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Very Important Paper

Si-Tethered Bis- and Tris-Malonates for the Regioselective Preparation of Fullerene Multi-Adducts

Franck Schillinger,^a Uwe Hahn,^a Sebastiano Guerra,^a Thi Minh Nguyet Trinh,^a David Sigwalt,^a Michel Holler,^a Iwona Nierengarten,^a and Jean-François Nierengarten^{*a}^a Laboratoire de Chimie des Matériaux Moléculaires, Université de Strasbourg et CNRS (UMR 7042, LIMA), École Européenne de Chimie, Polymères et Matériaux, 25 rue Becquerel, FR-67087 Strasbourg Cedex 2, France, e-mail: nierengarten@unistra.fr

Dedicated to Prof. Robert Deschenaux on the occasion of his retirement and in recognition for his outstanding contributions in the design of liquid crystalline materials.

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Bis- and tris-malonates constructed around a silicon atom have been prepared by reaction of malonate derivatives bearing an alcohol function with di-*tert*-butylsilyl bis(trifluoromethanesulfonate) and *tert*-butyl(trichloro)silane, respectively. These compounds have been used for the regioselective bis- and tris-functionalization of C₆₀ under *Bingel* conditions. By changing the nature of the linker between the central Si atom and the reactive malonate groups, the malonate precursors have been optimized to produce specific bis- and tris-adducts with excellent regioselectivity. A complete understanding of the electronic and stereochemical factors governing the regioselectivity has been obtained by combining computational studies with a complete analysis of the by-products formed during the reactions of the Si-tethered tris-malonates with C₆₀. Finally, desilylation reactions of the resulting fullerene bis- and tris-adducts have been carried out to generate the corresponding acyclic fullerene bis- and tris-adducts bearing alcohol functions.

Keywords: *Bingel* reaction, cyclopropanation, fullerenes, regioselectivity, trialkoxysilane.

Introduction

Fullerene chemistry has generated unique stereochemical problems related to the large number of possible isomers obtained when several addends are grafted onto the carbon sphere.^[1–5] The first powerful approach for the regioselective preparation of fullerene multiple adducts has been reported by *Diederich* and relies on macrocyclization reactions.^[6–8] Specifically, a linker between the first addend and the reactive unit acts as a directing tether and the addition reaction takes place onto a specific double bond of the fullerene mono-adduct. Following this first example, the same group has developed direct macro-

cyclization reactions between bis-malonate reagents and C₆₀ for the preparation of well-defined fullerene bis-adducts.^[9] This powerful principle has been extensively used for the preparation of a wide range of regioisomerically pure fullerene bis-adducts.^[10–23] The synthesis of C₆₀ higher adducts is a more challenging task given the high number of possible isomers. For instance, the number of theoretically possible regioisomers raises from 9 for C₆₀ bis-adducts to 46 for tris-adducts.^[24] A few examples of direct regioselective synthesis of fullerene tris-adducts have been reported so far.^[25–35] They are either based on the cyclization of tripodal or macrocyclic tris-malonate derivatives onto the C₆₀ core. In recent year, macrocyclic fullerene

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/hlca.202300026>¹Some of the structures reported in Reference [25] have been revised, see Reference [26].

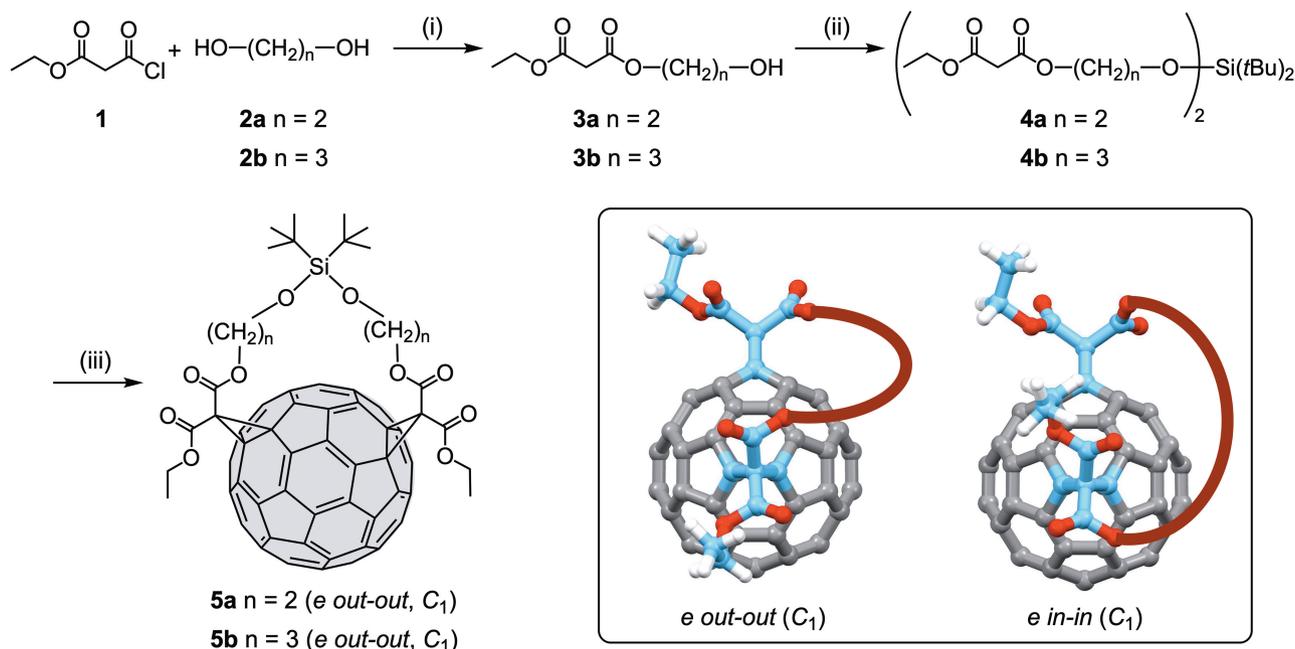
receptors have been used to hide some reactive positions of an encapsulated fullerene host and thus direct its multi-functionalization in a regioselective manner.^[36–43] While very elegant, this methodology is still in its infancy and not easily applicable for the large-scale preparation of fullerene multi-adduct building blocks.

As part of this research, our group has shown that macrocyclic di-*tert*-butylsilylene-tethered bis- and tris-malonates are attractive building blocks for the regioselective functionalization of C₆₀ in multiple *Bingel* cyclopropanations.^[44–46] In this particular case, the bridging di-*tert*-butylsilylene moiety is not only a directing tether for the macrocyclization step, it is also a protecting group that can be readily cleaved to afford the corresponding acyclic fullerene polyols.^[44–46] We have also reported a preliminary communication on the threefold *Bingel* reaction between C₆₀ and *tert*-butyl(trialkoxo)silane derivatives bearing three malonate groups for the regioselective tris-functionalization of C₆₀.^[47] We now report a full account on this work and provide a detailed stereochemical analysis of the bis- and tris-functionalization of C₆₀. Moreover, a complete series of *tert*-butyl(trialkoxo)silane derivatives has been prepared to show the limits of this methodology for the preparation of fullerene tris-adducts. Finally, desilylation

reactions of the resulting C₆₀ bis- and tris-adducts have been optimized to produce the corresponding diols and triols.

Results and Discussion

For a complete understanding of the tris-functionalization of C₆₀ with *tert*-butyl(trialkoxo)silane tris-malonates, it was important to first investigate the regioselectivity of the two-fold *Bingel* functionalization of C₆₀ with corresponding linear di-*tert*-butylsilylene-tethered bis-malonates. For this reason, bis malonates were prepared from diethyl malonyl chloride (**1**) as depicted in *Scheme 1*. Esterification of **1** with a large excess of diols **2a** and **2b** in the presence of pyridine (pyr) gave **3a** and **3b**. By using a large excess of diols **2a** and **2b**, the formation of the corresponding bis-malonates is largely prevented and compounds **3a** and **3b** were thus prepared in good yields. Treatment of **3a** and **3b** with di-*tert*-butylsilyl bis(trifluoromethanesulfonate) (TBDS ditriflate) in DMF in the presence of pyr afforded the Si-bridged malonates **4a** and **4b**. Reactions of bis-malonates **4a** and **4b** with C₆₀ were then carried out under modified *Bingel* conditions.^[9,48] In this particular case, the α -iodo-malonate intermediates are produced *in situ* by reaction of the malonate



Scheme 1. Preparation of fullerene bis-adducts **5a** and **5b**. *Reagents and conditions:* (i) pyr, THF, 0 °C to r.t. (**3a**: 87%; **3b**: 72%); (ii) TBDS ditriflate, pyr, DMF, r.t. (**4a**: 44%; **4b**: 52%); (iii) C₆₀, I₂, PhMe, –15 °C (**5a**: 23%; **5b**: 48%). Inset: schematic representation of the two possible diastereomers for an equatorial macrocyclic bis-adduct; steric considerations based on molecular modeling revealed that only the *out-out* isomer is reasonable in the particular case of **5a** and **5b**.

carbanions with iodine. The cyclopropanation is then achieved by addition of the α -iodo-malonate carbanion to a double bond of C_{60} followed by displacement of iodine by the anionic center generated on the fullerene moiety. It was also decided to perform the *Bingel* reactions at -15°C in order to prevent unwanted desilylation side reactions. Moreover, the reactions were carried out at low concentrations (ca. 0.7 mM) to favor the macrocyclizations onto the fullerene core. Treatment of C_{60} with **4a** and **4b** in the presence of I_2 and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene (PhMe) at -15°C gave regioisomerically pure fullerene bis-adducts **5a** and **5b**. In both cases, by-products were mainly [2+2] and [3+3] macrocycles obtained as mixtures of regioisomers that were not further investigated. Traces of other bis-adducts were also detected but these by-products could not be isolated in a pure form and were obtained in too small quantities thus preventing their characterization.

Mass spectrometry confirmed the [1+1] macrocyclic structures of both **5a** and **5b**. The expected molecular ion peaks were effectively observed at m/z 1210.2 for **5a** ($[M+H]^+$, calc. for $[C_{82}H_{36}O_{10}Si+H]^+$: 1210.3) and 1237.3 for **5b** ($[M+H]^+$, calc. for $[C_{84}H_{40}O_{10}Si+H]^+$: 1237.3). It was then important to disclose the relative positions of the two cyclopropane rings onto the carbon sphere in **5a** and **5b**. As shown in *Figure 1*, there are in principle eight possible regioisomers for a fullerene bis-adduct bearing two identical addends.^[49] In this particular case, the symmetry of the bis-addition pattern can be either D_{2h} (*trans*-1), C_2 (*cis*-3, *trans*-2 and *trans*-3) or C_s (*cis*-1, *cis*-2, *e* and *trans*-4). In principle, each macrocyclic regioisomer resulting from the reaction of a bis-malonate such as **5a** and **5b** with C_{60} can afford different diastereoisomers depending on the relative orientation of the two CO_2Et residues (*in-in*, *in-out* and *out-out* isomerism).^[5] Taking into considerations the pairs of enantiomers for C_1 - and C_2 -symmetrical compounds, 37 isomeric macrocyclic bis-adducts are theoretically possible (*Figure S1*). For fullerene derivatives bearing two malonate addends, the addition pattern is conveniently disclosed from their absorption spectra. Effectively, the colors of such C_{60} bis-adducts, and accordingly their UV/vis spectra, are highly dependent on the relative position of the two cyclopropane rings onto the fullerene core.^[9,50] They are indeed characteristic for each of the regioisomers. The absorption spectra recorded for compounds **5a** and **5b** were identical and clearly showed the characteristic fingerprints of bis-adducts with an *equatorial* addition

