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# Regioselective Preparation of Fullerene Bis-adducts From Cleavable Macrocyclic Bis-malonates

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Dedicated to Prof. Remi Chauvin on the occasion of his 60<sup>th</sup> birthday

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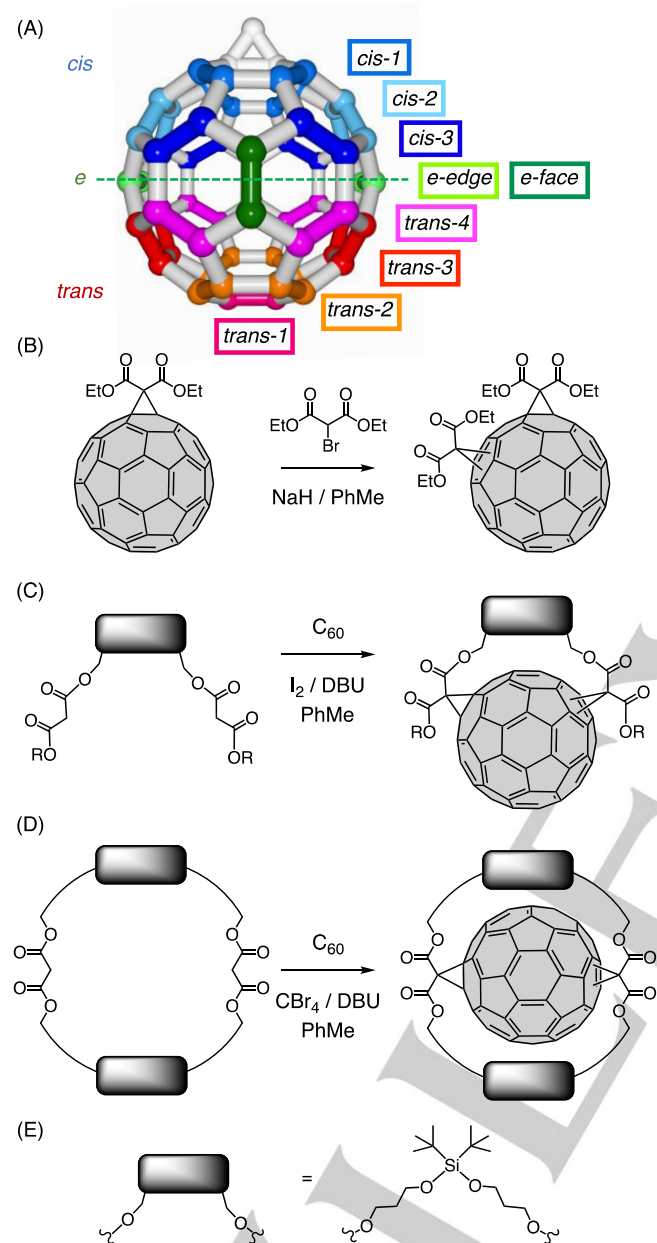
**Abstract:** A series of macrocyclic bis-malonates incorporating either di-*tert*-butylsilylene or tetra-*iso*-propylidisiloxane subunits have been prepared and used for the regioselective bis-functionalization of [60]fullerene by double Bingel cyclopropanations. By systematically changing the length and the rigidity of the spacer units linking the malonate moieties to the silylated protecting groups, fullerene bis-adducts with different addition patterns have been obtained. Finally, the bridging di-*tert*-butylsilylene groups have been cleaved to afford the corresponding acyclic fullerene bis-adducts bearing four alcohol functions.

## Introduction

The cyclopropanation of [60]fullerene with stabilized  $\alpha$ -halocarbanions, the so-called Bingel reaction, is one of the most efficient tools for the preparation of methanofullerenes.<sup>[1-3]</sup> This reaction proceeds by addition of a stabilized  $\alpha$ -halocarbanion to one of the 6-6 double bonds of C<sub>60</sub> (bonds at the junction between two six-membered rings), followed by an intramolecular displacement of the halide by the anionic center generated on the C<sub>60</sub> core. As all the thirty 6-6 double bonds of plain C<sub>60</sub> are equivalent, only one mono-addition product is possible. In contrast, monofunctionalized fullerene derivatives possess nine different 6-6 double bonds (Figure 1).<sup>[4]</sup> Addition of a second addend to a C<sub>2v</sub>-symmetrical C<sub>60</sub> mono-adduct can in principle lead to nine different regioisomeric bis-adducts. Relative to the first addend, the second one can be located either in the same hemisphere (*cis*), in the opposite one (*trans*), or on the equatorial belt (*e*).<sup>[4]</sup> The sequential double Bingel cyclopropanation of C<sub>60</sub> with diethyl bromomalonate has been investigated in details by Hirsch and co-workers (Figure 1B).<sup>[5]</sup> In this particular case, the two addends are identical and the symmetry of the C<sub>60</sub> bis-adducts can be either C<sub>2</sub> (*cis*-3, *trans*-2, *trans*-3), C<sub>s</sub> (*cis*-1, *cis*-2, *e*, *trans*-4), or D<sub>2h</sub> (*trans*-1). Moreover, a second addition onto the *e*-edge or *e*-face position leads to identical products (simply noted *e* in this particular case). Out of the eight possible bis-adducts, only the *cis*-1 has not been obtained for steric reasons. The product distribution is however not statistical and the preferred reaction products are the *e* and *trans*-3 isomers.<sup>[5]</sup> The difference in reactivity of the different

double bonds is nicely correlated with their LUMO coefficients in C<sub>60</sub>(CO<sub>2</sub>Et)<sub>2</sub>. Despite a preferential functionalization of specific double bonds, the preparative synthesis of fullerene bis-adducts by successive reactions at the C<sub>60</sub> core remains limited as complex mixtures are produced and tedious chromatographic separations are necessary for their purification. The development of selective routes to produce isomerically pure fullerene multi-adducts became rapidly a central topic in fullerene chemistry. The first powerful strategy for the regioselective preparation of fullerene multiple adducts has been introduced by Diederich in 1994 and is based on tether-directed remote functionalization.<sup>[6,7]</sup> The same group has also reported a direct bis-functionalization of C<sub>60</sub> based on the macrocyclization of bis-malonate derivatives onto the fullerene core (Figure 1C).<sup>[8]</sup> The linker between the two malonate moieties acts as a directing tether thus allowing a highly regioselective double Bingel addition to one carbon sphere.<sup>[9,10]</sup> This methodology has been further extended by Hirsch and co-workers to macrocyclic malonates.<sup>[11-13]</sup> In this case, the regioselectivity is not only governed by the length of the spacer but also by the even distribution of the strain within the macrocyclic malonates. As a result, formation of C<sub>2</sub>-symmetrical bis-adducts is favored when starting from macrocyclic malonates containing alkane chain spacers of identical length.<sup>[11]</sup> As part of this research, we have incorporated di-*tert*-butylsilylene protecting groups in the bridging units of linear and macrocyclic bis-malonates (Figure 1D).<sup>[14,15]</sup> Upon regioselective bis-functionalization of C<sub>60</sub>, our preliminary results have also shown that a desilylation reaction is possible to afford the corresponding acyclic polyols.<sup>[14]</sup> In this full paper, we now report a complete series of macrocyclic bis-malonates incorporating either di-*tert*-butylsilylene or tetra-*iso*-propylidisiloxane subunits in order to fully explore their potential for the regioselective bis-functionalization of C<sub>60</sub>. By systematically changing the length and the rigidity of the spacer units linking the malonate moieties to the silylated protecting groups, fullerene bis-adducts with different addition patterns became accessible. Interestingly, introduction of the silylene and disiloxane groups brings additional flexibility and influence the overall strain of the system. In contrast to the observation of Hirsch with macrocyclic malonates containing alkane chain spacers, the bis-addition patterns with rotational symmetry are not favored anymore by reaction of C<sub>60</sub> with symmetrical

macrocyclic bis-malonates incorporating di-*tert*-butylsilylene or tetra-*iso*-propylidisiloxane subunits. Finally, the di-*tert*-butylsilylene protecting groups have been cleaved to afford the corresponding acyclic fullerene bis-adducts bearing four alcohol functions.



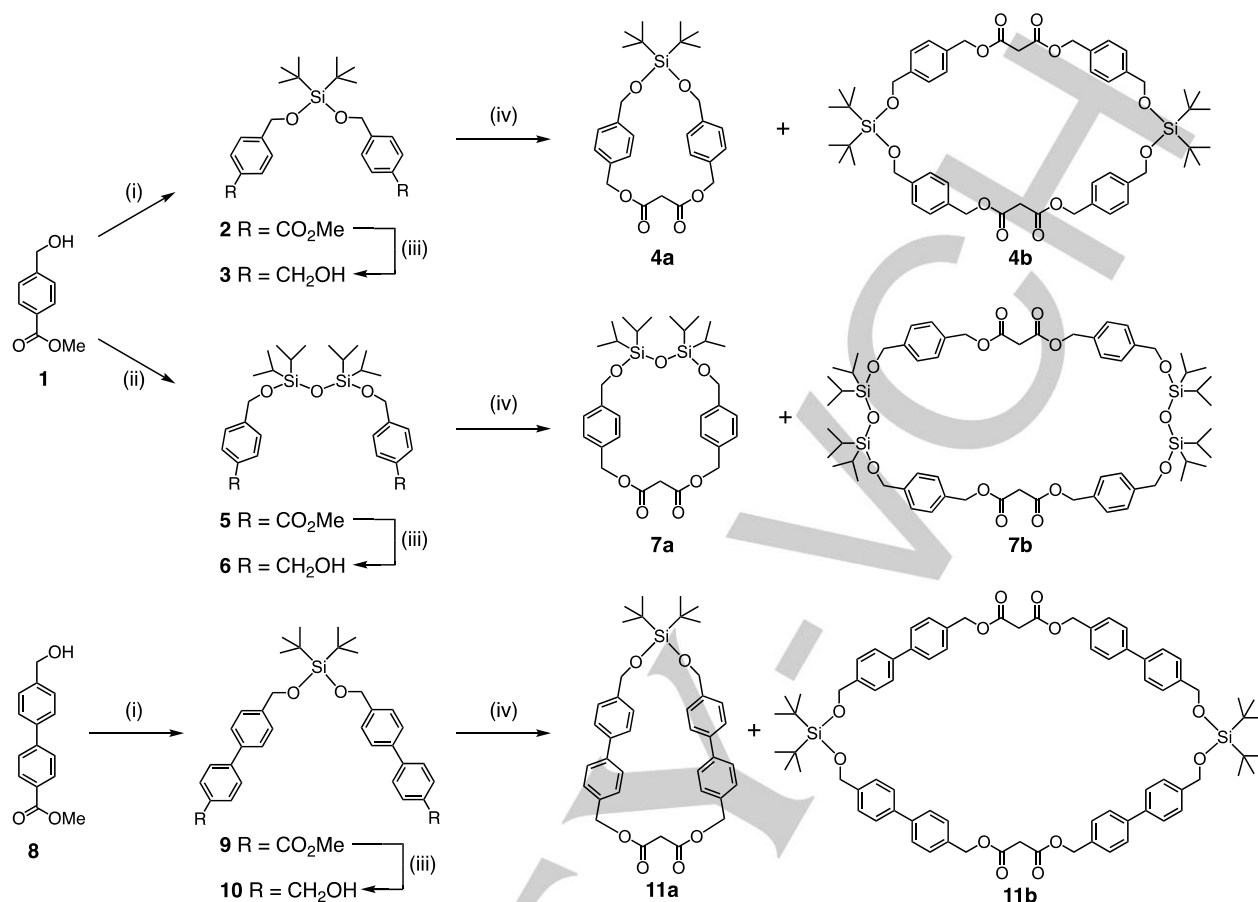
**Figure 1.** (A) Positional relationships of the different 6,6 double bonds relative to a first addend in a fullerene monoadduct.<sup>[4]</sup> (B) Double Bingel cyclopropanation investigated in details by Hirsch and co-workers.<sup>[5]</sup> (C) Regioselective preparation of  $C_{60}$  bis-adducts based on the reaction of linear bis-malonates with  $C_{60}$  reported by Diederich and co-workers.<sup>[8]</sup> (D) Regioselective preparation of  $C_{60}$  bis-adducts based on the reaction of macrocyclic bis-malonates with  $C_{60}$  reported by Hirsch and co-workers.<sup>[11]</sup> (E) Our group has developed linear and macrocyclic bis-malonates incorporating bridging di-*tert*-butylsilylene protecting groups that can be readily cleaved to afford the corresponding acyclic fullerene polyols upon the regioselective bis-functionalization of  $C_{60}$ .<sup>[14]</sup>

### Preparation of macrocyclic bis-malonates.

A first series of macrocyclic bis-malonates incorporating rigid aromatic spacer units between the malonate moieties to the silylated protecting groups were prepared as shown in Scheme 1. Reaction of methyl 4-(hydroxymethyl)benzoate (**1**) with di-*tert*-butylsilylene bis(trifluoromethanesulfonate) ( $tBu_2Si(OTf)_2$ ) in DMF in the presence of pyridine (pyr) afforded **2** in 92% yield. The reduction of the ester functions of **2** was first attempted with  $LiAlH_4$ . Under these conditions, the desired diol was not obtained due to the concomitant cleavage of the silyl ethers. In contrast, when diisobutylaluminum hydride (DIBAL-H) was used as the reducing agent, compound **3** was obtained in good yields (92%). Reaction of diol **3** with malonyl chloride was then performed in the presence of 4-dimethylaminopyridine (DMAP) under pseudo-high dilution conditions. A mixture of cyclooligomers and polymers was thus obtained. Macrocyclus **4a** and **4b** were isolated by repeated chromatographic separations. The 20-membered ring macrocyclic mono-malonate **4a** was thus isolated in 49% yield. The corresponding 40-membered ring macrocyclic bis-malonate was obtained in 9% yield. Compounds **7a** and **7b** were prepared from alcohol **1** by following a similar synthetic route. Reaction of **1** with 1,3-dichloro-1,1,3,3-tetraisopropylidisiloxane (TIPDSiCl<sub>2</sub>) followed by DIBAL-H reduction of the resulting **5** provided diol **6**. Treatment of **6** with malonyl chloride was then carried out under pseudo-high dilution conditions to afford the 22- and 44-membered ring macrocyclus **7a** and **7b** in 73% and 5% yields, respectively. In order to further increase the ring size of the macrocyclic bis-malonate incorporating rigid spacers, macrocyclus **11a** and **11b** were prepared starting from biphenyl derivative **8**. Treatment of **8** with  $tBu_2Si(OTf)_2$  provided **9** in 86% yield. Reduction of **9** with DIBAL-H in  $CH_2Cl_2$  at  $-15^\circ C$  gave diol **10** in 67% yield. Finally, the 28- and 56-membered ring macrocyclus **11a** and **11b** were obtained in low yields by reaction of **10** with malonyl chloride. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of macrocyclus **4a-b**, **7a-b** and **11a-b** were in full agreement with their cyclooligomeric structures. It was however not possible to fully confirm the proposed structures by mass spectrometry due to high levels of fragmentation resulting from the cleavage of the benzylic ester moieties during the MS analysis. Nonetheless, based on the elution order of the compounds and on their relative yields, compounds **4a**, **7a** and **11a** are likely the cyclomonomeric derivative, and **4b**, **7b** and **11b** the corresponding cyclodimers. This was fully confirmed upon functionalization of  $C_{60}$  with **4b**, **7b** and **11b** (*vide infra*).

Macrocyclic bis-malonates **18a-e** were prepared starting from alkanediols **12a-e** (Scheme 2). Initial attempts to produce **18a-e** by reaction of the corresponding di-*tert*-butyl silylene-bridged diols and malonyl chloride provided mainly [1+1] cyclization products and the desired [2+2] products were obtained in very low yields. A stepwise synthetic route was therefore developed in order to obtain the targeted bis-malonates more efficiently. Specifically, a first malonate subunit was first decorated with two appropriate groups bearing terminal alcohol groups. The resulting diol was then engaged in the macrocyclization step with malonyl chloride to generate the desired bis-malonates as the [1+1] cyclization products.

