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Regioselective Synthesis of Fullerene Tris-adducts for the Preparation of Clickable Fullerene [3:3]-Hexa-adduct Scaffolds

Eric Meichsner,^[a] Franck Schillinger,^[a] Thi Minh Nguyet Trinh,^[a] Sebastiano Guerra,^[a] Uwe Hahn,^[a] Iwona Nierengarten,^[a] Michel Holler,^[a] and Jean-François Nierengarten^{*[a]}

Dedicated to Prof. Luis Echegoyen on the occasion of his 70th birthday

[a] Dr. E. Meichsner, Dr. F. Schillinger, Dr. T. M. N. Trinh, Dr. S. Guerra, Dr. U. Hahn, Dr. I. Nierengarten, Dr. M. Holler, Dr. J.-F. Nierengarten
Laboratoire de Chimie des Matériaux Moléculaires
Université de Strasbourg et CNRS (UMR 7042 LIMA), Ecole Européenne de Chimie, Polymères et Matériaux
25 rue Becquerel, 67087 Strasbourg Cedex 2, France
E-mail : nierengarten@unistra.fr – Homepage URL: <http://nierengartengroup.com>

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Abstract: Macrocyclic tris-malonates incorporating cleavable di-*tert*-butylsilylene protecting groups have been prepared by a stepwise approach and used for the regioselective tris-functionalization of C₆₀. Fullerene tris-adducts with an *e,e,e* addition pattern have been thus obtained. The bridging di-*tert*-butylsilylene protecting groups have been cleaved to liberate the terminal alcohol functions of the fullerene tris-adduct. This key building block has been further functionalized to generate a clickable fullerene [3:3]-hexa-adduct scaffold allowing the successive introduction of two azide reagents.

Introduction

With their compact three-dimensional structure, *T_h*-symmetrical fullerene hexa-adducts are unique hard cores for the preparation of multifunctional nanomaterials.^[1-3] This class of fullerene derivatives have been introduced by Hirsch in 1994.^[4] Their synthesis is conveniently achieved in a one-step procedure by reaction of C₆₀ with malonate reagents.^[5] Amongst all the possible addition patterns for fullerene hexa-adducts, the octahedral one is the most stable due to the local aromaticity of its eight isolated six-membered rings.^[4,5] The key for the successful preparation of *T_h*-symmetrical fullerene hexa-adducts is based on the reversible addition of either 9,10-dimethylantracene (DMA) moieties^[4] or bromoform anions^[3c,6] onto the fullerene core during the multiple cyclopropanation reaction. In this way, dynamic covalent chemistry operates and the thermodynamic equilibrium is driven towards the formation of the most stable multi-adduct.^[3c] While very efficient when starting from relatively simple malonates, the direct preparation of fullerene hexa-adducts from more sophisticated reagents is however generally very low yielding.^[6] In order to solve this problem, our group has developed clickable fullerene hexa-adduct derivatives (Figure 1A).^[7] As these compounds are prepared from simple malonate starting materials, the C₆₀ hexa-adduct building blocks are obtained in high yields.^[7] Their post-functionalization is then typically achieved under copper-catalyzed alkyne-azide cycloaddition (CuAAC) reactions.^[7-9]

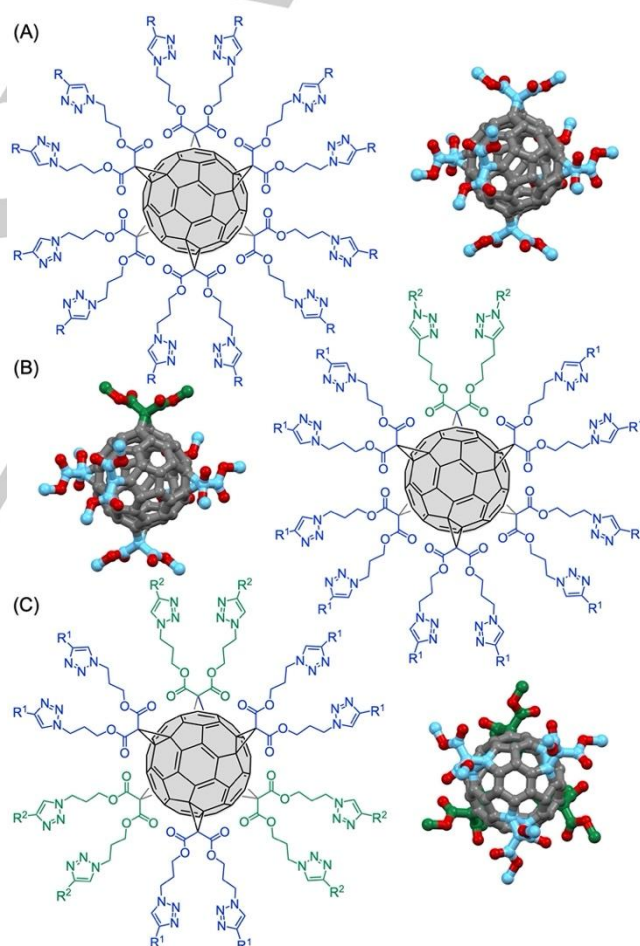


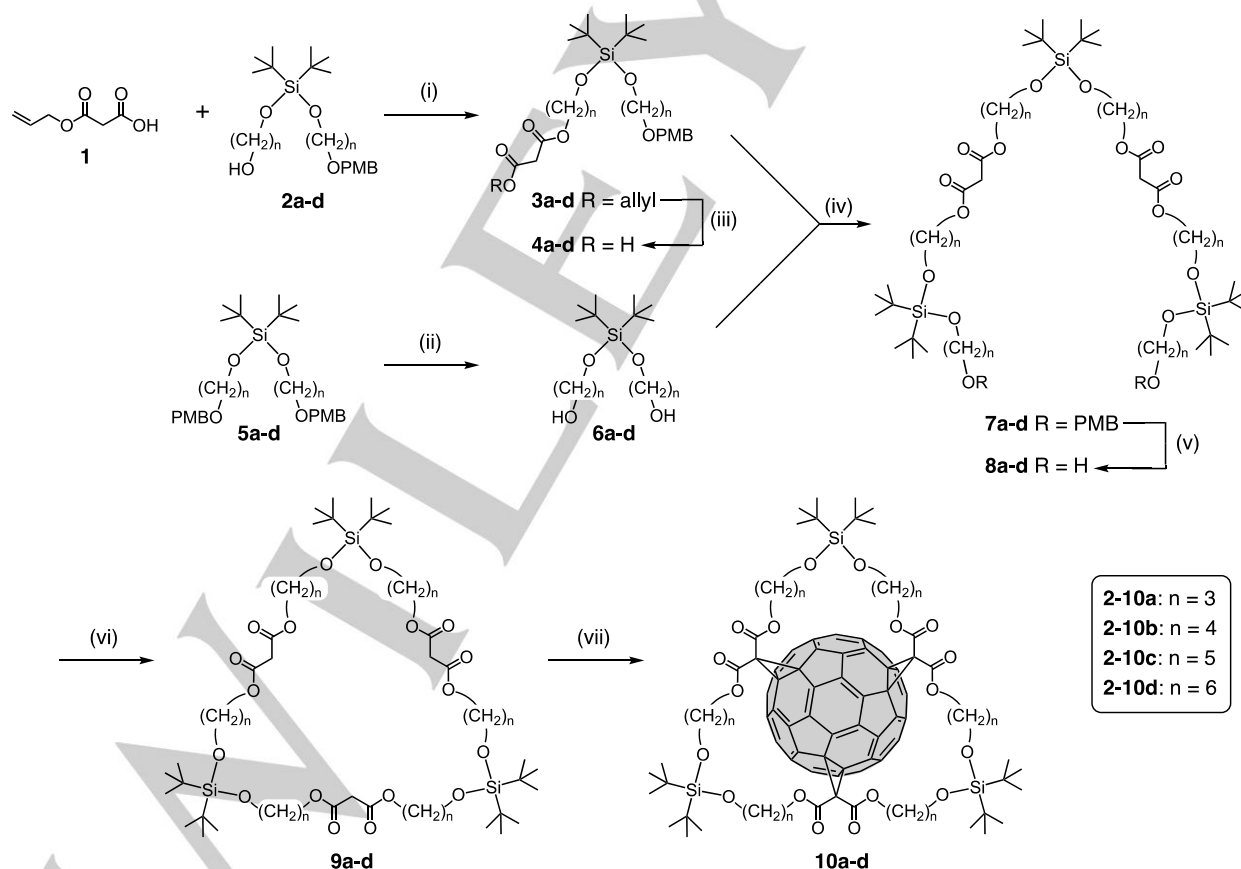
Figure 1. (A) The *T_h*-symmetrical fullerene hexakis-adduct core and an example of fully clicked derivative incorporating 12 identical peripheral functional groups. (B) The *C_{2v}*-symmetrical fullerene [5:1]-hexa-adduct core and an example of fully clicked derivative incorporating two different functional groups. (C) The *C₃*-symmetrical fullerene [3:3]-hexa-adduct core and an example of fully clicked derivative.