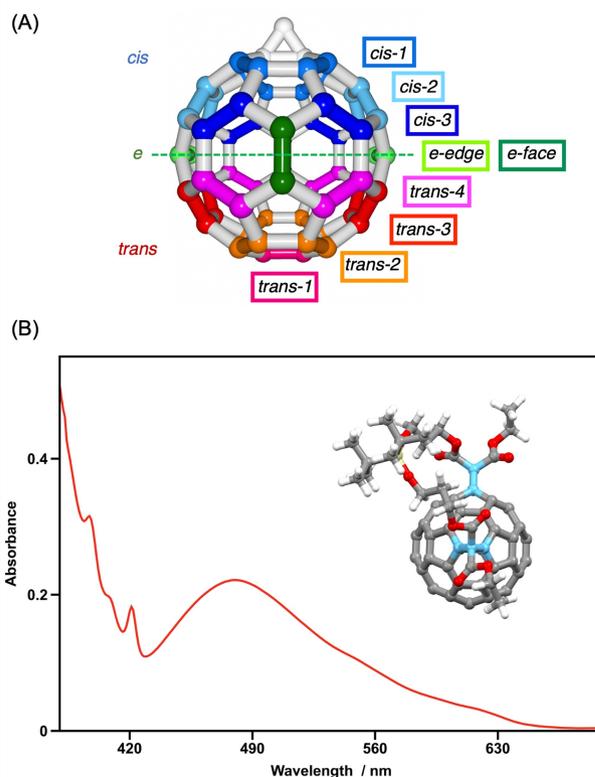


Figure 1. (A) Positional relationships of the different 6,6 double bonds relative to a first addend in a fullerene monoadduct; for bis-adducts, the two addends can be located either in the same hemisphere (*cis*), in the opposite one (*trans*), or on the equatorial belt (*e*); a second addition onto the *e*-edge or *e*-face position leads to the same bis-adducts (simply noted *e*) when the two addends are identical. (B) Absorption spectrum (CH_2Cl_2) of fullerene bis-adduct **5b** showing the characteristic features of the *e* bis-addition pattern. Inset: calculated structure of **5b**, the C-atoms of the cyclopropane rings are highlighted in blue.

pattern. As a typical example, the UV/vis spectrum recorded for compound **5b** is depicted in *Figure 1*. The molecular symmetry (C_1) deduced from the 1H - and ^{13}C -NMR spectra of **5a** and **5b** was also fully consistent with the proposed *equatorial* addition pattern. In principle, two diastereomers are possible for a macrocyclic *e* bis-adduct (inset *Scheme 1*). In both cases, molecular modeling studies revealed that the *in-in* diastereoisomer is highly strained as the linker between the two cyclopropane rings is too short (*Figure S2*). Therefore, only the *out-out equatorial* isomer is possible for both **5a** and **5b**. As only one diastereoisomer was formed during the cyclization of **4a** and **4b** onto the fullerene core, the bis-functionalization was at the same time regio- and diastereoselective.

To gain further understanding about the outcome of these reactions, computational studies were also performed. The molecular geometry of all the possible diastereoisomers for the *cis-2*, *cis-3*, *e*, *trans-4* and *trans-3* regioisomers resulting from the cyclization of **4a** and **4b** onto the fullerene core were optimized at the PM6 semi-empirical level (Figure S2). The *cis-1* regioisomer is typically not obtained in bis-Bingel cyclopropanation reactions of C₆₀ for obvious steric reasons^[49] and the linker between the two malonate subunits is too short to form *trans-1* and *trans-2* products, these regioisomers were thus not calculated. The relative heat of formation obtained for all the macrocyclization products are gathered in Table S1. For the sake of clarity, only the most reasonable bis-adducts (*out-out* diastereomers) are listed in Table 1.

In both cases, the *cis-3* and *trans-3* regioisomers were notably high in energy whatever the chain length of the Si-tether. Steric constraints resulting from the stereochemical preferences of the silylene linker (*cis-3*) or from the limited length of the linker between the two cyclopropane rings (*trans-3*) prevent the formation of these particular macrocyclic regioisomers. In the case of the cyclization products obtained from **4b**, the *e* regioisomer was the most stable in apparent agreement with the formation of **5b** from **4b** and C₆₀. In contrast, the *trans-4* regioisomer was found to be lowest in energy for the calculated cyclization products of **4a** and not the *e* derivative obtained experimentally (**4b**). Nonetheless, the differences in energy between the *cis-2*, *e* and *trans-4* regioisomers were rather small in both cases and do not explain the experimentally observed preferential formation of the *e* regioisomer. Indeed, ring strain plays an important role but the cyclization reactions on the C₆₀ core are also governed by the relative reactivity of the different double bonds in the mono-functionalized fullerene intermediate obtained upon the first cyclopropanation. The regioselectivity results actually from an interplay between steric factors and

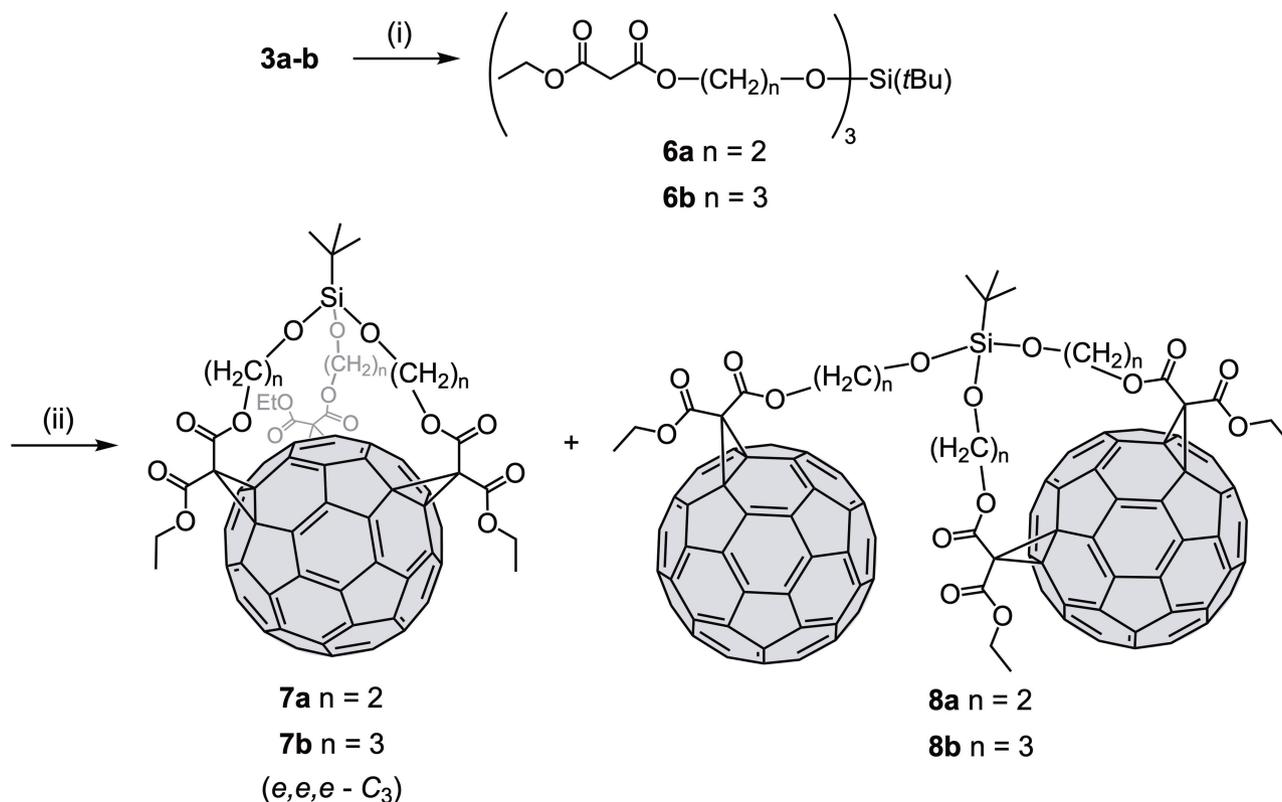
kinetic effects.^[45,46] In the intermediate mono-adduct, the most reactive double bonds are the *e-face* ones followed by the *trans-3* and the *cis-2* ones. These are actually the positions where the lowest-unoccupied molecular orbitals (LUMO) are mainly located (Figure S3). The regioselectivity observed for the macrocyclization of **4a** and **4b** onto the fullerene sphere results most likely from the highest reactivity of the *e-face* double bonds of the mono-adduct intermediate and compounds **5a** and **5b** must be therefore kinetic products. As the reactions were performed at low temperature (−15 °C), kinetic effects were further accentuated thus explaining well the observed regioselectivity.

After the successful regioselective bis-functionalization of C₆₀ with bis-malonates **4a** or **4b**, the strategy was then extended to Si-tethered tris-malonates to prepare fullerene tris-adducts (Scheme 2). Reaction of **3a** or **3b** with *tert*-butyl(trichloro)silane (^tBuSiCl₃) in dry DMF in the presence of imidazole (Im) provided tris-malonates **6a** and **6b**. These intermediates were found only moderately stable but their purification by column chromatography was possible. Complete decomposition was observed upon a few days of storage even at low temperature. Compounds **6a** and **6b** were therefore typically used for the next step immediately after their purification. Treatment of C₆₀ with **6a** and **6b** in the presence of DBU and I₂ in toluene at −15 °C afforded tris-adducts **7a** and **7b** as well as the corresponding bis-fullerene derivatives **8a** and **8b**. Due to the formation of byproducts **8a** and **8b**, it was necessary to use an excess of C₆₀ (1.5 equiv.) to obtain the desired tris-adducts with optimized yields. When compared to **6a** and **6b**, fullerene derivatives **7a**, **7b**, **8a** and **8b** were found to be more stable. However, partial decomposition was still observed after several weeks of storage at low temperature. This is, however, not a major problem as the corresponding products obtained upon desilylation are perfectly stable.

Compounds **7a**, **7b**, **8a** and **8b** have been characterized by ¹H- and ¹³C-NMR, IR and UV-vis spectroscopies. Their MALDI-TOF mass spectra were also in agreement with the proposed structures. The ¹H- and ¹³C-NMR spectra of compounds **8a** and **8b** revealed C₁-symmetrical structures fully consistent with a macrocyclic fullerene equatorial bis-adduct bearing a fullerene mono-adduct. This structural assignment was further supported by the products formed upon their desilylation (*vide infra*). In the case of **7a** and **7b**, the relative position of the three cyclopropane rings on the fullerene core was deduced from their molecular symmetry (C₃) based on the analysis of their ¹H- and

Table 1. Relative heat of formation in kJ/mol calculated at the PM6 semi-empirical level for the most probable fullerene bis-adducts obtained from the reaction of **4a** and **4b** with C₆₀.

	Bis-adduct obtained from 4a	Bis-adduct obtained from 4b
<i>cis-2</i>	+5.3	+7.0
<i>cis-3</i>	+14.0	+24.7
<i>e</i>	+8.6	0
<i>trans-4</i>	0	+4.1
<i>trans-3</i>	+82.5	+30.0



Scheme 2. Preparation of fullerene tris-adducts **7a** and **7b**. Reagents and conditions: (i) $t\text{BuSiCl}_3$, 1m, DMF, r.t. (**6a**: 77%; **6b**: 66%); (ii) C_{60} , I_2 , PhMe, -15°C (**7a**: 8% and **8a**: 20%; **7b**: 27% and **8b**: 11%).

^{13}C -NMR spectra. As a typical example, the ^{13}C -NMR spectrum recorded for tris-adduct **7a** is depicted in Figure 2. A total of 20 resonances are clearly observed for the fullerene C-atoms. Specifically, the two fullerene sp^3 C-atoms (a and b) are observed at $\delta = 71.1$ and 70.3 ppm while 18 resonances are detected between $\delta = 147.5$ and 140.8 ppm for the different fullerene sp^2 C-atoms. Compound **7a** is therefore a C_3 -symmetrical tris-adduct. This is further supported by the observation of nine resonances for the C-atoms of the Si-bridged tripodal substructure. Amongst all the possible addition patterns for fullerene tris-adducts, only three are C_3 -symmetrical: *cis-1,cis-1,cis-1*; *e,e,e* and *trans-3,trans-3,trans-3*. Owing to steric crowding, the formation of the *cis-1,cis-1,cis-1* isomer is highly unfavorable. Discrimination between the two possible addition patterns was finally achieved by comparison of the UV/vis spectra of **7a** and **7b** with those reported in the literature for *e,e,e* and *trans-3,trans-3,trans-3* fullerene tris-adducts.^[24–33] As discussed in the case of bis-adducts, the absorption spectra of fullerene multi-adducts are dependent on the addition pattern and highly characteristic for each regioisomer. The UV-vis

spectra of **7a** and **7b** revealed clearly the typical absorption features observed for *e,e,e* tris-adducts thus providing a definitive stereochemical assignment. This specific addition pattern was also fully consistent with the regiochemistry observed for the reaction of the corresponding Si-tethered bis-malonates **4a** and **4b** with C_{60} . Effectively, the stepwise *Bingel* reaction of tris-malonates **6a** and **6b** onto the fullerene core is expected to produce the same addition pattern for the intermediate bis-adduct leading to **7a** and **7b**, namely the *equatorial* regioisomer.

