Optically Active Macrocyclic *cis-3* Bis-Adducts of C_{60}: Regio- and Stereoselective Synthesis, Exciton Chirality Coupling, and Determination of the Absolute Configuration, and First Observation of Exciton Coupling between Fullerene Chromophores in a Chiral Environment

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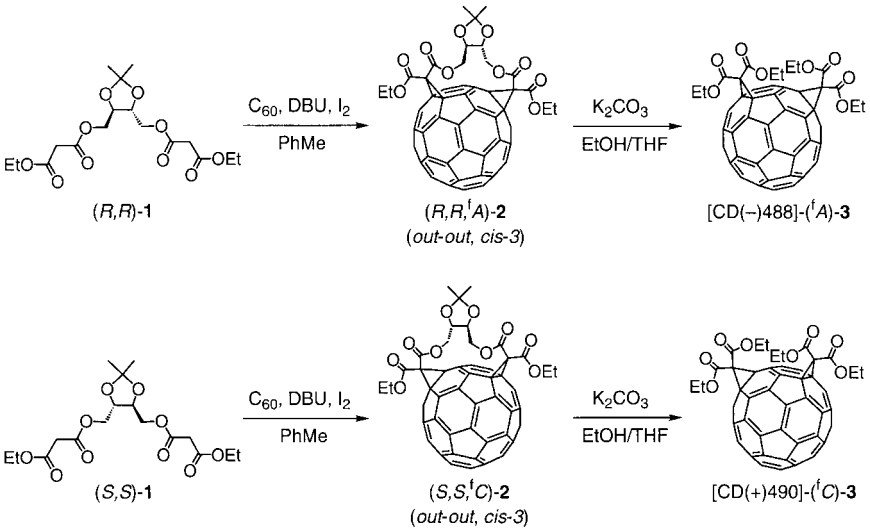
A series of optically active *cis-3* bis-adducts, such as (*R*,*R*,^{f}*C*)-**16** (*Scheme 6*), was obtained regio- and diastereoselectively by *Bingel* macrocyclization of C_{60} with bis-malonates, which contain optically active tethers derived from 1,2-diols. The absolute configuration of the inherently chiral addition pattern in *cis-3* bis-adducts had previously been determined by comparison of calculated and experimental circular dichroism (CD) spectra. Full confirmation of these earlier assignments was now obtained by an independent method based on semiempirical AM1 ('Austin Model 1') and OM2 ('Orthogonalization Method 2') calculations combined with ^{1}H-NMR spectroscopy. It was found computationally that bis-malonates $[CHR(OCOCH_2COOEt)]_2$, which contain (*R*,*R*)- or (*S*,*S*)-butane-2,3-diol derivatives as optically active tethers, preferentially form *out-out cis-3* bis-adducts of C_{60} as a single diastereoisomer in which the alkyl groups R adopt a *gauche* conformation, while the two glycolic H-atoms are in an *antiperiplanar* (*ap*) and the ester linkages to the fullerene in a *gauche* relationship (*Figs. 2* and *5*). In contrast, in the less favorable diastereoisomer, which should not form, the alkyl groups R adopt an *ap* and the H-atoms a *gauche* conformation, while the ester bridges to the fullerene remain, for geometric reasons, locked in a *gauche* conformation. According to the OM2 calculations, the geometry of the fully staggered tether in the free bis-malonates closely resembles the conformation of the tether fragment in the bis-adducts formed. These computational predictions were confirmed experimentally by the measurement of the coupling constant between the vicinal glycolic H-atoms in the ^{1}H-NMR spectrum. For (*R*,*R*,^{f}*C*)-**16**, ^{3}J(H,H) was determined as 7.9 Hz, in agreement with the *ap* conformation, and, in combination with the calculations, this allowed assignment of the ^{f}*C*-configuration to the inherently chiral addition pattern. This conformational analysis was further supported by the regio- and diastereoselective synthesis of *cis-3* bis-adducts from bis-malonates, including tethers derived from cyclic glycol units with a fixed *gauche* conformation of the alkyl residues R at the glycolic C-atoms. Thus, a bis-malonate of (*R*,*R*)-cyclohexane-1,2-diol provided exclusively *cis-3* bis-adduct (*R*,*R*,^{f}*C*)-**20** in 32% yield (*Scheme 7*). Incorporation of a tether derived from methyl 4,6-*O*,*O*-benzylidene-α-D-glucopyranoside into the bis-malonate and *Bingel* macrocyclization diastereoselectively produced the *cis-3* stereoisomer (α,D,^{f}*A*)-**22** (*Scheme 8*) as the only macrocyclic bis-adduct. If the geometry of the alkyl groups R at the glycolic C-atoms of the tether component deviates from a *gauche* relationship, as in the case of tethers derived from *exo cis*- and *trans*-norbornane-2,3-diol or from *trans*-cyclopentane-1,2-diol, hardly any macrocyclic product is formed (*Schemes 5* and *9*). The absolute configurations of the various optically active *cis-3* bis-adducts were also assigned by comparison of their CD spectra, which are dominated by the chiroptical contributions of the inherently chiral fullerene chromophore (*Figs. 1*, *3*, and *4*). A strong chiral exciton coupling was observed for optically active macrocyclic *cis-3* bis-adducts of C_{60} with two appended 4-(dimethylamino)benzoate ((*S*,*S*,^{f}*C*)-**26**; *Fig. 6*) or *meso*-tetraphenylporphyrin ((*R*,*R*,^{f}*C*)-**28**; *Fig. 7*) chromophores. Chiral exciton coupling between two fullerene chromophores was observed for the first time in the CD spectrum of the threitol-bridged bis-fullerene (*R*,*R*)-**35** (*Fig. 9*).