## Results and Discussion



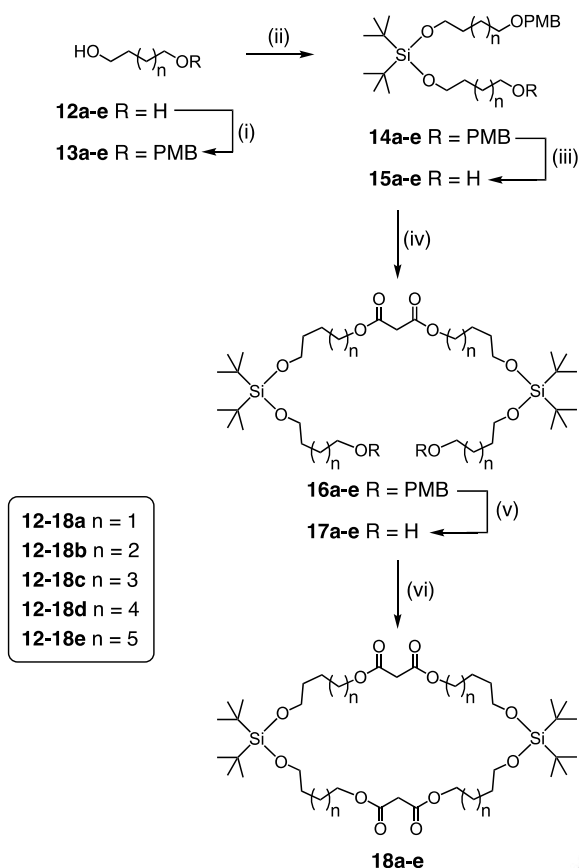
**Scheme 1.** Preparation of macrocyclic bis-malonates **4b**, **7b** and **11b**. *Reagents and conditions:* (i)  $t\text{Bu}_2\text{Si}(\text{OTf})_2$ , DMF, pyr, rt (**2**: 92%; **9**: 86%); (ii) TIPDSiCl<sub>2</sub>, DMF, pyr, rt (99%); (iii) DIBAL-H, CH<sub>2</sub>Cl<sub>2</sub>, -15°C (**3**: 92%; **6**: 77%; **10**: 67%); (iv) malonyl chloride, CH<sub>2</sub>Cl<sub>2</sub>, DMAP, rt (**4a**: 49% and **4b**: 9%; **7a**: 73% and **7b**: 5%; **11a**: 12% and **11b**: 8%).

The selective mono-protection of diols **12a-e** was carried out by treatment with Ag<sub>2</sub>O and *p*-methoxybenzyl chloride (PMBCl) according to the conditions reported by Bouzide and Sauvé.<sup>[16]</sup> Reaction of the resulting mono-protected derivatives **13a-e** with  $t\text{Bu}_2\text{Si}(\text{OTf})_2$  in the presence of pyr in DMF provided **14a-e**. Treatment of **14a-e** with 1 equiv. of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ)<sup>[17]</sup> in CH<sub>2</sub>Cl<sub>2</sub> containing a small amount of water gave the corresponding mono-protected diols **15a-e**. Subsequent reaction with malonyl chloride in the presence of DMAP afforded malonates **16a-e**. The choice of the appropriate protecting groups for the two terminal alcohol functions of **16a-e** was essential to achieve their deprotection without affecting the acid-sensitive bridging di-*tert*-butyl silylene groups and the base-sensitive ester functions. The PMB protecting group was perfectly suited for our purpose as its oxidative cleavage by treatment with DDQ was performed under neutral conditions.<sup>[17]</sup> Both the ester functions and the di-*tert*-butyl silylene groups remained intact under these conditions and diols **17a-e** were thus obtained in good yields. Macrocyclic bis-malonates **18a-e** were then prepared by reaction of diols **17a-e** with malonyl chloride in the presence of DMAP. In all the cases, only the [1+1] cyclization product was formed and by-products

were polymers. Their purification by column chromatography was therefore easily achieved. Considering their ring size ranging from 32 to 48 atoms, macrocycles **18a-e** were thus produced in good yields. Their structure was fully confirmed by NMR spectroscopy and mass spectrometry.

#### Bis-functionalization of C<sub>60</sub> with macrocyclic bis-malonates.

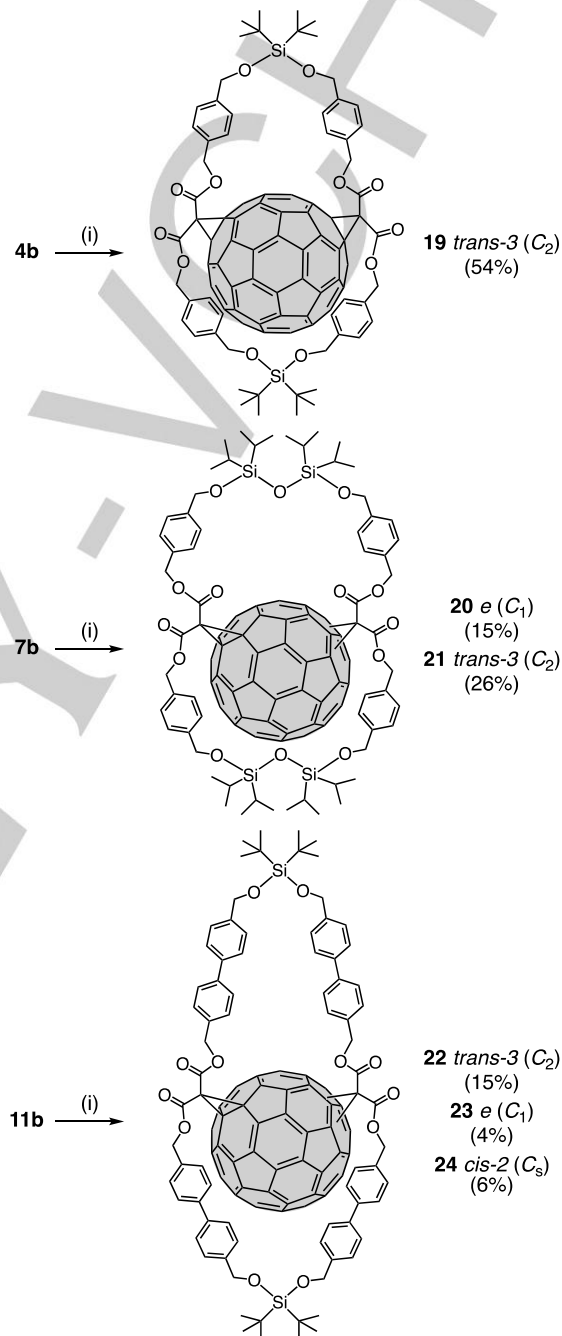
Reactions of macrocyclic bis-malonates **4b**, **7b** and **11b** with C<sub>60</sub> were carried out under the typical conditions developed by Diederich for the preparation of bis-adducts (Scheme 3).<sup>[8]</sup> Specifically, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added to a solution of C<sub>60</sub>, iodine and the appropriate macrocyclic bis-malonate (**4b**, **7b** or **11b**) in PhMe at room temperature. Under these conditions, the  $\alpha$ -iodo malonate intermediates needed for the cyclopropanation of C<sub>60</sub> are generated *in situ* by reaction of the malonates with iodine. To favor the macrocyclizations onto the C sphere and prevent intermolecular Bingel cyclopropanations between monofunctionalized intermediates, all the reactions were performed at low concentrations (ca. 0.3 mM for C<sub>60</sub>).



**Scheme 2** Preparation of macrocyclic bis-malonates **18a-e**. *Reagents and conditions:* (i) PMBCl, Ag<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, rt (**13a**: 95%; **13b**: 91%; **13c**: 92%; **13d**: 90%; **13e**: 69%); (ii) *t*Bu<sub>2</sub>Si(OTf)<sub>2</sub>, DMF, pyr, rt (**14a**: 60%; **14b**: 91%; **14c**: 59%; **14d**: 79%; **14e**: 83%); (iii) DDQ (1 equiv.), CH<sub>2</sub>Cl<sub>2</sub>, H<sub>2</sub>O, rt (**15a**: 47%; **15b**: 47%; **15c**: 60%; **15d**: 51%; **15e**: 50%); (iv) malonyl chloride (0.5 equiv.), CH<sub>2</sub>Cl<sub>2</sub>, DMAP, rt (**16a**: 67%; **16b**: 94%; **16c**: 93%; **16d**: 96%; **16e**: 90%); (v) DDQ (2.5 equiv.), CH<sub>2</sub>Cl<sub>2</sub>, H<sub>2</sub>O, rt (**15a**: 47%; **15b**: 47%; **15c**: 60%; **15d**: 51%; **15e**: 50%); (vi) malonyl chloride, CH<sub>2</sub>Cl<sub>2</sub>, DMAP, rt (**16a**: 67%; **16b**: 94%; **16c**: 93%; **16d**: 96%; **16e**: 90%); (vi) malonyl chloride (1 equiv.), CH<sub>2</sub>Cl<sub>2</sub>, DMAP, rt (**18a**: 50%; **18b**: 28%; **18c**: 30%; **18d**: 19%; **18e**: 19%).

Under these conditions, reaction of **4b** with C<sub>60</sub> was highly regioselective and *trans*-3 bis-adduct **19** was the only cyclization product. It was obtained in a good yield (54%). In the case of **7b**, the reaction with C<sub>60</sub> afforded two regioisomeric bis-adducts. Upon purification by column chromatography, *e* bis-adduct **20** and *trans*-3 bis-adduct **21** were obtained pure in 15% and 26% yields, respectively. Incorporation of the slightly longer and more flexible disiloxane moieties in the starting macrocycle clearly influenced the outcome of the reaction, the bis-functionalization remained however regioselective. In contrast, very limited regioselectivity was observed when the largest macrocyclic bis-malonate (**11b**) was used as the starting material. Three regioisomers were isolated in pure form by column chromatography. Compounds **22** (*trans*-3), **23** (*e*) and **24** (*cis*-2) were thus obtained in 15%, 4% and 6% yields, respectively. Traces of several other bis-adducts were also observed but these products could not be isolated in pure form and/or were obtained in too small quantities to achieve complete characterization. Despite the long rigid biphenyl units in **11b**, the presence of the silylene linkers is at the origin of a large conformational flexibility preventing the regioselective bis-functionalization of C<sub>60</sub> from **11b**. In the case of **4b** and **7b**, the

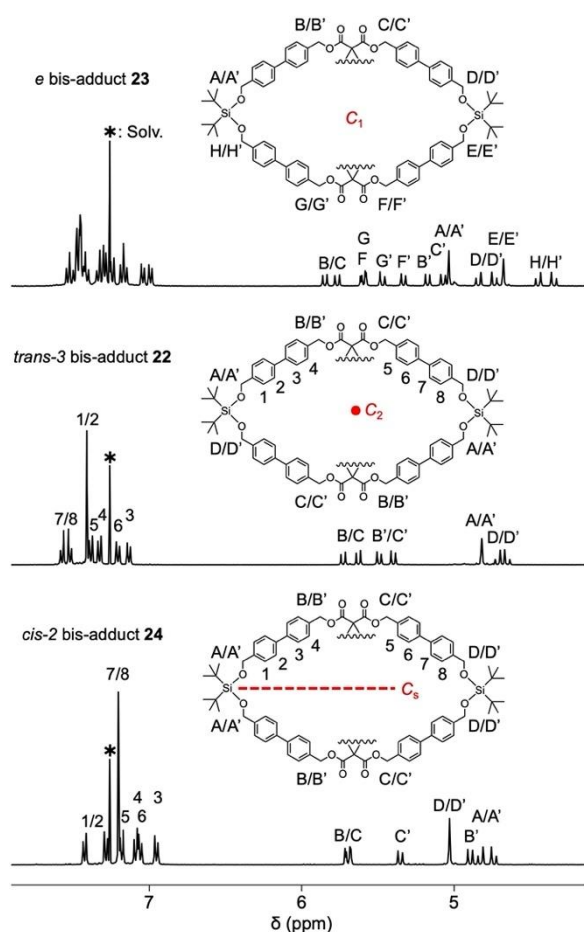
shorter xylylene rigid spacers restricts the intramolecular distance between the two reactive malonate moieties in **4a** and **7a** over a shorter range. In this way, despite the conformational freedom resulting from the presence of the silylated linkers, the reaction of **4a** and **7a** with C<sub>60</sub> remains regioselective.



**Scheme 3.** Preparation of fullerene bis-adducts **19-24**. *Reagents and conditions:* (i) C<sub>60</sub>, DBU, I<sub>2</sub>, PhMe, rt.

Bis-adducts **19-24** were characterized by <sup>1</sup>H and <sup>13</sup>C NMR, UV-vis and IR spectroscopies. Their structure was also confirmed by their MALDI-TOF mass spectra showing the expected pseudo-molecular ion peak in all the cases. To determine the relative position of the two cyclopropane rings on the fullerene core in

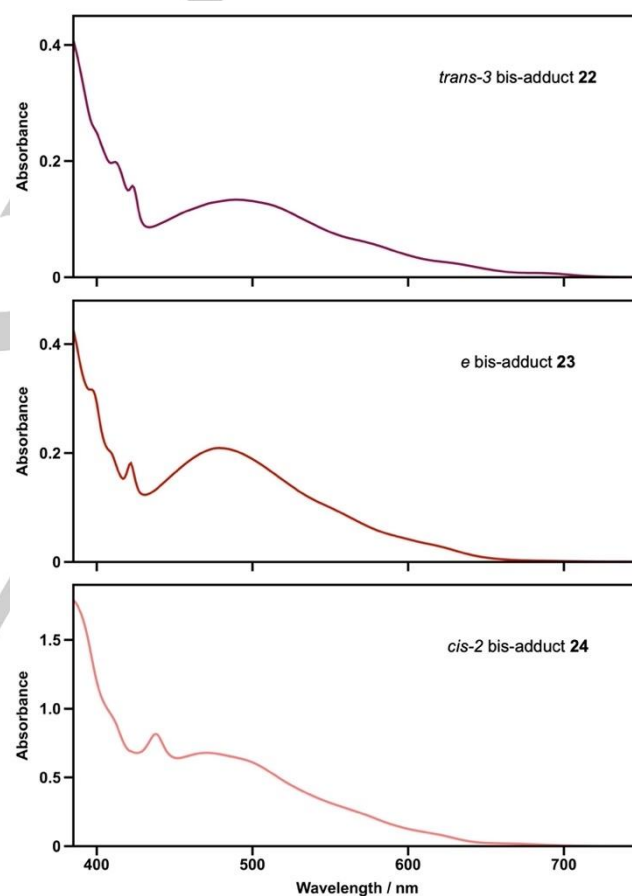
**19-24**, detailed analysis of their  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra was necessary to first deduce their molecular symmetry. As typical examples, the  $^1\text{H}$  NMR spectra recorded for compounds **22-24** in  $\text{CDCl}_3$  are depicted in Figure 2. The spectrum of **23** is by far more complex when compared to those of **22** and **24**. The different diastereotopic benzylic  $\text{CH}_2$  units are non-equivalent in the case of **23** as attested by the presence of eight AB quartets between 4.4 and 5.2 ppm. Compound **23** is therefore  $C_1$  symmetric. This was also confirmed by the complex set of signals observed in the aromatic region corresponding to eight different AA'XX' systems for the protons of the different *p*-disubstituted phenyl units. For a fullerene derivative obtained from a macrocyclic bis-malonate, the only possible bis-addition pattern with a  $C_1$  symmetry is *e*. Owing to the presence of a macrocyclic link joining the two cyclopropane rings in **23**, the  $C_s$  symmetry of the equatorial bis-addition pattern is reduced to  $C_1$ .