To fully understand the stereochemical and electronic factors governing the formation of **7a**, **7b**, **8a** and **8b**, detailed computational studies were performed. This is shown in Figure 3 for the functionalization of C_{60} with tris-malonate **6a**. The two first *Bingel* reactions of **6a** with C_{60} are expected to produce a bis-adduct intermediate with an *equatorial* addition pattern based on the regioselectivity observed for the bis-cyclopropanation of C_{60} with the corresponding Si-tethered bis-malonate (**4a**). Owing to the chirality of the resulting macrocyclic equatorial bis-adduct, the tetra-substituted silicon atom becomes stereogenic in

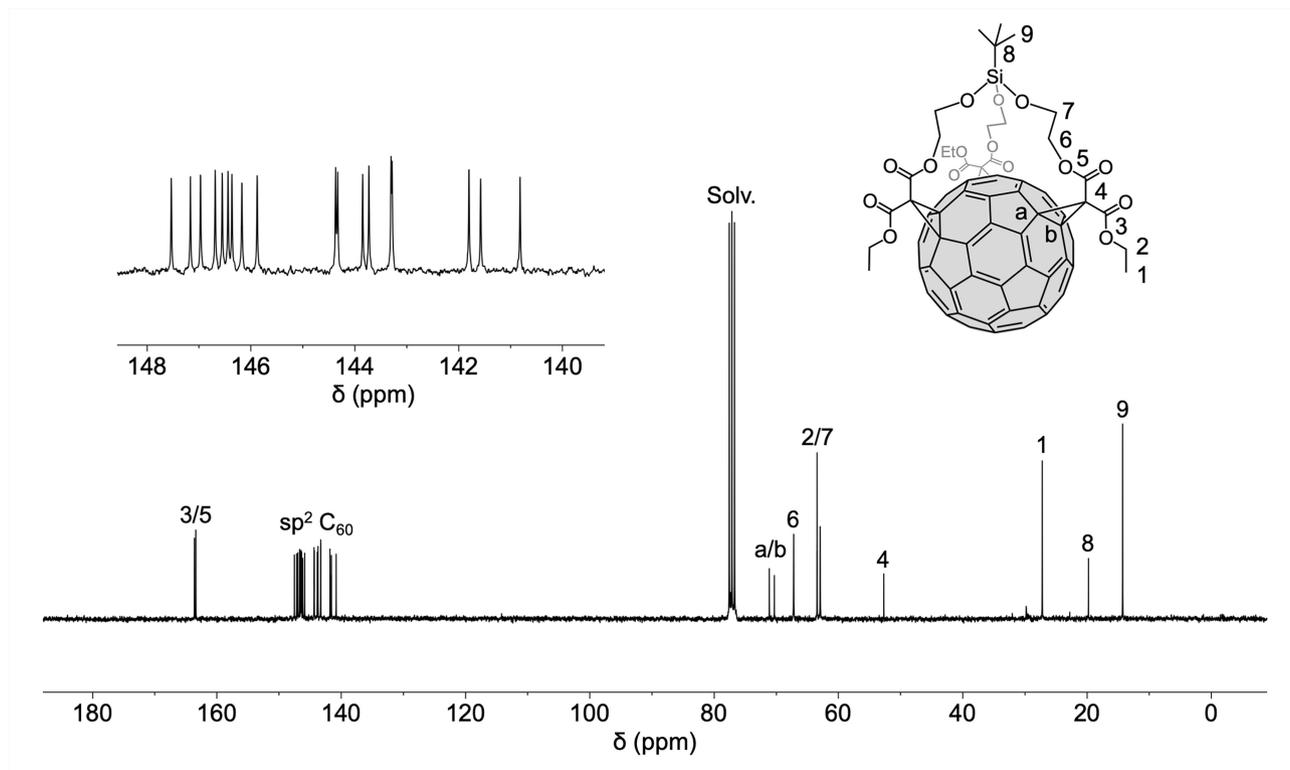


Figure 2. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of compound **7a**.

this intermediate. As a result, two pairs of enantiomeric diastereomers are possible (**A/ent-A** and **B/ent-B**). A third intramolecular cyclopropanation reaction is then supposed to generate a fullerene tris-adduct. As the reaction is performed under kinetic control, cyclopropanation of the most reactive double bond is expected to be favored. These bonds are located on two equatorial positions based on the LUMO of the bis-adduct (*Figure S4*) and are highlighted in blue in the structures of **A/ent-A** and **B/ent-B**.

The reactive malonate group is perfectly oriented in **B** and *ent-B* to generate a C_3 -symmetrical *e,e,e* tris-adduct with all the CO_2Et groups in an *out* orientation (**7a** and *ent-7a*). In contrast, reaction with the other equatorial position in **B** and *ent-B* is prevented as it would generate a highly strained C_1 -symmetrical tris-adduct with the $t\text{Bu}$ group in an *endo* orientation (**E** and *ent-E*). In theory, cyclization of **A** and *ent-A* would form fullerene tris-adducts **C/ent-C** and **D/ent-D**. These cyclization products are however highly strained due to the *endo* orientation of the bulky $t\text{Bu}$ group (**D/ent-D**) or to the *in* orientation of one CO_2Et subunit (**C/ent-C**) making their formation highly unfavorable. As the cyclization of **A** and *ent-A* is prevented due to an unfavorable orientation of their reactive malonate

group, these intermediates react in an intermolecular manner with a second fullerene sphere to generate bis-fullerenes **8a** and *ent-8a*. In conclusion of this theoretical analysis, it appears that the formation of **7a** is limited by the stereochemistry of its bis-adduct precursor as only two of the four possible diastereomers have an appropriate orientation for a cyclization reaction. The two other diastereomers react in an intermolecular manner with a second fullerene molecule to generate bis-fullerene **8a**. On the other hand, the regioselectivity observed for the formation of **7a** results most likely from kinetic effects that favor reactions onto the most reactive *equatorial* positions in the intermediate mono- and bis-adducts.

To further evaluate the potential of this strategy for the regioselective tris-functionalization of C_{60} , additional tris-malonates constructed on a *t*-butyl(trialkoxy)silane core were prepared from diols **2c–2g** (*Scheme 3*). Mono-esterification of **2c–2g** with **1** and subsequent treatment of the resulting **3c–3g** with $t\text{BuSiCl}_3$ afforded tris-malonates **6c–6g**. Functionalization of C_{60} with **6c–6g** was then achieved under the conditions optimized for the preparation of **7a**, **7b**, **8a** and **8b** from **6a** and **6b**. Except for **6g**, all the reactions provided the cherry-red *e,e,e* fullerene tris-

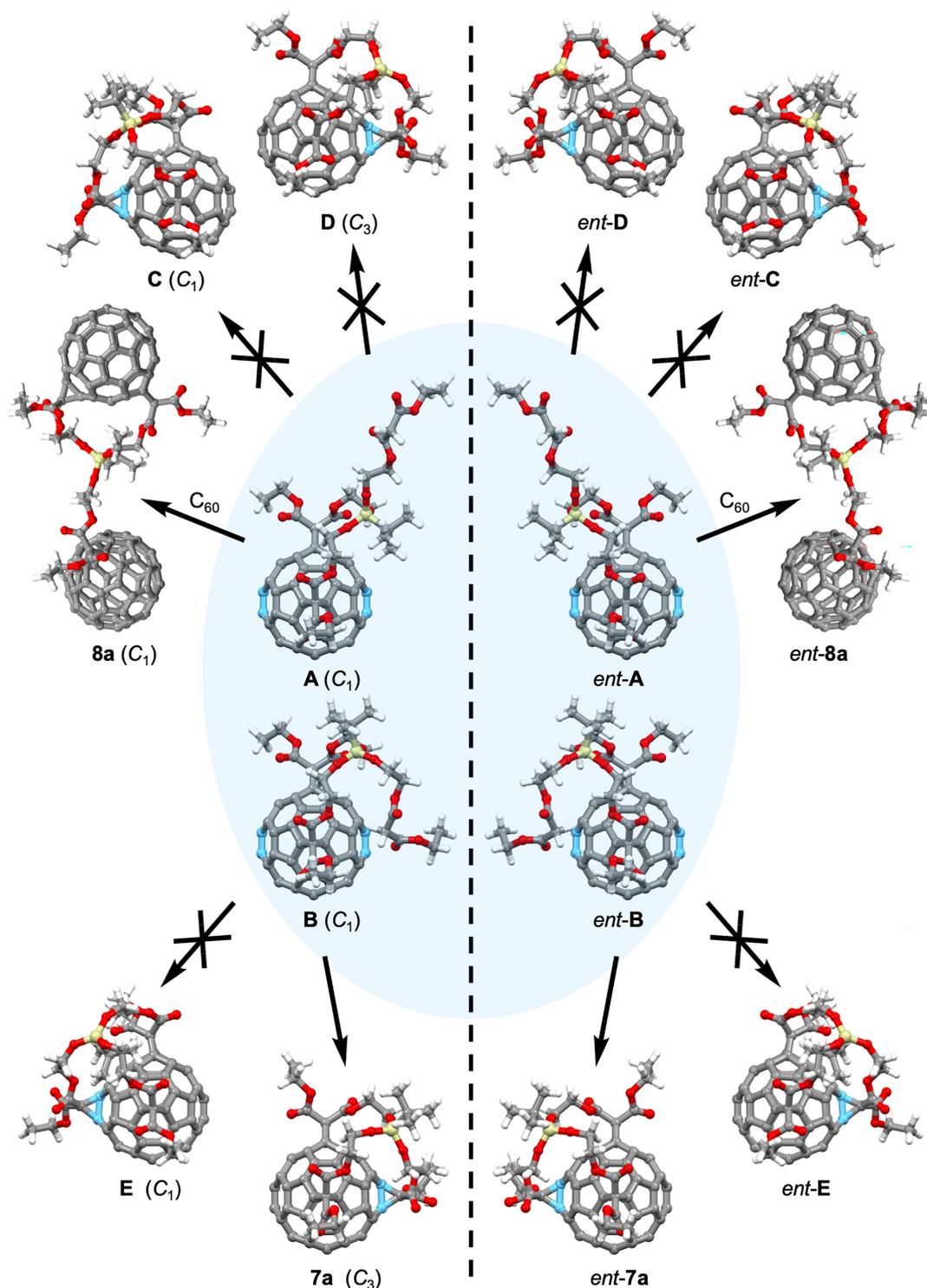
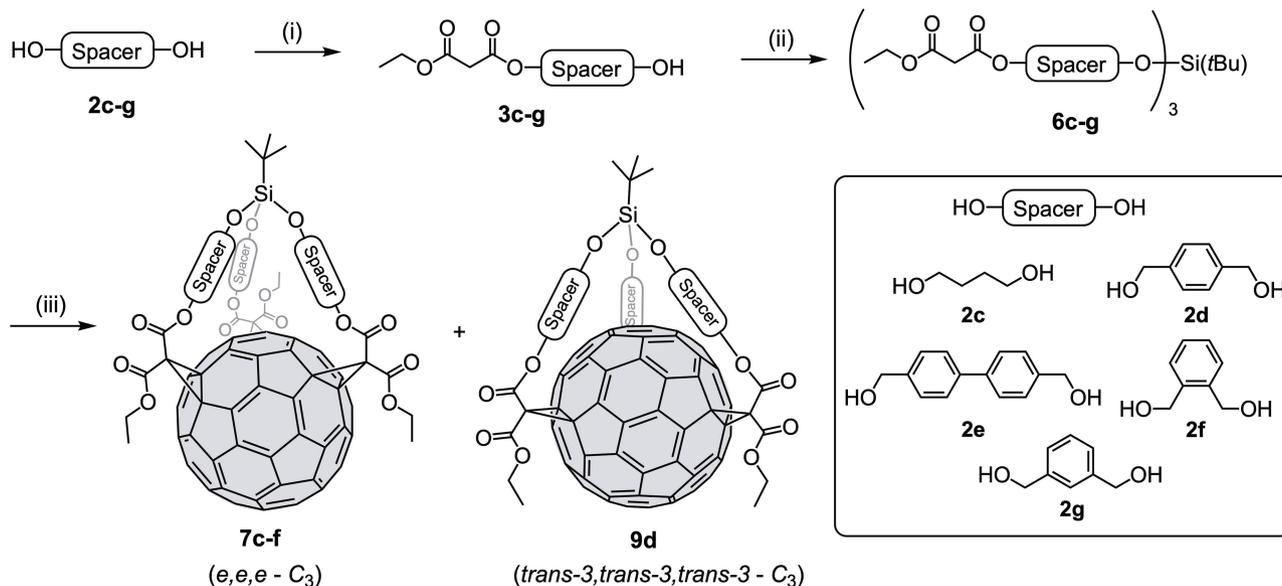


Figure 3. PM6 optimized structures of the four possible bis-adduct intermediates resulting from the bis-cyclopropanation of C_{60} with **6a** (**A**, *ent-A*, **B** and *ent-B*) for which the most reactive equatorial double bonds are highlighted in blue) and the theoretically possible *e,e,e* tris-adducts resulting from an intramolecular *Bingel* reaction (in the cyclization products, the fullerene C-atoms of the newly formed cyclopropane ring are highlighted in blue). For steric reasons, the orientation of the reactive malonate group of **A** and *ent-A* is highly unfavorable and intermolecular reactions with C_{60} occurs to generate **8a** and *ent-8a*. In contrast, the orientation of the reactive malonate group of **B** and *ent-B* is well suited to generate **7a** and *ent-7a*, respectively, but reaction with the other equatorial double bond leading to **E** and *ent-E* is unfavorable.