Importantly, this strategy gave access to a large variety of functionalized fullerene hexa-adduct derivatives that would be barely accessible by using the direct functionalization of C₆₀.^[3] These compounds found applications in different fields. Examples include polycationic derivatives for gene delivery,^[10] bioactive glycoclusters,^[11] multivalent enzyme inhibitors,^[12] liquid crystals^[13] and photoactive molecular devices.^[14] In order to introduce different functional subunits onto the fullerene core, we have also developed fullerene [5:1]-hexa-adduct scaffolds bearing complementary reactive groups allowing the grafting of different building blocks via successive click reactions (Figure 1B).^[8] This construction principle has been intensively used for the preparation of new advanced materials^[15] and bioactive compounds.^[16] As part of this research, we became interested in the development of mixed fullerene [3:3]-hexa-adduct scaffolds (Figure 1C). Whereas [5:1]-hexa-adducts are easily accessible by introduction of five malonate reagents to a mono-functionalized fullerene starting material,^[17] the preparation of the targeted mixed scaffold is by far more challenging.^[18,19] This requires effectively the functionalization of C₆₀ with three first addends in very specific positions. In this paper, we now report an efficient strategy allowing the controlled preparation of a fullerene tris-adduct precursor with the appropriate addition pattern for the construction of a clickable fullerene [3:3]-hexa-adduct scaffold. The synthetic approach relies on the use of a cleavable di-*tert*-butylsilylene-tethered macrocyclic tris-malonate

for the regioselective tris-functionalization of C₆₀. With the three first addends in place, the targeted clickable fullerene [3:3]-hexa-adduct has been achieved by desilylation to liberate the functional groups of the three first addends on the fullerene core followed by the introduction of three additional malonate addends. Successive click reactions have finally been carried out to fully functionalize the fullerene [3:3]-hexa-adduct scaffold.

Results and Discussion

To prepare the targeted clickable fullerene [3:3]-hexa-adduct scaffold, our first task was to develop an efficient synthesis of the appropriate fullerene tris-adduct precursor with an *e,e,e* addition pattern and bearing terminal functional groups allowing further chemical transformations (Scheme 1). The regioselective preparation of *e,e,e* fullerene derivatives is possible by the direct functionalization of C₆₀ with acyclic^[20] or macrocyclic malonates.^[21] As part of this research, we have shown in a preliminary communication that reaction of C₆₀ with a macrocyclic tris-malonate incorporating di-*tert*-butylsilylene moieties afforded a fullerene tris-adduct with the desired addition pattern.^[22]



Scheme 1. Preparation of macrocyclic tris-malonates and their reaction with C₆₀. *Reagents and conditions:* (i) DCC, DMAP, CH₂Cl₂, 0°C to rt (**3a**: 73%; **3b**: 71%; **3c**: 100%; **3d**: 96%); (ii) DDQ, CH₂Cl₂, H₂O, rt (**6a**: 86%; **6b**: 91%; **6c**: 90%; **6d**: 89%); (iii) Pd(PPh₃)₄, morpholine, THF, rt, then (iv) DCC, DMAP, CH₂Cl₂, 0°C to rt (**7a**: 61%; **7b**: 75%; **7c**: 66%; **7d**: 55%); (v) DDQ, CH₂Cl₂, H₂O, rt (**8a**: 98%; **8b**: 89%; **8c**: 53%; **8d**: 65%); (vi) malonyl chloride, CH₂Cl₂, DMAP, rt (**9a**: 53%; **9b**: 26%; **9c**: 63%; **9d**: 43%); (vii) C₆₀, DBU, I₂, PhMe, rt (**10a**: 61%; **10b**: 39%; **10c**: 15%; **10d**: 6%).

This particular compound appears to be a perfect precursor for the preparation of clickable fullerene [3:3]-hexa-adduct as the bridging di-*tert*-butylsilylene subunits can be in principle readily cleaved to liberate the terminal alcohol functions of the malonate addends.^[23] However, the direct synthesis of the macrocyclic tris-malonate precursor by reaction of the corresponding diol with malonyl chloride is low yielding. We thus decided to first optimize the preparation of this key building block by using a stepwise strategy. On the other hand, structural parameters have been also modified to optimize the size of the macrocyclic tris-malonates in order to obtain the desired *e,e,e* fullerene tris-adducts with high yields. The stepwise synthesis of the macrocyclic tris-malonates is depicted in Scheme 1. Esterification of malonic acid monoallyl ester **1** with *p*-methoxybenzyl (PMB) mono-protected diols **2a-d** under Steglich conditions^[24] afforded the corresponding mono-malonates **3a-d**. The allyl ester function of **3a-d** was then cleaved to generate the corresponding carboxylic acids. The choice of the allyl ester function was the key to generate **4a-d** without affecting the other functions. The allyl groups were cleaved under mild conditions by treatment with Pd(PPh₃)₄ in the presence of an excess of morpholine.^[25] Under these conditions, the alkyl ester function and both PMB and di-*tert*-butylsilylene protecting groups remained unchanged thus affording the desired carboxylic acids **4a-d** as attested by total disappearance of the typical allyl signals in their ¹H NMR spectra. Compounds **4a-d** thus obtained were used in the next step without further purification. Diols **6a-b** were prepared by deprotection of the corresponding PMB bis-protected derivatives **5a-d** under oxidative conditions using 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in CH₂Cl₂ containing a small amount of water.^[26] Treatment of **4a-d** with *N,N*-dicyclohexylcarbodiimide (DCC) and diols **6a-d** in the presence of 4-(dimethylamino)pyridine (DMAP) gave bis-malonates **7a-d**. Subsequent deprotection with DDQ afforded the corresponding diols **8a-d**. Macrocyclic tris-malonates **9a-d** were then obtained by reaction of diols **8a-d** with malonyl chloride in the presence of DMAP. In all the cases, compounds **9a-d** were the only cyclooligomeric products under these conditions and by-products were mainly polymers. Their purification by column chromatography was therefore easily achieved. Considering their ring size ranging from 42 to 60 atoms, macrocycles **9a-d** were thus produced in good to excellent yields. Interestingly, odd-even effects seem to play a role in these macrocyclization reactions despite the large ring size of **9a-d** and the presence of flexible silylene subunits in acyclic precursors **8a-d**.^[27] Effectively, the yields were significantly higher for the compounds with linkers having an odd number of CH₂ subunits (**9a** and **9c**). The structures of macrocyclic tris-malonates **9a-d** were fully confirmed by NMR spectroscopy and mass spectrometry. Reactions of macrocyclic tris-malonates **9a-d** with C₆₀ were carried out under the typical Bingel conditions (Scheme 1).^[28] Specifically, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added to a solution of C₆₀, iodine and **9a-d** in PhMe at room temperature. Under these conditions, the α -iodo malonate intermediates are generated *in situ* by reaction of the malonates with iodine. The cyclopropanation occurred by addition of the α -iodomalonate carbanion to C₆₀ followed by an intramolecular displacement of iodine by the anionic center generated on the C₆₀ core. To favor intramolecular Bingel cyclopropanations between mono- or bis-functionalized intermediates, all the reactions were performed at low concentrations (ca. 0.4 mM for

C₆₀). Under these conditions, reaction of **9a-b** with C₆₀ was highly regioselective and *e,e,e* tris-adducts **10a-b** were the only cyclization products. They were thus obtained in high yields (**10a**: 61% and **10b**: 39%). In contrast, very limited regioselectivity was observed when the largest macrocyclic tris-malonates (**9c-d**) were used for the tris-functionalization of C₆₀. In both cases, the corresponding *e,e,e* fullerene tris-adducts **10c-d** were obtained in low yields (**10c**: 8% and **10d**: 5%). Traces of several other tris-adducts were also formed but these products could not be isolated in a pure form. The position of the three cyclopropane rings on the fullerene core in **10a-d** were unambiguously determined based on their C₃ symmetry deduced from their ¹H and ¹³C NMR spectra. Moreover, their cherry-red color was in complete agreement with the proposed addition pattern. Indeed, their absorption spectra revealed the diagnostic features previously reported for *e,e,e* fullerene tris-adducts.^[20,21] As a typical example, the absorption spectrum recorded for compound **10b** in CH₂Cl₂ is given in Figure 2.

