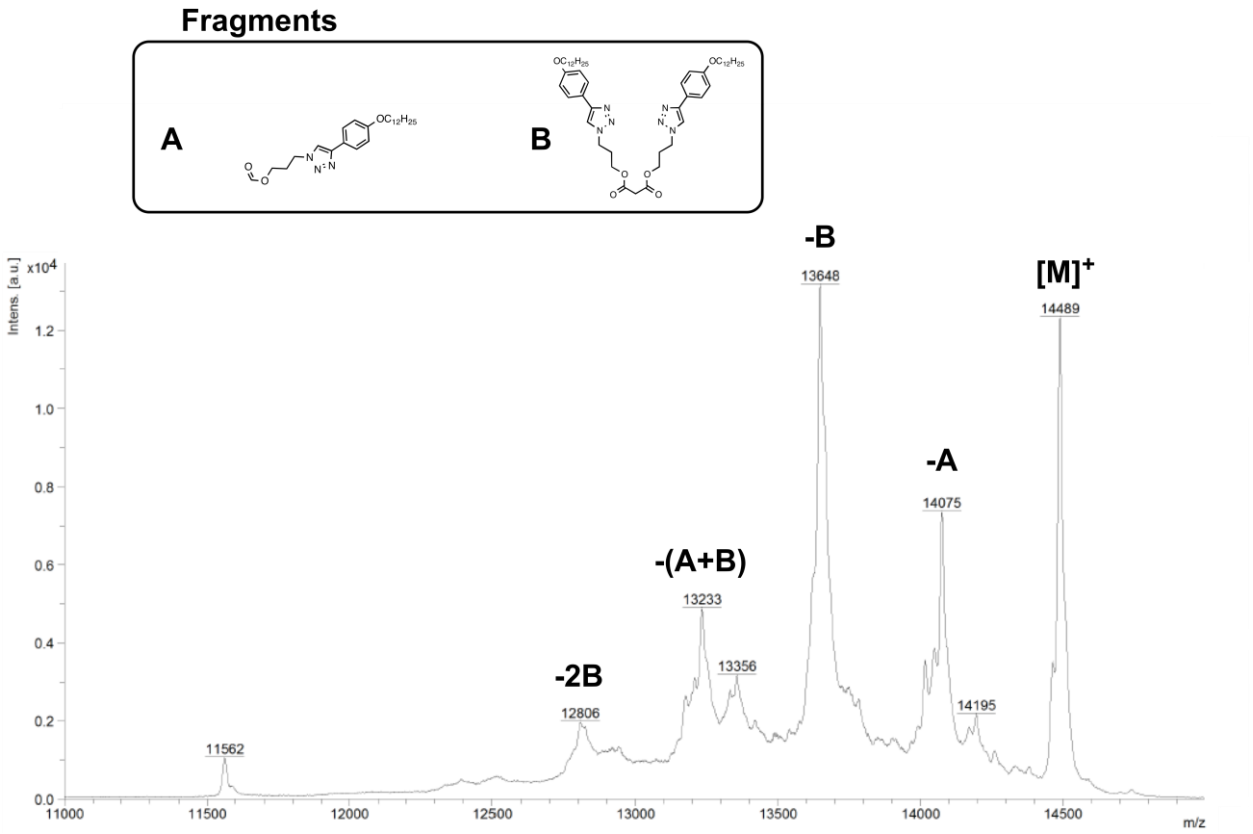


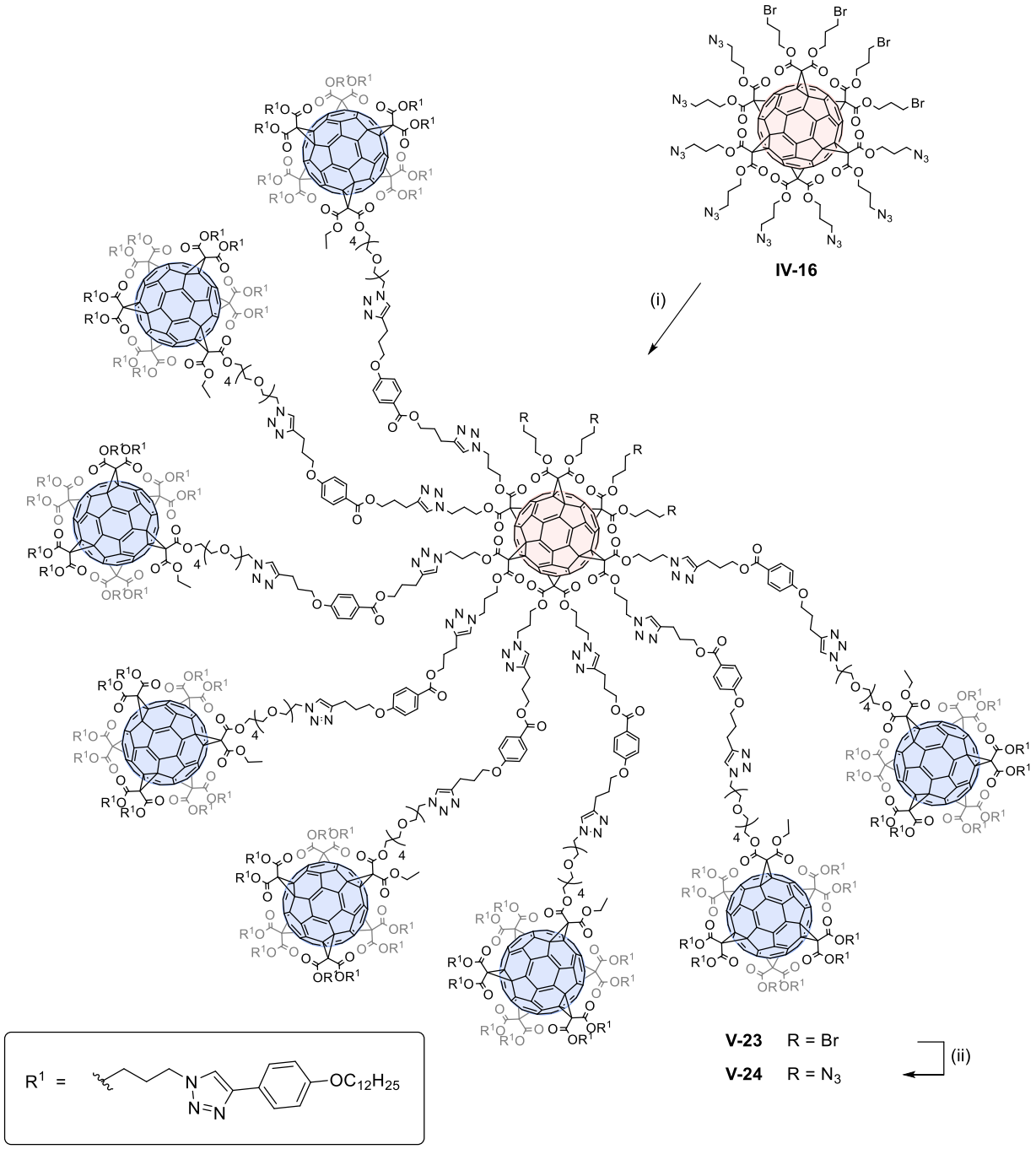
*Figure V-8 : MALDI-TOF mass spectrum of **V-20** showing the characteristic fragmentations.*

Compounds **V-20-22** are decorated with two types of functions in a 20:10, 30:6 and 40:8 ratio, respectively. Each peripheral C_{60} hexa-adduct bears 10 dodecoxyphenyl groups and the central C_{60} hexa-adducts 6 to 10 phenyl groups. Compounds **V-20-22** represent new examples of multi- and poly- functional molecules synthesized with a perfect control of the regiochemistry.

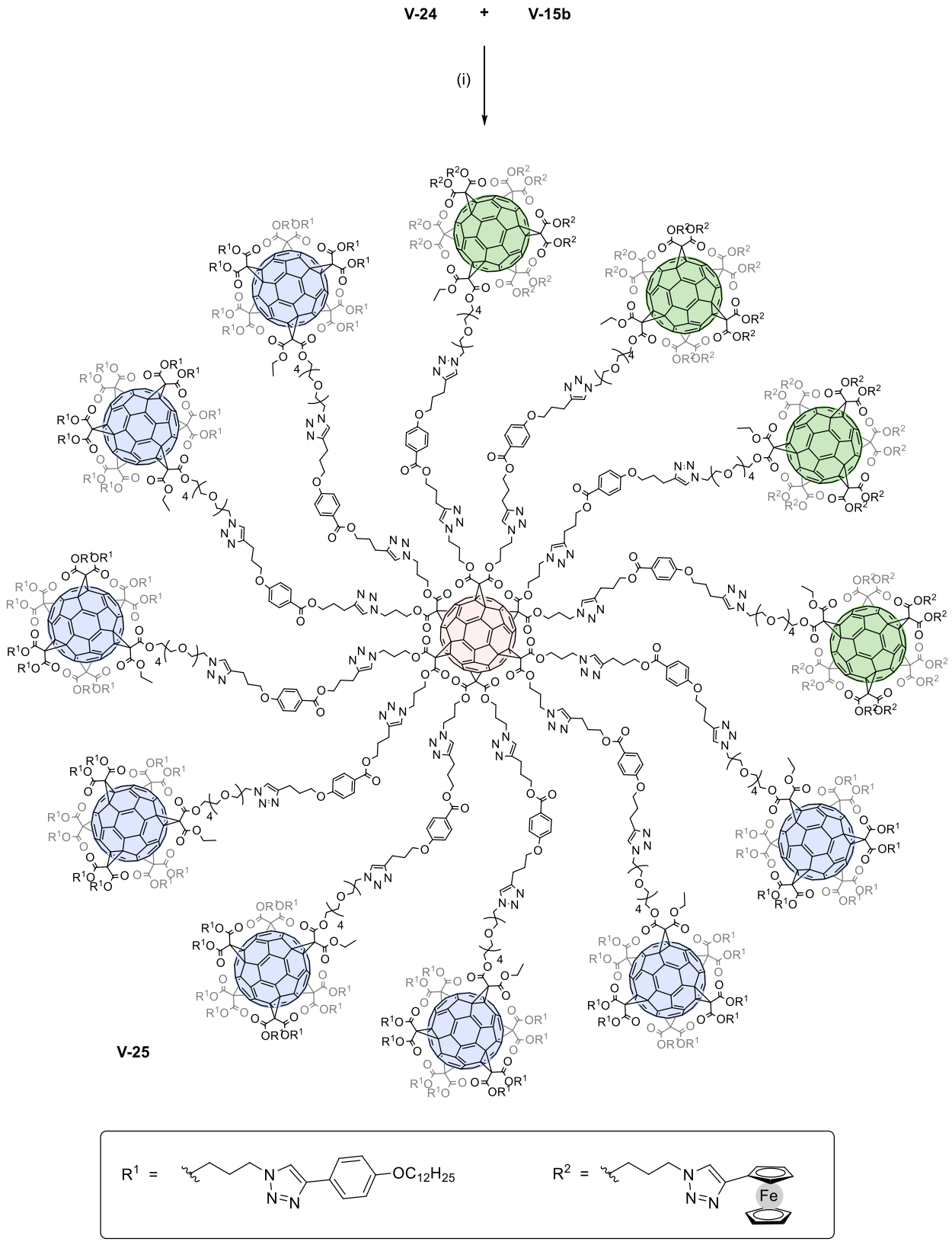
3. Giant mixed C_{60} hexa-adducts dendrimer.