1. Introduction. – With the introduction of the tether-directed remote-functionalization methodology [1][2] – a versatile strategy for the regio- and stereoselective formation of multiple adducts of C_{60} – *cis-3* bis-adducts of the C-sphere (for the nomenclature of bis-adduct isomers, see [3]) have been prepared and studied in

increasing numbers. A particular interest in such compounds was derived from the fact that the *cis-3* addition pattern is inherently chiral [3][4]. Thus, we reported an enantioselective synthesis of optically active *cis-3* bis-adducts in which the chirality results exclusively from the addition pattern [5]. Starting from (*R*,*R*)-**1** and (*S*,*S*)-**1**, which were prepared from the corresponding optically pure diols and ethyl 2-(chlorocarbonyl)acetate, the two enantiomeric *cis-3* bis-adducts, (*R*,*R*,^{f}*A*)-**2** and (*S*,*S*,^{f}*C*)-**2** (for the definition of the configurational descriptors ^{f}*C* and ^{f}*A*, see [6])[1]), respectively, were obtained with high diastereoselectivity (diastereoisomeric excess (de) > 97%; *Scheme 1*). In each *Bingel* macrocyclization, two diastereoisomeric *out-out cis-3* adducts can possibly form due to the chirality of both the tether and the newly generated addition pattern; however, the high asymmetric induction by the optically active bis-malonates in the second (intramolecular) addition step led to the formation of (*R*,*R*,^{f}*A*)-**2** and (*S*,*S*,^{f}*C*)-**2** only. Transesterification finally yielded the *cis-3* tetraethyl esters [CD(−)488]-(^{f}*A*)-**3** and [CD(+)490]-(^{f}*C*)-**3** with an enantiomeric excess (ee) higher than 99% ((^{f}*A*)-**3**) and 97% ((^{f}*C*)-**3**) (HPLC), reflecting the ee's of the corresponding commercial starting diols.

Scheme 1. *Synthesis of [CD(−)488]-(^{f}A)-***3** *and [CD(+)490]-(^{f}C)-***3** *by Diastereoselective Tether-Directed Bis-Cyclopropanation of C_{60}, Followed by Transesterification* [5]



Two other examples of the formation of optically active *cis-3* bis-adducts (in which the chirality results exclusively from the addition pattern) by highly diastereoselective macrocyclizations using non-racemic tethers, followed by removal of the tether, have been reported by *Nakamura* and co-workers [7], and *Nishimura* and co-workers [8]. The former group used a double [3 + 2] cycloaddition of tethered vinylcarbenes, whereas the latter performed a double *Diels-Alder* addition with a tethered bis(*o*-

[1]) The configuration of C_{60} and C_{70} derivatives with a chiral functionalization pattern can easily be determined *via* the interactive webpage 'www.diederich.chem.ethz.ch/chirafull'.

quinodimethane). In this paper, we explore the structural requirements for chiral, non-racemic tethers derived from 1,2-diols to induce high diastereoselectivity in the *Bingel* macrocyclization leading to optically active *cis-3* bis-adducts of C_{60}.