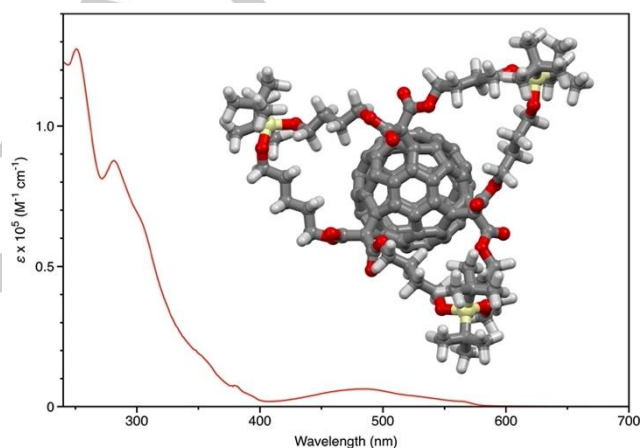


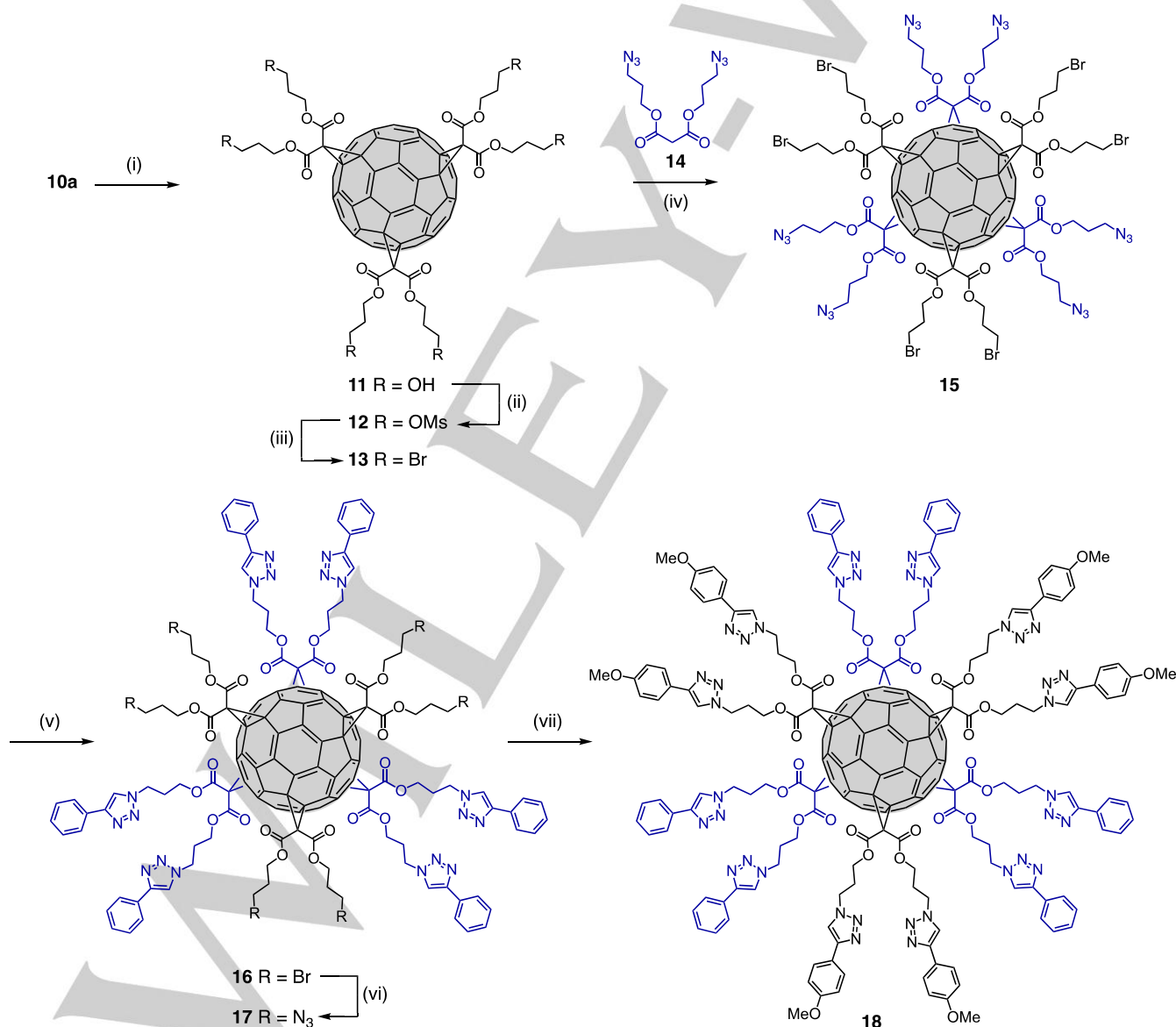
Figure 2. Absorption spectrum (CH₂Cl₂) of fullerene tris-adduct **10b** showing the characteristic features of the *e,e,e* tris-addition pattern. Inset: calculated structure of **10b**, the molecular geometry was optimized with *Spartan*¹⁸ Macintosh Parallel Edition (Wavefunction Inc., USA) at the AM1 semi-empirical level (C: gray, O: red, Si: pale yellow, H: white).

With their *e,e,e* addition pattern, compounds **10a-d** are perfectly suited starting materials for the construction of mixed C₆₀ hexa-adducts with an octahedral addition pattern. As shown in Scheme 2, this was carried out starting from compound **10a**. Desilylation was achieved by treatment of **10a** with an excess of BF₃·Et₂O in CH₂Cl₂/CH₃CN. The resulting hexaol (**11**) was only poorly-soluble in very polar solvents such as THF and was thus used in the next step without further purification. The six alcohol functions of **11** were directly mesylated by reaction of crude **11** with mesyl chloride (MsCl) in the presence of Et₃N. Compound **12** was thus obtained from **10a** with a 39% yield over the two steps. Treatment of **12** with an excess of LiBr in THF at 60°C afforded compound **13** in 82% yield. The three additional malonate addends were then introduced onto the fullerene core under the conditions developed by Sun for the preparation of fullerene hexa-adducts.^[6] Specifically, reaction of **13** with malonate **14** in the presence of an excess of CBr₄ and DBU gave hexa-adduct **15** in 63% yield. Importantly, the alkyl bromide units were not affected under these conditions and remained unchanged. Subsequent reaction with phenylacetylene under

the classical CuAAC conditions reported by Sharpless^[29] gave clicked derivative **16** in an almost quantitative yield. Finally, treatment of **16** with NaN₃ followed by reaction of the resulting hexa-azide **17** with 4-ethynylanisole in the presence of CuSO₄·5H₂O and sodium ascorbate in CH₂Cl₂/H₂O gave fully clicked derivative **18**.

Compounds **11–18** were characterized by combining several analytical tools. IR spectroscopy was useful to confirm that no unreacted azide residues (2097–2098 cm⁻¹) remained in compounds **16** and **18**. The NMR spectra of compounds **11–18** were also fully consistent with the proposed molecular structures. The ¹³C NMR spectra were particularly informative to confirm the stereochemistry of the compounds. Typical examples are shown in Figure 3. The ¹³C NMR spectrum of fullerene tris-adduct **13** is characterized by 20 resonances for the fullerene C atoms in full agreement with the C₃-symmetrical structure resulting from the e,e,e addition pattern. The spectrum is also characterized by the

diagnostic signals of its three equivalent malonate addends. Compound **18** is also C₃ symmetrical. However, only three signals are observed for the fullerene C atoms in its ¹³C NMR spectrum. This reveals the strong influence of the local symmetry and the three signals seen for the fullerene C atoms are reminiscent of those typically observed for T_h-symmetrical fullerene hexa-adducts.^[17,18] The expected signals of the phenyl and anisyl peripheral substituents are clearly observed in the ¹³C NMR spectrum of **18**. Their 6:6 ratio was further confirmed by the integration of their diagnostic signals in the ¹H NMR spectrum of **18**. Finally, hexa-adducts **15–18** are all pale orange compounds and their absorption spectra fully consistent with those typically reported for fullerene hexa-adducts with an octahedral addition pattern.^[17,18]



Scheme 2 Preparation of fullerene [3:3]-hexa-adduct **18**. *Reagents and conditions:* (i) $\text{BF}_3 \cdot \text{Et}_2\text{O}$, $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ 2:1, rt, then (ii) MsCl , Et_3N , THF, rt (39%); (iii) LiBr , THF, 60°C (82%); (iv) C_{60} , DBU, CBr_4 , PhMe, rt (63%); (v) phenylacetylene, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, sodium ascorbate, $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ (2:1), rt (99%); (vi) NaN_3 , DMF, rt (98%); (vi) 4-ethynylanisole, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, sodium ascorbate, $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ (2:1), rt (88%).