The synthesis of the giant mixed tridecafullerene **V-25** relies on the sequential grafting of two different peripheral C_{60} [5:1] hexa-adducts (**V-15a** and **V-15b**) onto a central mixed C_{60} hexa-adduct building block (**IV-16**). Reaction of **V-15a** with **IV-16** under CuAAC reaction conditions afforded the nonafullerene derivative **V-23** (**Scheme V-*8***). The ^{1}H NMR spectrum of **V-23** reveals the same characteristic features as described previously for compound **V-22**. In addition, the IR data show the absence of unreacted azide (2098 cm^{-1}) and alkyne (3315 cm^{-1}) residues. Treatment of **V-23** with sodium azide in DMF was next performed to afford compound **V-24**. The total conversion into azide functions was confirmed by the change in chemical shift for the terminal methylene group: from δ = 3.41 ppm for the CH_2Br signals to δ = 3.35 ppm for the CH_2N_3 signals. Finally, **V-25** was obtained by a second CuAAC reaction of **V-24** with **V-15b** (**Scheme V-*9***). The ^{1}H NMR spectrum of **V-25** is showed in Figure V-9. The signals relative to the substituents of the two different peripheral C_{60} hexa-adducts are clearly distinguishable. Furthermore, the resonances attributed to the aromatic protons of the 1,2,3-triazole and the $CH_2C_{triazole}$ of the linker sub-units are observed at δ = 7.45 and 2.85 ppm, respectively. The integration ratio of each different signal is also in agreement with the proposed structure. The ^{13}C NMR spectrum of **V-25** shows the strong influence of the high local symmetry (Figure V-9). The differentiation is only observed for the terminal sub-units grafted onto the peripheral C_{60} hexa-adducts. The characteristic signals of [$C_{18,27}$] and [$C_{19,26}$] of the linker subunits are detected at δ = 122.0 and 22.2 ppm. The signal of [C_{17}] is also detected at δ = 50.1 ppm. The MALDI-TOF experiment was not suited for compound **V-25** and only broad signals were observed. Nonetheless, these signals are in the expected molecular weight range.

Compound **V-25** is a first generation dendrimer possessing 120 peripheral functions. 80 dodecoxyphenyl groups are brought by 8 peripheral C_{60} hexa-adducts with the first CuAAC reaction and 40 ferrocene groups by 4 other peripheral C_{60} hexa-adducts with the second CuAAC reaction. Compound **V-25** is the first example of giant multi-functionalized fullerodendrimer synthesized with the control of the regiochemistry.



Scheme V-8. Reagents and conditions: (i) **V-15a**, $CuSO_4.5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, 30 °C, 12 h (70%); (ii) NaN_3, DMF, rt, 12 h (88%).



Scheme V-9. Reagents and conditions: (i) $CuSO_4.5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, 37 °C, 7 d (72%).

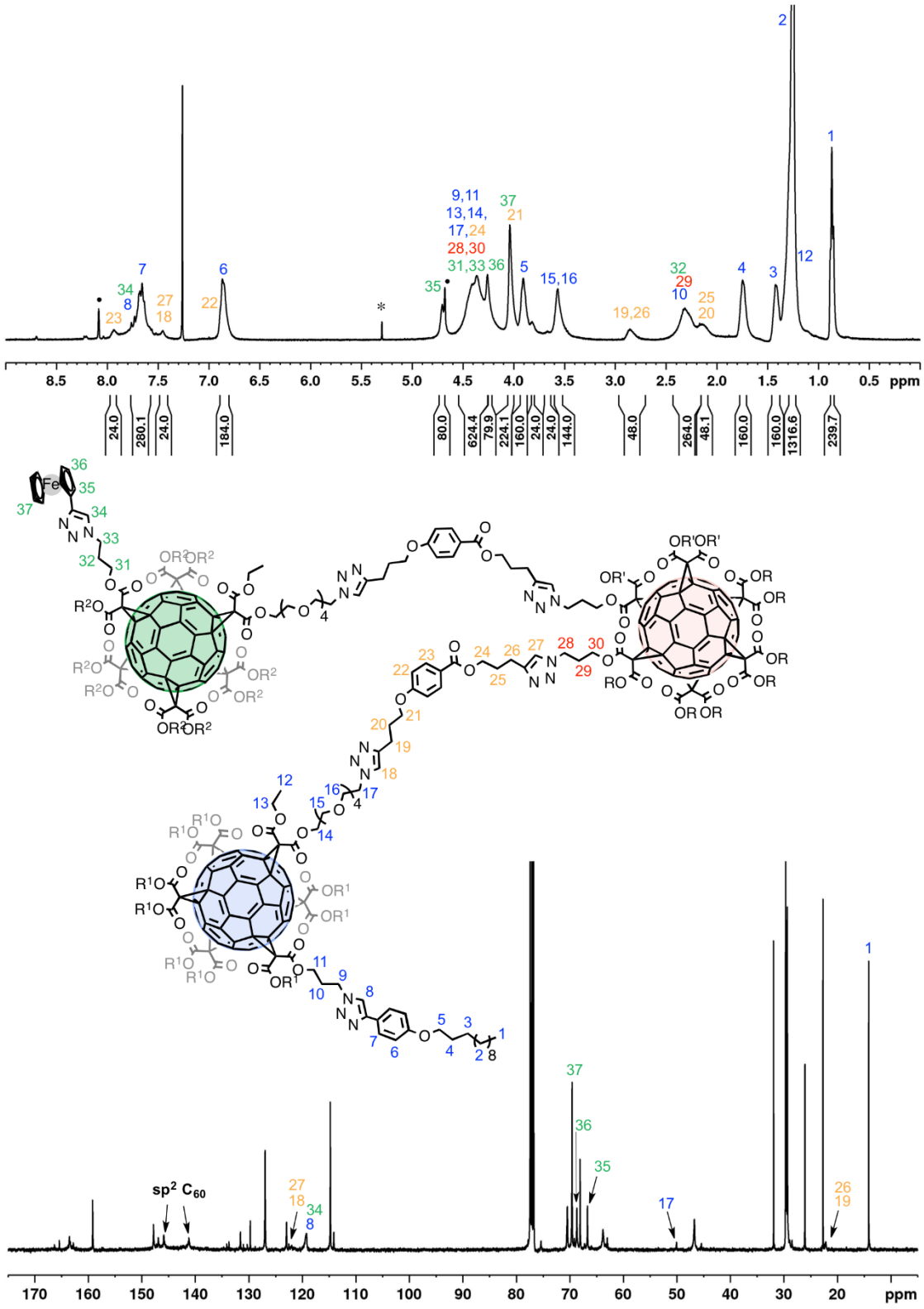


*Figure V-9 : (top) ^{1}H NMR spectrum (400MHz, $CDCl_3$) of **V-25**, * CH_2Cl_2, • impurities; (bottom) ^{13}C NMR spectrum (100MHz, $CDCl_3$) of **V-25**.*

4. Conclusion.

The synthesis of fullerodendrimers based on C_{60} mixed hexa-adduct building blocks has been achieved. The grafting of the peripheral C_{60} [5:1] hexa-adducts onto a central C_{60} hexa-adduct has been efficiently performed under CuAAC reaction conditions. Two defined function zones are thus generated. Different ratios of the functional groups have been thus obtained (20:10, 30:6, 40:8 and 80:40). Based on our different C_{60} hexa-adducts building blocks, the controlled elaboration of new nanomaterials and bioactive molecules should become easily accessible.

5. Bibliography.

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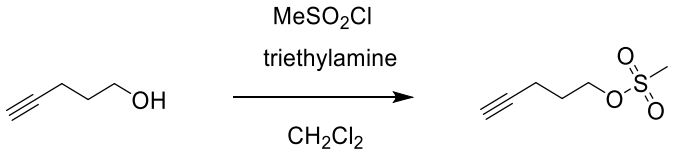
6. Experimental part.

General: Reagents and solvents were purchased as reagent grade and used without further purification. All reactions were performed in standard glassware under an inert Ar atmosphere. Evaporation and concentration were done at water aspirator pressure and drying in vacuo at 10^{-2} Torr. Column chromatography: silica gel 60 (230-400 mesh, 0.040-0.063 mm) was purchased from E. Merck. Thin Layer Chromatography (TLC) was performed on aluminum sheets coated with silica gel 60 F_{254} purchased from E. Merck. IR spectra (cm^{-1}) were recorded on a Perkin–Elmer Spectrum One Spectrophotometer. UV/Visible spectra were recorded on a Perkin-Elmer Lamda 35 UV/Vis Spectrometer. NMR spectra were recorded on a Bruker AC 300 or AC 400 with solvent peaks as reference at 25°C. MALDI-TOF-MS were obtained on a Bruker ULTRAFLEX TOF/TOF mass spectrometer with a dithranol matrix.

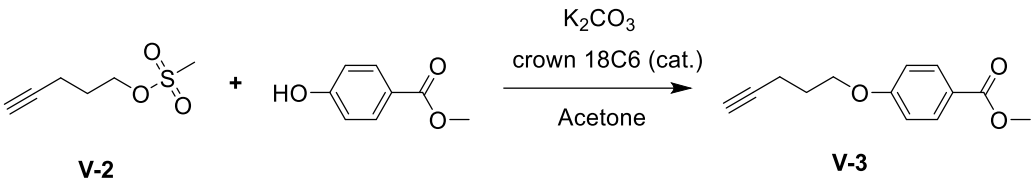
Synthesis.



V-2

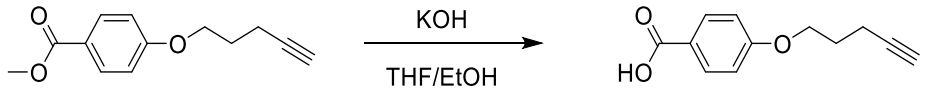
Compound V-2: Methanesulfonyl chloride (5 mL, 64 mmol) was added to a solution of 4-pentyn-1-ol (3 mL, 32 mmol) and triethylamine (9 mL, 64 mmol) in CH_2Cl_2 (100 mL). The resulting mixture was stirred at room temperature for 1 h, then filtered on SiO_2 (CH_2Cl_2) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 5:5 to CH_2Cl_2) yielded **V-2** (5 g, 30.8 mmol, 96%) as a white solid. IR (neat): υ = 3287 (C≡CH), 2119 (C≡C) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.36 (t, ^3J = 6 Hz, 2 H, CH_2CH_2O), 3.03 (s, 3 H, OSO_2CH_3), 2.37 (dt, ^3J = 6

Hz & ^4J = 2 Hz, 2 H, C≡CCH_2CH$_2$), 2.01 (t, ^4J = 2 Hz, 1 H, C≡CH), 1.97 (quint., ^3J = 6 Hz, 2 H, CH$_2$CH_2CH$_2$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 82.1, 69.8, 68.2, 37.3, 27.8, 14.7 ppm.



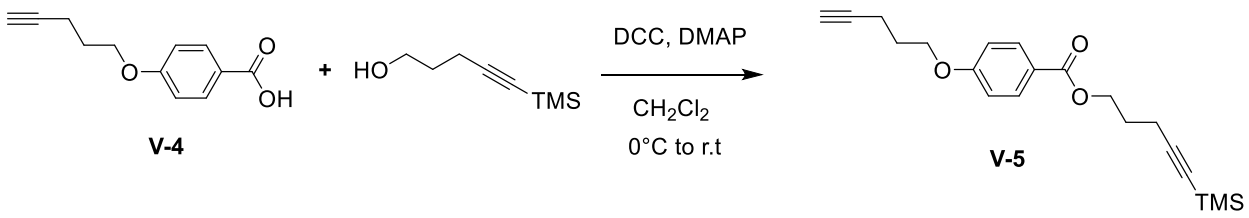
V-2 **V-3**

Compound V-3: V-2 (5.00 g, 30.8 mmol) was added to a solution of methyl 4-hydroxybenzoate (4.69 g, 30.8 mmol), K_2CO_3 (17 g, 123 mmol) and crown 18C6 (cat.) in acetone (250 mL). The resulting mixture was stirred under reflux for 1.5 days, then the salts was filtered and the product was extracted with Et_2O, washed with H_2O and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 7:3) yielded **V-3** (5.57 g, 25.5 mmol, 83%) as a white solid. IR (neat): υ = 3296 (C≡CH), 2119 (C≡C), 1712 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.98 (d, ^3J = 8 Hz, 2 H, ArH_o), 6.91 (d, ^3J = 8 Hz, 2 H, ArH_m), 4.12 (t, ^3J = 6 Hz, 2 H, CH$_2$CH_2OAr), 3.88 (s, 3 H, COOCH_3), 2.41 (dt, ^3J = 6 Hz & ^4J = 2 Hz, 2 H, C≡CCH_2CH$_2$), 2.02 (quint., ^3J = 6 Hz, 2 H, CH$_2$CH_2CH$_2$), 1.98 (t, ^4J = 2 Hz, 1 H, C≡CH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.8, 162.7, 131.6, 122.6, 114.6, 83.2, 69.1, 66.3, 51.8, 28.0, 15.1 ppm.