**Figure 2.**  $^1\text{H}$  NMR spectra of fullerene bis-adducts **22-24** ( $\text{CDCl}_3$ , 400 MHz).

For both **22** and **24**, only four sets of signals are observed for the benzylic  $\text{CH}_2$  groups thus revealing a two-fold symmetrical structure in both cases. The pattern observed for the protons of the *p*-disubstituted phenyl units is also consistent with this observation. Compounds **22** and **24** are therefore either  $C_s$  or  $C_2$  symmetric. Definitive conclusions about their symmetry was obtained by careful analysis of their  $^{13}\text{C}$  NMR spectra. In particular, 30 fullerene resonances are expected for a  $C_2$ -

symmetrical fullerene derivative (28  $\text{sp}^2$  C atoms and 2  $\text{sp}^3$  C atoms). This is the case for compound **22** thus suggesting either a *cis*-3, *trans*-3 or *trans*-2 addition pattern. In contrast, 32 resonances are expected for a  $C_s$ -symmetrical fullerene bis-adduct (30  $\text{sp}^2$  C atoms with four showing half-intensity and 2  $\text{sp}^3$  C atoms). This is observed for compound **24** thus suggesting either a *cis*-2 or *trans*-4 addition pattern. The relative position of the two cyclopropane rings on the  $\text{C}_{60}$  core suggested by the molecular symmetry is conveniently confirmed by their absorption spectra. The UV/vis spectra of fullerene bis-adducts and therefore their colors are dependent on the addition pattern and highly characteristic for each regioisomer.<sup>[5-8]</sup> As depicted in Figure 3, the UV/vis spectra recorded for compounds **22-24** clearly show the diagnostic features previously reported for *trans*-3 (**22**), *e* (**23**) and *cis*-2 (**24**) bis-adducts<sup>[5-8]</sup> thus providing definitive structural assignment for these compounds.



**Figure 3.** Absorption spectra ( $\text{CH}_2\text{Cl}_2$ ) of fullerene bis-adducts **22-24**. The characteristic features of *trans*-3 (**22**), *e* (**23**) and *cis*-2 (**24**) bis-addition patterns are clearly observed. Solutions of **22** (*trans*-3) are purplish-brown, of **23** (*e*) red and of **24** (*cis*-2) orange.

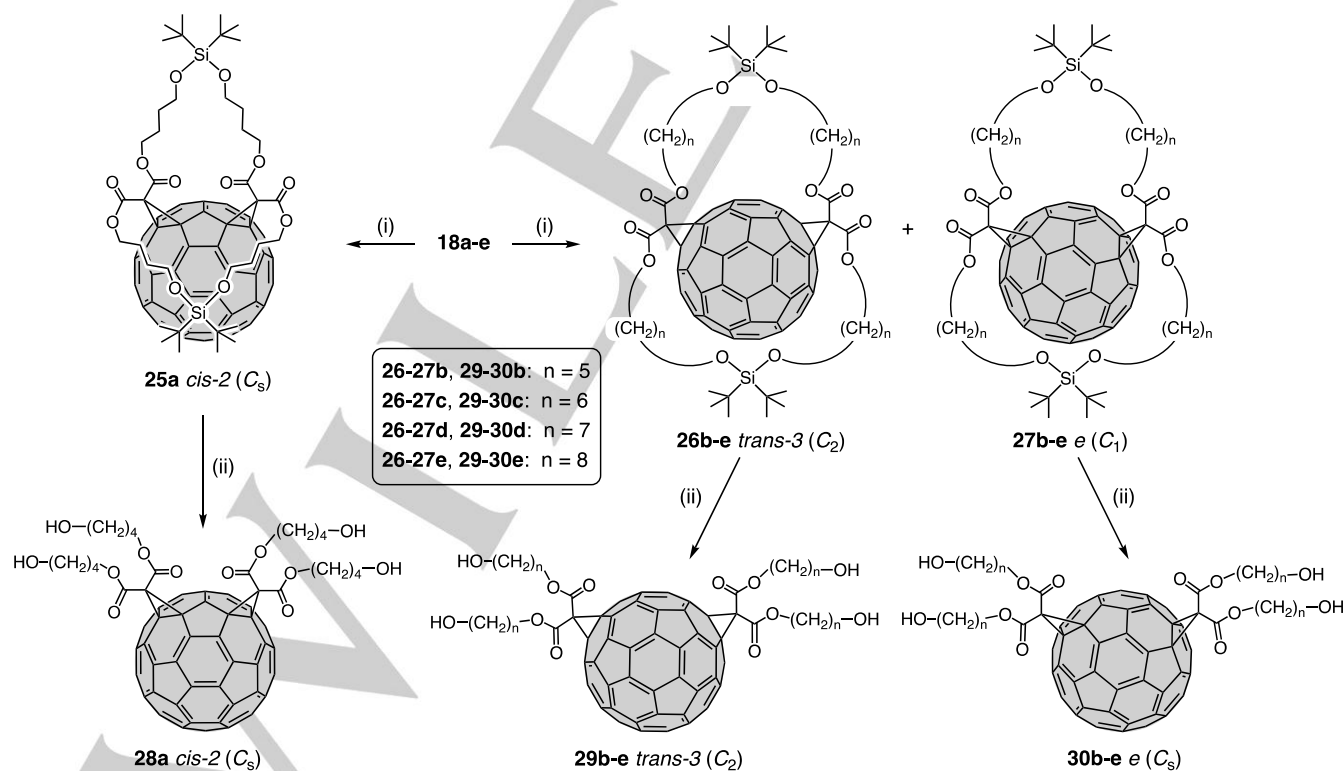
The bis-functionalization of  $\text{C}_{60}$  with macrocyclic bis-malonates **18a-e** was achieved under the same conditions (Scheme 4). Reaction of the smallest macrocycle (**18a**) with  $\text{C}_{60}$  in the presence of iodine and DBU afforded  $C_s$ -symmetrical **25a** with a *cis*-2 addition pattern. Treatment of the larger macrocyclic bis-malonate **18b-e** with  $\text{C}_{60}$  gave two regioisomeric bis-adducts, namely *trans*-3 **26b-e** and *e* **27b-e**. For the  $-(\text{CH}_2)_5-$  derivative,

the *trans*-3 isomer (**26b**) was the major product (44%) while the *e* isomer (**27b**) was only obtained in 12% yield. The *trans*-3/*e* ratio was progressively displaced in favor of the *e* isomer by increasing the size of the macrocyclic bis-malonate when going from **18b** to **18e**. Interestingly, the regioselectivity for the bis-cyclopropanation of  $C_{60}$  with **18a-e** is in apparent contradiction with the observations reported by Hirsch with macrocyclic bis-malonates containing linear alkane chain spacers of identical length.<sup>[11]</sup> In this particular case, the regioselectivity was mainly governed by the even distribution of the strain within the macrocyclic malonates thus favoring the formation of  $C_2$ -symmetrical fullerene bis-adducts.<sup>[11]</sup> Obviously, introduction of the silylene spacers generates different constraints within the macrocyclic bis-malonates and thus favors the formation of fullerene bis-adducts with different symmetries. To fully understand the outcome of these reactions, computational studies were also performed. The molecular geometry of all the possible regioisomers resulting from the cyclization of **18a-e** onto the  $C_{60}$  sphere were optimized at the AM1 semi-empirical level. The relative heat of formation obtained for all the possible regioisomers are summarized in Table 1. Interestingly, the  $C_2$ -symmetrical *cis*-3 regioisomer was notably high in energy whatever the chain length. The steric constraints resulting from the presence of the silylene linkers clearly prevents the formation of this particular isomer. In the case of **18a**, the *cis*-2 regioisomer was found lower in energy when compared to all the other regioisomers thus explaining well the exclusive formation of **25a** from **18a**.

**Table 1.** Relative heat of formation in kJ/mol calculated for all the possible regioisomeric fullerene bis-adducts obtained from the reaction **18a-e** with  $C_{60}$ .<sup>[a]</sup>

	<b>18a</b> -(CH <sub>2</sub> ) <sub>4</sub> -	<b>18b</b> -(CH <sub>2</sub> ) <sub>5</sub> -	<b>18c</b> -(CH <sub>2</sub> ) <sub>6</sub> -	<b>18d</b> -(CH <sub>2</sub> ) <sub>7</sub> -	<b>18e</b> -(CH <sub>2</sub> ) <sub>8</sub> -
<i>cis</i> -2 (C <sub>s</sub> )	0	0	0	+3	+20.6
<i>cis</i> -3 (C <sub>2</sub> )	+97.2	+121.0	+91.5	+79.8	+85.7
<i>e</i> (C <sub>1</sub> )	+30.8	+18.1	+7.3	+1.1	+12.1
<i>trans</i> -4 (C <sub>s</sub> )	+57.2	+28.4	+16.2	+14.5	+23.1
<i>trans</i> -3 (C <sub>2</sub> )	+30.3	+15.3	+21.3	0	+6.5
<i>trans</i> -2 (C <sub>2</sub> )	+219.2	+77.1	+53.2	+28.0	+31.6
<i>trans</i> -1 (D <sub>2h</sub> )		+71.3	+5.8	+39.0	0

[a] The molecular geometry of the various regioisomers was optimized with *Spartan* 18 Macintosh Parallel Edition (Wavefunction Inc., USA) at the AM1 semi-empirical level.



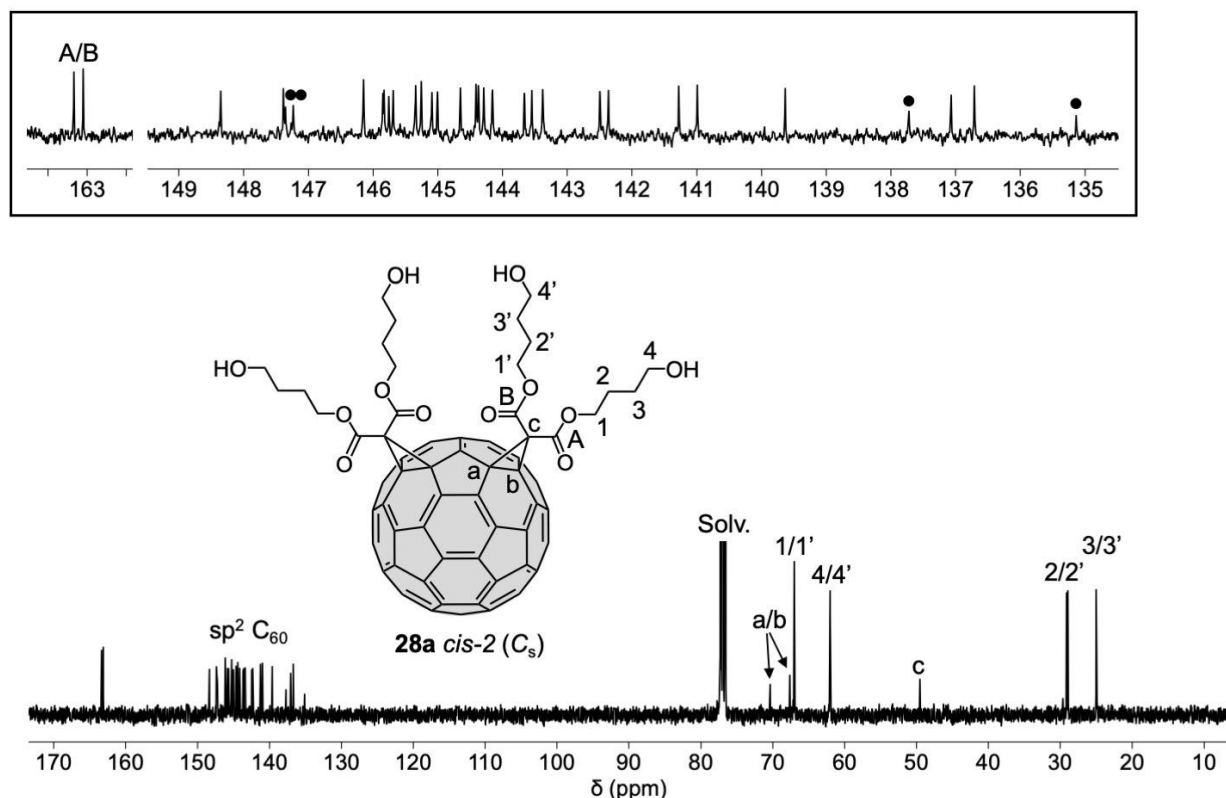
**Scheme 4.** Preparation of fullerene bis-adducts **25a**, **26b-e** and **27b-e** followed by their deprotection to afford tetraols **28a**, **29b-e** and **30b-e**. *Reagents and conditions:* (i)  $C_{60}$ , DBU, I<sub>2</sub>, PhMe, rt (**25a**: 39%; **26b**: 44% and **27b**: 12%; **26c**: 33% and **27c**: 27%; **26d**: 20% and **27d**: 30%; **26e**: 16% and **27e**: 21%); (ii)  $BF_3 \cdot Et_2O$ ,  $CH_2Cl_2/CH_3CN$  2:1, rt (**28a**: 88%; **29b**: 81%; **29c**: 89%; **29d**: 66%; **29e**: 56%; **30b**: 85%; **30c**: 80%; **30d**: 70%; **30e**: 82%).

In contrast, regioisomers **26b-e** and **27b-e** obtained experimentally from **18b-e** were not systematically the lowest in energy. Indeed, distribution of the ring strain within the macrocyclic bis-malonates plays an important role but the cyclization reactions on the C<sub>60</sub> core are also governed by the relative reactivity of the different 6-6 double bonds upon the first cyclopropanation. As soon as the ring strain is limited for the *e* and *trans*-3 products, these addition patterns are favored as they correspond also to the most reactive double bonds. The regioselectivity results therefore from an interplay between steric factors and kinetic effects. When compared to macrocyclic bis-malonates containing linear alkane chain spacers, the silylene linkers in **18a-e** generate specific ring strains owing to their stereochemical preferences and thus dramatically influence the outcome of the cyclization reactions on the fullerene sphere.