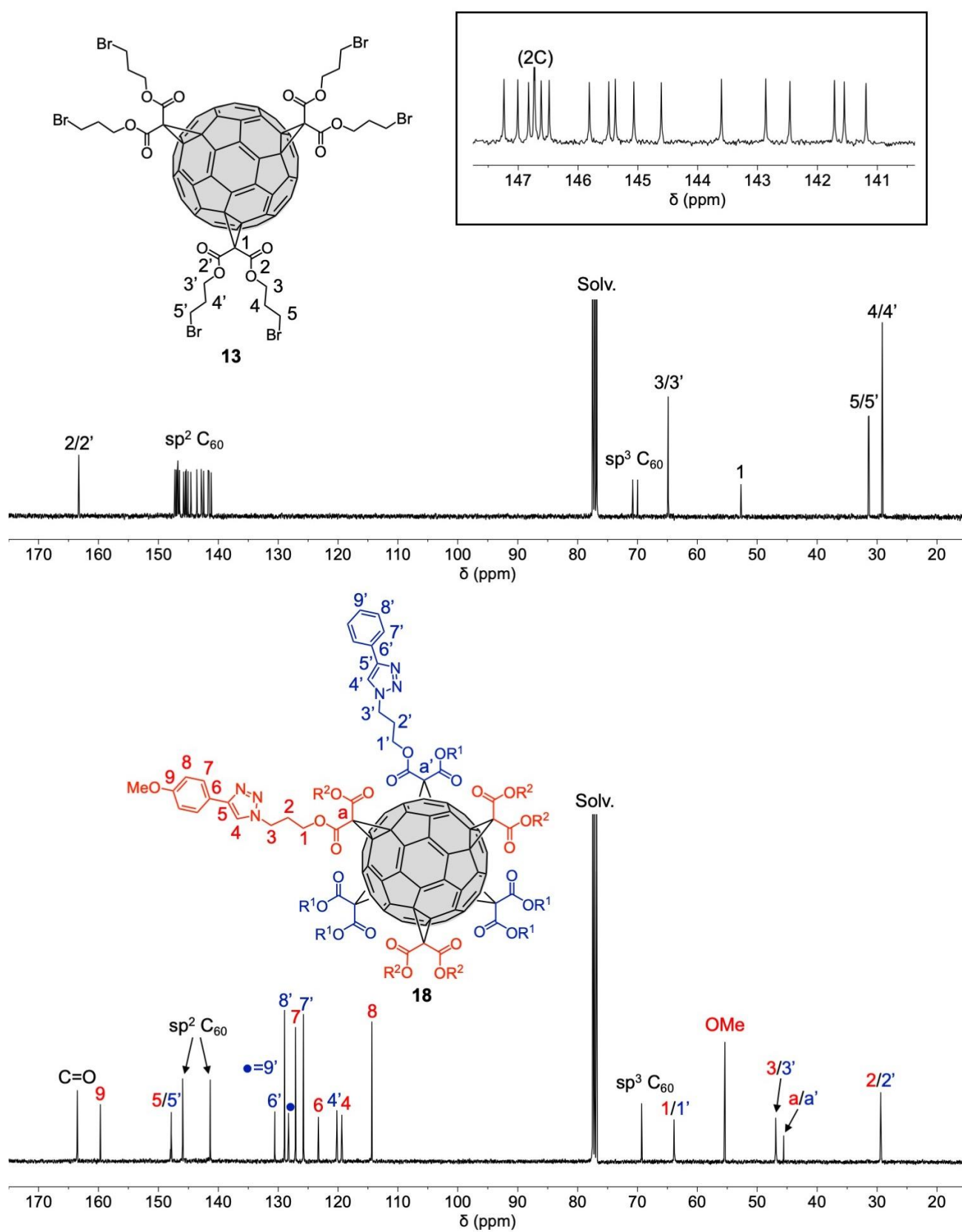


Figure 3. ^{13}C NMR spectra (CDCl₃, 100 MHz) of C₃-symmetrical fullerene tris-adduct **13** and fully clicked fullerene hexa-adduct **18**.

Conclusion

An efficient stepwise synthesis of macrocyclic tris-malonates incorporating di-*tert*-butylsilylene units has been developed. These compounds have been used to regioselectively functionalized C₆₀ by a triple Bingel cyclopropanation thus providing C₃-symmetrical fullerene tris-adducts with an *e,e,e* addition pattern. The bridging di-*tert*-butylsilylene moieties are not only directing group for the cyclization step onto the fullerene sphere, they are also protecting groups that can be cleaved to liberate the terminal alcohol functions of the three malonate addends. These building block has been used to construct a clickable fullerene [3:3]-hexa-adduct scaffold. As a proof of principle, this new scaffold has been functionalized with two different alkyne building blocks by two successive CuAAC reactions. The resulting fully clicked fullerene hexa-adduct has been thus decorated with two different functional groups in a 6:6 ratio. This construction principle will be further investigated to generate new giant amphiphilic compounds for various applications. Work in this direction is under way in our laboratory.

Experimental Section

General. Reagents were purchased as reagent grade and used without further purification unless specified. Compounds **1**,^[30] **2-d**,^[23] **5a-d**^[23] and **14**^[7] were prepared according to literature procedures. All reactions were performed in standard glassware under an inert Ar atmosphere. Column chromatography (CC) was performed on silica gel 60 (70-230 mesh, 0.063-0.200 mm) was purchased from E. Merck. Thin Layer Chromatography (TLC) was performed on aluminum sheets coated with silica gel 60 F₂₅₄ purchased from E. Merck. NMR spectra were recorded Bruker Avance I (300 MHz), Avance III HD (400 MHz) or Avance III HD (500 MHz) spectrometers with solvent peaks as reference. IR spectra (cm⁻¹) were recorded with a Perkin-Elmer Spectrum One spectrophotometer. Absorption spectral measurements were carried out in QS Hellma cuvettes with a PerkinElmer Lambda 365 spectrophotometer equipped with PCB 1500 water peltier system. MALDI-TOF mass spectra were recorded by the analytical service of the School of Chemistry (Strasbourg, France).

General procedure for the synthesis of compounds 3a-d. A mixture of **1a-d**, **2** and DMAP was dissolved in CH₂Cl₂ at 0 °C under argon and DCC was added. The mixture was stirred at 0°C for 1h and then allowed to warm to room temperature. The stirring was continued at this temperature for 12h. The mixture was filtered over silica (eluent: CH₂Cl₂), the filtrate evaporated, and the crude purified as indicated below.

Compound 3a. Prepared from **1a** (2.22 g, 5.38 mmol), **2** (853 mg, 5.92 mmol), DMAP (657 mg, 5.38 mmol) and DCC (2.22 g, 10.8 mmol) in CH₂Cl₂ (20 mL). Column chromatography on SiO₂ (eluent: CH₂Cl₂) gave **2a** (2.10 g, 73%). Colourless oil. IR (neat): $\tilde{\nu}$ = 1753 (C=O), 1736 (C=O) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 7.25 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 5.90 (m, 1H), 5.30 (m, 2H), 4.64 (td, *J* = 5.5 Hz, 1.5 Hz, 2H), 4.43 (s, 2H), 4.29 (t, *J* = 6.5 Hz, 2H), 3.92 (t, *J* = 6 Hz, 2H), 3.88 (t, *J* = 6 Hz, 2H), 3.80 (s, 3H), 3.58 (t, *J* = 6.5 Hz, 2H), 3.39 (s, 2H), 1.86 (m, 4H), 0.99 (s, 18H) ppm. ¹³C NMR (75 MHz, CDCl₃): 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 3b. Prepared from **1b** (2.21 g, 5.02 mmol), **2** (796 mg, 5.52 mmol), DMAP (610 mg, 4.99 mmol) and DCC (2.06 g, 10.0 mmol) in CH₂Cl₂ (40 mL). Column chromatography on SiO₂ (eluent: CH₂Cl₂) gave **2b** (2.04 g, 72%). Colourless oil. IR (neat): $\tilde{\nu}$ = 1754 (C=O), 1737 (C=O)

cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 7.26 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 5.91 (ddt, *J* = 17 Hz, 10.5 Hz, 6 Hz, 5.5 Hz, 1H), 5.29 (m, 2H), 4.65 (m, 2H), 4.44 (s, 2H), 4.18 (t, *J* = 6.5 Hz, 2H), 3.82 (t, *J* = 6 Hz, 4H), 3.80 (s, 3H), 3.48 (t, *J* = 6.5 Hz, 2H), 3.40 (s, 2H), 1.68 (m, 8H), 0.99 (s, 18H) ppm. ¹³C NMR (100 MHz, CDCl₃): 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 3c. Prepared from **1c** (2.36 g, 5.04 mmol), **2** (800 mg, 5.55 mmol), DMAP (616 mg, 5.04 mmol) and DCC (2.08 g, 10.1 mmol) in CH₂Cl₂ (20 mL). Column chromatography on SiO₂ (eluent: CH₂Cl₂/cyclohexane/MeOH 49:49:2) gave **5c** (3.00 g, 100%). Light yellow oil. IR (neat): $\tilde{\nu}$ = 1754 (C=O), 1737 (C=O) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 7.26 (d, *J* = 8.5 Hz, 2H), 8.87 (d, *J* = 8.5 Hz, 2H), 5.90 (m, 1H), 5.30 (m, 2H), 4.65 (m, 2H), 4.43 (s, 2H), 4.15 (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), 1.44 (m, 4H), 0.99 (s, 18H) ppm. ¹³C NMR (100 MHz, CDCl₃): 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 3d. Prepared from **1d** (1.51 g, 3.03 mmol), **2** (437 mg, 3.03 mmol), DMAP (370 mg, 3.03 mmol) and DCC (1.25 g, 6.06 mmol) in CH₂Cl₂ (8 mL). Column chromatography on SiO₂ (eluent: CH₂Cl₂/cyclohexane 7:3) gave **1d** (1.81 g, 96%). Light yellow oil. IR (neat): $\tilde{\nu}$ = 1754 (C=O), 1737 (C=O) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 7.26 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 5.91 (m, 1H), 5.30 (m, 2H), 4.64 (m, 2H), 4.43 (s, 2H), 4.14 (t, *J* = 6.5 Hz, 2H), 3.80 (m, 7H), 3.44 (t, *J* = 6.5 Hz, 2H), 3.40 (s, 2H), 1.61 (m, 8H), 1.38 (m, 8H), 0.99 (s, 18H) ppm. ¹³C NMR (75 MHz, CDCl₃): 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.

General procedure for the synthesis of compounds 6a-d. Water was added to a solution of **5a-d** and DDQ (2.1 equiv.) in CH₂Cl₂ at room temperature. After 6 h, the crude was filtered over a plug of silica (CH₂Cl₂/EtOAc, 9:1) and concentrated. The resulting product was purified as indicated below.

Compound 6a. Prepared from **5a** (2.54 g, 4.76 mmol), DDQ (2.27 g, 10 mmol) and water (4 mL) in CH₂Cl₂ (170 mL). Column chromatography on SiO₂ (eluent: CH₂Cl₂/MeOH 98:2) gave **6a** (1.21 g, 86%). Colourless oil. Analytical data identical to those reported in the literature for this compound.^[22]

Compound 6b. Prepared from **5b** (2.60 g, 4.64 mmol), DDQ (2.21 g, 9.74 mmol) and water (4 mL) in CH₂Cl₂ (170 mL). Colourless oil. Column chromatography on SiO₂ (eluent: CH₂Cl₂/MeOH 98:2) gave **6a** (1.35 g, 91%). Analytical data identical to those reported in the literature for this compound.^[22]

Compound 6c. Prepared from **5c** (2.43 g, 4.13 mmol), DDQ (1.97 g, 8.67 mmol) and water (4 mL) in CH₂Cl₂ (170 mL). Colourless oil. Column chromatography on SiO₂ (eluent: CH₂Cl₂/MeOH 98:2) gave **6a** (1.30 g, 90%). IR (neat): $\tilde{\nu}$ = 3327 (O-H) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 3.83 (t, *J* = 6.4 Hz, 4H), 3.65 (t, *J* = 6.6 Hz, 4H), 1.59 (m, 10H), 1.46 (m, 4H), 1.00 (s, 18H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 63.8, 63.1, 32.8, 32.6, 28.0, 22.1, 21.3 ppm.

Compound 6d. Prepared from **5d** (2.98 g, 4.83 mmol), DDQ (2.30 g, 10.1 mmol) and water (4 mL) in CH₂Cl₂ (170 mL). Colourless oil. Column chromatography on SiO₂ (eluent: CH₂Cl₂/MeOH 98:2) gave **6a** (1.62 g, 89%). IR (neat): $\tilde{\nu}$ = 3326 (O-H) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 3.81 (t, *J* = 6.4 Hz, 4H), 3.64 (t, *J* = 6.6 Hz, 4H), 1.57 (m, 10H), 1.39 (m, 8H), 0.99 (s, 18H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 63.8, 63.1, 33.0, 32.9, 28.0, 25.8, 25.7, 21.3 ppm.

General procedure for the synthesis of compounds 7a-d. *Step 1.* Morpholine and Pd(PPh₃)₄ were added to a solution of **3a-d** in dry THF under argon. After 4h, the solvent was evaporated, the crude was dissolved in CH₂Cl₂ and the solution was acidified with HCl 2M (10 mL). The organic layer was washed with water, dried (MgSO₄), filtered and evaporated to give **4a-d**. *Step 2.* Crude **4a-d** was dissolved under argon in CH₂Cl₂, **6a-d** and DMAP were added, and the mixture cooled to 0°C. DCC was added, the mixture was stirred at 0°C for 1h and then allowed to warm to room temperature. Stirring was continued at this temperature for 12h and the mixture filtered over silica (eluent: CH₂Cl₂) and evaporated. The resulting product was purified as indicated below.

Compound 7a. *Step 1.* Prepared from **3a** (493 mg, 0.915 mmol), morpholine (1.99 mL, 22.9 mmol) and Pd(PPh₃)₄ (211 mg, 0.183 mmol) in dry THF (5 mL) to give **4a**. *Step 2.* Prepared from crude **4a**, **6a** (134 mg, 0.458 mmol), DMAP (56 mg, 0.458 mmol) and DCC (283 mg, 1.37 mmol) in CH₂Cl₂ (10 mL). Column chromatography on SiO₂ (eluent: cyclohexane/diethyl ether 9:1) gave **6a** (349 mg, 61% over two steps). Colourless oil. IR (neat): $\tilde{\nu}$ = 1753 (C=O), 1736 (C=O) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 7.25 (d, *J* = 8.5 Hz, 4H), 6.87 (d, *J* = 8.5 Hz, 4H), 4.43 (s, 4H), 4.29 (t, *J* = 6.5 Hz, 4H), 4.27 (t, *J* = 6.5 Hz, 4H), 3.90 (m, 12H), 3.80 (s, 6H), 3.58 (t, *J* = 6 Hz, 4H), 3.36 (s, 4H), 1.87 (m, 12H), 0.99 (s, 54H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 166.7, 159.3, 130.8, 129.4, 113.9, 72.8, 66.8, 62.7, 60.3, 60.2, 55.4, 41.6, 33.2, 31.9, 28.0, 27.9, 21.3 ppm.