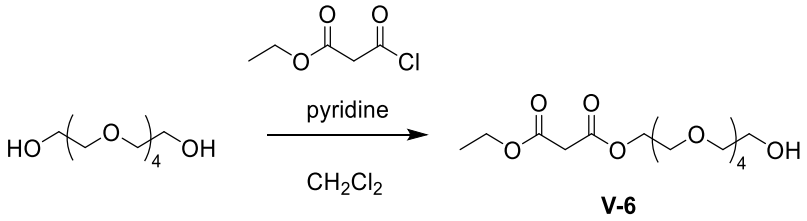
V-3 **V-4**

Compound V-4: A solution of **V-3** (1.60 g, 7.33 mmol) and KOH (4.14 g, 73.3 mmol) in THF/EtOH (200 : 100 mL) was stirred under reflux for 2.5 h. Then the solvent was removed under reduced pressure, resolubized in CH_2Cl_2/H_2O and acidified with HCl (aq). The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure yielded **V-4** (1.44 g, 7.1 mmol, 96%) as a white solid. IR (neat): υ = 3301 (C≡CH), 2116 (C≡C), 1685 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.06 (d, ^3J = 8 Hz, 2 H, OOCArH_o), 6.95 (d, ^3J = 8 Hz, 2 H, OOCArH_m), 4.15 (t, ^3J = 6 Hz, 2 H, OCH_2CH$_2$), 2.43 (dt, ^3J = 6 Hz & ^2J = 2 Hz, 2 H, CH$_2$CH_2C≡CH), 2.04 (quint., ^3J = 6 Hz, 2 H, CH$_2$CH_2CH$_2$), 1.99 (t, ^4J = 2 Hz, 1H, CH$_2$C≡CH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 171.4, 163.4, 132.4, 121.6, 114.2, 83.1, 69.1, 66.4, 28.0, 15.1 ppm.



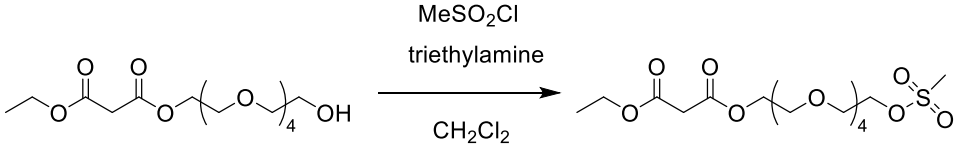
V-4 **V-5**

Compound V-5: DCC (557 mg, 2.7 mmol) was added to a solution of **V-4** (500 mg, 2.4 mmol), 5-trimethylsilyl-4-pentyn-1-ol (0.44 mL, 2.4 mmol), DMAP (61 mg, 0.5 mmol) in CH_2Cl_2 (40 mL) at 0°C. The resulting mixture was stirred at room temperature for 2.5 d. Then filtered on SiO_2 (CH_2Cl_2) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 5:5) yielded **V-5** (546 mg, 1.6 mmol, 65%) as a colorless oil. IR (neat): $\upsilon = 3301$ (C≡C-H), 2176 (C≡CSi), 2119 (C≡CH), 1713 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.98 (d, ^3J = 9 Hz, 2 H, ArH_o), 6.91 (d, ^{3}J = 9 Hz, 2 H, ArH_m), 4.37 (t, ^3J = 6 Hz, 2 H, COOCH_2CH$_2$), 4.13 (t, ^3J = 6 Hz, 2 H, ArOCH_2CH$_2$), 2.42 (m, 4H, CH$_2$CH_2C≡C), 2.05-1.96 (m, 5 H, CH$_2$CH_2CH$_2$ & C≡C*H*), 0.15 (s, 9 H, Si(CH_3)$_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.2, 162.6, 131.5, 122.6, 114.0, 105.8, 85.2, 83.1, 69.0, 66.2, 63.2, 27.9 (two peaks), 16.7, 15.0, 0.0 ppm.



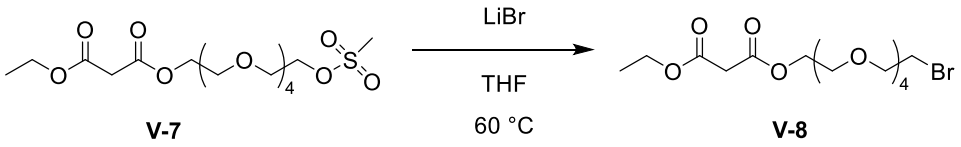
V-6

Compound V-6: Malonyl chloride (0.25 mL, 1.95 mmol) in CH_2Cl_2 (40 mL) was added dropwise to a solution of pentaethylene glycol (0.82 mL, 3.90 mmol) and pyridine (0.17 mL, 2.15 mmol) in CH_2Cl_2 (30 mL). The resulting mixture was stirred for 2 h at room temperature. The reaction mixture was filtered on SiO_2 and concentrated. Column chromatography (SiO_2, CH_2Cl_2/ether/MeOH 100:10:0 to 100:10:3) gave **V-6** (444 mg, 65%) as a colorless oil. IR (neat): υ = 3456 (br, OH), 1730 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.33 (t, ^3J = 4 Hz, 2 H, COOCH_2CH$_2$O), 4.22 (q, ^3J = 7 Hz, 2 H, COOCH_2CH$_3$), 3.74 (t, ^3J = 4 Hz, 4 H, CH_2(OCH$_2$CH$_2$)$_3$OCH_2), 3.71-3.66 (m, 12 H, CH$_2$(OCH_2CH_2)$_3$OCH$_2$), 3.43 (s, 2 H, OOCCH_2COO), 2.08 (s, 1 H, O*H*), 1.30 (t, ^3J = 7 Hz, 3 H, CH$_2$CH_3) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.7, 166.5, 72.5, 70.6, 70.5, 70.4, 68.8, 64.6, 61.8, 61.6, 41.5, 14.1 ppm.



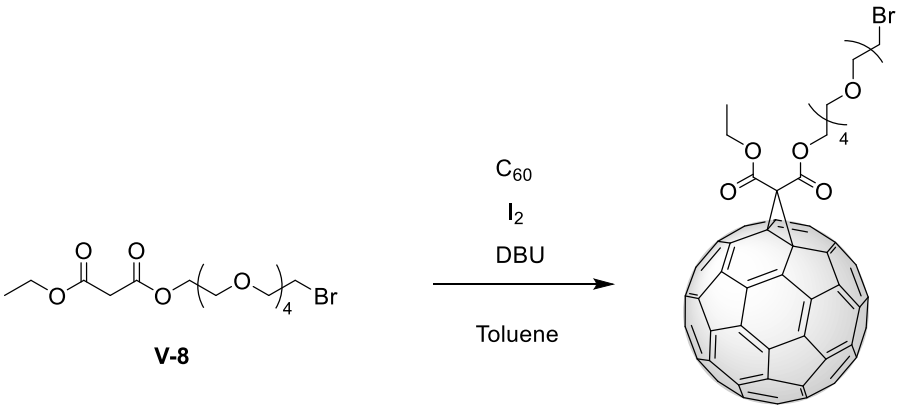
V-6 **V-7**

Compound V-7: Methanesulfonyl chloride (0.18 mL, 2.27 mmol) was added to a solution of **V-6** (400 mg, 1.14 mmol) and triethylamine (0.32 mL, 2.27 mmol) in CH_2Cl_2 (20 mL). The resulting mixture was stirred for 1 h at room temperature. The reaction mixture was filtered on SiO_2 and concentrated. Column chromatography (SiO_2, CH_2Cl_2/ether/MeOH 100:7:0 to 100:10:2) gave **V-7** (462 mg, 91%) as a colorless oil. IR (neat): υ = 1730 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.38 (t, ^3J = 4 Hz, 2 H, COOCH_2CH$_2$O), 4.30 (t, ^3J = 5 Hz, 2 H, CH$_2$CH_2OSO$_2$CH$_3$), 4.20 (q, ^3J = 7 Hz, 2 H, COOCH_2CH$_3$), 3.76 (t, ^3J = 4 Hz, 2 H, OCH_2CH$_2$OSO$_2$CH$_3$), 3.71 (t, ^3J = 4 Hz, 2 H, COOCH$_2$CH_2O), 3.68-3.62 (m, 12 H, CH$_2$(OCH_2CH_2)$_3$OCH$_2$), 3.40 (s, 2 H, OOCCH_2COO), 3.08 (s, 3 H, CH$_2$OSO$_2$CH_3), 1.27 (t, ^3J = 7 Hz, 3 H, CH$_2$CH_3) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.7, 166.5, 70.6, 70.6 (four peaks), 70.5, 69.3, 69.0, 68.9, 64.5, 61.6, 41.5, 37.7, 14.1 ppm.



V-7 **V-8**

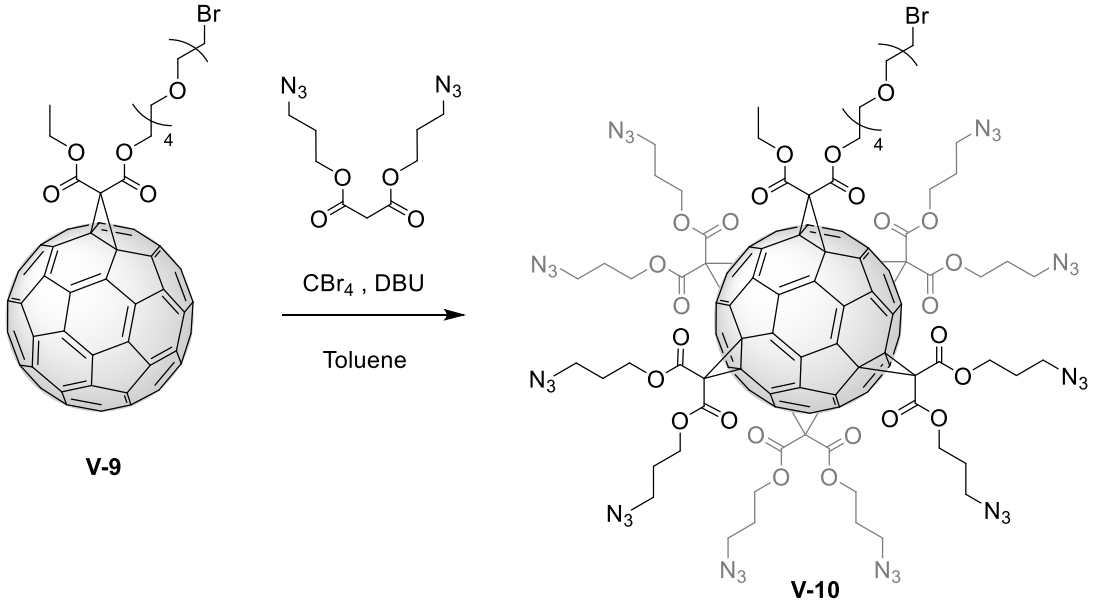
Compound V-8: A mixture of **V-7** (458 mg, 1.06 mmol) and LiBr (185 mg, 2.28 mmol) in THF anhydride was stirred at 60°C for 4 h. The reaction mixture was filtered on SiO_2 and concentrated. Column chromatography (SiO_2, CH_2Cl_2/ether/MeOH 100:10:0 to 100:10:1) gave **V-8** (386 mg, 87%) as a colorless oil. IR (neat): υ = 1731 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.30 (t, ^3J = 5 Hz, 2 H, COOCH_2CH$_2$O), 4.20 (q, ^3J = 7 Hz, 2 H, COOCH_2CH$_3$), 3.81 (t, ^3J = 6 Hz, 2 H, OCH_2CH$_2$Br), 3.71 (t, ^3J = 5 Hz, 2 H, COOCH$_2$CH_2O), 3.68-3.63 (m, 12 H, CH$_2$(OCH_2CH_2)$_3$OCH$_2$), 3.47 (t, ^3J = 6 Hz, 2 H, OCH$_2$CH_2Br), 3.40 (s, 2 H, OOCCH_2COO), 1.28 (t, ^3J = 7 Hz, 3 H, CH$_2$CH_3) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.7, 166.5, 71.2, 70.7 (two peaks), 70.6 (four peaks), 68.9, 64.6, 61.6, 41.5, 30.0, 14.1 ppm.