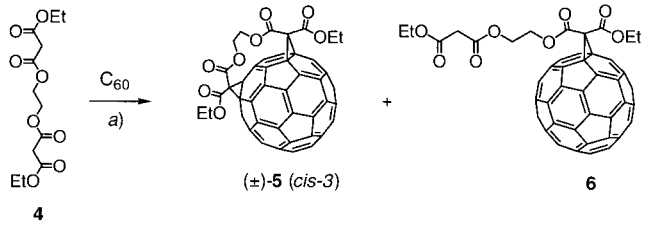
A major challenge in fullerene chemistry represents the assignment of the absolute configuration of inherently chiral fullerenes and their derivatives, as well as of fullerene adducts with an inherently chiral addition pattern. Straightforward experimental methods for assigning absolute configurations of these compounds are currently not available, and efforts to obtain X-ray-quality crystals have failed. Therefore, the determination of the absolute configuration relies on the theoretical calculation of the circular dichroism (CD) spectrum for one enantiomer and comparison with the experimental CD data [7c][9–11] (for the designation of enantiomers using CD data, see [12]). The absolute configuration of the optically active fullerene derivatives shown in *Scheme 1* was assigned this way [9]. Here, we report an independent determination of the absolute configuration of *cis-3* bis-adducts using ^{1}H-NMR spectroscopy in combination with computer-assisted calculations (for a related approach, see [8b]). In addition, first examples of chiral exciton coupling in fullerene chemistry are described. In particular, we show that two tethered C_{60} mono-adduct units in a chiral environment are suitable chromophores to display exciton coupling. Computer-assisted calculations of the sign and amplitude of the *Cotton* effects in the CD spectra featuring chiral exciton coupling could provide another independent determination of the absolute configuration of the inherently chiral addition pattern in *cis-3* bis-adducts of C_{60} [13][14].

2. Results and Discussion. – 2.1. *cis-3 Bis-Adducts by* Bingel *Macrocyclization with Bis-malonates Containing 1,2-Diol-Derived Tethers: Initial Studies.* In our first regio- and diastereoselective *Bingel* [15] macrocyclization to give *cis-3* bis-adducts, we had used bis-malonates containing the cyclic, conformationally rather rigid threitol derivatives (4*R*,5*R*)- and (4*S*,5*S*)-4,5-bis(hydroxymethyl)-2,2-dimethyl-1,3-dioxolane, respectively, as tethers (*Scheme 1*) [5]. Work by *Nakamura* and co-workers [7], and *Nishimura* and co-workers [8] suggested that less rigid, acyclic tethers were also suitable to achieve regioselective bis-functionalization. Therefore, we explored the use of conformationally more flexible but shorter, glycol-type tethers in the *Bingel* macrocyclization leading to *cis-3* bis-adducts.

When bis-malonate **4**, featuring a short ethane-1,2-diol-derived tether, was reacted with C_{60} in the presence of an excess of I_2 and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), *cis-3* bis-adduct (±)-**5** was isolated in 12% yield besides mono-adduct **6** (13%; *Scheme 2*). The reaction was quite regioselective, and no macrocyclic *cis-2* bis-adduct was detected despite the short tether length. However, the rather low yield of (±)-**5** and the isolation of its direct precursor, mono-adduct **6**, indicated that the ethane-1,2-diyl linker was not ideal for inducing formation of *cis-3* bis-adducts. In all previous *Bingel* macrocyclizations [1][5], we had been unable to isolate similar mono-adducts, due to their high propensity to undergo the second addition under formation of macrocyclic bis-adducts.