Compound 7b. *Step 1.* Prepared from **3b** (2.04 g, 3.60 mmol), morpholine (2.96 mL, 34.0 mmol) and Pd(PPh₃)₄ (198 mg, 0.171 mmol) in dry THF (20 mL) to give **4b**. *Step 2.* Prepared from crude **4b**, **6b** (545 mg, 1.70 mmol), DMAP (208 mg, 1.70 mmol) and DCC (1.23 g, 5.96 mmol) in CH₂Cl₂ (60 mL). Column chromatography on SiO₂ (eluent: CH₂Cl₂/EtOAc 9:1) gave **7b** (1.70 g, 75%). Colourless oil. IR (neat): $\tilde{\nu}$ = 1753 (C=O), 1736 (C=O) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 7.26 (d, *J* = 8.5 Hz, 4H), 6.87 (d, *J* = 8.5 Hz, 4H), 4.43 (s, 4H), 4.17 (m, 8H), 3.82 (m, 18H), 3.47 (t, *J* = 6.5 Hz, 4H), 3.37 (s, 4H), 1.68 (m, 24H), 0.99 (s, 54H) ppm. ¹³C NMR (100 MHz, CDCl₃): 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 7c. *Step 1.* Prepared from **3c** (3.01 g, 5.06 mmol), morpholine (6.61 mL, 75.9 mmol) and Pd(PPh₃)₄ (585 mg, 0.506 mmol) in dry THF (20 mL) to give **4c**. *Step 2.* Prepared from crude **4c**, **6c** (762 mg, 2.19 mmol), DMAP (540 mg, 4.42 mmol) and DCC (1.36 g, 6.59 mmol) in CH₂Cl₂ (10 mL). Column chromatography on SiO₂ (eluent: cyclohexane/diethyl ether 85:15) gave **7c** (2.06 g, 66% over two steps). Colourless oil IR (neat): $\tilde{\nu}$ = 1753 (C=O), 1736 (C=O) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 7.26 (t, *J* = 8.5 Hz, 4H), 6.87 (t, *J* = 8.5 Hz, 4H), 4.43 (s, 4H), 4.15 (m, 8H), 3.80 (m, 18H), 3.45 (t, *J* = 6.5 Hz, 4H), 3.55 (s, 4H), 1.59 (m, 24H), 1.44 (m, 12H), 0.99 (s, 54H) ppm. ¹³C NMR (100 MHz, CDCl₃): 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 7d. *Step 1.* Prepared from **3d** (1.81 g, 2.91 mmol), morpholine (1.27 mL, 14.5 mmol) and Pd(PPh₃)₄ (168 mg, 0.145 mmol) in dry THF (10 mL) to give **4d**. *Step 2.* Prepared from crude **4d**, **6d** (577 mg, 1.53 mmol), DMAP (380 mg, 3.11 mmol) and DCC (1.44 g, 6.98 mmol) in CH₂Cl₂ (10 mL). Column chromatography on SiO₂ (eluent: cyclohexane/diethyl ether 8:2) gave **7d** (1.26 g, 55% over two steps). Colourless oil. IR (neat): $\tilde{\nu}$ = 1753 (C=O), 1736 (C=O) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 7.26 (d, *J* = 8.5 Hz, 4H), 6.67 (d, *J* = 8.5 Hz, 4H), 4.43 (s, 4H), 4.14 (t, *J* = 6.5 Hz, 8H), 3.80 (m, 18H), 3.44 (t, *J* = 6.5 Hz, 4H), 3.36 (s, 4H), 1.60 (m, 24H), 1.38 (m, 24H), 0.99 (s, 54H) ppm. ¹³C NMR (100 MHz, CDCl₃): 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.

General procedure for the synthesis of compounds 8a-d. Water was added to a solution of **7a-d** and DDQ in CH₂Cl₂ at room temperature. After 6 h, the crude was filtered over a plug of silica and evaporated. The resulting product was purified as indicated below.

Compound 8a. Prepared from **7a** (348 mg, 0.278 mmol), DDQ (139 mg, 0.610 mmol) and water (1 mL) in CH₂Cl₂ (10 mL). Plug of silica (eluent: CH₂Cl₂/MeOH 95:5). Column chromatography on SiO₂ (eluent: CH₂Cl₂/MeOH 98:2) gave **8a** (274 mg, 97%). Colourless oil. IR (neat): $\tilde{\nu}$ = 3459 (O-H), 1752 (C=O), 1737 (C=O) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 4.30 (t, *J* = 6.5 Hz, 4H), 4.29 (t, *J* = 6.5 Hz, 4H), 4.02 (t, *J* = 5.5 Hz, 4H), 3.92 (m, 8H), 3.81 (t, *J* = 6 Hz, 4H), 3.37 (s, 4H), 2.05 (br s, 2H), 1.90 (m, 8H), 1.81 (m, *J* = 5.5 Hz, 4H), 1.01 (s, 36H), 0.99 (s, 18H) ppm. ¹³C NMR (100 MHz, CDCl₃): 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 8b. Prepared from **7b** (1.68 g, 1.26 mmol), DDQ (571 mg, 2.52 mmol) and water (1.5 mL) in CH₂Cl₂ (80 mL). Plug of silica (eluent: CH₂Cl₂/MeOH 97:3). Column chromatography on SiO₂ (eluent: CH₂Cl₂/MeOH 97:3) gave **8b** (1.23 g, 89%). Colourless oil. IR (neat): $\tilde{\nu}$ = 3454 (O-H), 1752 (C=O), 1736 (C=O) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 4.19 (t, *J* = 6.5 Hz, 8H), 3.85 (m, 12H), 3.67 (t, *J* = 6 Hz, 4H), 3.38 (s, 4H), 1.67 (m, 26H), 1.00 (s, 36H), 0.99 (s, 18H) ppm. ¹³C NMR (100 MHz, CDCl₃): 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 8c. Prepared from **7c** (2.06 g, 1.45 mmol), DDQ (658 mg, 2.90 mmol) and water (5 mL) in CH₂Cl₂ (50 mL). Plug of silica (eluent: CH₂Cl₂). Column chromatography on SiO₂ (eluent: CH₂Cl₂/diethyl ether 8:2) gave **8c** (916 mg, 54%). Colourless oil. IR (neat): $\tilde{\nu}$ = 3454 (O-H), 1752 (C=O), 1736 (C=O) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 4.15 (t, *J* = 6.5 Hz, 8H), 3.81 (m, 12H), 3.65 (t, *J* = 6.5 Hz, 4H), 3.35 (s, 4H), 1.58 (m, 38H), 0.99 (s, 54H) ppm. ¹³C NMR (100 MHz, CDCl₃): 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 8d. Prepared from **7d** (1.26 g, 0.836 mmol), DDQ (417 mg, 1.84 mmol) and water (3 mL) in CH₂Cl₂ (30 mL). Plug of silica (eluent: CH₂Cl₂/MeOH 99:1). Column chromatography on SiO₂ (eluent: cyclohexane/diethyl ether 7:3 to cyclohexane/diethyl ether/MeOH 7:3:0.1%) gave **8d** (683 mg, 65%). Colourless oil. IR (neat): $\tilde{\nu}$ = 3418 (O-H), 1752 (C=O), 1737 (C=O) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 4.14 (t, *J* = 7 Hz, 8H), 3.81 (m, 12H), 3.64 (t, *J* = 6.5 Hz, 4H), 3.36 (s, 4H), 1.66 (m, 8H), 1.56 (m, 16H), 1.40 (m, 26H), 0.99 (s, 54H) ppm. ¹³C NMR (100 MHz, CDCl₃): 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, 25.7, 25.6, 25.6, 21.3 ppm.

General procedure for the synthesis of compounds 9a-e. Malonyl chloride was added to a solution of **8a-e** and DMAP in CH₂Cl₂ under argon. After 1d, the mixture was filtered over a plug of silica and evaporated. The resulting product was purified as indicated below.

Compound 9a. Prepared from **8a** (405 mg, 0.40 mmol), DMAP (98 mg, 0.80 mmol) and malonyl chloride (57 mg, 0.40 mmol) in CH₂Cl₂ (50 mL). Plug of silica (eluent: CH₂Cl₂/EtOAc 9:1). Column chromatography on SiO₂ (eluent: CH₂Cl₂) gave **9a** (229 mg, 53%). Colourless oil. Analytical data identical to those reported in the literature for this compound.^[22]

Compound 9b. Prepared from **8b** (1.22 g, 1.11 mmol), DMAP (305 mg, 2.50 mmol) and malonyl chloride (156 mg, 1.11 mmol) in CH₂Cl₂ (300 mL). Plug of silica (eluent: CH₂Cl₂/EtOAc 9:1). Column chromatography on SiO₂ (eluent: CH₂Cl₂) gave **9b** (331 mg, 26 %). Colourless oil. IR (neat): $\tilde{\nu}$ = 1752 (C=O), 1735 (C=O) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 4.18 (t, *J* = 6.5 Hz, 12H), 3.84 (t, *J* = 6 Hz, 12H), 3.37 (s, 6H), 1.76 (q, *J* = 6.5 Hz, 12H), 1.61 (t, *J* = 6 Hz, 12H), 0.99 (s, 54H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 166.8, 65.5, 63.3, 41.8, 29.3, 28.0, 25.3, 21.3 ppm. MALDI-TOF MS: *m/z* = 1187.63 [M+Na]⁺, calcd for [C₅₇H₁₀₈O₁₈Si₃+Na]⁺ 1187.67.