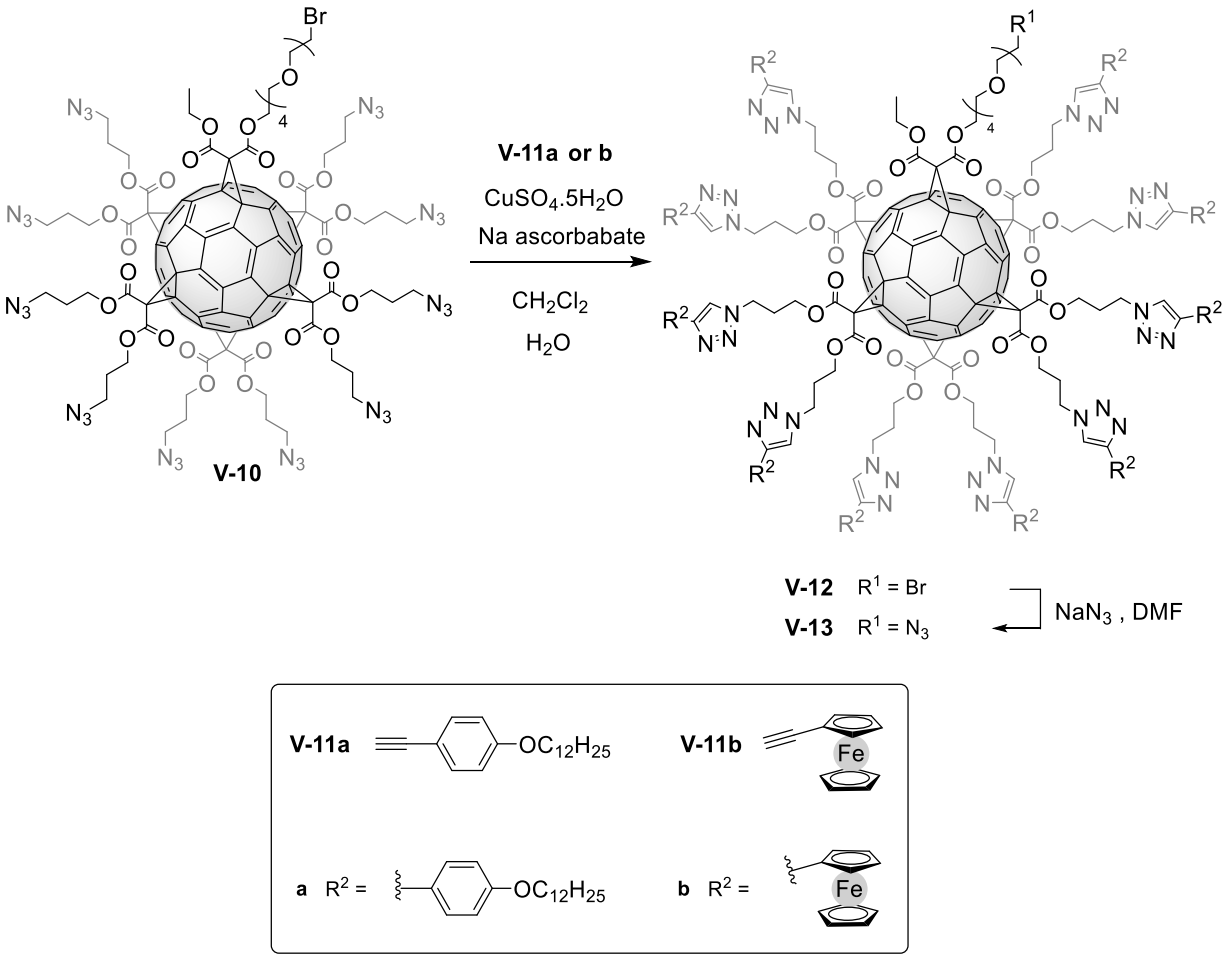
V-8 **V-9**

Compound V-9: DBU (0.37 mL, 2.5 mmol) was added to a solution of **V-8** (445 mg, 1.1 mmol), C_{60} (850 mg, 1.2 mmol) and I_2 (326 mg, 1.3 mmol) in toluene (1.7 L). The resulting mixture was stirred at room temperature for 30 min, then filtered on SiO_2 (CH_2Cl_2/THF, 9:1) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/THF, 94:6) yielded **V-9** (700

mg, 0.62 mmol, 57%) as a brown glassy solid. IR (neat): υ = 1743 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 260 ($1.3x10^5$), 330 ($4x10^4$), 394 (sh, $5x10^4$), 402 (sh, $4x10^3$), 414 (sh, $3x10^3$), 426 ($3x10^3$), 498 (sh, $2x10^3$), 631 (sh, $3x10^2$), 693 (sh, $2x10^2$) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.65 (m, 2 H, COOC*H*$_2$CH$_2$O), 4.56 (q, ^3J = 7 Hz, 2 H, COOC*H*$_2$CH$_3$), 3.88 (m, 2 H, COOCH$_2$C*H*$_2$O), 3.81 (t, ^3J = 6 Hz, 2 H, OC*H*$_2$CH$_2$Br), 3.71-3.64 (m, 12 H, (OC*H*$_2$C*H*$_2$)$_3$O), 3.47 (t, ^3J = 6 Hz, 2 H, OCH$_2$C*H*$_2$Br), 1.49 (t, ^3J = 7 Hz, 3 H, CH$_2$C*H*$_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz)**:** δ = 163.6, 163.4, 145.4, 145.3, 145.2 (two peaks), 144.9, 144.7, 144.6, 143.9 (two peaks), 143.1, 143.0 (three peaks), 142.2 (two peaks), 141.9 (two peaks), 141.0, 140.9, 139.2, 138.9, 71.5, 71.2, 70.7 (three peaks), 70.6 (two peaks), 68.8, 66.2, 63.5, 52.1, 30.3, 14.3 ppm. MS-MALDI-TOF: 1134.1 ($[M]^+$, calcd. for $C_{75}H_{25}O_8Br$: 1134.1).



Compound V-10: DBU (0.76 mL, 5.0 mmol) was added to a solution of **V-9** (285 mg, 251 μmol), **IV-27** (441 mg, 1.63 mmol) and CBr_4 (5.42 g, 16.3 mmol) in toluene (90 mL). The resulting mixture was stirred overnight at room temperature, then filtered on SiO_2 (CH_2Cl_2/Et_2O, 7:3) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/Et_2O, 9:1) yielded **V-10** (238 mg, 96 μmol, 38%) as an orange glassy solid. IR (neat): υ = 2095 (N_3), 1742 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.37 (m, 24 H, COOC*H*$_2$), 3.81 (t, ^3J = Hz, 2 H, COOCH$_2$C*H*$_2$O), 3.74-3.60 (m, 14 H, OC*H*$_2$C*H*$_2$OC*H*$_2$), 3.47 (t, ^3J = 6 Hz, 2 H, CH$_2$C*H*$_2$Br), 3.40 (t, ^3J = Hz, CH$_2$C*H*$_2$N$_3$), 1.97 (m, 20 H, CH$_2$C*H*$_2$CH$_2$N$_3$), 1.34 (t, ^3J = 7 Hz, 3 H, CH$_2$C*H*$_3$) ppm.



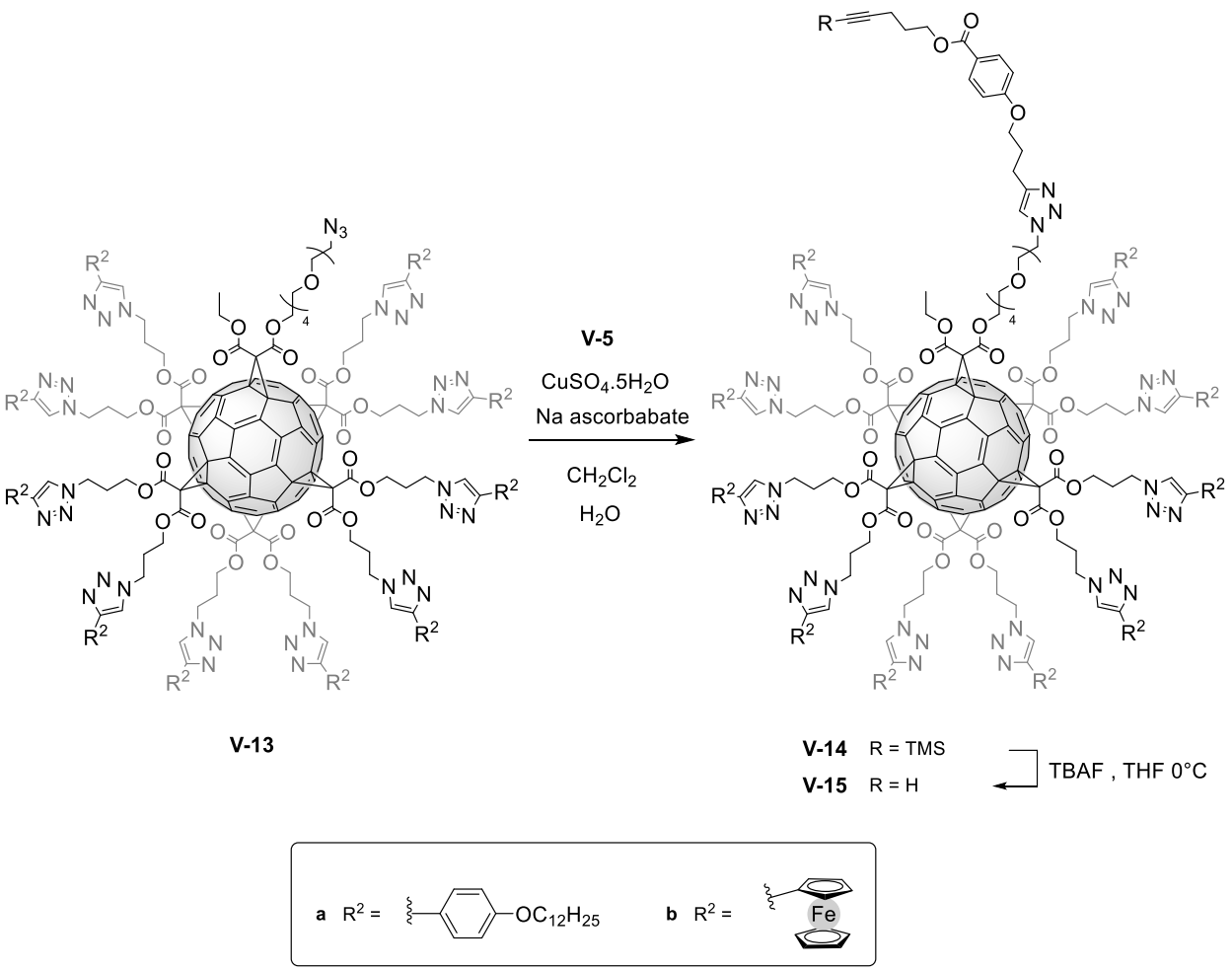
Compound V-12a: A solution of **V-10** (352 mg, 142 μmol), **V-11a** (541 mg, 1.89 mmol), $CuSO_4.5H_2O$ (3 mg, 11 μmol) and sodium ascorbate (4 mg, 22 μmol) in CH_2Cl_2/H_2O (2 : 1 mL) was stirred overnight at 30°C, then CH_2Cl_2 was added, washed with water and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 96:4) yielded **FS305** (737 mg, 138 μmol, 97%) as an orange glassy solid. IR (neat): υ = 1741 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 254 ($3.2x10^5$) nm. ^1H NMR ($CDCl_3$, 400 MHz): δ= 7.76-7.65 (m, 30 H, $H_{triazole}$ & ArH_o), 6.87 (m, 20 H, ArH_m), 4.40 (m, 44 H, $CH_2CH_2N_{triazole}$ & $COOCH_2$), 3.92 (m, 20 H, $OCH_2(CH_2)_{10}CH_3$) 3.76 (t, ^3J = 6 Hz, 2 H, OCH_2CH_2Br), 3.60 (m, 16 H, $COOCH_2CH_2(OCH_2CH_2)_3OCH_2CH_2Br$), 3.43 (t, ^3J = 6 Hz, 2 H, OCH_2CH_2Br), 2.32 (m, 20 H, $COOCH_2CH_2CH_2N_{triazole}$), 1.76 (m, 20 H, $OCH_2CH_2CH_2(CH_2)_8CH_3$) 1.43 (m, 20 H, $OCH_2CH_2CH_2(CH_2)_8CH_3$), 1.26 (m, 163 H, $OCH_2CH_2CH_2(CH_2)_8CH_3$ & $COOCH_2CH_3$), 0.87 (t, ^3J = 7 Hz, 30 H, $CH_2CH_2CH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 163.6, 159.2, 147.8, 145.9, 141.2, 127.0, 122.9, 119.2, 114.8, 71.2, 70.5, 69.2, 68.1, 63.8, 46.8, 45.4, 31.9, 30.5, 29.7, 29.5, 29.4, 29.3, 26.1, 22.7, 14.2 ppm. MS-MALDI-TOF: 5334.8 ($[M]^+$, calcd for $C_{320}H_{385}O_{38}N_{30}Br$: 5334.8 (monoisotopic)).