Scheme 3. Preparation of fullerene tris-adducts **7c–7f** and **9d**. Reagents and conditions: (i) **1**, pyr or Im, THF, 0 °C to r.t. (**3c**: 83%; **3d**: 46%; **3e**: 40%; **3f**: 47%; **3g**: 29%); (ii) $t\text{BuSiCl}_3$, Im, DMF, r.t. (**6c**: 67%; **6d**: 57%; **6e**: 54%; **6f**: 92%; **6g**: 59%); (iii) C_{60} , I_2 , PhMe, $-15\text{ }^\circ\text{C}$ (**7c**: 14%; **7d**: 10% and **9d**: 1%; **7e**: 3%; **7f**: 25%).

adducts (**7c–7f**). In all the cases, bis-fullerene by-products such as **8a** and **8b** were also obtained but these compounds were not further analyzed as most of them were obtained as an inseparable mixture of regioisomers resulting from different addition patterns of their bis-adduct moiety. The linker between the malonate subunits and the central *tert*-butylsilane core plays clearly an important role in the outcome of the reactions. Obviously, the 1,3-propane (**6b**) and the *o*-xylene (**6f**) linkers are the most appropriate to generate *e,e,e* fullerene tris-adducts in good yields. When longer spacers are used, *e,e,e* fullerene tris-adducts **7c–7e** were still obtained but in lower yields. Other regioisomeric tris-adduct by-products were also formed from **6c–6e** but most of them could not be isolated in a pure form. The only tris-adduct by-product that could be isolated and fully characterized was **9d**. In the particular case of **6g**, a complex mixture of tris-adducts was obtained and none of them could be isolated in a pure form. These observations suggest that the bis-adduct intermediate initially formed in the reaction of **6c–6g** with C_{60} is not exclusively *equatorial* due to the increased size of the linkers. This view is nicely supported by the formation of by-product **9d** with a *trans-3,trans-3,trans-3* addition pattern.

The addition patterns of fullerene tris-adducts **7c–7f** and **9d** were unambiguously deduced from their molecular symmetry and their diagnostic absorption spectra. ^1H - and ^{13}C -NMR revealed effectively a C_3 -

symmetrical structure for all these compounds. Diagnostic signatures of an *e,e,e* addition pattern were observed in the absorption spectra of **7c–7f**. As a typical example, the UV-vis spectrum recorded for compound **7d** is depicted in Figure 4. Compound **9d** is also C_3 -symmetrical and must therefore be the *trans-3,trans-3,trans-3* isomer as this is the only other possible addition pattern with this symmetry. As shown in Figure 4, the UV-vis spectrum recorded for **9d** is fully consistent with those previously reported

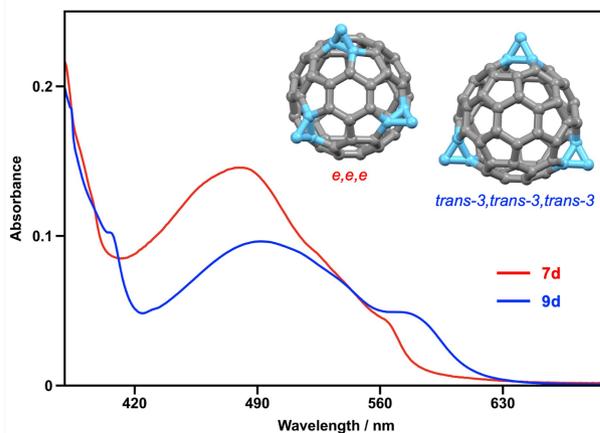
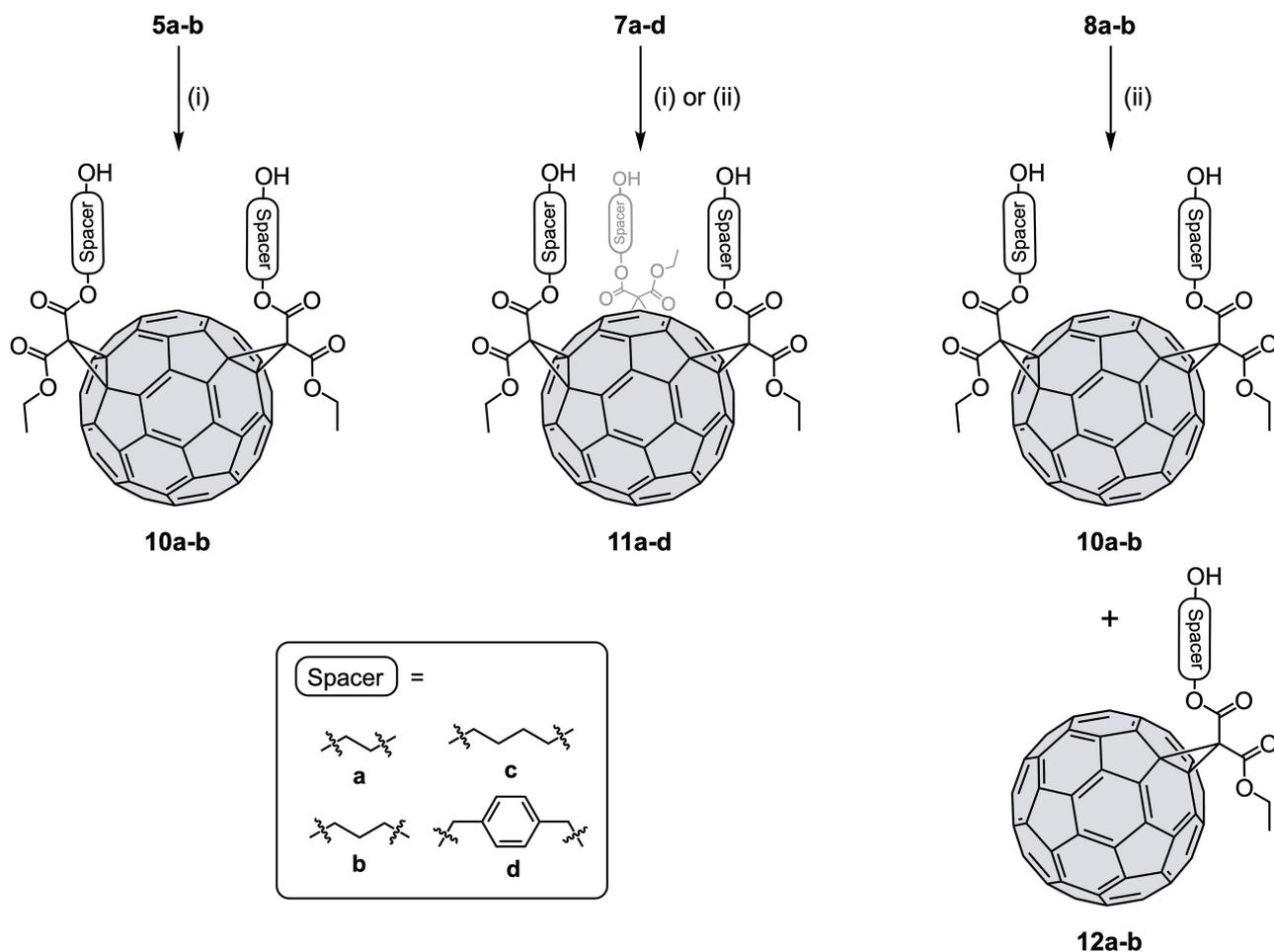


Figure 4. Absorption spectra (CH_2Cl_2) of fullerene tris-adducts **7d** and **9d**. Inset: position of the cyclopropane rings (in blue) in *e,e,e* and *trans-3,trans-3,trans-3* fullerene tris-adducts (view along the C_3 axis).

for tris-adducts with a *trans-3,trans-3,trans-3* addition pattern.^[24–33]

A major advantage of using silane-based connecting groups in the bis- and tris-malonates reagents is related to the possible cleavage of the Si–O bonds upon the regioselective multi-functionalization of the fullerene sphere. The resulting polyols thus obtained are valuable building blocks for further chemical transformations based on the reactivity of the alcohol functions. Desilylation reactions of **5a** and **5b** and **7a** and **7d** were thus attempted to produce the corresponding polyols (Scheme 4). Treatment of **5a** and **5b** with tetra-*n*-butylammonium fluoride (TBAF) gave mainly decomposition products. This was most probably related to the partial hydrolysis of some ester functions under such basic conditions. In contrast, fluoride was an effective reagent for the desilylation of **5a** and **5b** when the reactions were performed under acidic conditions. Desilylation of **5a** and **5b** with HF-

pyr in THF gave effectively diols **10a** and **10b** in good yields (80–90%). Alternatively, treatment of **5a** and **5b** with a large excess of BF₃·Et₂O (20 equiv.) in CH₂Cl₂ provided also **10a** and **10b** in good yields. Both desilylation conditions were efficient, the use of BF₃·Et₂O was however found to be more convenient from a practical point of view. These conditions do effectively not require HF-resistant equipment. In addition, traces of pyridine in the final products were sometimes difficult to remove in samples prepared by treatment with HF-pyr. The desilylation conditions used for the cleavage of the connecting di-*t*-butylsilylene protecting group in **5a** and **5b** were then applied to the *t*-butyl(trialkoxy)silane derivatives **7a–7d** and **8a** and **8b**. Triols **11a–11d** were thus obtained in good yields from **7a–7d**. In the case of **8a** and **8b**, desilylation produced two products, namely fullerene mono-adducts **12a** and **12b** and fullerene bis-adducts **10a** and **10b**. Importantly, samples of **10a** and **10b**



Scheme 4. Desilylation reactions. *Reagents and conditions:* (i) BF₃·Et₂O, CH₂Cl₂, CH₃CN, r.t. (**10a**: 91%; **10b**: 72%; **11b**: 97%; **11c**: 67%; **11d**: 82%); (ii): HF-pyr, THF, r.t. (**11a**: 88%; **10a**: 66% and **12a**: 55%; **10b**: 60% and **12b**: 76%).

thus obtained were rigorously identical to the ones prepared from **5a** and **5b**. The structural assignment proposed for compounds **8a** and **8b** was therefore fully confirmed.

Conclusions

The reaction of Si-tethered tris-malonates with C₆₀ gave easy access to *e,e,e* fullerene tris-adducts with an excellent regioselectivity and good yields when the linker between the Si core and the reactive malonate moieties has the appropriate length. A complete understanding of the stereochemical and electronic factors governing this tris-functionalization of C₆₀ has been obtained by combining computational studies with model bis-functionalization of C₆₀ with analogous Si-tethered bis-malonate derivatives. Overall, the regioselectivity of the tris-functionalization results from structural factors as the *tert*-butyl(trialkoxy)silane group acts as a directing tether but also from kinetic effects related to the difference in reactivity of the different double bonds in the intermediate mono- and bis-adducts. Indeed, the best yields in fullerene tris-adducts have been obtained when the tris-functionalization is carried out from precursors directing efficiently the second cyclopropanation onto the most reactive *equatorial* bonds. The final cyclization leading to the *e,e,e* tris-adducts is then conveniently achieved through cyclopropanation of the most reactive double bond of the bis-adduct intermediate. The tris-functionalization with Si-tethered tris-malonates is however limited by the stereochemistry of the Si atom in the bis-adduct intermediate. Effectively, only one of the two possible diastereomers of this key intermediate can form the desired tris-functionalized fullerene product. While very efficient for the preparation of fullerene tris-adducts with an *e,e,e* addition pattern, the direct tris-functionalization of C₆₀ with tripodes bearing three malonate moieties is not well suited to selectively produce related derivatives with other addition patterns. There is still a clear need to develop new strategies for this purpose. On the other hand, the *e,e,e* tris-adducts reported herein are ideal precursors for the construction of fullerene hexa-adducts with a controlled repartition of functional groups around the central fullerene core. Work in this direction is currently underway in our group to generate unprecedented globular nanomaterials.