#### Desilylation of fullerene bis-adducts.

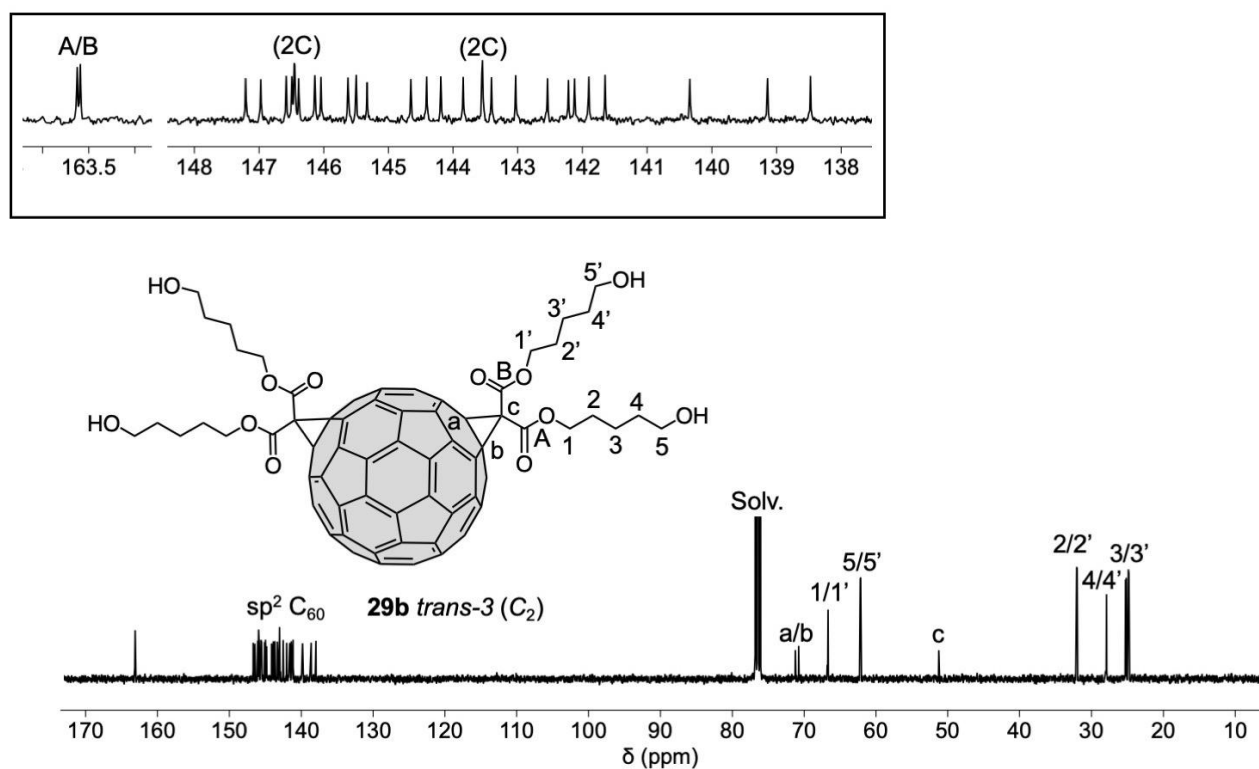
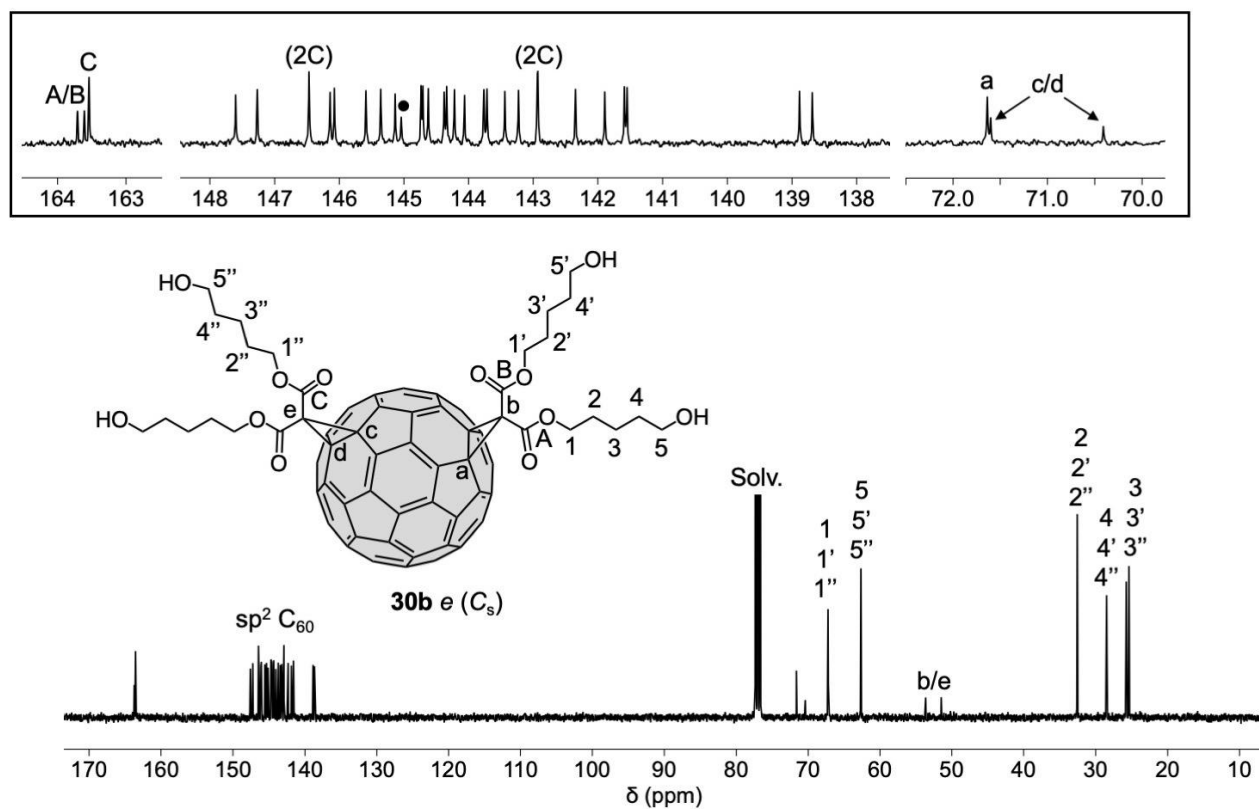
Cleavage of the connecting di-*tert*-butylsilylene protecting groups in bis-adduct regioisomers **25a**, **26b-e** and **27b-e** was achieved in good yields by treatment with an excess of BF<sub>3</sub>·Et<sub>2</sub>O in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN at room temperature (Scheme 4). The corresponding tetraols **28a**, **29b-e** and **30b-e** were thus obtained in 56-89% yields. Removal of the di-*tert*-butylsilylene groups was confirmed by disappearance of the typical *tert*-butyl signals in the <sup>1</sup>H and <sup>13</sup>C NMR spectra recorded for the final products. The symmetry deduced from the NMR spectra of tetraols **28a**, **29b-e**

and **30b-e** as well as their absorption spectra were fully consistent with the proposed addition patterns. Typical examples of <sup>13</sup>C NMR spectra are shown in Figures 4 and 5. For compound **28a**, the 32 expected fullerene resonances of a C<sub>s</sub>-symmetrical bis-adduct are clearly observed. In particular, the presence of four half intensity signals for four fullerene C atoms in the sp<sup>2</sup> region is an unambiguous signature of a C<sub>s</sub> symmetrical structure. The two fullerene sp<sup>3</sup> C atoms (a and b) are observed at δ = 70.5 and 67.7 ppm. The <sup>13</sup>C NMR for bis-adduct **28a** is thus fully consistent with the proposed *cis*-2 addition pattern. This was further confirmed by the UV/vis spectrum of **28a** showing the diagnostic signatures of a *cis*-2 bis-adduct. Compound **30b** with its *e* addition pattern is also C<sub>s</sub> symmetric. There are also 28 pairs of equivalent C fullerene atoms and four unique ones for **30b**. However, out of the three possible C<sub>s</sub>-symmetrical addition patterns (*cis*-2, *e* and *trans*-4), the only one for which three resonances are expected for the sp<sup>3</sup> fullerene C atoms is the *e* bis-adduct. This was further confirmed by the presence of three resonances for the carbonyl C atoms. Finally, the <sup>13</sup>C NMR spectrum of compound **29b** reveals a C<sub>2</sub>-symmetrical structure. The spectrum of **29b** is effectively characterized by 28 resonances of similar intensity for the fullerene sp<sup>2</sup> C atoms and two signals for the sp<sup>3</sup> fullerene C atoms. In addition to its typical absorption spectrum for a *trans*-3 C<sub>60</sub> bis-adduct, the stereochemistry of **29b** was thus unambiguously elucidated.





**Figure 4.**  $^{13}\text{C}$  NMR spectrum of fullerene bis-adduct **28a** ( $\text{CDCl}_3$ , 100 MHz). Four resonances corresponding to  $\text{sp}^2$  C atoms show half intensity (indicated by a black dot), these signals correspond to the four unique fullerene  $\text{sp}^2$  C atoms located in the plane of symmetry. The 26 other resonances correspond each to a pair of equivalent  $\text{sp}^2$  fullerene C atoms.



**Figure 5.**  $^{13}\text{C}$  NMR spectra of fullerene bis-adducts **29b** and **30b** ( $\text{CDCl}_3$ , 100 MHz). In the case of **30b**, the observation of three  $\text{sp}^3$  C fullerene atoms in a 2:1:1 ratio and a  $\text{sp}^2$  fullerene signal with half intensity (indicated by a black dot) is an unambiguous evidence for the  $\text{C}_s$ -symmetrical e addition pattern. The spectrum of

**29b** showing 28 resonances of similar intensity for the fullerene  $sp^2$  C atoms as well as two resonances for the  $sp^3$  fullerene C atoms is typical for a  $C_2$ -symmetrical fullerene bis-adduct.

## Conclusion

Cleavable silylated-tethered macrocyclic bis-malonates have been used for the regioselective preparation of fullerene bis-adducts. By systematically changing the length and the rigidity of the spacer units linking the two malonate moieties to the silyl units, fullerene bis-adducts with different addition patterns have been prepared. The regioselectivity results from the interplay between structural factors and kinetic effects. The formation of bis-adducts corresponding to the most reactive double bonds in the mono-cyclopropanated fullerene intermediates are largely favored. For this reason, mainly *trans*-3 and *e* bis-adducts have been obtained. For the smallest macrocyclic precursor (**18a**), steric constraints are too important in the *e* or *trans*-3 regioisomers and their formation is not possible anymore. In this particular case, the *cis*-2 fullerene bis-adduct is preferentially obtained. In contrast, when the macrocyclic bis-adduct is too large and contains long rigid units (**11b**), the bis-cyclopropanation of  $C_{60}$  is poorly regioselective. Finally, desilylation of the macrocyclic fullerene bis-adducts has been successfully achieved to generate the corresponding acyclic fullerene bis-adducts bearing four terminal alcohol functions. Easy access to these valuable building blocks opens new perspective in the chemistry of multi-functionalized fullerene derivatives for applications in biology or in materials science.

## Experimental Section

### General methods

Reagents were purchased as reagent grade and used without further purification unless specified. All reactions were performed in standard glassware under an inert Ar atmosphere. Evaporation and concentration were done at water aspirator pressure and drying in vacuo at  $10^{-2}$  Torr. Column chromatography: silica gel 60 (230-400 mesh, 0.040-0.063 mm) was purchased from E. Merck. Thin Layer Chromatography (TLC) was performed on aluminum sheets coated with silica gel 60  $F_{254}$  purchased from E. Merck. NMR spectra were recorded with a Bruker AC 300 or AC 400 spectrometer 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 on a Bruker ULTRAFLEX TOF/TOF mass spectrometer by the analytical service of the School of Chemistry (Strasbourg, France).

**Compound 2.**  $tBu_2Si(OTf)_2$  (5.0 g, 11.35 mmol) was added slowly to a solution of **1** (3.96 g, 23.8 mmol) and pyridine (2.1 mL, 26.1 mmol) in dry DMF (13 mL). The resulting mixture was stirred overnight at room temperature, then water was added and the product was extracted with  $Et_2O$ . The organic layer was washed, dried ( $MgSO_4$ ) and concentrated. Column chromatography ( $SiO_2$ ,  $CH_2Cl_2$ /cyclohexane 8:2) gave **2** (4.94 g, 92%) as a colorless glassy product. IR (neat): 1723 ( $C=O$ )  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 8.00 (d,  $J$  = 8 Hz, 4H), 7.36 (d,  $J$  = 8 Hz, 4H), 4.96 (s, 4H), 3.92 (s, 6H), 1.11 (s, 18H) ppm.  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 167.0, 146.2, 129.6, 128.9, 125.5, 65.2, 52.0, 27.9, 21.4 ppm.

**Compound 3.** A solution of DIBAL-H in  $CH_2Cl_2$  (1 M, 22 mL, 22 mmol) was added dropwise to a stirred solution of **2** (2.42 g, 5.12 mmol) in dry  $CH_2Cl_2$  (20 mL) at  $-15^\circ C$ . After 3 h, MeOH and  $NH_4Cl$  (aq.) were added carefully. The resulting mixture was filtered (Celite) and concentrated. Column chromatography ( $SiO_2$ ,  $CH_2Cl_2$ /MeOH, 98:2) yielded **3** (1.97 g, 92%) as a glassy product. IR (neat): 3321 (O-H)  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.32 (s, 8H), 4.93 (s, 4H), 4.68 (s, 4H), 1.10 (s, 18H) ppm.  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 140.7, 139.5, 127.0, 126.0, 65.4, 65.3, 28.0, 21.4 ppm.

**Compounds 4a and 4b.** A solution of malonyl chloride (0.5 mL, 5.2 mmol) in  $CH_2Cl_2$  (100 mL) was added dropwise to a solution of **3** (1.97 g, 4.73 mmol) and DMAP (1.27 g, 10.4 mmol) in  $CH_2Cl_2$  (430 mL). The resulting mixture was stirred at room temperature for 2 h, then filtered ( $SiO_2$ ,  $CH_2Cl_2$ ) and concentrated. Column chromatography ( $SiO_2$ ,  $CH_2Cl_2$ /cyclohexane, 9:1) yielded **4a** (1.13 g, 49%) and **4b** (0.21 g, 9%) as glassy products. **4a**: IR (neat): 1732 ( $C=O$ )  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.01 (s, 8H), 5.13 (s, 4H), 4.88 (s, 4H), 3.51 (s, 2H), 1.14 (s, 18H) ppm.  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 166.0, 141.0, 133.5, 127.3, 126.0, 66.8, 65.7, 42.4, 28.2, 21.3 ppm. **4b**:  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.25 (s, 16H), 5.14 (s, 8H), 4.87 (s, 8H), 3.47 (s, 4H), 1.10 (s, 36H) ppm.  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 166.2, 141.4, 133.8, 128.2, 125.9, 67.1, 65.2, 41.7, 28.0, 21.4 ppm.

**Compound 5.** TIPDSiCl<sub>2</sub> (2.47 mL, 7.9 mmol) was added to a solution of **1** (2.77 g, 16.7 mmol) and pyridine (1.5 mL, 18.5 mmol) in DMF (9 mL). The mixture was stirred overnight at room temperature, then  $H_2O$  was added and the product was extracted with ether. The organic layer was dried ( $MgSO_4$ ), filtered and concentrated. Column chromatography ( $SiO_2$ ,  $CH_2Cl_2$ /cyclohexane, 8:2) yielded **5** (4.53 g, 99%) as a glassy product. IR (neat): 1724 ( $C=O$ )  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.98 (d,  $J$  = 8 Hz, 4H), 7.34 (d,  $J$  = 8 Hz, 4H), 4.88 (s, 4H), 3.91 (s, 6H), 1.06 (m, 28H) ppm.  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 167.0, 146.3, 129.5, 128.8, 125.5, 63.8, 52.0, 17.4, 17.3, 13.0 ppm.

**Compound 6.** A solution of DIBAL-H in THF (1 M, 33 mL, 33 mmol) was added dropwise to a stirred solution of **5** (4.51 g, 7.85 mmol) in dry THF (35 mL) at  $-15^\circ C$ . After 3 h, MeOH and  $NH_4Cl$  (aq.) were added. The resulting mixture was filtered (Celite) and concentrated. Column chromatography ( $SiO_2$ ,  $CH_2Cl_2$ /cyclohexane, 8:2 to  $CH_2Cl_2$ /MeOH, 95:5) yielded **6** (3.15 g, 77%) as a glassy product. IR (neat): 3325 (O-H)  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.27 (s, 8H), 4.84 (s, 4H), 4.65 (s, 4H), 1.08 (m, 28H) ppm.  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 140.7, 139.4, 126.9, 126.1, 65.2, 64.0, 17.4, 17.4, 13.1 ppm.

**Compounds 7a and 7b.** A solution of malonyl chloride (0.94 g, 6.67 mmol) in  $CH_2Cl_2$  (100 mL) was added dropwise to a solution of **6** (3.14 g, 6.05 mmol) and DMAP (1.77 g, 14.5 mmol) in  $CH_2Cl_2$  (590 mL). After 2 h, the resulting mixture was filtered ( $SiO_2$ ,  $CH_2Cl_2$ ) and concentrated. Column chromatography ( $SiO_2$ ,  $CH_2Cl_2$ /cyclohexane, 9:1) gave **7a** (2.59 g, 4.4 mmol, 73%) and **7b** (177 mg, 0.14 mmol, 5%) as glassy products. **7a**: IR (neat): 1734 ( $C=O$ )  $cm^{-1}$ .  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 7.13 (d,  $J$  = 8 Hz, 4H), 7.04 (d,  $J$  = 8 Hz, 4H), 5.12 (s, 4H), 4.85 (s, 4H), 3.49 (s, 2H), 1.11 (s, 28H) ppm.  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  = 166.0, 141.1, 133.4, 127.8, 125.9, 67.0, 63.9, 42.3, 17.4 (two peaks), 13.1 ppm. **7b**:  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.22 (m, 16H), 5.12 (s, 8H), 4.77 (s, 8H), 3.44 (s, 4H), 1.07 (s, 56H) ppm.  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 166.3, 141.7, 133.7, 128.2, 125.9, 67.1, 63.8, 41.5, 17.4, 13.0 ppm.