Compound V-12b: A solution of **V-10** (238 mg, 96 μmol), ethynylferrocene (**V-11b**) (262 mg, 1.25 mmol), $CuSO_4.5H_2O$ (3 mg, 11 μmol) and sodium ascorbate (4 mg, 22 μmol) in CH_2Cl_2/H_2O

(2 : 1 mL) was stirred overnight at 30°C, then CH_2Cl_2 was added, washed with a solution of EDTA (aq) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 95:5) yielded **V-12b** (383 mg, 84 μmol, 87%) as an orange glassy solid. IR (neat): υ = 1740 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 232 ($2.5x10^5$), 269 ($1.5x10^5$), 344 (sh, $3x10^4$) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.56 (m, 10 H, $H_{triazole}$), 4.72 (s, 20 H, $H_{ferrocene}$), 4.39 (m, 44 H, $COOCH_2$ & $CH_2N_{triazole}$), 4.28 (s, 20 H, $H_{ferrocene}$), 4.06 (s, 50 H, $H_{ferrocene}$), 3.78 (t, ^3J = 6 Hz, $COOCH_2CH_2O$), 4.71-4.60 (m, 14 H, $OCH_2CH_2OCH_2$), 3.45 (t, ^3J = 6 Hz, CH_2CH_2Br), 2.34 (m, 20 H, $CH_2CH_2CH_2N_{triazole}$), 1.31 (t, ^3J = 7 Hz, 3 H, CH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.5, 147.0, 146.0, 145.9, 145.7, 141.5, 141.2, 119.3, 75.5, 71.2, 70.6, 69.1, 68.7, 66.7, 63.8, 46.7, 45.3, 30.5, 29.3, 14.1 ppm. MS-MALDI-TOF: 4575.1 (100%, $[M]^+$, calcd for $C_{240}H_{185}O_{28}N_{30}BrFe_{10}$: 4575.7), 3887.5 (54%, $[M-(Malonate-Fe)]^+$, calcd for $C_{207}H_{153}O_{24}N_{24}BrFe_8$: 3887.5).

Compound V-13a: V-12a (706 mg, 132 μmol) and NaN_3 (50 mg, 769 μmol) in DMF/THF (6:2 mL) were stirred at room temperature for 18 h. THF was removed under reduced pressure, then extracted with CH_2Cl_2, washed with H_2O and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 96:4) yielded **V-13a** (650 mg, 123 μmol, 93%) as an orange glassy solid. IR (neat): υ = 2101 (N_3), 1741 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.76-7.65 (m, 30 H, $H_{triazole}$ & ArH_o), 6.87 (m, 20 H, ArH_m), 4.40 (m, 44 H, $CH_2CH_2N_{triazole}$ & $COOCH_2$), 3.92 (m, 20 H, $OCH_2(CH_2)_{10}CH_3$), 3.60 (m, 18 H, $COOCH_2CH_2(OCH_2CH_2)_3OCH_2CH_2N_3$), 3.43 (t, ^3J = 6 Hz, 2 H, OCH_2CH_2Br), 2.32 (m, 20 H, $COOCH_2CH_2CH_2N_{triazole}$), 1.76 (m, 20 H, $OCH_2CH_2CH_2(CH_2)_8CH_3$) 1.43 (m, 20 H, $OCH_2CH_2CH_2(CH_2)_8CH_3$), 1.26 (m, 163 H, $OCH_2CH_2CH_2(CH_2)_8CH_3$ & $COOCH_2CH_3$), 0.87 (t, ^3J = 7 Hz, 30 H, $CH_2CH_2CH_3$) ppm.

Compound V-13b: V-12b (129 mg, 28 μmol) and NaN_3 (11 mg, 169 μmol) in DMF (2 mL) were stirred at room temperature for 18 h. The product was precipitated with Et_2O/H_2O then resolubilized with CH_2Cl_2, washed with H_2O and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 96:4) yielded **V-13b** (120 mg, 26 μmol, 94%) as an orange glassy solid. IR (neat): υ = 2102 (N_3), 1743 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.56 (m, 10 H, $H_{triazole}$), 4.72 (s, 20 H, $H_{ferrocene}$), 4.39 (m, 44 H, $COOCH_2$ & $CH_2N_{triazole}$), 4.28 (s, 20 H, $H_{ferrocene}$), 4.06 (s, 50 H, $H_{ferrocene}$), 3.78 (t, ^3J = 6 Hz, $COOCH_2CH_2O$), 4.71-4.60 (m, 14 H, $OCH_2CH_2OCH_2$), 3.36 (t, ^3J = 6 Hz, $CH_2CH_2N_3$), 2.34 (m, 20 H, $CH_2CH_2CH_2N_{triazole}$), 1.31 (t, ^3J = 7 Hz, 3 H, CH_2CH_3) ppm.



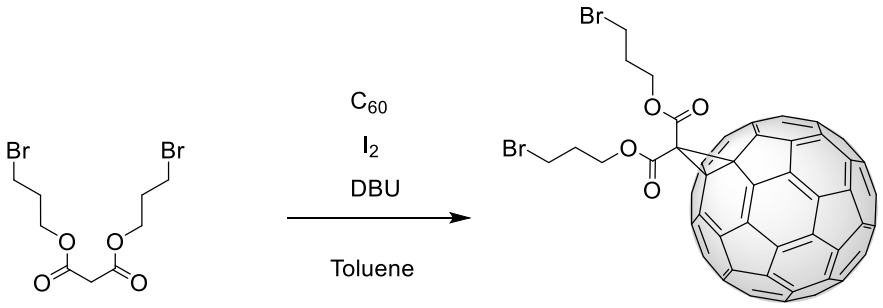
Compound V-14a: V-13a (200 mg, 38 μmol) was engaged in a solution of **V-5** (25 mg, 75 μmol), $CuSO_4.5H_2O$ (1 mg, 5 μmol) and sodium ascorbate (3 mg, 15 μmol) in CH_2Cl_2/H_2O (2/1 mL). The resulting mixture was stirred at 30°C for 2.5 h, then CH_2Cl_2 was added to the mixture, washed with H_2O and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 97:3) yielded **V-14a** (211 mg, 37 μmol, 99%) as an orange glassy solid. IR (neat): υ = 2178 (C≡CSi), 1741 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 255 ($2.8x10^5$) nm. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.96 (d, ^3J = 9 Hz, 2 H, OOCArH_o), 7.76-7.64 (m, 30 H, OArH_m & $H_{triazole}$-ArOC$_{12}$), 7.47 (s, 1 H, $H_{triazole}$-ArCOO), 6.87 (m, 22 H, OOCArH_m & OArH_o), 4.46-4.27 (m, 48 H), 4.05 (t, ^3J = 6 Hz, 2 H, OOCArOCH_2CH$_2$), 3.92 (m, 20 H, ArOCH_2CH$_2$), 3.81 (t, ^3J = 6 Hz, 2 H, N$_{triazole}$CH$_2$CH_2O), 3.66 (m, 2 H, COOCH$_2$CH_2O), 3.57 (m, 12 H, CH_2(OCH_2CH_2)$_3$OCH$_2$), 2.89 (t, ^3J = 6 Hz, 2 H, C$_{triazole}$CH_2CH$_2$), 2.40 (t, ^3J = 6 Hz, 2 H, CH$_2$CH_2C≡C), 2.32 (m, 20 H, COOCH$_2$CH_2CH$_2$N$_{triazole}$) 2.18 (m, 2 H, OCH$_2$CH_2CH$_2$C$_{triazole}$), 1.96 (quint., ^3J = 6 Hz, 2 H, CH$_2$CH_2CH$_2$C≡C), 1.75 (m, 20 H, OCH$_2$CH_2CH$_2$), 1.43 (m, 20 H, OCH$_2$CH$_2$CH_2CH$_2$), 1.26 (br s, 163 H, CH$_2$(CH_2)$_8$CH$_3$ & COOCH$_2$CH_3), 0.87 (t, ^3J = 7 Hz, 30 H, CH$_2$CH$_2$CH_3) 0.14 (s, 9 H, Si(CH_3)$_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.1, 163.5, 163.4, 162.7, 159.1, 147.7 (two peaks), 145.8, 145.6, 141.4, 141.2, 141.1, 141.0, 131.5, 126.9, 122.8, 122.5, 122.2, 119.1 (two peaks), 119.0, 114.7, 114.0, 105.8, 85.2, 70.4, 69.4, 69.0, 68.5, 68.4, 68.0, 67.0, 63.7, 63.2, 46.7, 45.3, 31.8,

29.6, 29.5 (two peaks), 29.4, 29.3, 29.2, 27.8, 26.0, 22.6, 16.7, 14.0, 0.0 ppm. MS-MALDI-TOF: 5638.5 ($[M]^+$, calcd for $C_{340}H_{411}O_{41}N_{33}Si$: 5640.5 (exact mass)).

Compound V-14b: V-13b (76 mg, 17 μmol) was engaged in a solution of **V-5** (12 mg, 33 μmol), $CuSO_4.5H_2O$ (1 mg, 5 μmol) and sodium ascorbate (3 mg, 15 μmol) in CH_2Cl_2/H_2O (2/1 mL). The resulting mixture was stirred at 30°C for 2.5 h, then CH_2Cl_2 was added to the mixture, washed with H_2O and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 96:4) yielded **V-14b** (72 mg, 15 μmol, 88%) as an orange glassy solid. IR (neat): υ = 2175 (C≡CSi), 1742 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 231 (2.7x10^5), 246 (sh, 2.1x10^5), 269 (1.7x10^5) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.96 (d, ^3J = 9 Hz, 2 H, OOCArH_o), 7.58-7.56 (m, 10 H, $H_{triazole}$-Fe), 7.47 (s, 1 H, $H_{triazole}$-ArCOO), 6.89 (d, ^3J = 9 Hz, 2 H, OOCArH_m), 4.71 (br s, 20 H, $H_{ferrocene}$), 4.46-4.30 (m, 48 H, COOCH_2 & CH_2N$_{triazole}$), 4.26 (br s, 20 H, $H_{ferrocene}$), 4.04 (m, 52 H, $H_{ferrocene}$ & CH_2CH_2OAr), 3.81 (m, 2 H, $OCH_2CH_2N_{triazole}$), 3.68 (m, 2 H, $COOCH_2CH_2O$), 3.56 (m, 12 H, $O(CH_2CH_2O)_3$), 2.89 (t, ^3J = 6 Hz, 2 H, $CH_2CH_2C_{triazole}$), 2.40-2.33 (m, 22 H, $CH_2CH_2CH_2N_{triazole}$ & CH_2C≡C), 2.18 (m, 2 H, $CH_2CH_2CH_2C_{triazole}$), 1.96 (quint., ^3J = 6 Hz, 2 H, $CH_2CH_2CH_2C$≡C), 1.29 (t, ^3J = 7 Hz, 3 H, CH_2CH_3), 0.14 (s, 9 H, $Si(CH_3)_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.1, 163.4, 163.3, 163.2, 162.6, 146.8, 146.7, 145.8 (two peaks), 145.7, 145.6, 141.3, 141.3, 141.0 (two peaks), 131.5, 122.5, 122.0, 119.2, 114.0, 105.8, 85.2, 75.2, 70.5, 70.4, 70.3, 69.5, 69.0, 68.6, 67.0, 66.6, 63.7, 63.2, 50.0, 46.6, 45.2, 29.2, 28.7, 27.8, 22.0, 16.7, 13.9, 0.0 ppm. MS-MALDI-TOF: 4879.2 ($[M]^+$, calcd for $C_{260}H_{211}O_{31}N_{33}SiFe_{10}$: 4880.2 (molecular weight)).