Experimental Section

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 expect for the reactions with hydrogen fluoride pyridine (hydrogen fluoride *ca.* 70%, pyridine *ca.* 30%, CAS number: 62778-11-4, purchased from *Sigma-Aldrich* Ref. 184225), which were carried out under argon in a *Teflon* flask. NOTE: Gel preparations of calcium gluconate should be within reach when working with hydrogen fluoride pyridine to treat possible hydrofluoric acid burns. 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 *PerkinElmer Spectrum One* Spectrophotometer. NMR spectra were recorded on *Bruker Avance I* (300 MHz) or *Avance III HD* (400 MHz) spectrometers with solvent peaks as reference. MALDI-TOF mass spectra were recorded on a *Bruker ULTRAFLEX* TOF/TOF mass spectrometer with a dithranol matrix by the analytical service of the École Européenne de Chimie, Polymères et Matériaux, Strasbourg, France.

General Procedure for the Preparation of Malonates **3a–3g**

A solution of **1** in anhydrous THF was added dropwise within 30 min to a solution of the diol (**2a–2g**) and pyridine or imidazole in anhydrous THF at 0 °C under argon. The mixture was allowed to slowly warm to room temperature and stirring was continued at this temperature overnight. The resulting mixture was filtered through silica, concentrated, and purified as indicated.

Compound 3a. Prepared from **1** (4.2 mL, 32.8 mmol), **2a** (36.8 mL, 660 mmol) and pyridine (3.3 mL, 40.8 mmol) in anhydrous THF (80 mL). Column chromatography (SiO₂; eluent: CH₂Cl₂/AcOEt 8:2) gave **3a** (5.0 g, 87%). Colorless oil. ¹H-NMR (CDCl₃, 300 MHz): 4.31–4.27 (m, 2H), 4.20 (q, *J* = 7, 2H), 3.82 (q, *J* = 4, 2H), 3.42 (s, 2H), 2.43 (t, *J* = 4, 1H), 1.28 (t, *J* = 7, 3H). ¹³C-NMR (CDCl₃, 75 MHz): 167.0, 166.8, 67.0, 61.8, 60.7, 41.5, 14.1.

Compound 3b. Prepared from **1** (1.0 mL, 7.81 mmol), **2b** (1.1 mL, 15.2 mmol) and pyridine

(1.1 mL, 13.6 mmol) in anhydrous THF (75 mL). Column chromatography (SiO₂; eluent: CH₂Cl₂/cyclohexane 8:2 to CH₂Cl₂/AcOEt 97:3) gave **3b** (1.07 g, 72%). Colorless oil. ¹H-NMR (CDCl₃, 300 MHz): 4.32 (t, *J* = 6, 2H), 4.20 (q, *J* = 7, 2H), 3.72 (t, *J* = 6, 2H), 3.38 (s, 2H), 1.90–1.63 (m, 3H), 1.28 (t, *J* = 7, 3H). ¹³C-NMR (CDCl₃, 100 MHz): 167.0, 166.8, 62.8, 61.8, 59.3, 41.7, 31.6, 14.2.

Compound 3c. Prepared from **1** (1.9 mL, 14.8 mmol), **2c** (5.4 mL, 60.9 mmol) and pyridine (2.3 mL, 28.4 mmol) in anhydrous THF (130 mL). Column chromatography (SiO₂; eluent: CH₂Cl₂ to CH₂Cl₂/AcOEt 97:3) gave **3c** (2.52 g, 83%). Colorless oil. ¹H-NMR (CDCl₃, 300 MHz): 4.24–4.17 (m, 4H), 3.68 (q, *J* = 6, 2H), 3.37 (s, 2H), 1.83–1.65 (m, 4H), 1.43 (s, 1H), 1.28 (t, *J* = 7, 3H). ¹³C-NMR (CDCl₃, 75 MHz): 166.6 (2 C), 65.5, 62.4, 61.7, 41.8, 29.1, 25.1, 14.2.

Compound 3d. Prepared from **1** (2.3 mL, 18.0 mmol), **2d** (5.0 g, 36.2 mmol) and pyridine (2.8 mL, 34.6 mmol) in anhydrous THF (300 mL). Column chromatography (SiO₂; eluent: CH₂Cl₂/cyclohexane 8:2 to CH₂Cl₂) gave **3d** (2.08 g, 46%). Colorless oil. ¹H-NMR (CDCl₃, 300 MHz): 7.36 (s, 4H), 5.18 (s, 2H), 4.70 (d, *J* = 5, 2H), 4.19 (q, *J* = 7, 2H), 3.41 (s, 2H), 1.73 (s, 1H), 1.25 (t, *J* = 7, 3H). ¹³C-NMR (CDCl₃, 75 MHz): 166.6 (2 C), 141.3, 134.9, 128.7, 127.3, 67.1, 65.1, 61.8, 41.8, 14.2.

Compound 3e. Prepared from **1** (0.8 mL, 6.25 mmol), **2e** (2.5 g, 11.7 mmol) and imidazole (0.79 g, 11.6 mmol) in anhydrous THF (150 mL). Column chromatography (SiO₂; eluent: CH₂Cl₂/cyclohexane, 8:2 to CH₂Cl₂) gave **3e** (0.82 g, 40%). Colorless oil. ¹H-NMR (CDCl₃, 400 MHz): 7.60 (d, *J* = 7, 2H), 7.58 (d, *J* = 7, 2H), 7.45 (d, *J* = 7, 2H), 7.43 (d, *J* = 7, 2H), 5.23 (s, 2H), 4.75 (s, 2H), 4.20 (q, *J* = 7, 2H), 3.44 (s, 2H), 1.61 (s, 1H), 1.26 (t, *J* = 7, 3H). ¹³C-NMR (CDCl₃, 100 MHz): 166.63, 166.57, 141.2, 140.3, 140.2, 134.5, 129.0, 127.7, 127.5, 127.4, 67.1, 65.2, 61.8, 41.8, 14.2.

Compound 3f. Prepared from **1** (1.4 mL, 10.9 mmol), **2f** (3.0 g, 21.7 mmol) and pyridine (1.7 mL, 21.0 mmol) in anhydrous THF (100 mL). Column chromatography (SiO₂; eluent: CH₂Cl₂/cyclohexane 8:2 to CH₂Cl₂/AcOEt 97:3) gave **3f** (1.30 g, 47%). Colorless oil. ¹H-NMR (CDCl₃, 300 MHz): 7.49–7.28 (m, 4H), 5.31 (s, 2H), 4.75 (s, 2H), 4.18 (q, *J* = 7, 2H), 3.41 (s, 2H), 2.19 (s, 1H), 1.24 (t, *J* = 7, 3H). ¹³C-NMR (CDCl₃, 75 MHz): 166.7, 166.4, 139.7, 133.2, 130.2, 129.3, 129.2, 128.3, 65.3, 63.0, 61.9, 41.8, 14.1.

Compound 3g. Prepared from **1** (1.8 mL, 14.1 mmol), **2g** (3.0 g, 21.7 mmol), and pyridine (2.3 mL, 28.4 mmol) in anhydrous THF (100 mL). Column chromatography (SiO₂; eluent: CH₂Cl₂/cyclohexane 8:2 to CH₂Cl₂) gave **3g** (1.03 g, 29%). Colorless oil. ¹H-NMR (CDCl₃, 300 MHz): 7.26–7.43 (m, 4H), 5.20 (s, 2H), 4.72 (s, 2H), 4.20 (q, *J* = 7, 2H), 3.42 (s, 2H), 1.66 (s, 1H), 1.26 (t, *J* = 7, 3H). ¹³C-NMR (CDCl₃, 75 MHz): 166.6 (2 C), 141.5, 135.7, 128.9, 127.5, 127.1, 126.8, 67.2, 65.0, 61.7, 41.7, 14.1.

General Procedure for the Preparation of Bismalonates **4a** and **4b**

TBDS ditriflate was added to a solution of the alcohol (**3a** or **3b**) and pyridine in anhydrous DMF under argon and the mixture was stirred at room temperature as indicated. Et₂O was added and the organic phase was extracted with water, dried with MgSO₄, concentrated, and purified as indicated.

Compound 4a. Prepared from **3a** (1.14 g, 6.45 mmol), pyridine (0.52 mL, 6.45 mmol) and TBDS ditriflate (0.80 mL, 2.45 mmol) in anhydrous DMF (15 mL) after stirring at room temperature for 12 h. Column chromatography (SiO₂; eluent: CH₂Cl₂/AcOEt 9:1) gave **4a** (529 mg, 44%). Colorless oil. ¹H-NMR (CDCl₃, 300 MHz): 4.26 (t, *J* = 5, 4H), 4.19 (q, *J* = 7, 4H), 4.04 (t, *J* = 5, 4H), 3.38 (s, 4H), 1.28 (t, *J* = 7, 6H), 1.00 (s, 18H). ¹³C-NMR (CDCl₃, 75 MHz): 166.8, 166.5, 66.7, 61.8, 61.7, 41.6, 27.7, 21.3, 14.2.

Compound 4b. Prepared from **3b** (1.00 g, 5.26 mmol), pyridine (0.43 mL, 5.26 mmol) and TBDS ditriflate (0.78 mL, 2.39 mmol) in anhydrous DMF (20 mL) after stirring at room temperature for 2 h. Column chromatography (SiO₂; eluent: CH₂Cl₂) gave **4b** (650 mg, 52%). Colorless oil. ¹H-NMR (CDCl₃, 300 MHz): 4.29 (t, *J* = 7, 4H), 4.18 (q, *J* = 7, 4H), 3.89 (t, *J* = 6, 4H), 3.35 (s, 4H), 1.89 (quint, *J* = 6, 4H), 1.26 (t, *J* = 7, 6H), 0.98 (s, 18H). ¹³C-NMR (CDCl₃, 100 MHz): 166.7, 166.6, 62.6, 61.6, 60.2, 41.7, 31.8, 27.9, 21.2, 14.2.

General Procedure for the Preparation of C₆₀ Bis-adducts **5a** and **5b**

DBU was added to a solution of C₆₀, the bis-malonate (**4a** or **4b**) and I₂ in toluene under argon at –15 °C. The resulting mixture was stirred for 1 h at –15 °C, then directly filtered (SiO₂; eluent: cyclohexane to CH₂Cl₂), concentrated, and purified as indicated.

Compound 5a. Prepared from **4a** (106 mg, 0.22 mmol), C₆₀ (155 mg, 0.22 mmol), I₂ (137 mg, 0.54 mmol) and DBU (0.27 mL, 1.81 mmol) in toluene (310 mL). Column chromatography (SiO₂; eluent: CH₂Cl₂/cyclohexane 3:2) gave **5a** (59 mg, 23%). Dark brown glassy solid. IR (neat): 1744 (C=O). UV/vis (CH₂Cl₂): 251 (89000), 307 (sh, 35400), 366 (sh, 10670), 397 (3900), 408 (sh, 2630), 421 (2400), 479 (2700). ¹H-NMR (300 MHz, CDCl₃): 4.71–4.82 (ddd, *J* = 10, 9, 5, 1H), 4.41–4.56 (m, 5H), 4.29–4.38 (m, 1H), 4.00–4.28 (m, 4H), 3.84–3.94 (m, 1H), 1.44 (t, *J* = 7, 6H), 1.09 (s, 9H) 0.94 (s, 9H). ¹³C-NMR (75 MHz, CDCl₃): 164.0, 163.6, 163.5, 163.1, 148.7, 147.5, 147.4, 146.63, 146.57, 146.51, 146.45, 146.3, 146.22, 146.20, 145.9, 145.61, 145.57, 145.53, 145.46, 145.41, 145.3, 145.12, 145.06, 144.98, 144.92, 144.85, 144.76, 144.73, 144.67, 144.58, 144.40, 144.38, 144.20, 144.11, 144.07, 143.93, 143.89, 143.83, 143.74, 143.58, 143.56, 143.48, 143.2, 143.1, 142.2, 142.1, 142.0, 141.9, 141.6, 141.5, 140.6, 140.4, 140.0, 139.8, 139.0, 138.6, 71.7, 70.3, 68.1, 66.7, 63.56, 63.49, 62.4, 60.8, 53.8, 51.2, 28.1, 27.7, 21.7, 21.4, 14.34, 14.31. MALDI-TOF-MS: 1210.2 ([*M* + *H*]⁺, calc. for [C₈₂H₃₆O₁₀Si + *H*]⁺: 1210.3).