Compound 9c. Prepared from **8c** (916 mg, 0.775 mmol), DMAP (189 mg, 1.55 mmol) and malonyl chloride (109 mg, 0.773 mmol) in CH_2Cl_2 (250 mL). Plug of silica (eluent: CH_2Cl_2 /diethyl ether 1:1). Column chromatography on SiO_2 (eluent: cyclohexane/diethyl ether 1:1) gave **9c** (612 mg, 63%). Colourless oil. IR (neat): $\tilde{\nu}$ = 1753 (C=O), 1736 (C=O) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 4.15 (t, J = 6.5 Hz, 12H), 3.81 (t, J = 6.5 Hz, 12H), 3.35 (s, 6H), 1.68 (m, 12H), 1.58 (m, 12H), 1.45 (m, 12H), 0.99 (s, 54H) 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 = 1249.48 $[\text{M}+\text{Na}]^+$, calcd for $[\text{C}_{63}\text{H}_{120}\text{O}_{18}\text{Si}_3+\text{H}]^+$: 1249.79.

Compound 9d. Prepared from **8d** (682 mg, 0.539 mmol), DMAP (132 mg, 1.08 mmol) and malonyl chloride (83.5 mg, 0.592 mmol) in CH_2Cl_2 (70 mL). Plug of silica (eluent: CH_2Cl_2 /diethyl ether 1:1). Column chromatography on SiO_2 (eluent: CH_2Cl_2 /diethyl ether 7:3) gave **9d** (307 mg, 43%). Colourless oil. IR (neat): $\tilde{\nu}$ = 1753 (C=O), 1736 (C=O) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 4.14 (t, J = 6.5 Hz, 12H), 3.80 (t, J = 6 Hz, 12H), 3.36 (s, 6H), 1.66 (m, 12H), 1.55 (m, 12H), 1.39 (m, 24H), 0.99 (s, 54H) 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 = 1355.81 $[\text{M}+\text{Na}]^+$, calcd for $[\text{C}_{69}\text{H}_{132}\text{O}_{18}\text{Si}_3+\text{Na}]^+$: 1355.86.

General procedure for the synthesis of compounds 10a-d. DBU was added to a solution of C_{60} , **9a-d** and I_2 in toluene. The mixture was stirred at room temperature for 90 min, then filtered over a plug of silica (eluent: cyclohexane, then CH_2Cl_2) and evaporated. The resulting product was purified as indicated below.

Compound 10a. Prepared from C_{60} (108 mg, 0.150 mmol), **9a** (580 mg, 0.15 mmol), I_2 (131 mg, 0.52 mmol) and DBU (0.15 mL, 1.00 mmol) in toluene (250 mL). Column chromatography on SiO_2 (eluent: CH_2Cl_2 /cyclohexane 1:1) gave **10b** (204 mg, 39%). Cherry-red glassy solid. Analytical data identical to those reported in the literature for this compound.^[22]

Compound 10b. Prepared from C_{60} (201 mg, 0.280 mmol), **9b** (326 mg, 0.280 mmol), I_2 (248 mg, 0.977 mmol) and DBU (0.299 mL, 2.00 mmol) in toluene (400 mL). Column chromatography on SiO_2 (eluent: CH_2Cl_2 /cyclohexane 1:1) gave **10b** (204 mg, 39%). Cherry-red glassy solid. IR (neat): $\tilde{\nu}$ = 1748 (C=O), 1728 (C=O) cm^{-1} . UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 237 (123500), 251 (127500), 281 (87700), 304 (sh, 65800), 483 (6300), 568 (sh, $1700 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$) nm. ^1H NMR (400 MHz, CDCl_3): δ = 4.53 (m, 6H), 4.21 (m, 6H), 3.79 (m, 12H), 1.77 (m, 12H), 1.57 (m, 12H), 1.00 (s, 27H), 0.96 (s, 27H) ppm. ^{13}C NMR (100 MHz, CDCl_3): 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: m/z = 1881.71 $[\text{M}+\text{H}]^+$, calcd for $[\text{C}_{117}\text{H}_{102}\text{O}_{18}\text{Si}_3+\text{H}]^+$: 1880.65.

Compound 10c. Prepared from C_{60} (188 mg, 0.261 mmol), **9c** (326 mg, 0.261 mmol), I_2 (232 mg, 0.913 mmol) and DBU (0.273 mL, 1.83 mmol), in toluene (700 mL). Column chromatography on SiO_2 (eluent: CH_2Cl_2) gave **10c** (77 mg, 15%). Cherry-red glassy solid. IR (neat): $\tilde{\nu}$ = 1746 (C=O) cm^{-1} . UV/vis (CH_2Cl_2): λ_{max} (ϵ) = 239 (91600), 250 (92300), 281 (63000), 307 (sh, 45900), 484 (4500), 564 (sh, $1400 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$) nm. ^1H NMR (400 MHz, CDCl_3): δ = 4.49 (m, 6H), 4.19 (m, 6H), 3.81-3.70 (m, 12H), 1.70 (m, 12H), 1.55 (m, 12H), 1.41 (m, 12H), 0.98 (s, 54H) 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: m/z = 1963.94 $[\text{M}+\text{H}]^+$, calcd for $[\text{C}_{123}\text{H}_{114}\text{O}_{18}\text{Si}_3+\text{H}]^+$: 1963.74.

Compound 10d. Prepared from C_{60} (158 mg, 0.219 mmol), **9d** (293 mg, 0.219 mmol), I_2 (195 mg, 0.768 mmol) and DBU (0.250 mL, 1.67 mmol), in toluene (316 mL). Column chromatography on SiO_2 (eluent: CH_2Cl_2) gave **10d** (25.4 mg, 6%). Cherry-red glassy solid. IR (neat): $\tilde{\nu}$ = 1748

(C=O) cm^{-1} . UV/vis (CH_2Cl_2): λ_{max} (ϵ) = 242 (99500), 248 (98700), 285 (sh, 58600), 483 (4300), 564 (sh, $1600 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$) nm. ^1H NMR (400 MHz, CDCl_3): δ = 4.70 (m, 4H), 4.41 (m, 4H), 4.23 (m, 4H), 3.78 (m, 12H), 1.70 (m, 12H), 1.39 (m, 36H), 0.99 (m, 54H) 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 = 2047.95 $[\text{M}+\text{H}]^+$, calcd for $[\text{C}_{129}\text{H}_{126}\text{O}_{18}\text{Si}_3+\text{H}]^+$: 2047.83.

Compound 12. $\text{BF}_3\cdot\text{Et}_2\text{O}$ (0.24 mL, 1.9 mmol) was added to a solution of **10a** (174 mg, 0.097 mmol) in CH_2Cl_2 (6 mL) and MeCN (3 mL) under argon. The mixture was stirred at room temperature for 1 d. The crude product was filtered over silica (eluent: THF/MeOH 9:1) to afford **11**, which was used without further purification in the next step. Crude **11** was dissolved under argon in anhydrous THF (5 mL), triethylamine (0.14 mL, 0.97 mmol) was added followed by the addition of MeSO_2Cl (0.075 mL, 0.97 mmol). The mixture was stirred at room temperature for 36 h and then evaporated. Column chromatography on SiO_2 (eluent: CH_2Cl_2 to CH_2Cl_2 /MeOH 99:1) yielded **12** (70 mg, 39% over 2 steps). Red glassy solid. ^1H NMR (400 MHz, CDCl_3): δ = 4.50 (t, J = 6 Hz, 6H), 4.44 (t, J = 6 Hz, 6H), 4.32 (t, J = 6 Hz, 6H), 4.29 (t, J = 6 Hz, 6H), 3.04 (s, 9H), 3.03 (s, 9H), 2.21 (m, 6H), 2.17 (m, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 163.2, 163.2, 147.1, 147.0, 146.9, 146.8, 146.7, 146.6, 146.5, 145.9, 145.6, 145.2, 144.9, 144.7, 143.6, 142.8, 142.6, 141.8, 141.6, 141.2, 70.8, 70.0, 66.0, 66.0, 63.1, 63.1, 52.7, 37.6, 37.6, 28.6, 28.5 ppm.