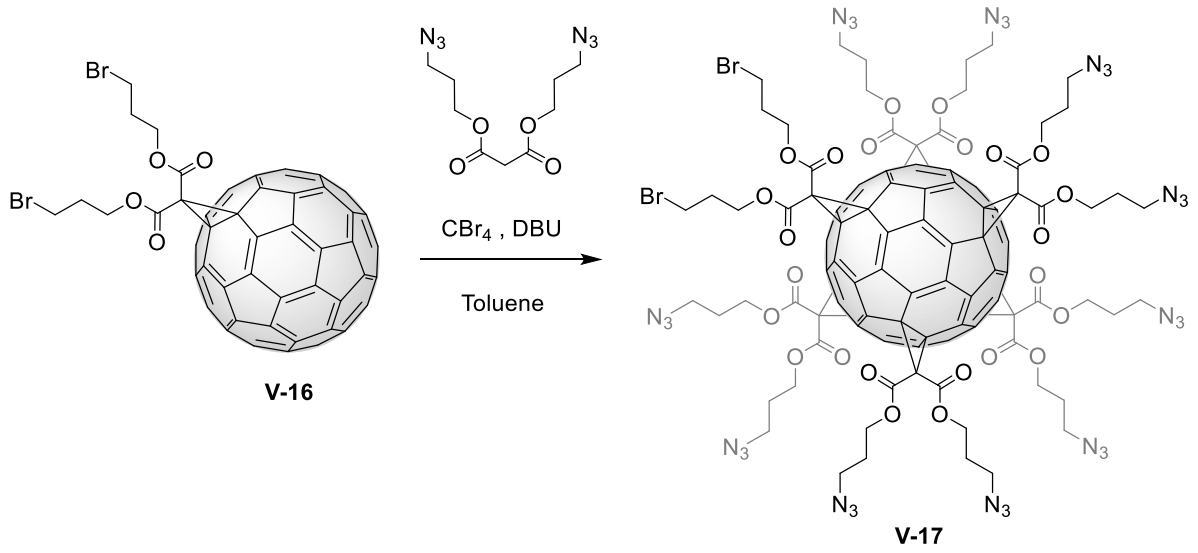
Compound V-15a: TBAF 1M in THF (0.24 mL, 240 μmol) was added to a solution of **V-14a** (903 mg, 160 μmol) in THF (15 mL) at 0°C. The resulting mixture was stirred at 0°C for 20 min, then water was added. THF was removed under reduced pressure and the product was solubized in CH_2Cl_2. The organic layer was washed with water and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 97:3) yielded **V-15a** (884 mg, 159 μmol, 99%) as an orange glassy solid. IR (neat): υ = 3315 (C≡C-H), 1741 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 256 (2.6x10^5) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.96 (d, ^3J = 9 Hz, 2 H, OOCArH_o), 7.76-7.64 (m, 30 H, OArH_m & $H_{triazole}$-ArOC$_{12}$), 7.47 (s, 1 H, $H_{triazole}$-ArCOO), 6.94 (d, ^3J = 9 Hz, 2 H, OOCArH_m), 6.87 (m, 20 H, OArH_o), 4.55 (t, ^3J = 6 Hz, 2 H, $ArCOOCH_2CH_2$), 4.46-4.27 (m, 48 H), 4.05 (t, ^3J = 6 Hz, 2 H, $OOCArOCH_2CH_2$), 3.92 (m, 20 H, $ArOCH_2CH_2$), 3.81 (t, ^3J = 6 Hz, 2 H, $N_{triazole}CH_2CH_2O$), 3.67 (m, 2 H, $COOCH_2CH_2O$), 3.57 (m, 12 H, $CH_2(OCH_2CH_2)_3OCH_2$), 2.89 (t, ^3J = 6 Hz, 2 H, $C_{triazole}CH_2CH_2$), 2.37-2.27 (m, 22 H, CH_2CH_2C≡C & $COOCH_2CH_2CH_2N_{triazole}$), 2.17 (m, 2 H, $OCH_2CH_2CH_2C_{triazole}$), 1.97 (m, 3 H, $CH_2CH_2CH_2C$≡C*H*), 1.75 (m, 20 H, $OCH_2CH_2CH_2$), 1.43 (m, 20 H, $OCH_2CH_2CH_2CH_2$), 1.26 (br s, 163 H, $CH_2(CH_2)_8CH_3$ & $COOCH_2CH_3$), 0.87 (t, ^3J = 7 Hz, 30 H, $CH_2CH_2CH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.2, 163.5, 162.8, 159.2, 147.8 (two peaks), 145.9, 141.2, 131.6, 127.0, 123.0, 122.5, 122.1, 119.2, 114.8, 114.1, 83.1, 70.5, 69.5, 69.1 (two peaks), 68.1, 67.1, 63.8, 63.2, 56.8, 45.4, 31.9, 29.7 (two peaks), 29.6, 29.5, 29.4, 29.3, 28.8, 27.8, 26.1, 22.7, 22.1, 15.4, 14.1 ppm. MS-MALDI-TOF: 5566.3 ($[M]^+$, calcd for $C_{337}H_{403}O_{41}N_{33}$: 5568.0 (exact mass)).

Compound V-15b: TBAF 1M in THF (0.02 mL, 18 μmol) was added to a solution of **V-14b** (44 mg, 9 μmol) in THF (4 mL) at 0°C. The resulting mixture was stirred at 0°C for 20 min, then water was added. THF was removed under reduced pressure and the product was solubized in CH_2Cl_2. The organic layer was washed with water and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 96:4) yielded **V-15b** (40 mg, 8.3 μmol, 92%) as an orange glassy solid. IR (neat): υ = 3296 (C≡C-H), 1741 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 269 (sh, 9x10^4) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.96 (d, ^3J = 9 Hz, 2 H, OOCArH_o), 7.58-7.56 (m, 10 H, $H_{triazole}$-Fe), 7.47 (s, 1 H, $H_{triazole}$-ArCOO), 6.89 (d, ^3J = 9 Hz, 2 H, OOCArH_m), 4.72 (br s, 20 H, $H_{ferrocene}$), 4.46-4.30 (m, 48 H, COOCH_2 & CH_2N$_{triazole}$), 4.28 (br s, 20 H, $H_{ferrocene}$), 4.06 (m, 52 H, $H_{ferrocene}$ & CH_2CH_2OAr), 3.82 (m, 2 H, $OCH_2CH_2N_{triazole}$), 3.68 (m, 2 H, $COOCH_2CH_2O$), 3.57 (m, 12 H, $O(CH_2CH_2O)_3$), 2.89 (t, ^3J = 6 Hz, 2 H, $CH_2CH_2C_{triazole}$), 2.40-2.33 (m, 22 H, $CH_2CH_2CH_2N_{triazole}$ & CH_2C≡C), 2.18 (m, 2 H, $CH_2CH_2CH_2C_{triazole}$), 1.98 (m, 3 H, $CH_2CH_2CH_2C{\equiv}CH$), 1.30 (m, 3 H, CH_2CH_3), ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.3, 163.5, 162.8, 147.0, 146.8, 145.9, 141.1, 131.6, 122.5, 122.1, 119.3, 114.1, 83.2, 75.4, 70.5, 69.6, 69.1, 68.7, 67.1, 66.7, 63.8, 63.2, 50.1, 46.7, 45.1, 29.3, 28.8, 27.8, 22.1, 15.4, 14.1 ppm. MS-MALDI-TOF : 4808.1 ([M]$^+$, calcd for $C_{257}H_{203}O_{31}N_{33}Fe_{10}$: 4808.0 (molecular weight)).

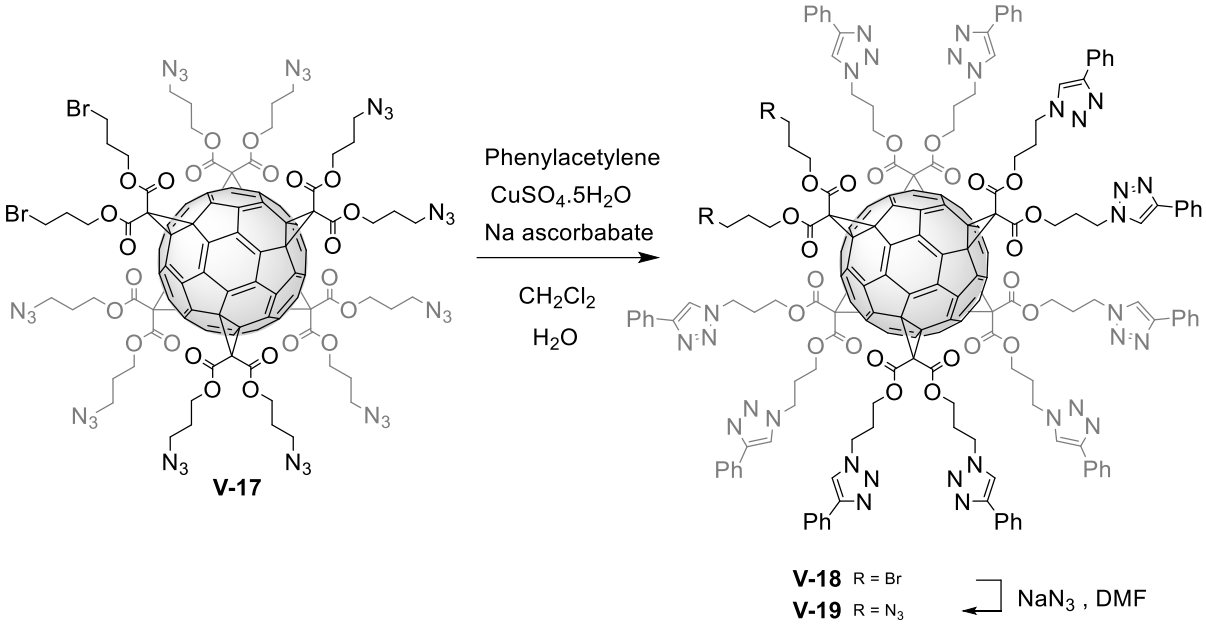


IV-27 **V-16**

Compound V-16: DBU (0.18 mL, 1.2 mmol) was added to a solution of **IV-27** (191 mg, 0.55 mmol), C_{60} (400 mg, 0.55 mmol) and I_2 (169 mg, 0.66 mmol) in toluene (0.8 L). The resulting mixture was stirred at room temperature for 30 min, then filtered on SiO_2 (CH_2Cl_2) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2/cyclohexane, 3:7) yielded **V-16** (302 mg, 0.28 mmol, 51%) as a brown glassy solid. IR (neat): υ = 1743 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.67 (t, ^3J = 6 Hz, 4 H, $COOCH_2CH_2$), 3.58 (t, ^3J = 6 Hz, 4 H, CH_2CH_2Br), 2.41 (quint., ^3J = 6 Hz, 4 H, $CH_2CH_2CH_2Br$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.4, 145.3, 145.2, 145.0, 144.9, 144.7 (two peaks), 144.6, 143.9, 143.1 (two peaks), 143.0, 142.2, 141.9, 141.0, 139.0, 71.3, 65.0, 51.8, 31.4, 29.0 ppm.



Compound V-17: DBU (0.23 mL, 1.3 mmol) was added to a solution of **V-16** (80 mg, 75 μmol), **IV-12** (142 mg, 0.53 mmol) and CBr_4 (1.74 g, 5.3 mmol) in toluene (50 mL). The resulting mixture was stirred overnight at room temperature, then filtered on SiO_2 (CH_2Cl_2/Et_2O, 7:3) and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/Et_2O, 9:1) yielded **V-17** (100 mg, 42 μmol, 55%) as an orange glassy solid. IR (neat): υ = 2094 (N_3), 1740 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.44 (t, ^3J = 6 Hz, 4 H, COOC*H*$_2$CH$_2$CH$_2$Br), 4.37 (t, ^3J = 6 Hz, 20 H, COOC*H*$_2$CH$_2$CH$_2$N$_3$), 3.47 (t, ^3J = 6 Hz, 4 H, CH$_2$C*H*$_2$Br), 3.40 (t, ^3J = 6 Hz, 20 H, CH$_2$C*H*$_2$N$_3$), 2. 25 (quint., ^3J = 6 Hz, 4 H, COOCH$_2$C*H*$_2$CH$_2$Br), 1.97 (quint., ^3J = 6 Hz, 20 H, COOCH$_2$C*H*$_2$CH$_2$N$_3$) ppm.