Compound 5b. Prepared from **4b** (291 mg, 0.56 mmol), C₆₀ (400 mg, 0.56 mmol), I₂ (352 mg, 1.39 mmol) and DBU (0.42 mL, 2.81 mmol) in toluene (800 mL). Column chromatography (SiO₂; eluent: CH₂Cl₂/cyclohexane 3:2) gave **5b** (332 mg, 48%). Dark brown glassy solid. IR (neat): 1751 (C=O). UV/vis (CH₂Cl₂): 310 (sh, 38670), 361 (sh, 13450), 398 (3850), 409 (sh, 2410), 421 (2260), 479 (sh, 2740). ¹H-NMR (300 MHz, CD₂Cl₂): 4.65–4.80 (m, 2H), 4.31–4.55 (m, 6H), 3.79–3.93 (m, 4H), 1.91–2.06 (m, 4H), 1.41 (t, *J* = 7, 6H), 1.03 (s, 9H), 0.91 (s, 9H). ¹³C-NMR (100 MHz, CDCl₃): 164.1, 163.6, 163.4, 163.3, 148.8, 147.3, 147.0, 146.6, 146.5, 146.4, 146.20, 146.18, 146.1, 145.8, 145.6, 145.4, 145.33, 145.30, 145.26, 145.15, 145.09, 144.97, 144.89, 144.82, 144.72, 144.69, 144.65, 144.63, 144.51, 144.36, 144.16, 144.14, 143.9, 143.8, 143.7, 143.6, 143.52, 143.50, 143.47, 143.2, 143.1, 142.55, 142.52, 142.0, 141.9, 141.80, 141.76, 141.71, 141.5, 141.2, 140.5, 139.73, 139.68, 138.8, 138.7, 71.7, 71.7, 70.5, 64.3, 63.5, 63.4, 63.4, 60.4, 59.8, 54.0, 51.6, 32.2, 31.8, 27.8, 27.8, 27.0, 21.3, 14.3. MALDI-TOF-MS: 1237.3 ([*M* + *H*]⁺, calc. for [C₈₄H₄₀O₁₀Si + *H*]⁺: 1237.3).

General Procedure for the Preparation of Tris-malonates **6a–6g**

A mixture of ^tBuSiCl₃, the alcohol (**3a–3g**) and imidazole in anhydrous DMF was stirred at room

temperature overnight. Water was added and the aqueous layer was extracted with Et₂O. The organic layer was washed several times with water, dried with MgSO₄, concentrated, and purified as indicated.

Compound 6a. Prepared from **3a** (2.00 g, 11.4 mmol), imidazole (0.77 g, 11.3 mmol) and ^tBuSiCl₃ (0.62 g, 3.24 mmol) in anhydrous DMF (10 mL). Column chromatography (SiO₂; eluent: CH₂Cl₂/AcOEt 95:5) gave **6a** (1.52 g, 77%). Colorless oil. ¹H-NMR (300 MHz, CDCl₃): 4.27–4.22 (m, 6H), 4.19 (q, *J* = 7, 6H), 4.00–3.96 (m, 6H), 3.39 (s, 6H), 1.27 (t, *J* = 7, 9H), 0.95 (s, 9H). ¹³C-NMR (75 MHz, CDCl₃): 166.7, 166.5, 66.3, 61.7, 61.3, 41.5, 26.1, 17.8, 14.2.

Compound 6b. Prepared from **3b** (1.06 g, 5.57 mmol), imidazole (0.43 g, 6.32 mmol) and ^tBuSiCl₃ (0.34 g, 1.78 mmol) in anhydrous DMF (11 mL). Column chromatography (SiO₂; eluent: CH₂Cl₂ to CH₂Cl₂/AcOEt 97:3) gave **6b** (0.76 g, 66%). Colorless oil. ¹H-NMR (CDCl₃, 300 MHz): 4.27 (t, *J* = 7, 6H), 4.20 (q, *J* = 7, 6H), 3.85 (t, *J* = 6, 6H), 3.37 (s, 6H), 1.90 (quint, *J* = 6, 6H), 1.28 (t, *J* = 7, 9H), 0.94 (s, 9H). ¹³C-NMR (CDCl₃, 75 MHz): 166.8, 166.7, 62.5, 61.7, 59.7, 41.7, 31.6, 26.4, 17.8, 14.2.

Compound 6c. Prepared from **3c** (1.00 g, 4.90 mmol), imidazole (0.36 g, 5.29 mmol) and ^tBuSiCl₃ (0.29 g, 1.51 mmol) in anhydrous DMF (10 mL). Column chromatography (SiO₂; eluent: CH₂Cl₂ to CH₂Cl₂/AcOEt 97:3) gave **6c** (0.66 g, 67%). Colorless oil. ¹H-NMR (CDCl₃, 300 MHz): 4.24–4.16 (m, 12H), 3.79 (t, *J* = 6, 6H), 3.37 (s, 6H), 1.7–1.69 (m, 6H), 1.66–1.58 (m, 6H), 1.28 (t, *J* = 7, 9H), 0.94 (s, 9H). ¹³C-NMR (CDCl₃, 75 MHz): 166.8, 166.7, 65.5, 62.7, 61.7, 41.8, 29.0, 26.5, 25.2, 17.9, 14.2.

Compound 6d. Prepared from **3d** (1.5 g, 5.95 mmol), imidazole (0.44 g, 6.46 mmol) and ^tBuSiCl₃ (0.36 g, 1.88 mmol) in anhydrous DMF (12 mL). Column chromatography (SiO₂; eluent: CH₂Cl₂/cyclohexane 8:2 to CH₂Cl₂) gave **6d** (0.97 g, 57%). Colorless oil. ¹H-NMR (CDCl₃, 300 MHz): 7.30 (s, 12H), 5.18 (s, 6H), 4.86 (s, 6H), 4.19 (q, *J* = 7, 6H), 3.42 (s, 6H), 1.25 (t, *J* = 7, 9H), 1.05 (s, 9H). ¹³C-NMR (CDCl₃, 75 MHz): 166.61, 166.57, 140.9, 134.3, 128.5, 126.5, 67.2, 64.9, 61.7, 41.8, 26.5, 18.1, 14.2.

Compound 6e. Prepared from ^tBuSiCl₃ (0.15 g, 0.78 mmol), **3e** (0.82 g, 2.50 mmol) and imidazole (0.19 g, 2.79 mmol) in anhydrous DMF (10 mL). Column chromatography (SiO₂; eluent: CH₂Cl₂/cyclohexane 8:2 to CH₂Cl₂) gave **6e** (0.48 g, 54%). Colorless oil. ¹H-NMR

(CDCl₃, 400 MHz): 7.57 (d, *J* = 7, 6H), 7.53 (d, *J* = 7, 6H), 7.42 (d, *J* = 7, 6H), 7.38 (d, *J* = 7, 6H), 5.23 (s, 6H), 4.95 (s, 6H), 4.20 (q, *J* = 7, 6H), 3.44 (s, 6H), 1.26 (t, *J* = 7, 9H), 1.12 (s, 9H). ¹³C-NMR (CDCl₃, 100 MHz): 166.64, 166.57, 141.3, 140.1, 139.6, 134.4, 129.0, 127.4, 127.2, 126.9, 67.1, 65.0, 61.8, 41.8, 26.6, 18.2, 14.2.

Compound 6f. Prepared from **3f** (1.00 g, 3.96 mmol), imidazole (0.30 g, 4.41 mmol) and ^tBuSiCl₃ (0.24 g, 1.25 mmol) in anhydrous DMF (15 mL). Column chromatography (SiO₂; eluent: CH₂Cl₂/cyclohexane 8:2 to CH₂Cl₂) gave **6f** (1.04 g, 92%). Colorless oil. ¹H-NMR (CDCl₃, 300 MHz): 7.43–7.19 (m, 12H), 5.15 (s, 6H), 4.87 (s, 6H), 4.15 (q, *J* = 7, 6H), 3.35 (s, 6H), 1.22 (t, *J* = 7, 9H), 1.02 (s, 9H). ¹³C-NMR (CDCl₃, 75 MHz): 166.5, 166.4, 138.7, 132.9, 129.2, 128.7, 127.8, 127.5, 64.6, 63.0, 61.7, 41.6, 26.5, 18.0, 14.1.

Compound 6g. Prepared from **3g** (1.00 g, 3.96 mmol), imidazole (0.21 g, 3.09 mmol) and ^tBuSiCl₃ (0.17 g, 0.89 mmol) in anhydrous DMF (15 mL). Column chromatography (SiO₂; eluent: CH₂Cl₂/cyclohexane 8:2 to CH₂Cl₂) gave **6g** (0.47 g, 59%). Colorless oil. ¹H-NMR (CDCl₃, 300 MHz): 7.35–7.18 (m, 12H), 5.12 (s, 6H), 4.85 (s, 6H), 4.15 (q, *J* = 7, 6H), 3.37 (s, 6H), 1.21 (t, *J* = 7, 9H), 1.05 (s, 9H). ¹³C-NMR (CDCl₃, 75 MHz): 166.5, 166.5, 141.0, 135.4, 128.7, 127.2, 126.3, 126.2, 67.2, 64.9, 61.6, 41.6, 26.5, 18.0, 14.1.

General Procedure for the Preparation of Fullerene Derivatives **7a–7f**, **8a**, **8b** and **9d**

DBU was added to a solution of C₆₀, the tris-malonate (**6a–6f**) and I₂ in toluene under argon at –15 °C. The resulting mixture was stirred for 1 h at –15 °C, then directly filtered (SiO₂; eluent: cyclohexane to CH₂Cl₂), concentrated, and purified as indicated.

Compounds 7a and 8a. Prepared from **6a** (468 mg, 0.77 mmol), C₆₀ (828 mg, 1.15 mmol), I₂ (681 mg, 2.68 mmol) and DBU (0.87 mL, 5.82 mmol) in toluene (1.65 L). Column chromatography (SiO₂; eluent: CH₂Cl₂) gave **7a** (83 mg, 8%) and **8a** (320 mg, 20%). *Data of 7a:* Cherry-red glassy solid. IR (neat): 1745, 1727 (C=O). UV/Vis (CH₂Cl₂): 251 (103180), 282 (74700), 303 (sh, 61730), 381 (6200), 484 (5420), 565 (sh, 1100). ¹H-NMR (300 MHz, CDCl₃): 5.02–4.94 (m, 3H), 4.41 (q, *J* = 7, 6H), 3.76–4.04 (m, 9H), 1.39 (t, *J* = 7, 9H), 0.97 (s, 9H). ¹³C-NMR (75 MHz, CDCl₃): 163.6, 163.4, 147.5, 147.2, 147.0, 146.7, 146.6, 146.44, 146.36, 146.2, 145.9, 144.4, 144.3, 143.9, 143.7, 143.30, 143.28, 141.8, 141.6, 140.8, 71.1, 70.3, 67.2, 63.4, 62.9, 52.7, 27.2, 19.8, 14.3. MALDI-TOF-

MS: 1324.2 (*M*⁺, calc. for [C₈₅H₃₆O₁₅Si]⁺): 1324.2. *Data of 8a:* Brown glassy solid. IR (neat): 1743, 1728 (C=O). ¹H-NMR (300 MHz, CDCl₃): 4.89–4.81 (m, 1H), 4.43–4.70 (m, 9H), 3.97–4.34 (m, 8H), 1.51–1.41 (m, 9H), 0.88 (s, 9H). ¹³C-NMR (75 MHz, CDCl₃): 164.1, 163.7, 163.6, 163.5, 163.4, 163.0, 148.4, 147.40, 147.39, 146.61, 146.60, 146.58, 146.54, 146.46, 146.29, 146.21, 146.19, 145.8, 145.63, 145.58, 145.44, 145.39, 145.35, 145.32, 145.28, 145.24, 145.20, 145.16, 145.15, 145.14, 145.13, 145.08, 145.01, 144.98, 144.85, 144.82, 144.79, 144.75, 144.74, 144.72, 144.67, 144.63, 144.53, 144.4, 144.2, 144.1, 144.0, 143.9, 143.8, 143.7, 143.58, 143.53, 143.48, 143.23, 143.16, 143.10, 143.0, 142.35, 142.31, 142.29, 142.23, 142.1, 142.02, 141.97, 141.92, 141.85, 141.6, 141.5, 141.12, 141.08, 141.05, 140.8, 140.7, 140.0, 139.9, 139.2, 139.1, 139.0, 138.5, 71.79, 71.72, 71.69, 71.64, 70.4, 68.0, 67.5, 63.61, 63.58, 61.8, 61.2, 60.8, 53.7, 52.2, 51.3, 26.8, 26.3, 17.8, 14.5, 14.4. MALDI-TOF-MS: 2045.1 (*[M + H]*⁺, calc. for [C₁₄₅H₃₆O₁₅Si + H]⁺): 2045.2).