In the next step, we intended to introduce stereogenic centers into the 1,2-diol-derived tether to make the bis-addition diastereoselective. Readily available derivatives of L-tartaric acid, however, failed to give satisfactory results. The reaction of bis-

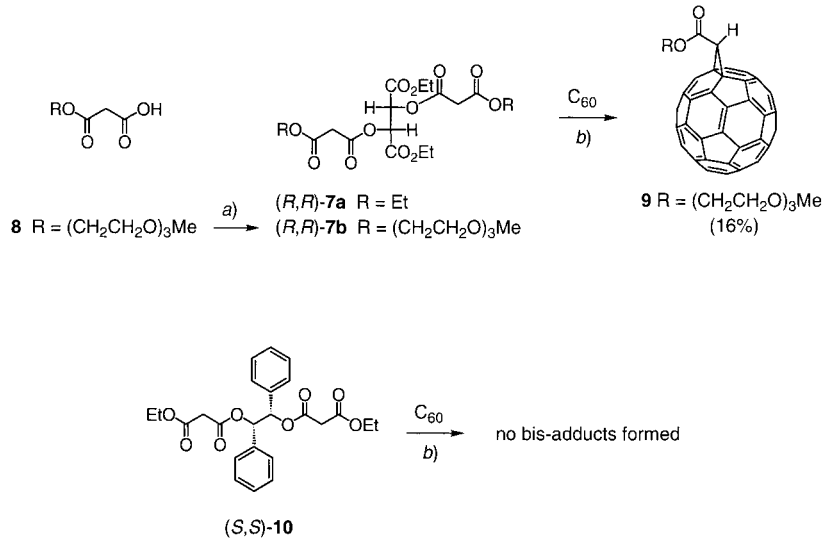
Scheme 2. Bingel *Macrocyclization with a Bis-malonate Containing a Tether Derived from Ethane-1,2-diol*



a) DBU, I_2, PhMe, 20°, 12 h; 12% ((±)-**5**); 13% (**6**).

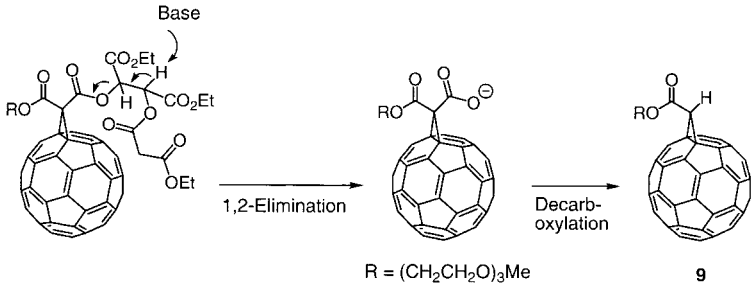
malonate (*R*,*R*)-**7a** (*Scheme 3*) provided a mono-adduct (according to UV/VIS spectroscopy [16]), which was quite insoluble in common solvents such as PhMe or CH_2Cl_2 and, therefore, difficult to isolate. To enhance the solubility, bis-malonate (*R*,*R*)-**7b** was prepared from **8**, which, in turn, was formed from triethyleneglycol monomethyl ether and 2,2-dimethyl-1,3-dioxane-4,6-dione. When (*R*,*R*)-**7b** was reacted with C_{60}, the more soluble mono-ester **9** was isolated as the only major product in 16% yield. Apparently, decomposition of bis-malonates (*R*,*R*)-**7a** and (*R*,*R*)-**7b** after the first addition step is faster than the second, intramolecular cyclopropanation of the C-sphere. This decomposition could possibly occur by a mechanism similar to the one proposed in *Scheme 4*. We presume that the second addition step is disfavored, as compared to base-induced decomposition, since the

Scheme 3. *Attempted* Bingel *Macrocyclizations with Bis-malonates Containing Tethers Derived from* L*-Tartrate or* (S,S)*-Dihydrobenzoin*



a) Diethyl (*R*,*R*)-tartrate, *N*,*N*′-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), THF, 12 h, 0° → 20°; 60%. *b*) DBU, I_2, PhMe, 20°, 12 h; 16%.