**Compound 9.**  $tBu_2Si(OTf)_2$  (2.0 mL, 6.1 mmol) was added to a solution of **8** (3.19 g, 13.2 mmol) and pyridine (1.1 mL, 13.5 mmol) in DMF (2 mL). The resulting mixture was stirred overnight at rt, then water was added and the product was extracted with  $CH_2Cl_2$ . The organic layer was washed with  $H_2O$ , dried ( $MgSO_4$ ) and concentrated. Column

chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane 7:3) yielded **9** (3.31 g, 86%) as a glassy product. IR (neat): 1721 (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.09 (d, *J* = 8 Hz, 4H), 7.66 (d, *J* = 8 Hz, 4H), 7.60 (d, *J* = 8 Hz, 4H), 7.43 (d, *J* = 8 Hz, 4H), 5.01 (s, 4H), 3.94 (s, 6H), 1.14 (s, 18H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 167.0, 145.4, 141.3, 138.6, 130.1, 128.8, 127.1, 126.9, 126.3, 65.3, 52.1, 28.0, 21.4 ppm.

**Compound 10.** A solution of DIBAL-H in THF (1M, 20.3 mL, 20.3 mmol) was added dropwise to a stirred solution of **9** (3.03 g, 4.8 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) at -15°C. After for 3h, MeOH and NH<sub>4</sub>Cl (aq) were added. The resulting mixture was filtered (Celite) and concentrated. Column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 96:4) yielded **10** (1.85 g, 67%) as a glassy product. IR (neat): 3311 (br, O-H) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.59 (d, *J* = 8 Hz, 4H), 7.56 (d, *J* = 8 Hz, 4H), 7.43 (d, *J* = 8 Hz, 4H), 7.41 (d, *J* = 8 Hz, 4H), 5.01 (s, 4H), 4.74 (s, 4H), 1.14 (s, 18H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 140.5, 140.4, 139.7, 139.4, 127.5, 127.2, 126.9, 126.3, 65.4, 65.1, 28.0, 21.4 ppm.

**Compounds 11a and 11b.** A solution of malonyl chloride (0.32 mL, 3.29 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) was added dropwise to a solution of **10** (1.85 g, 3.2 mmol) and DMAP (1.47 g, 12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (300 mL). The resulting mixture was stirred at room temperature for 2 h, then filtered (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>) and concentrated. Column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane/ether, 7:2:1) yielded **11a** (250 mg, 12%) and **11b** (170 mg, 8%) as colorless glassy products. **11a:** IR (neat): 1754 (C=O), 1725 (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.29 (d, *J* = 8 Hz, 4H), 7.21 (d, *J* = 8 Hz, 4H), 7.19 (d, *J* = 8 Hz, 4H), 7.07 (d, *J* = 8 Hz, 4H), 5.22 (s, 4H), 4.98 (s, 4H), 3.56 (s, 2H), 1.17 (s, 18H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 166.1, 140.7, 140.3, 138.5, 133.8, 128.2, 127.0, 126.4 (two peaks), 67.0, 66.0, 42.3, 28.3, 21.5 ppm. **11b:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.54-7.46 (m, 16H), 7.40-7.32 (m, 16H), 5.21 (s, 8H), 4.99 (s, 8H), 3.53 (s, 4H), 1.16 (s, 36H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 166.2, 141.1, 140.4, 139.1, 134.0, 128.9, 128.8, 127.1, 126.9, 126.3, 67.0, 65.4, 41.9, 28.1, 21.5 ppm.

**General procedure for the mono-protection of diols (12a-e).** A solution of PMB-Cl (1 eq.) in CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to a solution of the appropriate diol (**12a-e**) (2-3 eq.) and Ag<sub>2</sub>O (1 eq.) in CH<sub>2</sub>Cl<sub>2</sub>. The resulting mixture was stirred overnight at room temperature, then filtered through a plug (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/EtOAc, 9:1) and concentrated. Column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/EtOAc) gave **13a-e**.

**Compound 13a.** Prepared from **12a** (10.0 g, 111 mmol), PMB-Cl (5.0 mL, 36.7 mmol) and obtained as a colorless oil (7.4 g, 95%). IR (neat): 3392 (br, OH) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.25 (d, *J* = 8 Hz, 2H), 6.87 (d, *J* = 8 Hz, 2H), 4.43 (s, 2H), 3.80 (s, 3H), 3.62 (t, *J* = 7 Hz, 2H), 3.45 (t, *J* = 7 Hz, 2H), 1.79 (m, 4H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 159.2, 130.2, 129.3, 113.8, 72.7, 70.1, 62.7, 55.3, 30.2, 26.8 ppm.

**Compound 13b.** Prepared from **12b** (10.0 g, 96 mmol), PMB-Cl (4.4 mL, 32.3 mmol) and obtained as a colorless oil (6.6 g, 91%). IR (neat): 3392 (br, OH) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.25 (d, *J* = 8 Hz, 2H), 6.87 (d, *J* = 8 Hz, 2H), 4.43 (s, 2H), 3.80 (s, 3H), 3.62 (t, *J* = 7 Hz, 2H), 3.45 (t, *J* = 7 Hz, 2H), 1.58 (m, 4H), 1.43 (m, 2H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 159.1, 130.7, 129.1, 113.7, 72.6, 70.0, 62.8, 55.3, 32.5, 29.5, 22.4 ppm.

**Compound 13c.** Prepared from **12c** (10.0 g, 85 mmol), PMB-Cl (3.8 mL, 27.9 mmol) and obtained as a colorless oil (6.1 g, 92%). IR (neat): 3378 (br, OH) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.25 (d, *J* = 8 Hz, 2H), 6.87 (d, *J* = 8 Hz, 2H), 4.43 (s, 2H), 3.80 (s, 3H), 3.62 (t, *J* = 7 Hz, 2H), 3.44 (t, *J* = 7 Hz, 2H), 1.58 (m, 4H), 1.37 (m, 4H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 159.1, 130.7, 129.2, 113.7, 72.6, 70.0, 63.0, 55.3, 32.7, 29.7, 26.0, 25.6 ppm.

**Compound 13d.** Prepared from **12d** (10.0 g, 76 mmol), PMB-Cl (4.1 mL, 30.1 mmol) and obtained as a colorless oil (6.9 g, 90%). IR (neat): 3378 (br, OH) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.26 (d, *J* = 8 Hz, 2H),

6.87 (d, *J* = 8 Hz, 2H), 4.43 (s, 2H), 3.80 (s, 3H), 3.63 (t, *J* = 7 Hz, 2H), 3.43 (t, *J* = 7 Hz, 2H), 1.58 (m, 4H), 1.34 (m, 6H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 159.1, 130.7, 129.2, 113.7, 72.5, 70.1, 63.0, 55.3, 32.7, 29.7, 29.2, 26.0, 25.7 ppm.

**Compound 13e.** Prepared from **12e** (13.8 g, 94 mmol), PMB-Cl (4.3 mL, 31.6 mmol) and obtained as a colorless oil (5.8 g, 69%). IR (neat): 3400 (br, OH) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.26 (d, *J* = 8 Hz, 2H), 6.87 (d, *J* = 8 Hz, 2H), 4.43 (s, 2H), 3.80 (s, 3H), 3.63 (t, *J* = 7 Hz, 2H), 3.43 (t, *J* = 7 Hz, 2H), 1.57 (m, 4H), 1.32 (m, 8H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 159.1, 130.8, 129.2, 113.7, 72.5, 70.2, 63.1, 55.3, 32.8, 29.8, 29.4, 29.3, 26.1, 25.7 ppm.

**General procedure for the silylation of mono-protected diols (14a-e).** *t*Bu<sub>2</sub>Si(OTf)<sub>2</sub> (1 eq.) was added slowly to a solution of **13a-e** (2 eq.) and pyridine (or imidazole) (2 eq.) in DMF. The resulting mixture was stirred overnight at room temperature, then water was added and the product was extracted with Et<sub>2</sub>O. The organic layer was washed, dried (MgSO<sub>4</sub>) and concentrated. Column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane to CH<sub>2</sub>Cl<sub>2</sub>/MeOH) gave **14a-e**.

**Compound 14a.** Prepared from **13a** (7.30 g, 34.7 mmol), *t*Bu<sub>2</sub>Si(OTf)<sub>2</sub> (5.1 mL, 15.6 mmol) and obtained as a colorless oil (5.3 g, 60%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.25 (d, *J* = 8 Hz, 4H), 6.87 (d, *J* = 8 Hz, 4H), 4.43 (s, 4H), 3.81 (t, *J* = 6 Hz, 4H), 3.80 (s, 6H), 3.47 (t, *J* = 6 Hz, 4H), 1.69 (m, 4H), 1.61 (m, 4H), 0.98 (s, 18H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 159.0, 130.7, 129.2, 113.7, 72.5, 70.0, 63.6, 55.3, 29.6, 27.9, 26.2, 21.1 ppm.

**Compound 14b.** Prepared from **13b** (5.6 g, 25.0 mmol), *t*Bu<sub>2</sub>Si(OTf)<sub>2</sub> (3.7 mL, 11.3 mmol) and obtained as a colorless oil (6.1 g, 91%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.25 (d, *J* = 8 Hz, 4H), 6.87 (d, *J* = 8 Hz, 4H), 4.43 (s, 4H), 3.83 (m, 10H), 3.45 (t, *J* = 7 Hz, 4H), 1.59-1.45 (m, 12H), 0.99 (s, 18H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 159.1, 130.8, 129.1, 113.7, 72.5, 70.2, 63.7, 55.3, 32.7, 29.6, 27.9, 22.5, 21.2 ppm.

**Compound 14c.** Prepared from **13c** (6.4 g, 26.9 mmol), *t*Bu<sub>2</sub>Si(OTf)<sub>2</sub> (4.0 mL, 12.3 mmol) and obtained as a colorless oil (4.5 g, 59%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.25 (d, *J* = 8 Hz, 4H), 6.87 (d, *J* = 8 Hz, 4H), 4.43 (s, 4H), 3.80 (s, 6H), 3.79 (t, *J* = 6 Hz, 4H), 3.44 (t, *J* = 6 Hz, 4H), 1.63-1.58 (m, 8H), 1.40 (m, 8H), 0.99 (s, 18H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 159.1, 130.8, 129.2, 113.7, 72.6, 70.2, 63.7, 55.3, 32.9, 29.9, 27.9, 26.1, 25.7, 21.1 ppm.

**Compound 14d.** Prepared from **13d** (6.30 g, 25 mmol), *t*Bu<sub>2</sub>Si(OTf)<sub>2</sub> (5.0 mL, 15.3 mmol) and obtained as a colorless oil (7.85 g, 79%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.27 (d, *J* = 8 Hz, 4H), 6.87 (d, *J* = 8 Hz, 4H), 4.43 (s, 4H), 3.80 (s, 6H), 3.79 (t, *J* = 6 Hz, 4H), 3.43 (t, *J* = 6 Hz, 4H), 1.56 (m, 8H), 1.34 (m, 12H), 0.99 (s, 18H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 159.0, 130.8, 129.2, 113.7, 72.5, 70.2, 63.8, 55.3, 32.9, 29.8, 29.3, 27.9, 26.3, 25.8, 21.2 ppm.

**Compound 14e.** Prepared from **13e** (5.8 g, 21.8 mmol), *t*Bu<sub>2</sub>Si(OTf)<sub>2</sub> (3.2 mL, 9.8 mmol) and obtained as a colorless oil (5.5 g, 83%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.25 (d, *J* = 8 Hz, 4H), 6.87 (d, *J* = 8 Hz, 4H), 4.43 (s, 4H), 3.80 (s, 6H), 3.79 (t, *J* = 6 Hz, 4H), 3.43 (t, *J* = 6 Hz, 4H), 1.55 (m, 8H), 1.32 (m, 16H), 0.99 (s, 18H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 159.0, 130.8, 129.2, 113.7, 72.5, 70.3, 63.8, 55.3, 32.9, 29.9, 29.5, 29.4, 27.9, 26.2, 25.8, 21.2 ppm.

**General procedure for the synthesis of compounds 15a-e.** DDQ (1 eq.) was added to a solution of **14a-e** (1 eq.) in CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O. The resulting mixture was stirred at room temperature for 1 h, then filtered on SiO<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub>/EtOAc, 9:1) and concentrated. Column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH) gave the corresponding **15a-e**.

**Compounds 15a.** Prepared from **14a** (5.25 g, 9.4 mmol) and obtained as a colorless oil (1.94 g, 47%). IR (neat): 3403 (br, OH)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.25 (d,  $J$  = 8 Hz, 2H), 6.87 (d,  $J$  = 8 Hz, 2H), 4.44 (s, 2H), 3.82 (m, 4H), 3.80 (s, 3H), 3.66 (t,  $J$  = 6 Hz, 2H), 3.47 (t,  $J$  = 6 Hz, 2H), 1.63 (m, 8H), 1.00 (s, 18H) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 159.1, 130.7, 129.2, 113.7, 72.5, 70.0, 63.8, 63.7, 55.3, 29.9, 29.6, 27.9, 26.2, 21.2 ppm.

**Compounds 15b.** Prepared from **14b** (6.00 g, 10.2 mmol) and obtained as a colorless oil (2.26 g, 47%). IR (neat): 3399 (br, OH)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.25 (d,  $J$  = 8 Hz, 2H), 6.87 (d,  $J$  = 8 Hz, 2H), 4.43 (s, 2H), 3.81 (m, 7H), 3.63 (t,  $J$  = 7 Hz, 2H), 3.44 (t,  $J$  = 7, 2H), 1.59 (m, 8H), 1.43 (m, 4H), 1.00 (s, 18H) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 159.1, 130.7, 129.2, 113.7, 72.5, 70.2, 63.7, 63.6, 62.9, 55.3, 32.8, 32.6, 32.5, 29.6, 27.9, 22.5, 22.0, 21.2 ppm.

**Compounds 15c.** Prepared from **14c** (3.1 g, 5.0 mmol) and obtained as colorless oil (1.2 g, 48%). IR (neat): 3394 (br, OH)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.25 (d,  $J$  = 8 Hz, 2H), 6.87 (d,  $J$  = 8 Hz, 2H), 4.43 (s, 2H), 3.81 (m, 7H), 3.63 (t,  $J$  = 7 Hz, 2H), 3.44 (t,  $J$  = 7 Hz, 2H), 1.57 (m, 8H), 1.39 (m, 8H), 0.99 (s, 18H) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 159.1, 130.7, 129.2, 113.7, 72.6, 70.2, 63.8, 63.7, 63.0, 55.3, 32.8 (three peaks), 29.8, 27.9, 26.0, 25.8, 25.7, 25.6, 21.2 ppm.

**Compounds 15d.** Prepared from **14d** (5.7 g, 8.9 mmol) and obtained as colorless oil (2.37 g, 51%). IR (neat): 3380 (br, OH)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.26 (d,  $J$  = 8 Hz, 2H), 6.87 (d,  $J$  = 8 Hz, 2H), 4.43 (s, 2H), 3.80 (m, 7H), 3.63 (t,  $J$  = 6 Hz, 2H), 3.43 (t,  $J$  = 6 Hz, 2H), 1.55 (m, 8H), 1.35 (m, 12H), 0.99 (s, 18H) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 159.1, 130.7, 129.2, 113.7, 72.5, 70.2, 63.8 (two peaks), 63.0, 55.3, 32.8 (two peaks), 32.8, 29.8, 29.3 (two peaks), 27.9, 27.5, 26.3, 25.8, 21.2 ppm.