Compounds 7b and 8b. Prepared from **6b** (153 mg, 0.23 mmol), C₆₀ (250 mg, 0.35 mmol), I₂ (213 mg, 0.84 mmol) and DBU (0.26 mL, 1.74 mmol) in toluene (500 mL). Column chromatography (SiO₂; eluent: CH₂Cl₂/cyclohexane 1:1) followed by GPC (*Bio-Beads SX-1*, eluent: CH₂Cl₂) gave **7b** (86 mg, 27%) and **8b** (53 mg, 11%). *Data of 7b:* Cherry-red glassy solid. IR (neat): 1740 (C=O). UV/Vis (CH₂Cl₂): 251 (102000), 281 (67020), 302 (sh, 54100), 380 (6110), 483 (4500), 564 (sh, 1310). ¹H-NMR (CDCl₃, 300 MHz): 4.58–4.50 (m, 3H), 4.49–4.38 (m, 6H), 4.26–4.18 (m, 3H), 3.59 (t, *J* = 7, 6H), 1.98–1.89 (m, 6H), 1.38 (t, *J* = 7, 9H), 0.89 (s, 9H). ¹³C-NMR (CDCl₃, 100 MHz): 163.7, 163.4, 147.3, 147.1, 147.0, 146.8, 146.54, 146.50, 146.44, 146.37, 145.98, 144.4, 143.7, 143.4, 143.3, 143.2, 142.9, 141.9, 141.1, 71.0, 70.3, 64.0, 63.5, 59.9, 53.1, 31.8, 26.2, 17.6, 14.3. MALDI-TOF-MS: 1366.2 (*M*⁺, calc. for [C₈₈H₄₂O₁₅Si]⁺): 1366.2). *Data of 8b:* Brown glassy solid. IR (neat): 1740 (C=O). UV/Vis (CH₂Cl₂): 392 (sh, 11100), 408 (sh, 6900), 426 (5600), 481 (5300), 612 (sh, 1200), 689 (300). ¹H-NMR (CDCl₃, 300 MHz): 4.86–4.78 (m, 1H), 4.75–4.67 (m, 1H), 4.63 (t, *J* = 7, 2H), 4.60–4.35 (m, 8H), 4.05 (t, *J* = 6, 2H), 3.89–3.70 (m, 4H), 2.14 (quint, *J* = 6, 2H), 2.07–1.90 (m, 4H), 1.49 (t, *J* = 7, 3H), 1.44 (t, *J* = 7, 3H), 1.43 (t, *J* = 7, 3H), 0.91 (s, 9H). ¹³C-NMR (CDCl₃, 75 MHz): 163.8, 163.7, 163.5, 163.3 (2 C), 148.8, 147.5, 147.4, 147.0, 146.68, 146.64, 146.52, 146.49, 146.3, 146.2, 145.9, 145.7, 145.46, 145.40, 145.32, 145.30, 145.25, 145.17, 145.02, 145.00, 144.93, 144.83, 144.80, 144.77, 144.75, 144.73, 144.69, 144.61, 144.4, 144.3, 144.2, 144.02, 143.97, 143.85, 143.81, 143.76, 143.69, 143.61, 143.56, 143.50, 143.22, 143.20, 143.17, 143.12, 142.57,

142.54, 142.3, 142.2, 142.1, 142.0, 141.9, 141.68, 141.64, 141.4, 141.1, 140.7, 139.87, 139.85, 139.2, 139.0, 138.7, 71.91, 71.83, 71.77, 71.73, 70.64, 64.5, 63.7, 63.58, 63.56, 63.54, 63.3, 60.1, 59.8, 58.7, 54.0, 53.6, 52.4, 51.7, 32.2, 31.9, 31.6, 26.5, 17.7, 14.45, 14.43, 14.37. MALDI-TOF-MS: 2087.2 ($[M+H]^+$, calc. for $[C_{148}H_{42}O_{15}Si+H]^+$: 2087.2).

Compound 7c. Prepared from **6c** (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 (SiO_2 ; eluent: CH_2Cl_2 /cyclohexane 1:1) followed by GPC (*Bio-Beads SX-1*, eluent: CH_2Cl_2) gave **7c** (44 mg, 14%). Cherry-red glassy solid. IR (neat): 1747 (C=O). UV/Vis (CH_2Cl_2): 251 (75000), 282 (50900), 302 (sh, 40520), 380 (4600), 482 (3700), 564 (sh, 960). 1H -NMR ($CDCl_3$, 400 MHz): 4.52 (dt, $J=11, 7, 3H$), 4.35–4.47 (m, 6H), 4.09 (dt, $J=11, 7, 3H$), 3.63 (dtd, $J=11, 10, 5, 6H$), 1.72 (quint, $J=7, 6H$), 1.54–1.46 (m, 6H), 1.38 (t, $J=7, 9H$), 0.92 (s, 9H). ^{13}C -NMR ($CDCl_3$, 100 MHz): 163.5, 163.3, 147.03, 146.95, 146.83, 146.76, 146.6, 146.44, 146.41, 145.9, 144.33, 144.26, 143.8, 143.4, 143.0, 142.7, 142.4, 142.2, 141.1, 71.1, 70.2, 66.5, 63.4, 62.3, 53.1, 30.3, 28.3, 27.1, 26.5, 25.3, 18.0, 14.3. MALDI-TOF-MS: 1408.2 (M^+ , calc. for $[C_{91}H_{48}O_{15}Si]^+$: 1408.3).

Compounds 7d and 9d. Prepared from **6d** (1.59 g, 1.77 mmol), C_{60} (1.50 g, 2.08 mmol), I_2 (1.68 g, 6.62 mmol) and DBU (2.22 mL, 14.8 mmol) in toluene (3 L). Column chromatography (SiO_2 ; eluent: CH_2Cl_2 /cyclohexane 1:1) followed by slow vapor diffusion in THF/cyclohexane gave **7d** (302 mg, 11%) and **9d** (30 mg, 1%). *Data of 7d:* Cherry-red glassy solid. IR (neat): 1746 (C=O). UV/Vis (CH_2Cl_2): 249 (229700), 283 (153200), 305 (sh, 120600), 383 (2700), 479 (1500), 563 (sh, 500). 1H -NMR (300 MHz, $CDCl_3$): 7.09 (d, $J=8.0, 6H$), 6.88 (d, $J=8.0, 6H$), 5.51 (d, $J=13, 3H$), 5.13 (d, $J=13, 3H$), 4.49 (d, $J=12, 3H$), 4.42 (q, $J=7, 6H$), 4.22 (d, $J=12, 3H$), 1.37 (t, $J=7, 9H$), 1.05 (s, 9H). ^{13}C -NMR (75 MHz, $CDCl_3$): 163.8, 163.4, 147.04, 146.99, 146.85, 146.7, 146.6, 146.35, 146.50, 145.9, 144.6, 144.5, 144.2, 143.5, 143.1, 142.5, 142.4, 142.3, 141.1, 140.8, 134.0, 128.3, 126.6, 70.9, 70.2, 68.3, 65.4, 63.5, 53.1, 27.1, 26.4, 18.2, 14.3. MALDI-TOF-MS: 1552.3 (M^+ , calc. for $[C_{103}H_{48}O_{15}Si]^+$: 1552.3). *Data of 9d:* Purple-red glassy solid. IR (neat): 1745 (C=O). UV/Vis (CH_2Cl_2): 246 (42200), 302 (19300), 407 (sh, 1600), 493 (1500), 574 (sh, 760). 1H -NMR (400 MHz, $CDCl_3$): 7.39 (d, $J=8, 6H$), 7.17 (d, $J=8, 6H$), 5.96 (d, $J=11, 3H$), 5.01 (q, $J=7, 6H$), 4.98 (d, $J=11, 3H$), 4.52–4.41 (m, 6H), 1.44 (t, $J=7, 9H$), 1.11 (s, 9H). ^{13}C -NMR (100 MHz, $CDCl_3$): 163.7,

148.5, 147.7, 147.2, 146.3, 146.1, 145.8, 145.6, 145.5, 145.2, 145.2, 143.8, 143.1, 143.0, 142.9, 142.1, 141.9, 141.7, 141.4, 138.9, 133.6, 131.3, 124.9, 71.4, 71.0, 68.9, 64.8, 63.5, 50.5, 26.5, 19.4, 14.4. MALDI-TOF-MS: 1552.3 (M^+ , calc. for $[C_{103}H_{48}O_{15}Si]^+$: 1552.3).

Compound 7e. Prepared from **6e** (480 mg, 0.43 mmol), C_{60} (357 mg, 0.50 mmol), I_2 (399 mg, 1.57 mmol) and DBU (0.51 mL, 3.40 mmol) in toluene (720 mL). Column chromatography (SiO_2 ; eluent: CH_2Cl_2 /cyclohexane 1:1) followed by GPC (*Bio-Beads SX-1*, eluent: CH_2Cl_2) gave **7e** (25 mg, 3%). Cherry-red glassy solid. IR (neat): 1739 (C=O). UV/Vis (CH_2Cl_2): 252 (74070), 281 (42360), 304 (sh, 24700), 483 (2120), 565 (sh, 660). 1H -NMR (400 MHz, $CDCl_3$): 7.47 (d, $J=8, 6H$), 7.35 (d, $J=8, 6H$), 7.31 (d, $J=8, 6H$), 6.93 (d, $J=8, 6H$), 5.60 (d, $J=13, 3H$), 5.12 (d, $J=13, 3H$), 4.71 (d, $J=12, 3H$), 4.58 (d, $J=12, 3H$), 4.52–4.40 (m, 6H), 1.41 (t, $J=7, 9H$), 1.15 (s, 9H). ^{13}C -NMR (100 MHz, $CDCl_3$): 164.2, 163.6, 148.1, 147.0, 146.8, 146.7, 146.6, 146.4, 146.0, 145.7, 145.2, 144.4, 143.6, 143.4, 141.8, 141.4, 141.2, 141.1, 140.9, 140.0, 139.7, 133.9, 128.6, 128.0, 127.8, 127.1, 71.0, 70.0, 69.0, 65.7, 63.3, 52.8, 27.1, 26.5, 18.7, 14.4. MALDI-TOF-MS: 1780.5 (M^+ , calc. for $[C_{121}H_{60}O_{15}Si]^+$: 1780.4).

Compound 7f. Prepared from **6f** (388 mg, 0.43 mmol), C_{60} (500 mg, 0.69 mmol), I_2 (408 mg, 1.61 mmol) and DBU (0.54 mL, 3.60 mmol) in toluene (1 L). Column chromatography (SiO_2 ; eluent: CH_2Cl_2 /cyclohexane 1:1) followed by slow vapor diffusion in THF/cyclohexane gave **7f** (165 mg, 25%). Cherry-red glassy solid. UV/Vis (CH_2Cl_2): 373 (14600), 468 (6920), 555 (sh, 2120). 1H -NMR (300 MHz, $CDCl_3$): 7.28–7.45 (m, 12H), 5.50 (d, $J=12, 3H$), 5.34 (d, $J=12, 3H$), 4.86 (d, $J=13, 3H$), 4.67 (d, $J=13, 3H$), 4.51–4.40 (m, 6H), 1.40 (t, $J=7, 9H$), 0.94 (s, 9H). ^{13}C -NMR (75 MHz, $CDCl_3$): 164.4, 163.2, 147.3, 146.8, 146.6, 146.4, 146.3, 145.8, 145.7, 144.4, 144.2, 144.1, 143.3, 142.6, 142.4, 141.9, 141.1, 140.8, 139.4, 132.0, 130.8, 130.1, 127.93, 127.87, 70.3, 69.8, 66.4, 63.2, 62.5, 52.4, 26.2, 17.6, 14.3. MALDI-TOF-MS: 1552.3 (M^+ , calc. for $[C_{103}H_{48}O_{15}Si]^+$: 1552.3).

General Procedure for the BF_3 -Mediated Cleavage of the Silyl-Protecting Group

$BF_3 \cdot Et_2O$ was added to a solution of the appropriate fullerene derivative in CH_2Cl_2 and CH_3CN under argon at room temperature and the resulting mixture was stirred overnight. A saturated aqueous $NaHCO_3$ solution was added, and the aqueous layer was extracted with CH_2Cl_2 . The organic layer was washed with water,

dried with MgSO₄, concentrated, and purified as indicated.