Scheme 4. *Possible Mechanism for Formation of Mono-Adduct* **9**

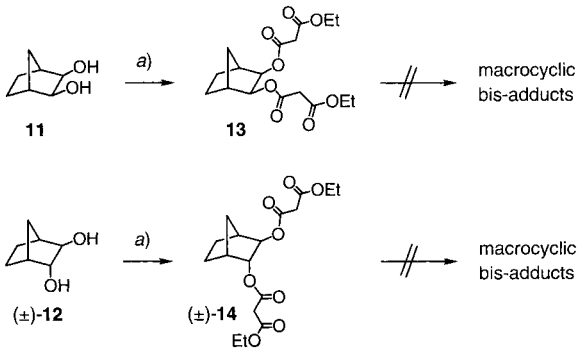


tartrate tether, with its bulky ester groups, may be unable to adopt a favorable conformation for macrocyclization.

Similar to the ester groups in the tartrate derivatives (*R*,*R*)-**7a** and (*R*,*R*)-**7b**, bulky Ph residues attached to the glycol-derived tether prevent a successful *Bingel* macrocyclization. Thus, bis-malonate (*S*,*S*)-**10**, prepared from (*S*,*S*)-dihydrobenzoin did not yield any bis-adducts upon reaction with C_{60} (*Scheme 3*).

We subsequently explored the use of rigid cyclic 1,2-diol-derived tethers in which the two OH groups are locked in a specific conformation. For this purpose, the *exo-cis*- and the *trans*-norbornane-2,3-diols **11** and (±)-**12** [17] were converted to bis-malonates **13** and (±)-**14**, respectively (*Scheme 5*). However, both **13** (with the two malonates in *synperiplanar* eclipsed conformation) and (±)-**14** (*anticlinal* eclipsed) failed to undergo efficient double *Bingel* addition, and only traces of bis-adducts were isolated.

Scheme 5. *Synthesis of Bis-malonates* **13** *and (±)-*__14__, *Which Failed to Undergo* Bingel *Macrocyclization with* C_{60}

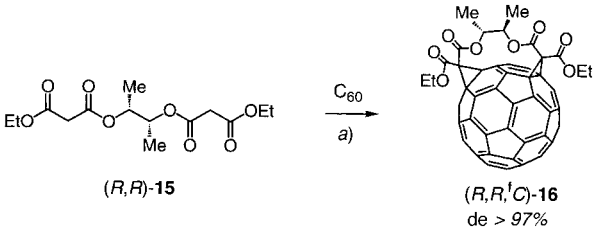


a) $EtOOCCH_2COCl$, pyridine, CH_2Cl_2, 0° → 20°, 12 h; 15% (**13**), 65% ((±)-**14**).

We then returned to conformationally more flexible tethers and explored the use of chiral butane-2,3-diols. Gratifyingly, the corresponding spacers led to a breakthrough. Starting from (*R*,*R*)- and (*S*,*S*)-butane-2,3-diol, bis-malonates (*R*,*R*)-**15** and (*S*,*S*)-**15** were prepared and reacted with C_{60} under the conditions of the *Bingel* macrocyclization. The conversion occurred with complete regio- and diastereoselectivity (de > 97%, HPLC) to yield the enantiomeric *cis-3* derivatives (*R*,*R*,^{f}*C*)-**16** and (*S*,*S*,^{f}*A*)-**16**, respectively, as the only isolable bis-adducts (*Scheme 6*). Since the chiroptical

contribution of side chains with stereogenic centers to the *Cotton* effects of fullerene derivatives with inherently chiral π-chromophores is almost negligible [4][18], the absolute configuration of the *cis-3* addition pattern in the two enantiomers could be identified by comparison of their CD spectra with those of (^{f}A)-**3** and (^{f}C)-**3** (*Fig. 1*). This configurational assignment is strongly supported by the experiments described below.

Scheme 6. *Regio- and Diastereoselective* Bingel *Macrocyclization of C_{60} with a Bis-malonate Containing a Tether Derived from (*R,R*)-Butane-2,3-diol*



(*R,R*)-**15** (*R,R,*^{f}C)-**16**
de > 97%

a) I_2, DBU, PhMe, 20°, 1.5 h; 24%.