Compound 13. A solution of **12** (40 mg, 0.0217 mmol) and LiBr (23 mg, 0.265 mmol) in Et_2THF (5 mL) was stirred overnight at 60°C, then filtered over silica (eluent: CH_2Cl_2) and evaporated. Column chromatography on SiO_2 (eluent: CH_2Cl_2 /cyclohexane 7:3) gave **13** (31 mg, 82%). Red glassy solid. IR (neat): $\tilde{\nu}$ = 1741 (C=O) cm^{-1} . UV/vis (CH_2Cl_2): λ_{max} (ϵ) = 235 (116600), 251 (116900), 282 (81200), 305 (sh, 62300), 484 (5900), 524 (sh, 3600), 565 (sh, $1700 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$) nm. ^1H NMR (400 MHz, CDCl_3): δ = 4.50 (m, 6H), 4.45 (m, 6H), 3.47 (t, J = 6 Hz, 6H), 3.45 (t, J = 6 Hz, 6H), 2.29 (m, 6H), 2.26 (m, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 163.3, 163.2, 147.2, 147.0, 146.8, 146.7, 146.7, 146.6, 146.5, 145.8, 145.5, 145.4, 145.1, 144.6, 143.6, 142.9, 142.5, 141.7, 141.6, 141.2, 70.8, 70.0, 64.9, 64.9, 52.7, 31.5, 31.4, 29.1 ppm. MALDI-TOF MS: m/z = 1747.79 $[\text{M}+\text{H}]^+$, calcd for $[\text{C}_{87}\text{H}_{36}\text{O}_{12}\text{Br}_6+\text{H}]^+$: 1746.74.

Compound 15. DBU (0.14 mL, 0.9 mmol) was added to a solution of **13** (102 mg, 0.058 mmol), **14** (94 mg, 0.35 mmol) and CBR_4 (965 mg, 2.91 mmol) in toluene (20 mL). The resulting mixture was stirred overnight at room temperature, filtered over silica (eluent: CH_2Cl_2 /MeOH 98:2) and evaporated. Column chromatography on SiO_2 (eluent: CH_2Cl_2 to CH_2Cl_2 /EtOAc 98:2) gave **15** (94 mg, 63%). Orange glassy solid. IR (neat): $\tilde{\nu}$ = 2097 (N_3), 1741 (C=O) cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 4.43 (t, J = 6 Hz, 12H), 4.37 (t, J = 6 Hz, 12H), 3.44 (t, J = 6 Hz, 12H), 3.40 (t, J = 6 Hz, 12H), 2.25 (quint, J = 6 Hz, 12H), 1.97 (quint, J = 6 Hz, 12H) ppm.

Compound 16. A solution of **15** (94 mg, 0.037 mmol), phenylacetylene (0.05 mL, 0.47 mmol), $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ (3 mg, 0.011 mmol) and sodium ascorbate (4 mg, 0.022 mmol) in CH_2Cl_2 (2 mL) and H_2O (1 mL) was stirred at 30°C. After 15 h, CH_2Cl_2 (20 mL) was added, and the organic layer washed with H_2O , dried (MgSO_4), filtered and evaporated. Column chromatography on SiO_2 (eluent: CH_2Cl_2 to CH_2Cl_2 /MeOH 98:2) gave **16** (116 mg, 99%). Orange glassy solid. IR (neat): $\tilde{\nu}$ = 1743 (C=O) cm^{-1} . UV/vis (CH_2Cl_2): λ_{max} (ϵ) = 246 (237200), 267 (sh, 126000), 281 (sh, 103200), 318 (sh, 61500), 336 (sh, $47200 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$) nm. ^1H NMR (400 MHz, CDCl_3): δ = 7.86 (s, 3H), 7.83 (s, 3H), 7.79 (m, 12H), 7.37 (m, 12H), 7.30 (m, 6H), 4.49-4.34 (m, 36H), 3.41 (t, J = 6 Hz, 6H), 3.39 (t, J = 6 Hz, 6H), 2.38 (quint, J = 6 Hz, 6H), 2.32 (quint, J = 6 Hz, 6H), 2.22 (quint, J = 6 Hz, 6H), 2.19 (quint, J = 6 Hz, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 163.6, 163.6, 163.6, 163.5, 148.1, 148.0, 146.1, 146.0, 145.9, 145.9, 141.4, 141.4, 141.3, 141.3, 141.2, 141.2, 130.6, 130.6, 129.0, 128.3, 125.9, 125.8, 120.2, 120.2, 69.3, 69.3, 69.3, 69.2, 64.9, 63.8, 63.8,

47.0, 45.5, 45.5, 31.4, 31.3, 29.5, 29.2, 29.2 ppm. MALDI-TOF MS: m/z = 3171.1 $[M+H]^+$, calcd for $[C_{162}H_{109}O_{24}N_{18}Br_6+H]^+$: 3171.3.

Compound 17. A mixture of **16** (113 mg, 0.035 mmol) and NaN_3 (23 mg, 0.356 mmol) in DMF (2 mL) was stirred at room temperature. After 17 h, the product was precipitated with H_2O/Et_2O and the crude dissolved in CH_2Cl_2 , the organic phase was washed with H_2O , separated and the solvents were evaporated. Column chromatography on SiO_2 (eluent: CH_2Cl_2 to $CH_2Cl_2/MeOH$ 98:2) afforded **17** (103 mg, 98%). Orange glassy solid. IR (neat): $\tilde{\nu}$ = 2098 (N_3), 1742 (C=O) cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ = 7.86 (s, 3H), 7.83 (s, 3H), 7.79 (m, 12H), 7.35 (m, 12H), 7.30 (m, 6H), 4.45 (m, 12H), 4.34 (m, 24H), 3.36 (t, J = 6 Hz, 6H), 3.33 (t, J = 6 Hz, 6H), 2.34 (m, 12H), 1.94 (quint, J = 6 Hz, 6H), 1.90 (quint, J = 6 Hz, 6H) ppm.

Compound 18. **17** (104 mg, 0.035 mmol) was added in a solution of 4-ethynylanisole (57 mg, 0.428 mmol), $CuSO_4 \cdot 5H_2O$ (3 mg, 0.011 mmol) and sodium ascorbate (4 mg, 0.022 mmol) in CH_2Cl_2/H_2O (2/1 mL). The resulting mixture was stirred at 30°C. After 15 h, CH_2Cl_2 was added to the mixture, washed with H_2O , dried ($MgSO_4$), filtered and evaporated. Column chromatography on SiO_2 (eluent: CH_2Cl_2 to $CH_2Cl_2/MeOH$ 97:3) gave **18** (117 mg, 89%). Orange glassy solid. IR (neat): $\tilde{\nu}$ = 1742 (C=O) cm^{-1} . UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 248 (266700), 318 (sh, 48800), 335 (sh, 38700 $mol^{-1}dm^3cm^{-1}$) nm. 1H NMR (400 MHz, $CDCl_3$): δ = 7.82 (s, 6H), 7.76 (d, J = 7 Hz, 12H), 7.71 (s, 6H), 7.67 (d, J = 7 Hz, 12H), 7.34 (t, J = 7 Hz, 12H), 7.28 (d, J = 7 Hz, 6H), 6.87 (d, J = 7 Hz, 12H), 4.41 (t, J = 7 Hz, 12H), 4.39 (t, J = 7 Hz, 12H), 4.33 (t, J = 6 Hz, 24H), 3.77 (s, 18H), 2.29 (m, 24H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.5, 159.7, 148.0, 147.9, 146.0, 141.4, 130.6, 129.0, 128.3, 127.1, 125.8, 123.3, 120.2, 119.4, 114.3, 69.3, 63.9, 55.4, 46.9, 46.8, 29.4 ppm. MALDI-TOF MS: m/z = 3734.9 $[M+H]^+$, calcd for $[C_{216}H_{156}O_{30}N_{36}+H]^+$: 3734.2). Elemental analysis calcd (%) for $C_{216}H_{156}O_{30}N_{36} \cdot CH_2Cl_2$: C 68.22, H 4.17, N 13.20; found: C 68.02, H 4.01, N 13.07.

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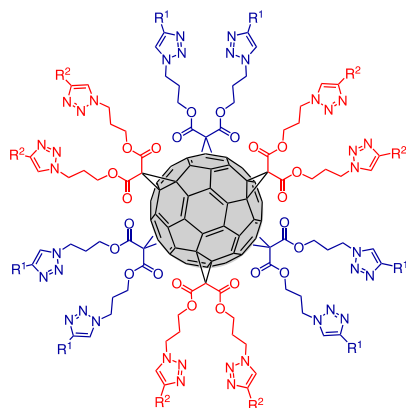
Keywords: Fullerene • Macrocycle • Bingel reaction • Regiochemistry • Silyl protecting groups

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Macrocyclic tris-malonate incorporating cleavable di-*tert*-butylsilylene protecting groups have been used for the regioselective tris-functionalization of C₆₀. Fullerene tris-adducts with an *e,e,e* addition pattern have been thus obtained. Further functionalization has been carried out to generate a clickable fullerene [3:3]-hexa-adduct scaffold allowing the successive introduction of two azide reagents.

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