Compound 10a. Prepared from **5a** (45.0 mg, 0.037 mmol) and BF₃·Et₂O (0.09 mL, 0.74 mmol) in CH₂Cl₂ (4 mL) and CH₃CN (2 mL). Column chromatography (SiO₂, eluent: CH₂Cl₂ to CH₂Cl₂/MeOH 97:3) gave **10a** (36.1 mg, 91%). Brown-red glassy solid. IR (neat): 3400 (br, OH), 1739 and 1729 (C=O). UV/vis (CH₂Cl₂): 253 (20110), 308 (sh, 7650), 397 (1380), 410 (sh, 830), 421 (800), 480 (990). ¹H-NMR (400 MHz, CDCl₃): 4.60–4.44 (m, 8H), 4.00–3.91 (m, 4H), 2.26 (s, 1H), 2.09 (s, 1H), 1.45 (t, *J* = 7, 3H), 1.44 (t, *J* = 7, 3H). ¹³C-NMR (75 MHz, CDCl₃): 163.9, 163.8, 163.7 (2 C), 147.9, 147.47, 147.45, 147.36, 146.66, 146.64, 146.33, 146.25, 146.22, 145.8, 145.7, 145.54, 145.51, 145.30, 145.27, 145.21, 144.95, 144.94, 144.89, 144.87, 144.80, 144.57, 144.54, 144.45, 144.44, 144.31, 144.25, 144.23, 143.92, 143.88, 143.81, 143.7, 143.6, 143.4, 143.12, 143.02, 142.95, 142.89, 142.79, 142.2, 142.12, 142.08, 141.74, 141.65, 141.4, 139.3, 138.9, 138.8, 71.60, 71.56, 70.4, 68.7, 68.5, 63.71, 63.68, 60.9, 53.6, 53.5, 51.3, 14.3. MALDI-TOF-MS: 1068.5 (*M*⁺, calc. for [C₇₄H₂₀O₁₀]⁺: 1068.1).

Compound 10b. Prepared from **5b** (96.1 mg, 0.078 mmol) and BF₃·Et₂O (0.19 mL, 1.55 mmol) in CH₂Cl₂ (4 mL) and CH₃CN (2 mL). Column chromatography (SiO₂, eluent: CH₂Cl₂ to CH₂Cl₂/MeOH 96:4) gave **10b** (61.2 mg, 72%). Brown-red glassy solid. IR (neat): 3420 (br, OH), 1740 (C=O). UV/vis (CH₂Cl₂): 306 (sh, 21900), 358 (sh, 7930), 397 (2350), 409 (sh, 1550), 421 (1450), 477 (sh, 1620). ¹H-NMR (400 MHz, CDCl₃): 4.58–4.45 (m, 8H), 3.80–3.74 (m, 4H), 2.06–1.98 (m, 4H), 1.96 (broad s, 3H), 1.44 (t, *J* = 7, 3H), 1.43 (t, *J* = 7, 3H). ¹³C-NMR (100 MHz, CDCl₃): 164.0, 163.8, 163.7, 163.6, 147.8, 147.6, 147.4, 146.6, 146.29, 126.26, 146.21, 145.8, 145.7, 145.5, 145.27, 145.25, 145.18, 144.90, 144.88, 144.86, 144.84, 144.76, 144.54, 144.51, 144.47, 144.43, 144.32, 144.28, 144.20, 143.92, 143.89, 143.86, 143.84, 143.60, 143.57, 143.29, 143.13, 143.10, 143.07, 142.7, 142.3, 142.06, 142.04, 141.9, 141.69, 141.67, 141.58, 139.1, 138.84, 138.82, 71.3, 64.34, 64.28, 63.6, 63.5, 59.2, 53.5, 51.3, 31.63, 31.57, 14.3. MALDI-TOF-MS: 1096.1 (*M*⁺, calc. for [C₇₆H₂₄O₁₀]⁺: 1096.1).

Compound 11b. Prepared from **7b** (252 mg, 0.18 mmol) and BF₃·Et₂O (0.32 mL, 2.59 mmol) in CH₂Cl₂ (4 mL) and CH₃CN (2 mL). Column chromatography (SiO₂; eluent: CH₂Cl₂/MeOH 96:4) gave **11b** (229 mg, 97%). Cherry-red glassy solid. IR (neat): 3390 (br, OH), 1737 (C=O). UV/Vis (CH₂Cl₂): 251 (115000), 282 (80000), 304 (sh, 60600), 353 (sh, 16400), 379 (sh,

7000), 485 (5100), 564 (sh, 1500). ¹H-NMR (300 MHz, CDCl₃): 4.56–4.28 (m, 12H), 3.67 (t, *J* = 6, 6H), 2.20 (s, 3H), 1.94 (quint, *J* = 6, 6H), 1.37 (t, *J* = 7, 9H). ¹³C-NMR (75 MHz, CDCl₃): 163.7, 163.5, 147.2, 147.0, 146.9, 146.8, 146.61, 146.57, 146.4, 146.0, 145.8, 144.9, 144.7, 144.4, 143.5, 142.8, 142.7, 142.1, 141.9, 141.1, 71.0, 70.2, 64.1, 63.4, 59.1, 53.0, 31.5, 14.3. MALDI-TOF-MS: 1284.1 (*M*⁺, calc. for [C₈₄H₃₆O₁₅]⁺: 1284.2).

Compound 11c. Prepared from **7c** (70 mg, 0.050 mmol) and BF₃·Et₂O (0.1 mL, 0.81 mmol) in CH₂Cl₂ (2 mL) and CH₃CN (1 mL). Column chromatography (SiO₂; eluent: CH₂Cl₂/MeOH 96:4) gave **11c** (44 mg, 67%). Cherry-red glassy solid. IR (neat): 3380 (br, OH), 1742 (C=O). UV/Vis (CH₂Cl₂): 251 (121000), 283 (84400), 305 (sh, 62800), 353 (sh, 17400), 380 (6600), 484 (5500), 565 (sh, 1600). ¹H-NMR (300 MHz, CDCl₃): 4.46–4.24 (m, 12H), 3.57 (t, *J* = 7, 6H), 2.01 (s, 3H), 1.82–1.73 (m, 6H), 1.66–1.56 (m, 6H), 1.37 (t, *J* = 7, 9H). ¹³C-NMR (75 MHz, CDCl₃): 163.7, 163.5, 147.3, 147.0, 146.9, 146.7, 146.64, 146.59, 146.4, 145.9, 145.8, 145.0, 144.8, 144.5, 143.6, 142.9, 142.6, 141.9, 141.1, 71.0, 70.3, 67.1, 63.4, 62.2, 53.1, 29.2, 25.1, 14.3.

Compound 11d. Prepared from **7d** (54 mg, 0.035 mmol) and BF₃·Et₂O (0.1 mL, 0.8 mmol) in CH₂Cl₂ (2 mL) and CH₃CN (1 mL). Column chromatography (SiO₂; eluent: CH₂Cl₂/MeOH 96:4) gave **11d** (42 mg, 82%). Cherry-red glassy solid. IR (neat): 3380 (br, OH), 1740 (C=O). UV/Vis (CH₂Cl₂): 251 (120800), 282 (82600), 305 (sh, 63100), 380 (6200), 484 (5300), 567 (sh, 1400). ¹H-NMR (300 MHz, CDCl₃): 7.33 (s, 12H), 5.30 (s, 6H), 4.63 (s, 6H), 4.37 (q, *J* = 7, 6H), 2.22 (s, 3H), 1.30 (t, *J* = 7, 9H). ¹³C-NMR (75 MHz, CDCl₃): 163.4, 147.2, 146.9, 146.8, 146.7, 146.58, 146.56, 146.4, 145.7, 145.6, 144.8, 144.7, 144.4, 143.5, 142.8, 142.6, 141.99, 141.96, 141.7, 141.0, 133.8, 129.2, 127.1, 70.7, 70.1, 68.7, 64.9, 63.4, 52.8, 14.2.

General Procedure for the HF-Pyridine-Mediated Cleavage of the Silyl-Protecting Group

A HF (approx. 70% in pyridine) solution was added to a solution of the appropriate fullerene derivative in THF in a Teflon flask under argon at room temperature. After 1 h, silica gel was added, the mixture concentrated, and the crude purified as indicated.

Compound 11a. Prepared from **7a** (158 mg, 0.12 mmol), hydrogen fluoride pyridine (0.15 mL, approx. 5.77 mmol, hydrogen fluoride ca. 70%, pyridine ca. 30%) solution in anhydrous THF (10 mL). Column

chromatography (SiO₂; eluent: THF) followed by GPC (*Bio-Beads SX-1*, eluent: CH₂Cl₂) and slow vapor diffusion of hexane in THF gave **11a** (131 mg, 88%). Red glassy solid. IR (neat): 3420 (br, OH), 1740 and 1736 (C=O). UV/Vis (CH₂Cl₂): 251 (sh, 183000), 282 (163000), 305 (sh, 51000), 380 (41000), 480 (5000), 565 (2000). ¹H-NMR (300 MHz, CDCl₃): 4.54–4.30 (m, 12H), 3.85 (t, *J* = 5, 6H), 2.42 (broad, 3H), 1.39 (t, *J* = 7 Hz, 9H). ¹³C-NMR (75 MHz, CDCl₃): 163.6, 163.5, 147.0 (2 C), 146.9, 146.8, 146.62, 146.59, 146.5, 146.2, 145.9, 144.52, 144.48, 144.42, 143.5, 143.1, 142.6, 142.4, 142.1, 141.1, 70.9, 70.1, 68.3, 63.5, 60.7, 52.9, 14.3. MALDI-TOF-MS: 1242.0 (100%, *M*⁺, calc. for [C₈₁H₃₀O₁₅]⁺: 1242.2).

Compounds 10a and 12a. Prepared from **8a** (186 mg, 0.091 mmol), hydrogen fluoride pyridine (0.15 mL, approx. 5.77 mmol, hydrogen fluoride *ca.* 70%, pyridine *ca.* 30%) solution in anhydrous THF (5 mL). Column chromatography (SiO₂; eluent: THF/cyclohexane 3:7 to THF) gave **10a** (64 mg, 66%) and **12a** (45 mg, 55%). *Data of 10a:* see above. *Data of 12a:* Brown glassy solid. IR (neat): 3390 (br, OH), 1733 (C=O). ¹H-NMR (300 MHz, CDCl₃): 4.67–4.63 (m, 2H), 4.58 (q, *J* = 7, 2H), 4.04 (q, *J* = 6, 2H), 2.03 (t, *J* = 6, 1H), 1.51 (t, *J* = 7, 3H). ¹³C-NMR (75 MHz, CDCl₃): 164.0, 163.9, 145.45 (2 C), 145.37, 145.36, 145.30, 145.22, 145.12, 145.07, 144.86, 144.85, 144.83, 144.81, 144.1, 144.0, 143.3, 143.2 (2 C), 143.1, 142.4 (2 C), 142.1, 142.0, 141.2, 141.1, 140.1, 139.5, 138.9, 71.5, 68.8, 63.8, 61.0, 53.6, 14.4. MALDI-TOF-MS: 893.9 (*M*⁺, calc. for [C₆₇H₁₀O₅]⁺: 894.1).

Compounds 10b and 12b. Prepared from **8b** (274 mg, 0.13 mmol), BF₃·Et₂O (0.32 mL, 2.59 mmol) in CH₂Cl₂ (4 mL) and CH₃CN (2 mL). Column chromatography (SiO₂; eluent: CH₂Cl₂/MeOH 96:4) gave **10b** (86 mg, 60%) and **12b** (90 mg, 76%). *Data of 10b:* see above. *Data of 12b:* Brown glassy solid. IR (neat): 3390 (br, OH), 1743 (C=O). UV/Vis (CH₂Cl₂): 258 (107700), 326 (33600), 394 (sh, 4000), 400 (sh, 2900), 414 (sh, 2100), 426 (3450), 488 (1300), 551 (sh, 860), 688 (180). ¹H-NMR (400 MHz, CDCl₃): 4.66 (t, *J* = 6, 2H), 4.57 (q, *J* = 7, 2H), 3.86 (t, *J* = 6, 2H), 2.11 (quint, *J* = 6, 2H), 1.66 (s, 1H), 1.49 (t, *J* = 6, 3H). ¹³C-NMR (100 MHz, CDCl₃): 164.0, 163.7, 145.44, 145.40, 145.35, 145.31, 145.28, 145.1, 144.9, 144.8, 144.1, 143.3, 143.19, 143.17, 143.14, 142.4, 142.1, 141.14, 141.12, 139.3, 139.1, 71.7, 64.5, 63.7, 59.3, 52.3, 31.8, 14.4. MALDI-TOF-MS: 908.0 (*M*⁺, calc. for [C₆₈H₁₂O₅]⁺: 908.1).

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Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Author Contribution Statement

F. S., U. H., S. G., T. M. N. T., D. S., M. H. and I. N. performed all the synthesis and characterization. U. H., M. H. and I. N. analyzed all the data and U. H. prepared the experimental section and the Supporting Information. J.-F. N. performed the molecular modeling, programmed, designed, and coordinated all the scientific activities and wrote the article through contributions of all the authors.

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