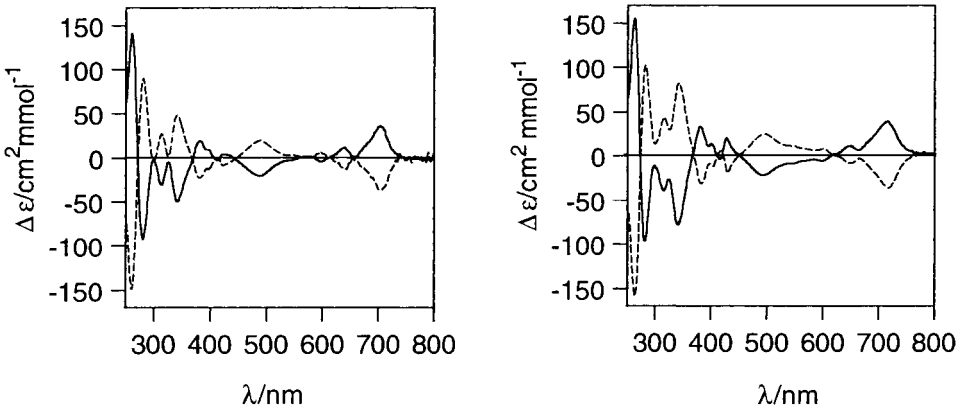


Fig. 1. *Experimental CD spectra in CH_2Cl_2 of [CD(−)488]-(*^{f}A*)-***3** (——) *and [CD(+)490]-(*^{f}C*)-***3** (– – –) (left) *and [CD(−)490]-(*S,S,^{f}A*)-***16** (——) *and [CD(+)491]-(*R,R,^{f}C*)-***16** (– – –) (right)

Remarkably, only traces of *cis-2* bis-adducts were formed in the double addition of (*R*,*R*)-**15** and (*S*,*S*)-**15** to C_{60}, despite the short length of the 1,2-diol tethers. This contrasts with the *Bingel* macrocyclization of bis-malonates (*R*,*R*)-**1** and (*S*,*S*)-**1** with the longer 1,4-diol- (threitol-) derived tethers, which had provided *cis-2* bis-adducts as the major products in *ca.* 20% yield in addition to the *cis-3* derivatives (*R*,*R*,^{f}A)-**2** and (*S*,*S*,^{f}C)-**2** (*Scheme 1*). To explain the remarkable selectivity in the double addition of bis-malonates with (*R*,*R*)- and (*S*,*S*)-butane-2,3-diol-derived tethers, computer-assisted calculations were undertaken.

2.2. *Computer Modeling to Rationalize the Regio- and Stereoselectivity of the* Bingel *Macrocyclization of (*R,R*)-***15** *and (*S,S*)-***15**. First calculations were performed with the program SPARTAN V. 4.0 [19] using the semiempirical AM1 ('Austin Model 1')

method [20]. In the modeling, the absolute configuration of the *cis-3* bis-addition pattern was fixed as (*ʳC*). (*S*,*S*)- and (*R*,*R*)-butane-2,3-diol-derived tethers were chosen, but the two *out-out* COOEt groups were replaced with H-atoms in order to simplify the computations. The two modeled compounds (*S*,*S*,*ʳC*)-**17** and (*R*,*R*,*ʳC*)-**18** (*Fig. 2*) are diastereoisomers; they are enantiomeric to (*R*,*R*,*ʳA*)-**17** and (*S*,*S*,*ʳA*)-**18**, respectively, which were, therefore, not considered in the calculations. The calculations were performed under the assumption that the product stabilities would be reflected in the transition states of the second addition step (the macrocyclization step) that determines the absolute configuration of the addition pattern (for other computational approaches to predict the regio- and stereoselectivity of tether-directed remote functionalizations of C_{60}, see [8b][21]). Such assumptions must be considered with caution since the *Bingel* cyclopropanation has been shown to be a kinetically controlled reaction [18b][22].