Compound V-18: A solution of **V-17** (100 mg, 42 μmol), phenylacetylene (0.06 mL, 499 μmol), $CuSO_4.5H_2O$ (3 mg, 11 μmol) and sodium ascorbate (4 mg, 22 μmol) in CH_2Cl_2/H_2O (2 : 1 mL) was stirred overnight at 30°C, then CH_2Cl_2 was added, washed with water and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 96:4) yielded **V-18** (113 mg, 33

μmol, 79%) as an orange glassy solid. IR (neat): υ = 1742 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 246 ($1.7x10^5$), 283 ($6x10^4$) nm. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.84-7.75 (m, 30 H, ArH_o & $H_{triazole}$), 7.37-7.28 (m, 30 H, Ar$H_{m,p}$), 4.47-4.32 (m, 44 H, COOCH_2CH$_2$ & CH$_2$CH_2N$_{triazole}$), 3.36 (t, ^3J = 6 Hz, 4 H, CH$_2$CH_2Br), 2.37-2.28 (m, 20 H, CH$_2$CH_2CH$_2$N$_{triazole}$), 2.17 (m, 4 H, CH$_2$CH_2CH$_2$Br) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.5, 163.4, 163.3, 147.9 (two peaks), 145.9 (three peaks), 145.8, 141.3, 141.2 (two peaks), 141.1, 130.5, 128.9, 128.2, 125.7, 120.1, 69.2 (two peaks), 69.1, 64.9, 63.8, 63.7 (two peaks), 46.8, 45.4, 31.1, 29.3, 29.1 ppm. MS-MALDI-TOF : 3429.6 ($[M]^+$, calcd for $C_{194}H_{132}O_{24}N_{30}Br_2$: 3427.1 (molecular mass)).

Compound V-19: V-18 (42 mg, 12 μmol) and NaN_3 (3 mg, 37 μmol) in DMF (2 mL) were stirred at room temperature. After 17 h, the product was precipitated with H_2O/Et_2O and resolubilized in CH_2Cl_2, washed with H_2O and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to CH_2Cl_2/MeOH, 96:4) yielded **V-19** (38 mg, 11 μmol, 93%) as an orange glassy solid. IR (neat): υ = 2098 (N_3), 1741 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.84-7.75 (m, 30 H, ArH_o & $H_{triazole}$), 7.38-7.29 (m, 30 H, Ar$H_{m,p}$), 4.48-4.29 (m, 44 H, COOCH_2CH$_2$ & CH$_2$CH_2N$_{triazole}$), 3.31 (t, ^3J = 6 Hz, CH$_2$CH_2N$_3$), 2.34 (m, 20 H, CH$_2$CH_2CH$_2$N$_{triazole}$), 1.89 (quint., ^3J = 6 Hz, 4 H, CH$_2$CH_2CH$_2$N$_3$) ppm.

Compound V-20: A solution of **V-19** (28 mg, 8 μmol), **V-15a** (97 mg, 17 μmol), $CuSO_4.5H_2O$ (3 mg, 11 μmol) and sodium ascorbate (4 mg, 22 μmol) in CH_2Cl_2/H_2O (2 : 1 mL) was stirred overnight at 30°C, then CH_2Cl_2 was added, washed with water and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to THF/MeOH, 92:8) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) yielded **V-20** (68 mg, 4.7 μmol, 56%) as an orange glassy solid. IR (neat): υ = 1742 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 251 ($8.9x10^5$) nm. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.92 (d, ^3J = 9 Hz, 4 H, OOCArH_o), 7.86-7.64 (m, 90 H, OArH_m & $H_{triazole}$-ArOC$_{12}$ & ArH_o & $H_{triazole}$-Ar), 7.47 (m, 4 H, $H_{triazole}$-ArCOO), 7.36-7.27 (m, 30 H, Ar$H_{m,p}$), 6.86 (m, 44 H, OArH_o & OOCArH_m), 4.48-4.27 (m, 144 H), 4.02 (m, 4 H, OOCArOCH_2CH$_2$), 3.91 (m, 40 H, ArOCH_2CH$_2$), 3.80 (m, 4 H, N$_{triazole}$CH$_2$CH_2O), 3.65 (m, 4 H, COOCH$_2$CH_2O), 3.56 (m, 24 H, CH$_2$(OCH_2CH_2)$_3$OCH$_2$), 2.87-2.80 (m, 8 H, C$_{triazole}$CH_2CH$_2$), 2.31 (m, 60 H, COOCH$_2$CH_2CH$_2$N$_{triazole}$), 2.17-2.08 (m, 8 H, CH$_2$CH_2CH$_2$C$_{triazole}$), 1.75 (m, 40 H, OCH$_2$CH_2CH$_2$), 1.42 (m, 40 H, OCH$_2$CH$_2$CH_2CH$_2$), 1.26 (br s, 326 H, CH$_2$(CH_2)$_8$CH$_3$ & COOCH$_2$CH_3) 0.87 (br s, 60 H, CH$_2$CH$_2$CH_3)ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.3, 163.5, 163.4 (two peaks), 162.8, 159.2, 147.8, 145.9, 145.7, 141.2, 131.6, 130.5, 128.9, 128.2, 127.0, 125.7, 123.0, 122.5, 122.0, 120.1, 119.2, 114.8, 114.1, 70.6, 70.5, 69.5, 69.2, 68.5, 68.1, 67.2, 66.0, 63.8, 46.8 (two peaks), 45.5, 45.4, 31.9, 29.7 (two peaks), 29.5, 29.4, 29.3, 28.8, 28.4, 26.1, 22.7, 22.1, 14.1, 14.0 ppm. MS-MALDI-TOF: 14487.4 ($[M]^+$, calcd for $C_{868}H_{938}O_{106}N_{102}$: 14485.1 (exact mass)).

Compound V-21: A solution of **IV-18** (22 mg, 8 μmol), **V-15a** (132 mg, 24 μmol), $CuSO_4.5H_2O$ (3 mg, 11 μmol) and sodium ascorbate (4 mg, 22 μmol) in CH_2Cl_2/H_2O (2 : 1 mL) was stirred overnight at 30°C, then CH_2Cl_2 was added, washed with water and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to THF/MeOH, 9:1) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) yielded **V-21** (95 mg, 4.9 μmol, 62%) as an orange

glassy solid. IR (neat): υ = 1742 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 253 ($9.2x10^5$)nm. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.94 (d, ^3J = 9 Hz, 6 H, OOCArH_o), 7.87-7.66 (m, 110 H, OArH_m & $H_{triazole}$-ArOC$_{12}$ & ArH_o & $H_{triazole}$-Ar), 7.47 (m, 6 H, $H_{triazole}$-ArCOO), 7.36-7.27 (m, 18 H, Ar$H_{m,p}$), 6.87 (m, 66 H, OArH_o & OOCArH_m), 4.46-4.27 (m, 186 H), 4.04 (m, 6 H, OOCArOCH_2CH$_2$), 3.91 (m, 60 H, ArOCH_2CH$_2$), 3.81 (m, 6 H, N$_{triazole}$CH$_2$CH_2O), 3.66 (m, 6 H, COOCH$_2$CH_2O), 3.57 (m, 36 H, CH$_2$(OCH_2CH_2)$_3$OCH$_2$), 2.86 (m, 12 H, C$_{triazole}$CH_2CH$_2$), 2.31 (m, 78 H, COOCH$_2$CH_2CH$_2$N$_{triazole}$), 2.15 (m, 12 H, CH$_2$CH_2CH$_2$C$_{triazole}$), 1.75 (m, 60 H, OCH$_2$CH_2CH$_2$), 1.42 (m, 60 H, OCH$_2$CH$_2$CH_2CH$_2$), 1.26 (br s, 498 H, CH$_2$(CH_2)$_8$CH$_3$ & COOCH$_2$CH_3) 0.87 (t, ^3J = 7 Hz, 90 H, CH$_2$CH$_2$CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.2, 163.5, 163.4, 162.8, 159.2, 147.9, 147.8, 147.7, 145.9, 145.8, 141.1, 131.6, 130.5, 128.8, 128.2, 127.0, 125.7, 123.0, 122.6, 122,2, 120.1, 119.2, 114.8, 114.1, 70.5, 69.5, 69.2, 69.1, 69.0, 68.5, 68.1, 67.2, 63.8 (two peaks), 63.7, 63.6, 63.5, 46.9, 46.8 (two peaks), 45.4 (two peaks), 31.9, 29.7 (two peaks), 29.6, 29.5, 29.4, 29.3, 26.1, 22.7, 14.1 ppm.

Compound V-22: A solution of **IV-24** (16 mg, 5.1 μmol), **V-15a** (116 mg, 21 μmol), $CuSO_4.5H_2O$ (3 mg, 11 μmol) and sodium ascorbate (4 mg, 22 μmol) in CH_2Cl_2/H_2O (2 : 1 mL) was stirred overnight at 30°C, then CH_2Cl_2 was added, washed with water and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to THF/MeOH, 9:1) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) yielded **V-22** (88 mg, 3.4 μmol, 68%) as an orange glassy solid. IR (neat): υ = 1742 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 253 ($1.4x10^6$) nm. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.94-7.63 (m, 160 H, OArH_m & $H_{triazole}$-ArOC$_{12}$ & ArH_o & $H_{triazole}$-Ar & OOCArH_o), 7.47 (m, 8 H, $H_{triazole}$-ArCOO), 7.36-7.27 (m, 24 H, Ar$H_{m,p}$), 6.87 (m, 88 H, OArH_o & OOCArH_m), 4.46-4.27 (m, 240 H), 4.04 (m, 8 H, OOCArOCH_2CH$_2$), 3.91 (m, 80 H, ArOCH_2CH$_2$), 3.81 (m, 8 H, N$_{triazole}$CH$_2$CH_2O), 3.66 (m, 8 H, COOCH$_2$CH_2O), 3.57 (m, 48 H, CH$_2$(OCH_2CH_2)$_3$OCH$_2$), 2.86 (m, 16 H, C$_{triazole}$CH_2CH$_2$), 2.31 (m, 104 H, COOCH$_2$CH_2CH$_2$N$_{triazole}$), 2.15 (m, 16 H, CH$_2$CH_2CH$_2$C$_{triazole}$), 1.75 (m, 80 H, OCH$_2$CH_2CH$_2$), 1.42 (m, 80 H, OCH$_2$CH$_2$CH_2CH$_2$), 1.26 (br s, 652 H, CH$_2$(CH_2)$_8$CH$_3$ & COOCH$_2$CH_3) 0.87 (br s, 120 H, CH$_2$CH$_2$CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.3, 163.6, 163.5 (two peaks), 163.4, 162.8, 159.2, 147.8, 145.9, 145.7, 141.3, 141.2, 141.1, 131.6, 130.5, 128.9, 128.2, 127.0, 125.7, 123.0, 122.5, 122.2, 120.1, 119.3, 114.8, 114.1, 70.5, 69.5, 69.2, 68.5, 68.1, 67.2, 66.0, 63.8, 50.1, 46.8, 45.6, 45.4, 31.9, 29.7 (two peaks), 29.5, 29.4, 29.3, 26.1, 22.7, 14.1 ppm.

Compound V-23: A solution of **IV-16** (16 mg, 6.4 μmol), **V-15a** (293 mg, 53 μmol), $CuSO_4.5H_2O$ (3 mg, 11 μmol) and sodium ascorbate (4 mg, 22 μmol) in CH_2Cl_2/H_2O (2 : 1 mL) was stirred at 30°C for 4 days, then CH_2Cl_2 was added, washed with water and concentrated. Column chromatography on SiO_2 (CH_2Cl_2 to THF/MeOH, 9:1) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) yielded **V-23** (212 mg, 4.5 μmol, 70%) as an orange glassy solid. IR (neat): υ = 1742 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 255 ($2.8x10^6$) nm. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.94 (m, 16 H, OOCArH_o), 7.76-7.66 (m, 240 H, OArH_m & $H_{triazole}$-ArOC$_{12}$), 7.46 (m, 16 H, $H_{triazole}$-ArCOO), 6.87 (m, 176 H, OArH_o & OOCArH_m), 4.46-4.27 (m, 424 H), 4.05 (m, 16 H, OOCArOCH_2CH$_2$), 3.91 (m, 160 H, ArOCH_2CH$_2$), 3.82 (m, 16 H,

$N_{triazole}CH_2CH_2O$), 3.66 (m, 16 H, $COOCH_2CH_2O$), 3.56 (m, 96 H, $CH_2(OCH_2CH_2)_3OCH_2$), 3.38 (m, 8 H, $CH_2CH_2N_3$), 2.86 (m, 32 H, $C_{triazole}CH_2CH_2$), 2.32 (m, 160 H, $COOCH_2CH_2CH_2N_{triazole}$), 2.16 (m, 40 H, $CH_2CH_2CH_2C_{triazole}$ & $CH_2CH_2CH_2Br$), 1.75 (m, 160 H, $OCH_2CH_2CH_2$), 1.42 (m, 160 H, $OCH_2CH_2CH_2CH_2$), 1.26 (br s, 1304 H, $CH_2(CH_2)_8CH_3$ & $COOCH_2CH_3$) 0.87 (br s, 240 H, $CH_2CH_2CH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 166.3, 163.6, 163.5 (two peaks), 163.4, 163.3, 162.8, 159.2, 147.8, 145.9, 141.2, 131.6, 127.0, 123.0, 122.6, 122.1, 119.2, 114.8, 114.1, 71.4, 70.5, 69.5, 69.1, 68.6, 68.1, 67.2, 65.3, 63.8, 50.1, 46.8, 45.4, 31.9, 31.2, 29.7 (two peaks), 29.5, 29.4, 29.3, 28.5, 26.1, 22.7, 22.3, 14.1 ppm.