**Compounds 15e.** Prepared from **14e** (5.4 g, 8.1 mmol) and obtained as a colorless oil (2.22 g, 50%). IR (neat): 3388 (br, OH)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.27 (d,  $J$  = 8 Hz, 2H), 6.87 (d,  $J$  = 8 Hz, 2H), 4.43 (s, 2H), 3.80 (m, 7H), 3.63 (t,  $J$  = 6 Hz, 2H), 3.43 (t,  $J$  = 6 Hz, 2H), 1.55 (m, 8H), 1.33 (m, 16H), 0.99 (s, 18H) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 159.1, 130.7, 129.2, 113.7, 72.5, 70.2, 63.8, 63.1, 55.3, 32.9, 32.8, 29.8, 29.5, 29.4 (two peaks), 27.9, 27.5, 26.2, 25.8, 25.7, 21.2 ppm.

**General procedure for the synthesis of compounds 16a-e.** Malonyl chloride (1 eq.) was added to a solution of **15a-e** (2 eq.) and DMAP (2.2 eq.) in  $\text{CH}_2\text{Cl}_2$ . The resulting mixture was stirred at room temperature for 2 h, then filtered on  $\text{SiO}_2$  ( $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ , 9:1) and concentrated. Column chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ ) gave **16a-e**.

**Compound 16a.** Prepared from **15a** (1.9 g, 4.3 mmol), malonyl chloride (0.3 g, 2.2 mmol) and obtained as a colorless oil (1.4 g, 67%). IR (neat): 1752 (C=O), 1735 (C=O)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.25 (d,  $J$  = 8 Hz, 4H), 6.87 (d,  $J$  = 8 Hz, 4H), 4.43 (s, 4H), 4.17 (t,  $J$  = 6 Hz, 4H), 3.82 (t,  $J$  = 6 Hz, 8H), 3.80 (s, 6H), 3.47 (t,  $J$  = 6 Hz, 4H), 3.37 (s, 2H), 1.77–1.59 (m, 18H), 0.97 (s, 36H) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.1, 159.1, 130.7, 129.2, 113.7, 72.5, 70.0, 65.5, 63.6, 63.1, 55.3, 41.6, 29.6, 29.1, 27.9, 26.3, 25.15, 21.2 ppm.

**Compound 16b.** Prepared from **15b** (2.30 g, 4.8 mmol), malonyl chloride (0.33 g, 2.4 mmol) and obtained as a colorless oil (2.24 g, 94%). IR (neat): 1753 (C=O), 1736 (C=O)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.25 (d,  $J$  = 8 Hz, 4H), 6.87 (d,  $J$  = 8 Hz, 4H), 4.43 (s, 4H), 4.14 (t,  $J$  = 7 Hz, 4H), 3.80 (s, 6H), 3.79 (t,  $J$  = 7 Hz, 8H), 3.45 (t,  $J$  = 7 Hz, 4H), 3.35 (s, 2H), 1.69–1.50 (m, 16H), 1.38 (m, 8H), 0.99 (s, 36H) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.6, 159.0, 130.7, 129.1, 113.7, 72.5, 70.2, 65.6, 63.7, 63.4, 55.3, 41.6, 32.9, 32.7, 29.8, 28.5, 27.9, 26.1, 25.7, 25.6, 25.5, 21.2 ppm.

**Compound 16c.** Prepared from **15c** (1.20 g, 2.3 mmol), malonyl chloride (0.16 g, 1.2 mmol) and obtained as a colorless oil (1.13 g, 93%). IR (neat): 1753 (C=O), 1736 (C=O)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.25 (d,  $J$  = 8 Hz, 4H), 6.87 (d,  $J$  = 8 Hz, 4H), 4.43 (s, 4H), 4.14 (t,  $J$  = 7 Hz, 4H), 3.80 (s, 6H), 3.79 (t,  $J$  = 6 Hz, 8H), 3.44 (t,  $J$  = 6 Hz, 4H), 3.36 (s, 2H), 1.69–1.50 (m, 18H), 1.38 (m, 14H), 0.99 (s, 36H) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.6, 159.0, 130.7, 129.2, 113.7, 72.5, 70.2, 65.6, 63.8, 63.6, 55.3, 41.6, 32.7, 32.4, 29.6, 28.3, 27.9, 22.5, 22.1, 21.2 ppm.

**Compound 16d.** Prepared from **15d** (2.30 g, 4.3 mmol), malonyl chloride (0.31 g, 2.2 mmol) and obtained as a colorless oil (2.36 g, 96%). IR (neat): 1753 (C=O), 1736 (C=O)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.26 (d,  $J$  = 8 Hz, 4H), 6.87 (d,  $J$  = 8 Hz, 4H), 4.43 (s, 4H), 4.13 (t,  $J$  = 7 Hz, 4H), 3.80 (s, 6H), 3.79 (t,  $J$  = 6 Hz, 8H), 3.43 (t,  $J$  = 6 Hz, 4H), 3.36 (s, 2H), 1.66–1.51 (m, 16H), 1.35 (m, 24H), 0.99 (s, 36H) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.6, 159.1, 130.8, 129.1, 113.7, 72.5, 70.2, 65.6, 63.8, 63.7, 55.3, 41.6, 32.9, 32.8, 29.8, 29.3, 29.0, 28.5, 28.0, 26.3, 25.8, 25.7, 21.2 ppm.

**Compound 16e.** Prepared from **15e** (2.30 g, 4.1 mmol), malonyl chloride (0.29 g, 2.0 mmol) and obtained as a colorless oil (2.18 g, 90%). IR (neat): 1753 (C=O), 1736 (C=O)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.25 (d,  $J$  = 8 Hz, 4H), 6.87 (d,  $J$  = 8 Hz, 4H), 4.43 (s, 4H), 4.13 (t,  $J$  = 7 Hz, 4H), 3.80 (s, 6H), 3.79 (t,  $J$  = 6 Hz, 8H), 3.43 (t,  $J$  = 6 Hz, 4H), 3.36 (s, 2H), 1.66–1.50 (m, 16H), 1.32 (m, 32H), 0.99 (s, 36H) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.7, 159.0, 130.8, 129.2, 113.7, 72.5, 70.2, 65.7, 63.8 (two peaks), 55.3, 41.7, 32.9, 29.8, 29.5, 29.4, 29.3, 29.2, 28.7, 27.5, 26.2, 25.8, 21.2 ppm.

**General procedure for the deprotection of compounds 17a-e.** DDQ (2.5 eq.) was added to a solution of **16a-e** (1 eq.) in  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$  (18:1). The resulting mixture was stirred at room temperature for 2 h, then filtered on  $\text{SiO}_2$  ( $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , 95:5) and concentrated. Column chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ ) gave **17a-e**.

**Compound 17a.** Prepared from **16a** (1.30 g, 1.37 mmol) and obtained as a colorless oil (0.68 g, 68%). IR (neat): 3388 (br, OH), 1752 (C=O), 1737 (C=O)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.21 (t,  $J$  = 7 Hz, 4H), 3.88 (m, 8H), 3.70 (t,  $J$  = 6 Hz, 4H), 3.40 (s, 2H), 1.80 (m, 4H), 1.73–1.61 (m, 12H), 1.03 (s, 36H) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.7, 65.5, 63.9, 63.2, 62.8, 41.6, 29.8, 29.6, 29.1, 27.9, 25.1, 21.2 ppm.

**Compound 17b.** Prepared from **16b** (2.30 g, 2.3 mmol) and obtained as a colorless oil (1.42 g, 81%). IR (neat): 3361 (br, OH), 1753 (C=O), 1736 (C=O)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.15 (t,  $J$  = 7 Hz, 4H), 3.82 (2t,  $J$  = 6 Hz, 8H), 3.65 (t,  $J$  = 7 Hz, 4H), 3.36 (s, 2H), 1.69 (m, 4H), 1.60 (m, 12H), 1.47 (m, 8H), 0.99 (s, 36H) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.7, 65.6, 63.7, 63.4, 62.9, 41.6, 32.6, 32.5, 32.4, 28.2, 27.9, 22.1, 22.0, 21.2 ppm.

**Compound 17c.** Prepared from **16c** (1.10 g, 1.0 mmol) and obtained as a colorless oil (0.69 g, 80%). IR (neat): 3363 (br, OH), 1753 (C=O), 1737 (C=O)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.14 (t,  $J$  = 7 Hz, 4H), 3.81 (2t,  $J$  = 6 Hz, 8H), 3.66 (t,  $J$  = 6 Hz, 4H), 3.37 (s, 2H), 1.66 (m, 4H), 1.60–1.50 (m, 12H), 1.40 (m, 16H), 0.99 (s, 36H) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.7, 65.6, 63.7, 63.6, 62.9, 41.6, 32.8 (three peaks), 28.5, 27.9, 25.6 (three peaks), 25.5, 21.2 ppm.

**Compound 17d.** Prepared from **16d** (2.30 g, 2.0 mmol) and obtained as a colorless oil (1.52 g, 84%). IR (neat): 3378 (br, OH), 1756 (C=O), 1732 (C=O)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.14 (t,  $J$  = 7 Hz, 4H), 3.80 (2t,  $J$  = 6 Hz, 8H), 3.64 (t,  $J$  = 6 Hz, 4H), 3.37 (s, 2H), 1.65 (m, 4H), 1.56 (m, 16H), 1.35 (m, 20H), 0.99 (s, 36H) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.7, 65.7, 63.8, 63.7, 63.0, 41.7, 32.9, 32.8 (two peaks), 29.4 (two peaks), 29.3, 29.0, 28.4, 27.9, 25.8 (two peaks), 25.7, 21.2 ppm.



= 14 Hz, 2H), 4.71 (d,  $^2J = 13$  Hz, 2H), 4.65 (d,  $^2J = 13$  Hz, 2H), 1.14 (s, 18H), 1.10 (s, 18H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 163.5, 163.4, 146.8, 146.6, 146.2, 146.1, 145.1, 145.8, 145.7, 145.6, 145.5, 145.4, 145.1, 145.0, 144.4, 144.1, 143.7, 143.5, 143.3, 143.2, 143.1, 142.5, 142.2, 142.0, 141.9, 141.8$  (two peaks), 141.6, 141.3, 140.5, 140.0, 139.3, 139.0, 138.8, 137.8, 133.5, 133.2, 130.4, 129.9, 127.4, 127.1, 126.9, 126.8 (two peaks), 126.4, 71.4, 70.9, 69.1, 68.9, 65.5, 65.3, 51.7, 28.2, 28.1, 21.3, 21.2 ppm. MALDI-TOF-MS:  $m/z = 1990.3$  ( $[\text{M}+\text{H}]^+$ , calcd for  $\text{C}_{138}\text{H}_{85}\text{O}_{12}\text{Si}_2$ : 1990.5).

**Compound 23.** Prepared from **11b** (0.170 g, 0.13 mmol) and obtained as a red-brown glassy product (12 mg, 4%). UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 255 (126000), 317 (sh, 27000), 397 (sh, 4500), 410 (sh, 2800), 422 (2600), 479 (sh, 3000), 620 nm (sh,  $410 \text{ M}^{-1}\text{cm}^{-1}$ ). IR (neat): 1747 (C=O)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.57\text{--}7.42$  (m, 16H), 7.37–7.26 (m, 8H), 7.20 (m, 4H), 7.04 (d,  $^3J = 8$  Hz, 2H), 6.99 (d,  $^3J = 8$  Hz, 2H), 5.85 (d,  $^2J = 11$  Hz, 1H), 5.77 (d,  $^2J = 12$  Hz, 1H), 5.60 (d,  $^2J = 12$  Hz, 1H), 5.59 (d,  $^2J = 11$  Hz, 1H), 5.47 (d,  $^2J = 12$  Hz, 1H), 5.33 (d,  $^2J = 11$  Hz, 1H), 5.17 (d,  $^2J = 11$  Hz, 1H), 5.07 (d,  $^2J = 12$  Hz, 1H), 5.03 (AB,  $^2J = 12$  Hz, 2H), 4.84 (d,  $^2J = 13$  Hz, 1H), 4.74 (d,  $^2J = 13$  Hz, 1H), 4.68 (AB,  $^2J = 12$  Hz, 2H), 4.45 (d,  $^2J = 13$  Hz, 1H), 4.34 (d,  $^2J = 13$  Hz, 1H), 1.15 (s, 18H), 1.10 (s, 18H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 163.9, 163.7, 163.4, 162.6, 147.6, 147.4, 147.1$  (two peaks), 146.4, 146.3 (two peaks), 146.2, 146.0, 145.9, 145.8, 145.5 (two peaks), 145.4, 145.2, 145.1, 145.0, 144.6 (two peaks), 144.5 (three peaks), 144.4, 144.3 (three peaks), 144.0 (two peaks), 143.7 (two peaks), 143.6, 143.4, 143.3, 143.2 (two peaks), 143.0 (two peaks), 142.9, 142.8, 142.7, 142.5, 142.3, 142.2, 142.0, 141.9, 141.7, 141.6, 141.5, 141.4, 141.3, 141.0, 140.8, 140.7, 140.6, 140.5 (two peaks), 139.4, 138.8, 138.7, 138.4, 138.3, 138.1, 133.7, 133.4 (two peaks), 133.1, 130.9, 130.2, 129.0, 128.9, 127.5, 127.4, 127.3, 127.2, 127.1, 126.9, 126.8, 126.6 (two peaks), 126.4, 125.9, 71.4 (three peaks), 69.0, 68.9, 68.7, 68.6, 66.2, 65.7, 65.3, 65.1, 51.0, 48.3, 28.3, 28.2, 28.1 (two peaks), 21.4, 21.2 (two peaks) ppm.

**Compound 24.** Prepared from **11b** (0.170 g, 0.13 mmol) and obtained as an orange-brown glassy product (16 mg, 6%). UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 250 (128000), 318 (sh, 39800), 389 (9500), 411 (sh, 5100), 439 (4500), 470 (3800), 621 nm (sh,  $450 \text{ M}^{-1}\text{cm}^{-1}$ ). IR (neat): 1746 (C=O)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.42$  (d,  $^3J = 8$  Hz, 4H), 7.28 (d,  $^3J = 8$  Hz, 4H), 7.20 (s, 8H), 7.18 (d,  $^3J = 8$  Hz, 4H), 7.09 (d,  $^3J = 8$  Hz, 4H), 7.06 (d,  $^3J = 8$  Hz, 4H), 6.95 (d,  $^3J = 8$  Hz, 4H), 5.70 (d,  $^2J = 12$  Hz, 2H), 5.69 (d,  $^2J = 12$  Hz, 2H), 5.35 (d,  $^2J = 12$  Hz, 2H), 5.03 (s, 4H), 4.90 (d,  $^2J = 12$  Hz, 2H), 4.83 (d,  $^2J = 13$  Hz, 2H), 4.74 (d,  $^2J = 13$  Hz, 2H), 1.23 (s, 9H), 1.21 (s, 9H), 1.18 (s, 9H), 1.15 (s, 9H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 163.3, 162.4, 147.4, 146.2, 145.9$  (two peaks), 145.7, 145.4, 145.3 (two peaks), 145.1, 145.0, 144.7, 144.6, 144.4, 144.2, 143.8, 143.6, 143.2, 142.5, 142.0, 141.0 (two peaks), 140.9, 140.5, 140.2, 139.4, 138.7 (two peaks), 138.4, 138.2, 137.5, 133.5, 133.4, 129.5, 128.3, 127.1, 127.0, 126.6 (three peaks), 126.5, 70.1, 68.6, 68.0, 67.7, 66.0, 65.6, 49.0, 28.5, 28.3, 28.2 (two peaks), 21.6, 21.5, 21.4, 21.2 ppm.