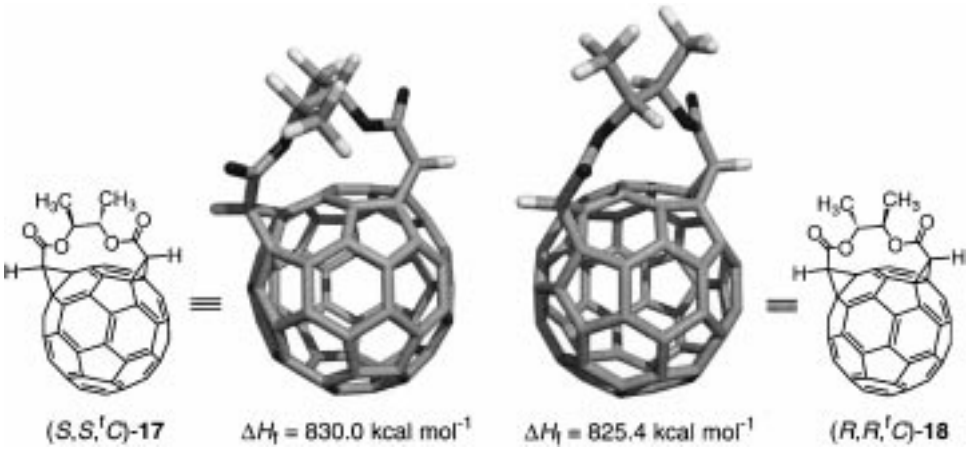


Fig. 2. *AM1-Optimized geometries and calculated heats of formation* ΔH_f [kcal mol^{-1}] *of the two diastereoisomeric bis-adducts (*S,S,*ʳ*C)-**17** *and (*R,R,*ʳ*C)-**18**. The OM2-generated geometries are very similar.

The AM1 calculations provided optimized geometries and heats of formation ΔH_f for the bis-adducts. In agreement with the experimental findings, they suggested that the (*R*,*R*)-configured butane-2,3-diol-derived tether would prefer incorporation into the (*ʳC*)-configured *cis-3* bis-adduct (*R*,*R*,*ʳC*)-**18**, which was calculated to be more stable ($\Delta\Delta H_f = 4.6$ kcal mol^{-1}) than (*S*,*S*,*ʳC*)-**17** (or its enantiomer (*R*,*R*,*ʳA*)-**17**). In both diastereoisomers, the tether adopts a staggered conformation, and the ester fragments connecting it to the fullerene are in a *gauche* alignment. We assume that this conformational array of the bridging ester residues is imposed mainly by steric constraints in the twelve-membered ring and less by the well-known *gauche* effect [23]. In the calculated more-stable diastereoisomer (*R*,*R*,*ʳC*)-**18**, the Me groups in the tether adopt a *gauche* conformation, whereas they prefer an *antiperiplanar* (*ap*) arrangement in the less-stable diastereoisomer (*S*,*S*,*ʳC*)-**17** (*Fig. 2*).

The AM1 method has, however, been shown to frequently introduce unsystematic errors in the treatment of torsional angles and rotational barriers about single bonds (see [24] and refs. cit. therein). Since the answer to the question addressed in this work

required an accurate description of torsional energies and relative stability of diastereoisomers, we decided to continue the calculations with the semiempirical OM2 method ('Orthogonalization Method 2') [24] as implemented in the MNDO97 ('Modified Neglect of Differential Overlap') program [25]. In contrast to other established semiempirical methods, OM2 introduces orthogonalization corrections, including three-center terms for the calculation of resonance integrals. Such correlations allow a better determination of conformational properties or energy differences between conformational and constitutional isomers [26]. Specifically, rotational and torsional barriers are improved with respect to other semiempirical methods [26]. The OM2 calculations also produced (*S*,*S*,^{f}*C*)-**17** as the higher-energy ($\Delta H_f = 540.0$ kcal mol^{-1}) and (*R*,*R*,^{f}*C*)-**18** as the lower-energy ($\Delta H_f = 538.8$ kcal mol^{-1}) diastereoisomers, but the difference in heat of formation was only $\Delta\Delta H_f = 1.2$ kcal mol^{-1}, which is quite small for a confident prediction of the diastereoisomeric preference. When the conformational relationships of the H-atoms and the Me groups in the tether were reversed, two local minima at much higher energy were computed. The heat of formation was calculated as $\Delta H_f = 548.7$ kcal mol^{-1} for (*S*,*S*,^{f}*C*)-**17** with *ap* glycolic H-atoms and as $\Delta H_f = 544.4$ kcal mol^{-1} for (*R*,*R*,^{f}*C*)-**18** with *ap* Me groups. Thus, the OM2 calculations clearly show that the (*S*,*S*,^{f}*C*)-configured product prefers the Me groups in the *ap* (*vs. gauche*) conformation ($\Delta\Delta H_f = 8.7$ kcal mol^{-1}), whereas the *gauche* (*vs. ap*) conformation of these groups is preferentially adopted by the (*R*,*R*,^{f}*C*)-diastereoisomer ($\Delta\Delta H_f = 5.6$ kcal mol^{-1}).