Compound V-24: V-23 (110 mg, 2.3 μmol) and NaN_3 (22 mg, 338 μmol) in DMF (2 mL) were stirred at room temperature. After 17 h, the product was precipitated with H_2O/Et_2O and resolubilized in CH_2Cl_2. The organic layer was washed with H_2O, dried over $MgSO_4$ and concentrated. Gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) yielded **V-24** (97 mg, 2.1 μmol, 88%) as an orange glassy solid. IR (neat): υ = 2099 (N_3), 1741 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.94 (m, 16 H, OOCArH_o), 7.76-7.66 (m, 240 H, OArH_m & $H_{triazole}$-ArOC_{12}), 7.47 (m, 16 H, $H_{triazole}$-ArCOO), 6.87 (m, 176 H, OArH_o & OOCArH_m), 4.46-4.27 (m, 424 H), 4.05 (m, 16 H, $OOCArOCH_2CH_2$), 3.91 (m, 160 H, $ArOCH_2CH_2$), 3.82 (m, 16 H, $N_{triazole}CH_2CH_2O$), 3.66 (m, 16 H, $COOCH_2CH_2O$), 3.57 (m, 96 H, $CH_2(OCH_2CH_2)_3OCH_2$), 3.36 (m, 8 H, $CH_2CH_2N_3$), 2.86 (m, 32 H, $C_{triazole}CH_2CH_2$), 2.32 (m, 160 H, $COOCH_2CH_2CH_2N_{triazole}$), 2.16 (m, 32 H, $CH_2CH_2CH_2C_{triazole}$), 1.95 (m, 8 H, $CH_2CH_2CH_2N_3$), 1.75 (m, 160 H, $OCH_2CH_2CH_2$), 1.42 (m, 160 H, $OCH_2CH_2CH_2CH_2$), 1.26 (br s, 1304 H, $CH_2(CH_2)_8CH_3$ & $COOCH_2CH_3$) 0.87 (br s, 240 H, $CH_2CH_2CH_3$) ppm.

Compound V-25: A solution of **V-24** (94 mg, 2 μmol), **V-15b** (60 mg, 12 μmol), $CuSO_4.5H_2O$ (3 mg, 11 μmol) and sodium ascorbate (4 mg, 22 μmol) in CH_2Cl_2/DMF/H_2O (2 : 1 : 1 mL) was stirred at 37°C for 7 days, then CH_2Cl_2 was added, washed with water and concentrated. Column chromatography on SiO_2 (CH_2Cl_2) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) yielded **V-25** (95 mg, 1.4 μmol, 72%) as an orange glassy solid. IR (neat): υ = 1741 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 254 (2.7x10^6) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.93 (m, 24 H, OOCArH_o), 7.76-7.59 (m, 280 H, OArH_m & $H_{triazole}$-ArOC_{12} & $H_{triazole}$-Fe), 7.45 (m, 24 H, $H_{triazole}$-ArCOO), 6.87 (m, 184 H, OArH_o & OOCArH_m), 4.70 (m, 80 H, $H_{ferrocene}$), 4.48-4.29 (m, 624 H, $COOCH_2$ & $CH_2N_{triazole}$), 4.26 (m, 80 H, $H_{ferrocene}$), 4.04 (m, 224 H, $H_{ferrocene}$ & CH_2CH_2OAr), 3.91 (m, 160 H, $ArOCH_2CH_2$), 3.82 (m, 24 H, $N_{triazole}CH_2CH_2O$), 3.68 (m, 24 H, $COOCH_2CH_2O$), 3.57 (m, 144 H, $CH_2(OCH_2CH_2)_3OCH_2$), 2.86 (m, 48 H, $C_{triazole}CH_2CH_2$), 2.33 (m, 264 H, $COOCH_2CH_2CH_2N_{triazole}$), 2.15 (m, 48 H, $CH_2CH_2CH_2C_{triazole}$), 1.75 (m, 160 H, $OCH_2CH_2CH_2$), 1.42 (m, 160 H, $OCH_2CH_2CH_2CH_2$), 1.25 (m, 1316 H, $CH_2(CH_2)_8CH_3$ & $COOCH_2CH_3$), 0.87 (m, 240 H, $CH_2CH_2CH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 166.3, 163.5, 163.4, 162.8, 159.2, 147.8, 146.9, 145.9, 145.7, 141.3, 141.2, 141.1, 131.6, 127.0, 123.0, 122.5, 122.0, 119.2, 119.2, 114.8, 114.1, 75.4, 70.5, 69.6, 69.1, 68.7, 68.1, 67.2, 66.7, 63.8, 50.1, 46.7, 45.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 28.9, 28.5, 26.1, 22.7, 22.3, 22.2, 14.1, 14.0 ppm.

Chapter VI : General conclusions.

The first part of this work is concerned with the development of now methodologies for the regioselective multifunctionalization of C_{60}. Our main concern was to include sub-units allowing to easily generate useful fullerene building blocks.

In a first instance, a macrocyclic approach has been investigated. For this purpose, bis-malonate macrocycles incorporating silyl groups were synthesized. Three parameters of the macrocycles have been modified: (1) the ring size, (2) the rigidity/flexibility of the spacer unit and (3) the nature of the protecting silyl groups. The reaction of the macrocycles bis-malonate with C_{60} gave three regioisomers of C_{60} bis-adducts with good regioselectivity. The cleavage of the silyl groups has been easily performed to afford the corresponding acyclic fullerene polyols. This new strategy opens new perspectives for the post-functionalization of fullerene multi-adducts derivatives.

Macrocyclic tris-malonates have been also synthesized. A stepwise synthesis has been developed in order to form the macrocycle in sufficient amount. For two macrocyclic tris-malonates, excellent results have been obtained with the exclusive formation of the C_{60} *e,e,e* tris-adduct.

The macrocyclic approach has proved to be interesting for the regioselective functionalization of C_{60}. However, in the case of the macrocyclic tris-malonates, the high number of steps for the synthesis of the macrocycles led us to develop a “tether-directed” type approach for the regioselective tris-functionalization of C_{60}. This strategy relies on a threefold Bingel reaction between C_{60} and a trialkoxysilane derivative bearing three malonate substituents. The C_{60} tris-adducts have been obtained in only three steps from commercially available starting materials. High regioselectivity has been observed for the *e,e,e* addition pattern. The easy deprotection of the silyl group afforded C_{60} tris-adducts bearing three alcohol functions which can be post-functionalized.

Optically pure *e,e,e* fullerene tris-adducts have been also prepared by using our synthetic approach. In this case, optically pure tris-malonates have been used to functionalize the fullerene core thus affording easily separable diastereoisomers differing by the absolute configuration of the inherently chiral addition pattern on the fullerene core. The absolute configuration of the inherently chiral *e,e,e* addition pattern has been unambiguously determined using X-ray crystal structure analysis for the first time.

Our “tether-directed” strategy furnishes a fast, simple, regio- and stereoselective access to C_{60} *e,e,e* tris-adduct suitable for the formation of C_{60} hexa-adducts with an octahedral addition pattern.

The second part of this work has been dedicated to the syntheses of mixed C_{60} hexa-adducts, based on the “tether-directed” methodology developed in the first part.

Three mixed C_{60} hexa-adducts building blocks have been synthesized from *e* bis-adduct and *e,e,e* tris-adducts. The post-functionalization of the mixed C_{60} hexa-adducts building blocks has been achieved by sequential CuAAC and esterification reactions. The functionalized mixed C_{60} hexa-adducts have been obtained in very good yields. Up to three different addend zones could be predefined based on the control of the regio- and stereochemistry provided

by our methodology. The high tolerance of the CuAAC reactions to a wide variety of functions will provide an easy access to the preparation of unprecedented globular multifunctional nanomaterials with a controlled distribution of functional groups on the spherical framework.

In the last part of this work, the mixed C_{60} hexa-adducts building blocks have been used to synthesize original fullerodendrimers. A convergent approach has been used to graft peripheral C_{60} hexa-adducts onto a central mixed C_{60} hexa-adduct. Our different scaffolds gave access to numerous poly- and multi-functionalized molecules. Based on our methodologies, the controlled elaboration of new nanomaterials and bioactive molecules should be easily achieved.

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Fonctionnalisation Multiple d'Hexa-adduits du C_{60} par Chimie « Click »

Résumé

Dans un premier temps, la bis- et tris-fonctionnalisation du C_{60} a été effectuée par une approche macrocyclique. Différents bis- et tris-adduits du C_{60} ont été obtenus avec de bonnes régioselectivités. Dans un deuxième temps, la tris-fonctionnalisation du C_{60} a été effectuée par une approche « tête directrice ». Par cette approche, un accès rapide, simple, régio- et stéréo-sélectif à des tris-adduits *e,e,e* approprié à la formation d'hexa-adduits d'ordre d'addition octaédrique a été obtenu. La synthèse et la séparation de tris-adduits *e,e,e* optiquement purs ont également été réalisées. Les dérivés polyols obtenus par déprotection des groupes silylés ouvrent de nouvelles perspectives pour la post-fonctionnalisation de multi-adduits de C_{60}. A partir de nos méthodologies de synthèse de bis- et tris-adduits de C_{60}, des synthons d'hexa-adduits mixtes de C_{60} ont été préparés. La post-fonctionnalisation de ces synthons a été effectuée par réaction de cycloaddition 1,3-dipolaire de type Huisgen mais aussi par réaction d'estérification, afin d'obtenir des hexa-adduits de C_{60} multifonctionnels. La méthodologie de synthèse d'hexa-adduits de C_{60} multifonctionnels a été mise à profit pour l'élaboration d'édifices hyperfonctionnels comportant plusieurs hexa-adduits de C_{60} autour d'un hexa-adduit de C_{60} central. La post-fonctionnalisation des synthons hexa-adduits mixtes par chimie « click » donne accès à la préparation contrôlée de nouveaux nanomatériaux globulaires multifonctionnels.

Mots clés : [60]fullerène, chimie « click », régiochimie, stéréochimie, multi-adduits, réaction de Bingel.

Abstract

In a first instance, the bis- and tris-functionalization of C_{60} was performed by a macrocyclic approach. Different bis- and tris-adducts of C_{60} were obtained with good regioselectivity. In a second instance, the tris-functionalization of C_{60} was performed by a "tether-directed" approach. By this approach, a fast, simple, regio- and stereoselective access to C_{60} *e,e,e* tris-adduct suitable for the formation of C_{60} hexa-adducts with an octahedral addition pattern was obtained. The synthesis and the separation of optically pure *e,e,e* tris-adducts was also realized. The polyol derivatives obtained by deprotection of the silyl groups open new perspectives for the post-functionalization of C_{60} multi-adducts. Using our synthesis methodologies of bis- and tris-adducts of C_{60}, mixed hexa-adducts building blocks were prepared. The post-functionalization of these building blocks was carried out by copper catalyzed azide-alkyne 1,3-dipolar cycloadditions but also by esterification reactions to obtain multifunctional C_{60} hexa-adducts. The methodology for the synthesis of multifunctional C_{60} hexa-adducts was used for the elaboration of fullerodendrimers containing several C_{60} hexa-adducts around a central C_{60} hexa-adduct. The post-functionalization of the mixed hexa-adducts building blocks by "click" chemistry gave access to the controlled preparation of new globular and multifunctional nanomaterials.

Keywords : [60]fullerene, « click » chemistry, regiochemistry, stereochemistry, multi-adducts, Bingel reaction.