**Compound 25a.** Prepared from **18a** (0.286 g, 0.37 mmol) and obtained as an orange-brown glassy product (212 mg, 39%). UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 259 (141000), 319 (sh, 43200), 380 (sh, 14100), 439 (3900), 470 (3400), 621 nm (sh,  $420 \text{ M}^{-1}\text{cm}^{-1}$ ). IR (neat): 1746 (C=O)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 4.57$  (m, 2H), 4.50 (m, 2H), 4.39 (m, 2H), 4.26 (m, 2H), 3.95 (t,  $J = 4$  Hz, 4H), 3.85 (m, 4H), 1.99 (m, 4H), 1.84 (m, 4H), 1.75 (m, 4H), 1.63 (m, 4H), 1.07 (s, 9H), 1.04 (2s, 18H), 0.95 (s, 9H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 163.3, 163.2, 148.2, 147.4, 147.3$  (two peaks), 146.8, 146.2, 146.0, 145.8, 145.7, 145.5, 145.3, 145.0 (two peaks), 144.7, 144.6, 144.4 (two peaks), 144.1, 143.6 (two peaks), 143.5, 142.5, 142.4, 141.3, 141.1, 140.1, 137.1, 136.4, 136.1, 135.6, 70.6, 67.7, 66.7 (two peaks), 63.2, 62.8, 50.3, 28.8, 28.5, 27.9 (three peaks), 27.8, 26.9, 25.5, 25.0, 21.4, 21.3, 21.2 ppm. MALDI-TOF-MS:  $m/z = 1515.38$  (100%,  $[\text{M}+\text{Na}]^+$ , calcd for  $\text{C}_{98}\text{H}_{68}\text{O}_{12}\text{Si}_2\text{Na}$ : 1515.41), 1493.33 (81%,  $[\text{M}+\text{H}]^+$ , calcd for  $\text{C}_{98}\text{H}_{69}\text{O}_{12}\text{Si}_2$ : 1493.43), 1531.36 (26%,  $[\text{M}+\text{K}]^+$ , calcd for  $\text{C}_{98}\text{H}_{68}\text{O}_{12}\text{Si}_2\text{K}$ : 1531.39).

**Compound 26b.** Prepared from **18b** (0.430 g, 0.52 mmol) and obtained as a brown glassy product (350 mg, 44%). UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 250 (130800), 318 (sh, 40400), 377 (sh, 11000), 399 (sh, 5030), 412 (4100), 423 (3400), 490 (2900), 574 (sh, 1300), 628 (sh, 550), 684 nm (sh,  $170 \text{ M}^{-1}\text{cm}^{-1}$ ). IR (neat): 1749 (C=O), 1724 (C=O)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 4.81$  (m, 2H), 4.57 (m, 2H), 4.40 (m, 4H), 3.62–2.52 (m, 8H), 1.90 (m, 2H), 1.75 (m, 6H), 1.50–1.34 (m, 16H), 0.93 (s, 18H), 0.92 (s, 18H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 164.8, 163.4, 147.5$  (two peaks), 147.3, 147.2, 146.6, 146.4 (two peaks), 146.3, 145.5, 145.4, 145.1, 144.8, 144.4, 144.3, 144.0, 143.7, 143.6, 143.5, 142.7, 142.6, 142.0, 141.7, 141.1 (two peaks), 140.0, 139.6, 138.8, 71.7, 71.4, 68.2, 67.3, 64.2, 64.0, 53.4, 32.7, 32.5, 28.7, 27.9, 27.8, 26.9, 23.4, 21.1 (two peaks) ppm. MALDI-TOF-MS:  $m/z = 1571.80$  ( $[\text{M}+\text{Na}]^+$ , calcd for  $\text{C}_{102}\text{H}_{76}\text{O}_{12}\text{Si}_2\text{Na}$ : 1571.48).

**Compound 27b.** Prepared from **18b** (0.430 g, 0.52 mmol) and obtained as a red-brown glassy product (95 mg, 12%). UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 248 (134100), 310 (sh, 47800), 356 (sh, 22000), 397 (5100), 409 (sh, 3100), 421 (3100), 480 (3800), 620 nm (sh,  $500 \text{ M}^{-1}\text{cm}^{-1}$ ). IR (neat): 1744 (C=O)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 4.73\text{--}4.53$  (m, 4H), 4.36 (m, 2H), 4.25 (m, 2H), 3.88 (m, 2H), 3.83–3.66 (m, 5H), 3.54 (m, 1H), 1.77 (m, 8H), 1.66–1.50 (m, 16H), 1.00 (s, 18H), 0.97 (s, 9H), 0.90 (s, 9H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 164.3, 163.6, 163.0, 162.8, 149.0, 147.4, 147.2, 147.1, 146.6, 146.5, 146.3$  (two peaks), 146.1, 146.0 (two peaks), 145.7, 145.6, 145.4 (two peaks), 145.1, 145.0, 144.9, 144.8, 144.7 (two peaks), 144.6 (two peaks), 144.3 (two peaks), 144.1, 143.9 (two peaks), 143.8, 143.7 (two peaks), 143.5, 143.4, 143.3, 143.2, 143.1 (two peaks), 142.9, 142.4, 142.0, 141.7, 141.4, 141.2, 140.0, 139.9, 139.7, 139.5, 138.7, 138.4, 71.9, 71.8, 71.7, 70.4, 67.8, 67.4, 66.9, 64.3, 64.0, 63.4 (two peaks), 53.8, 53.1, 33.3, 32.8, 32.3, 32.2, 29.2, 28.3, 28.2, 27.9 (several peaks), 27.7, 23.5, 23.2, 22.3, 22.2, 21.3 (two peaks), 21.1 (two peaks) ppm. MALDI-TOF-MS:  $m/z = 1571.82$  ( $[\text{M}+\text{Na}]^+$ , calcd for  $\text{C}_{102}\text{H}_{76}\text{O}_{12}\text{Si}_2\text{Na}$ : 1571.48).

**Compound 26c.** Prepared from **18c** (0.210 g, 0.24 mmol) and obtained as a brown glassy product (125 mg, 33%). UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 250 (147000), 318 (sh, 45000), 377 (sh, 13300), 399 (sh, 5300), 412 (4400), 423 (3600), 489 (3000), 573 (sh, 1400), 630 (sh, 600), 687 nm (sh,  $200 \text{ M}^{-1}\text{cm}^{-1}$ ). IR (neat): 1749 (C=O), 1727 (C=O)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 4.78$  (m, 2H), 4.52 (m, 2H), 4.38 (m, 4H), 3.64 (m, 8H), 1.80 (m, 4H), 1.69 (m, 4H), 1.50–1.19 (m, 24H), 0.93 (s, 18H), 0.91 (s, 18H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 164.4, 163.8, 147.3, 147.2, 147.0, 146.9, 146.7$  (two peaks), 146.5, 146.4 (two peaks), 145.8, 145.4, 145.3, 144.7, 144.4, 144.3, 144.0, 143.6 (two peaks), 143.0, 142.6, 142.0, 141.7 (two peaks), 141.6, 140.2, 139.0, 138.2, 71.7, 71.6, 67.5, 63.8, 63.7, 53.1, 33.0, 32.9, 29.7, 28.8, 28.7, 27.6, 26.5, 26.3, 25.6, 25.4, 21.2, 21.1 ppm. MALDI-TOF-MS:  $m/z = 1627.56$  ( $[\text{M}+\text{Na}]^+$ , calcd for  $\text{C}_{106}\text{H}_{84}\text{O}_{12}\text{Si}_2\text{Na}$ : 1627.54).

**Compound 27c.** Prepared from **18c** (0.210 g, 0.24 mmol) and obtained as a red-brown glassy product (102 mg, 27%). UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 252 (136000), 309 (sh, 52000), 356 (sh, 21400), 397 (5000), 409 (sh, 3100), 421 (3000), 480 (3700), 621 nm (sh,  $450 \text{ M}^{-1}\text{cm}^{-1}$ ). IR (neat): 1745 (C=O)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 4.72$  (m, 1H), 4.57 (m, 3H), 4.33 (m, 2H), 4.16 (m, 2H), 3.80 (m, 7H), 3.71 (m, 1H), 1.77 (m, 8H), 1.64–1.13 (m, 24H), 1.00 (s, 9H), 0.97 (s, 18H), 0.91 (s, 9H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 163.7, 163.5, 163.2, 147.4, 147.2, 146.6, 146.4, 146.1, 145.7, 145.6, 145.4, 145.2, 144.8, 144.7, 144.6, 144.4, 144.1, 144.0, 143.9$  (two peaks), 143.5 (two peaks), 143.3, 142.5, 142.1, 141.6 (two peaks), 140.6, 139.6 (two peaks), 138.6 (two peaks), 71.8, 67.7, 67.3, 66.9 (two peaks), 64.2, 63.6, 63.4, 51.9, 33.2, 32.8, 32.7 (two peaks), 28.6, 28.2, 28.0, 27.9, 27.2, 26.9, 26.5, 26.1, 25.5, 25.2, 25.1 (two peaks), 25.0 (two peaks), 21.1 (three peaks) ppm. MALDI-TOF-MS:  $m/z = 1627.65$  (100%,  $[\text{M}+\text{Na}]^+$ , calcd for  $\text{C}_{106}\text{H}_{84}\text{O}_{12}\text{Si}_2\text{Na}$ : 1627.54), 1643.59 (30%,  $[\text{M}+\text{K}]^+$ , calcd for  $\text{C}_{106}\text{H}_{84}\text{O}_{12}\text{Si}_2\text{K}$ : 1643.51), 1605.61 (12%,  $[\text{M}]^+$ , calcd for  $\text{C}_{106}\text{H}_{85}\text{O}_{12}\text{Si}_2$ : 1605.56).

**Compound 26d.** Prepared from **18d** (0.288 g, 0.30 mmol) and obtained as a brown glassy product (102 mg, 20%). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) = 250 (132000), 318 (sh, 40700), 377 (sh, 11300), 399 (sh, 5200), 412 (4200), 423 (3500), 487 (2900), 573 (sh, 1300), 630 (sh, 500), 687 nm (sh, 150 M<sup>-1</sup>cm<sup>-1</sup>). IR (neat): 1742 (C=O), 1728 (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.77 (m, 2H), 4.43 (m, 6H), 3.66 (m, 8H), 1.82 (m, 4H), 1.70 (m, 4H), 1.50–1.19 (m, 32H), 0.93 (s, 36H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 163.9 (two peaks), 147.2, 147.0, 146.8, 146.6 (two peaks), 146.5, 146.4, 146.3 (two peaks), 146.0, 145.5, 145.4, 144.6, 144.3, 144.2, 143.9, 143.6, 143.4, 142.9, 142.5, 142.2 (two peaks), 141.9, 141.6, 140.3, 138.5, 137.8, 71.9, 71.6, 67.5, 67.3, 63.8, 63.7, 53.0, 32.8, 32.7, 29.0, 28.8, 28.7, 28.6, 27.9 (two peaks), 26.4, 26.0, 25.9, 25.6, 21.1 (two peaks) ppm. MALDI-TOF-MS:  $m/z$  = 1663.44 ([M+H]<sup>+</sup>, calcd for C<sub>110</sub>H<sub>93</sub>O<sub>12</sub>Si<sub>2</sub>: 1663.08), 1683.61 ([M+Na]<sup>+</sup>, calcd for C<sub>110</sub>H<sub>92</sub>O<sub>12</sub>Si<sub>2</sub>Na: 1683.60).

**Compound 27d.** Prepared from **18d** (0.288 g, 0.30 mmol) and obtained as a red-brown glassy product (150 mg, 30%). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) = 253 (135300), 309 (sh, 52000), 356 (sh, 20400), 397 (5300), 409 (sh, 3300), 421 (3050), 480 (3800), 619 nm (sh, 530 M<sup>-1</sup>cm<sup>-1</sup>). IR (neat): 1747 (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.68–4.46 (m, 4H), 4.35–4.19 (m, 4H), 3.82–3.74 (m, 6H), 3.67 (m, 2H), 1.76 (m, 8H), 1.53 (m, 8H), 1.49–1.13 (m, 24H), 0.99 (s, 9H), 0.98 (s, 9H), 0.97 (s, 9H), 0.93 (s, 9H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 163.9, 163.6, 163.5, 163.3, 148.6, 147.5, 147.3, 147.2, 146.5 (two peaks), 146.4, 146.2, 146.1 (two peaks), 146.0, 145.6, 145.5, 145.2, 145.1 (two peaks), 145.0 (two peaks), 144.8, 144.7 (two peaks), 144.6 (three peaks), 144.5, 144.3 (two peaks), 144.1, 144.0, 143.8 (two peaks), 143.7 (three peaks), 143.5, 143.3 (two peaks), 143.0 (two peaks), 142.7, 142.3, 142.2, 142.1, 141.9 (two peaks), 141.6, 141.5, 141.1, 140.8, 139.3, 138.6 (two peaks), 71.8, 70.4, 67.4, 67.3, 67.2, 63.9 (two peaks), 63.7, 63.6, 53.8, 51.9, 33.1, 32.8, 32.8, 32.7, 32.3, 29.5, 29.0, 28.7, 28.6 (two peaks), 28.4 (two peaks), 28.2, 27.9 (two peaks), 26.8, 26.0, 25.9, 25.8, 25.7, 25.5, 25.4, 21.2, 21.1 (two peaks) ppm. MALDI-TOF-MS:  $m/z$  = 1683.61 ([M+Na]<sup>+</sup>, calcd for C<sub>110</sub>H<sub>92</sub>O<sub>12</sub>Si<sub>2</sub>Na: 1683.60), 1663.64 ([M+H]<sup>+</sup>, calcd for C<sub>110</sub>H<sub>93</sub>O<sub>12</sub>Si<sub>2</sub>: 1663.08).

**Compound 26e.** Prepared from **18e** (0.280 g, 0.28 mmol) and obtained as a brown glassy product (79 mg, 16%). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) = 250 (137500), 318 (sh, 43200), 377 (sh, 13700), 399 (sh, 5300), 411 (4300), 423 (3400), 487 (2900), 573 (sh, 1300), 629 (sh, 540), 688 nm (sh, 160 M<sup>-1</sup>cm<sup>-1</sup>). IR (neat): 1751 (C=O), 1732 (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.73 (m, 2H), 4.41 (m, 6H), 3.70 (m, 8H), 1.82 (m, 4H), 1.69 (m, 4H), 1.50–1.19 (m, 40H), 0.95 (s, 36H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 163.9, 163.8, 147.2, 147.0, 146.8, 146.6, 146.5, 146.3 (two peaks), 146.1, 145.5, 145.4, 144.6, 144.4, 144.1, 143.8, 143.5, 143.4, 143.0, 142.5, 142.2, 141.9, 141.6, 140.4, 138.6, 138.4, 137.7, 71.8, 71.6, 67.5, 67.2, 63.8, 52.9, 32.9 (two peaks), 29.4 (two peaks), 29.1, 29.0, 28.7, 28.6, 27.9 (two peaks), 26.2, 26.0, 25.9, 25.7, 21.1 (two peaks) ppm. MALDI-TOF-MS:  $m/z$  = 1719.83 ([M+H]<sup>+</sup>, calcd for C<sub>114</sub>H<sub>101</sub>O<sub>12</sub>Si<sub>2</sub>: 1719.19).

**Compound 27e.** Prepared from **18e** (0.280 g, 0.28 mmol) and obtained as a red-brown glassy product (102 mg, 21%). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) = 253 (114000), 310 (sh, 43200), 357 (sh, 17000), 397 (4700), 409 (sh, 3000), 422 (2700), 481 (3200), 620 nm (sh, 440 M<sup>-1</sup>cm<sup>-1</sup>). IR (neat):  $\nu$  = 1744 (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.63–4.23 (m, 8H), 3.79 (m, 4H), 3.69 (t,  $J$  = 7 Hz, 4H), 1.75 (m, 8H), 1.48–1.13 (m, 40H), 1.00 (s, 9H), 0.99 (s, 9H), 0.96 (s, 9H), 0.94 (s, 9H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 163.9, 163.6, 163.4, 148.5, 147.5, 147.3, 147.2, 146.4 (two peaks), 146.2, 146.1 (two peaks), 146.0, 145.6, 145.5, 145.3, 145.2 (two peaks), 145.0, 144.9, 144.8, 144.7 (two peaks), 144.6, 144.5, 144.4, 144.2, 144.1, 144.0 (two peaks), 143.8, 143.7, 143.5, 143.3 (two peaks), 142.9 (two peaks), 142.8, 142.6, 142.3, 142.0, 141.9, 141.6, 141.5, 141.2, 140.8, 138.9 (two peaks), 138.6 (two peaks), 71.9, 71.6, 70.4, 67.4, 67.3, 67.2, 63.9, 63.8, 63.5, 53.8, 51.9, 33.1, 32.9, 32.8, 29.7, 29.4, 29.3 (two peaks), 29.2 (two peaks), 28.9 (two peaks), 28.8, 28.7, 28.4 (two peaks), 27.9, 26.5, 26.3, 26.0, 25.7, 25.6 (two peaks), 25.0 (two peaks), 21.1

(three peaks) ppm. MALDI-TOF-MS:  $m/z$  = 1718.00 ([M+H]<sup>+</sup>, calcd for C<sub>114</sub>H<sub>101</sub>O<sub>12</sub>Si<sub>2</sub>: 1718.69).

**General procedure for the desilylation of bis-adducts.** BF<sub>3</sub>·OEt<sub>2</sub> (10–15 eq.) was added to a solution of the appropriate bis-adducts (**25a**, **26b-e** or **27b-e**, 1 eq.) in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (2:1). The resulting mixture was stirred at rt overnight, then filtered through a plug (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 95:5) and concentrated. Column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH) gave the corresponding bis-adducts **28a**, **29b-e** or **30b-e**.

**Compound 28a.** Prepared from **25a** (77 mg, 52  $\mu$ mol) and obtained as an orange-brown glassy product (55 mg, 88%). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) = 257 (147000), 321 (sh, 45000), 379 (sh, 15100), 438 (4100), 470 (sh, 3500), 623 nm (sh, 450 M<sup>-1</sup>cm<sup>-1</sup>). IR (neat): 3340 (br, OH), 1741 (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.40 (m, 8H), 3.68 (m, 8H), 1.96–1.62 (m, 16H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 163.4, 163.1, 148.4, 147.4 (two peaks), 147.3, 146.2, 145.9 (two peaks), 145.8, 145.7, 145.4, 145.3, 145.1, 145.0, 144.7, 144.4 (two peaks), 144.2, 143.7, 143.6, 143.4, 142.5, 142.4, 141.3, 141.0, 139.7, 137.8, 137.1, 136.7, 135.2, 70.5, 67.7, 67.1, 62.2, 62.1, 49.6, 29.2, 29.1, 25.1, 25.0 ppm. MALDI-TOF-MS:  $m/z$  = 1212.44 ([M]<sup>+</sup>, calcd for C<sub>82</sub>H<sub>36</sub>O<sub>12</sub>: 1212.22).

**Compound 29b.** Prepared from **26b** (118 mg, 76  $\mu$ mol) and obtained as a brown glassy product (78 mg, 81%). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) = 249 (126000), 318 (sh, 46000), 377 (sh, 11300), 399 (sh, 5000), 411 (4200), 422 (3400), 488 (2900), 573 (sh, 1300), 630 (sh, 540), 687 nm (sh, 160 M<sup>-1</sup>cm<sup>-1</sup>). IR (neat): 3326 (br, OH), 1737 (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.52 (t,  $J$  = 7 Hz, 4H), 4.42 (2t,  $J$  = 7 Hz, 4H), 3.68 (t,  $J$  = 7 Hz, 4H), 3.62 (t,  $J$  = 7 Hz, 4H), 1.90 (m, 4H), 1.80 (m, 4H), 1.75 (OH, 4H), 1.65–1.47 (m, 16H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 163.6 (two peaks), 147.2, 147.0, 146.6, 146.5, 146.4 (two peaks), 146.1, 146.0, 145.6, 145.5, 145.3, 144.6, 144.4, 144.2, 143.8, 143.5, 143.4, 143.0, 142.5, 142.2, 142.1, 141.9, 141.6, 140.3, 139.1, 138.4, 71.8, 71.3, 67.3, 67.2, 62.5 (two peaks), 51.8, 32.2, 32.1, 28.4, 28.3, 22.4, 22.3 ppm. MALDI-TOF-MS:  $m/z$  = 1268.35 (100%, [M]<sup>+</sup>, calcd for C<sub>86</sub>H<sub>44</sub>O<sub>12</sub>: 1268.28), 1291.34 (27%, [M+Na]<sup>+</sup>, calcd for C<sub>86</sub>H<sub>44</sub>O<sub>12</sub>Na: 1291.27).

**Compound 30b.** Prepared from **27b** (82 mg, 53  $\mu$ mol) and obtained as a red-brown glassy product (57 mg, 85%). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) = 248 (123000), 309 (sh, 48200), 356 (sh, 20300), 397 (5000), 409 (sh, 3100), 421 (3000), 481 (3700), 620 nm (sh, 500 M<sup>-1</sup>cm<sup>-1</sup>). IR (neat): 3339 (br, OH), 1739 (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.43 (m, 8H), 3.64 (m, 8H), 1.85 (m, 12H), 1.60 (m, 8H), 1.51 (m, 8H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 163.7, 163.6, 163.5, 147.5, 147.2, 146.4, 146.1 (two peaks), 145.6, 145.3, 145.1, 145.0, 144.7 (two peaks), 144.6, 144.3 (two peaks), 144.2, 144.0, 143.7 (two peaks), 143.4, 143.1, 142.9, 142.8, 142.3, 141.9, 141.6 (two peaks), 138.9, 138.7, 71.7, 71.6, 70.4, 67.3, 67.2, 62.5, 53.7, 53.44, 51.5, 32.2, 32.1, 28.3, 22.3 (two peaks) ppm. MALDI-TOF-MS:  $m/z$  = 1268.47 ([M]<sup>+</sup>, calcd for C<sub>86</sub>H<sub>44</sub>O<sub>12</sub>: 1268.28).

**Compound 29c.** Prepared from **26c** (96 mg, 60  $\mu$ mol) and obtained as a brown glassy product (71 mg, 89%). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) = 249 (131000), 319 (sh, 39200), 377 (sh, 11400), 399 (sh, 4800), 411 (4000), 423 (3300), 489 (2800), 575 (sh, 1300), 631 (sh, 520), 689 nm (sh, 160 M<sup>-1</sup>cm<sup>-1</sup>). IR (neat): 3325 (br, OH), 1741 (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.51 (t,  $J$  = 7 Hz, 4H), 4.40 (t,  $J$  = 7 Hz, 4H), 3.66 (t,  $J$  = 6 Hz, 4H), 3.62 (t,  $J$  = 6 Hz, 4H), 1.91–1.73 (m, 12H), 1.65–1.38 (m, 20H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 163.6 (two peaks), 147.2, 147.0, 146.6, 146.5 (two peaks), 146.4, 146.2, 146.1, 145.6, 145.5, 145.4, 144.7, 144.4, 144.2, 143.9, 143.6, 143.4, 143.1, 142.6, 142.2, 142.1, 142.0, 141.7, 140.4, 139.2, 138.5, 71.8, 71.3, 67.4, 67.3, 62.8 (two peaks), 51.8, 32.6 (two peaks), 28.6, 28.5, 25.9, 25.8, 25.5, 25.4 ppm. MALDI-TOF-MS:  $m/z$  = 1324.38 ([M]<sup>+</sup>, calcd for C<sub>90</sub>H<sub>52</sub>O<sub>12</sub>: 1324.35).

**Compound 30c.** Prepared from **27c** (82 mg, 51  $\mu$ mol) and obtained as a red-brown glassy product (54 mg, 80%). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) = 252 (132800), 310 (sh, 50000), 358 (sh, 19400), 397 (sh, 5000), 409 (3000), 421 (2900), 480 (3600), 620 nm (sh, 500 M<sup>-1</sup>cm<sup>-1</sup>). IR (neat): 3338 (br,

OH), 1741 (C=O)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.42 (m, 8H), 3.64 (m, 8H), 1.81 (m, 8H), 1.58 (m, 8H), 1.51–1.38 (m, 12H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 163.7, 163.6 (two peaks), 147.6, 147.3, 146.5, 146.2, 146.1, 145.6, 145.4, 145.2, 145.1, 144.7 (two peaks), 144.6, 144.4 (two peaks), 144.2, 144.1, 143.8, 143.7, 143.5, 143.2, 143.0, 142.4, 141.9, 141.6 (two peaks), 138.9, 138.7, 71.7, 71.6, 70.4, 67.3, 62.7, 53.7, 51.5, 32.6 (two peaks), 28.5 (two peaks), 28.4, 25.8 (two peaks), 25.7, 25.4 (two peaks), 25.3 ppm. MALDI-TOF-MS:  $m/z$  = 1324.45 (100%,  $[\text{M}]^+$ , calcd for  $\text{C}_{90}\text{H}_{52}\text{O}_{12}$ : 1324.34), 1347.35 (15%,  $[\text{M}+\text{Na}]^+$ , calcd. for  $\text{C}_{90}\text{H}_{52}\text{O}_{12}\text{Na}$ : 1347.34), 1363.26 (20%,  $[\text{M}+\text{K}]^+$ , calcd for  $\text{C}_{90}\text{H}_{52}\text{O}_{12}\text{K}$ : 1363.31).

**Compound 29d.** Prepared from **26d** (70 mg, 42  $\mu\text{mol}$ ) and obtained as a brown glassy product (38 mg, 66%). UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 249 (137000), 317 (sh, 43000), 378 (sh, 11300), 399 (sh, 5300), 411 (4400), 421 (3400), 487 (3000), 577 (sh, 1300), 632 (sh, 530), 688 nm (sh, 160  $\text{M}^{-1}\text{cm}^{-1}$ ). IR (neat): 3336 (br, OH), 1743 (C=O)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.51 (t,  $J$  = 7 Hz, 4H), 4.40 (t,  $J$  = 7 Hz, 4H), 3.65 (t,  $J$  = 7 Hz, 4H), 3.62 (t,  $J$  = 7 Hz, 4H), 1.87 (m, 4H), 1.77 (m, 4H), 1.56 (m, 16H), 1.43–1.34 (m, 20H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 163.6 (two peaks), 147.2, 146.9, 146.5 (two peaks), 146.4, 146.1, 146.0, 145.6, 145.5, 145.3, 144.6, 144.4, 144.1, 143.8, 143.5 (two peaks), 143.4, 143.0, 142.5, 142.2, 142.1, 141.9, 140.6, 140.3, 139.1, 138.4, 71.8, 71.4, 67.4, 67.3, 62.8 (two peaks), 51.9, 32.6 (two peaks), 29.0 (two peaks), 28.6, 28.5, 25.9 (two peaks), 25.8, 25.7 ppm. MALDI-TOF-MS:  $m/z$  = 1380.40 ( $[\text{M}]^+$ , calcd for  $\text{C}_{94}\text{H}_{60}\text{O}_{12}$ : 1380.41).

**Compound 30d.** Prepared from **27d** (95 mg, 57  $\mu\text{mol}$ ) and obtained as a red-brown glassy product (55 mg, 70%). UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 252 (142500), 309 (sh, 55100), 357 (sh, 21500), 397 (5300), 409 (sh, 3400), 421 (3100), 481 (3800), 619 nm (sh, 550  $\text{M}^{-1}\text{cm}^{-1}$ ). IR (neat): 3316 (br, OH), 1741 (C=O)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.40 (m, 8H), 3.64 (m, 8H), 1.79 (m, 8H), 1.58 (m, 12H), 1.48–1.34 (m, 24H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 163.6, 163.5, 147.6, 147.2, 146.4, 146.1, 146.0, 145.5, 145.3, 145.1, 145.0, 144.7 (two peaks), 144.6, 144.4 (two peaks), 144.1, 144.0, 143.7 (two peaks), 143.4, 143.3, 143.1, 142.9, 142.3, 141.9, 141.6, 141.5, 138.7, 138.6, 71.7, 70.5, 67.3, 62.8, 53.7, 51.5, 32.6, 28.9 (two peaks), 28.5, 25.8 (two peaks), 25.9, 25.8, 25.7 ppm. MALDI-TOF-MS:  $m/z$  = 1380.36 ( $[\text{M}]^+$ , calcd for  $\text{C}_{94}\text{H}_{60}\text{O}_{12}$ : 1380.41).

**Compound 29e.** Prepared from **26e** (60 mg, 35  $\mu\text{mol}$ ) and obtained as a brown glassy product (28 mg, 56%). UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 249 (127200), 319 (sh, 39500), 377 (sh, 11000), 399 (sh, 5200), 411 (4300), 422 (3400), 488 (2900), 576 (sh, 1220), 633 (sh, 500), 688 nm (sh, 150  $\text{M}^{-1}\text{cm}^{-1}$ ). IR (neat): 3330 (br, OH), 1746 (C=O)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.51 (t,  $J$  = 7 Hz, 4H), 4.40 (t,  $J$  = 7 Hz, 4H), 3.64 (t,  $J$  = 7 Hz, 4H), 3.63 (t,  $J$  = 7 Hz, 4H), 1.86 (m, 4H), 1.77 (m, 4H), 1.56 (m, 16H), 1.43–1.31 (m, 28H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 163.6 (two peaks), 147.2, 146.9, 146.5, 146.4 (two peaks), 146.2, 146.0, 145.6, 145.5, 145.3, 144.6, 144.4, 144.1, 143.8, 143.5 (two peaks), 143.4, 143.0, 142.5, 142.2, 142.1, 141.9, 141.6, 140.3, 139.1, 138.4, 71.8, 71.4, 67.4, 67.3, 62.9 (two peaks), 51.9, 32.7 (two peaks), 29.4 (two peaks), 29.2 (two peaks), 28.6, 28.5, 26.0, 25.9, 25.7 (two peaks) ppm. MALDI-TOF-MS:  $m/z$  = 1436.46 ( $[\text{M}]^+$ , calcd for  $\text{C}_{98}\text{H}_{68}\text{O}_{12}$ : 1436.47).

**Compound 30e.** Prepared from **27e** (73 mg, 43  $\mu\text{mol}$ ) and obtained as a red-brown glassy product (50 mg, 82%). UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 252 (117000), 309 (sh, 46600), 357 (sh, 17900), 397 (sh, 4500), 409 (sh, 2900), 421 (2700), 478 (3300), 630 nm (sh, 310  $\text{M}^{-1}\text{cm}^{-1}$ ). IR (neat): 3330 (br, OH), 1741 (C=O)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.40 (m, 8H), 3.64 (m, 8H), 1.79 (m, 8H), 1.58 (m, 12H), 1.45–1.34 (m, 32H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 163.6 (two peaks), 163.5, 147.6, 147.2, 146.4, 146.1, 146.0, 145.5, 145.3, 145.1, 145.0, 144.7, 144.6, 144.5, 144.4, 144.0 (two peaks), 143.8, 143.7, 143.4, 143.3, 143.2, 142.9, 142.3, 141.8, 141.6, 141.5, 138.6, 71.7, 70.4, 67.3, 62.9, 53.7, 51.5, 32.7, 29.3 (two peaks), 29.2 (two peaks), 29.1, 28.5 (two peaks), 28.4, 25.9 (two

peaks), 25.8, 25.7 (two peaks), 25.6 ppm. MALDI-TOF-MS:  $m/z$  = 1436.26 ( $[\text{M}]^+$ , calcd for  $\text{C}_{98}\text{H}_{68}\text{O}_{12}$ : 1436.47).

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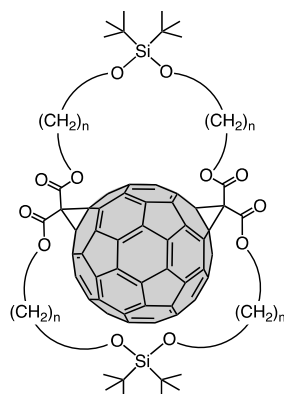
**Keywords:** Bingel reaction • Fullerene • Macrocyclic • Regiochemistry • Silyl protecting groups

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A series of macrocyclic bis-malonates incorporating cleavable di-*tert*-butylsilylene subunits have been prepared and used for the regioselective bis-functionalization of [60]fullerene by double Bingel cyclopropanations. Upon functionalization of the fullerene sphere, the bridging di-*tert*-butylsilylene groups have been cleaved to afford the corresponding acyclic fullerene bis-adducts bearing four alcohol functions.

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