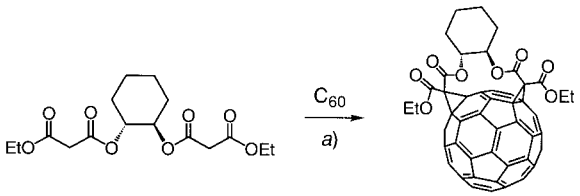
As already mentioned, the consideration of product stabilities to evaluate the preferred configuration of the *cis-3* addition pattern formed in the second step of the macrocyclization may not be a satisfactory approach, since the *Bingel* addition occurs under kinetic control. Therefore, we analyzed computationally the geometry of the formal precursor (*R*,*R*)-[CH(Me)OCOCH$_3$]$_2$ to (*R*,*R*,^{f}*C*)-**18**, in order to explore whether the diastereoselectivity would possibly be determined by the best match between the geometries of starting material and product. First, the distance between the two C-atoms in the formal precursor, which end up as methano bridge C-atoms in bis-adduct (*R*,*R*,^{f}*C*)-**18**, was constrained to the distance seen in the latter ($d = 5.73$ Å). It should, in particular, correspond to the distance between the corresponding C-atoms in the mono-adduct that undergoes the second, configuration-determining cyclopropanation. OM2 Calculations revealed a strong preference for a staggered tether with *gauche* orientations of both the Me and AcO groups. The heat of formation of the corresponding conformer with a *gauche*-ester array but an *ap* alignment of the Me groups was computed to be higher in energy by $\Delta\Delta H_f = 4.5$ kcal mol^{-1}.

OM2 Calculations were also performed on the free, unrestricted 'computational precursor' to (*R*,*R*,^{f}*C*)-**18**. If Me and ester groups are in a *gauche* array, respectively, the distance between the C-atoms, which end up as the methano bridge C-atoms in the product is 5.72 Å, matching well the corresponding distance (5.73 Å) in (*R*,*R*,^{f}*C*)-**18**, whereas it increases to $d = 6.81$ Å if the Me groups are in an *ap* and the ester groups in a *gauche* orientation. Thus, the geometry of the formal precursor, with both *gauche* Me and ester ('*gauche* effect' [23]) groups, fits very well with the geometry of the formal product, (*R*,*R*,^{f}*C*)-**18**, in which the same conformational array is maintained, and this could explain the observed diastereoselective formation of *Bingel*-type *cis-3* bis-adducts starting from bis-malonates of (*R*,*R*)- or (*S*,*S*)-butane-2,3-diol. We, therefore,

propose that the productive conformation of bis-malonates with 1,2-dialkyl-substituted 1,2-diol-derived tethers with *like* absolute configurations of both stereogenic centers (and the corresponding fullerene mono-adduct) in double *Bingel* reactions with C_{60} is the one containing *gauche* arrays of both the alkyl and malonate groups.

2.3. Bingel *Macrocyclizations with Bis-malonates Containing 1,2-Diol Tethers with Enforced* gauche *Conformation of Both the Alkyl and the Ester Residues.* In (*R*,*R*)-**19** (*Scheme 7*), with a tether derived from (*R*,*R*)-cyclohexane-1,2-diol, the *gauche* array of both the two alkyl and the two malonate residues is fixed in the 1,2-diequatorial conformer. According to the calculations, this geometry should be particularly favorable for regio- and stereoselective bis-adduct formation. Indeed, macrocyclization of (*R*,*R*)-**19** with C_{60} yielded exclusively *cis-3* bis-adduct (*R*,*R*,^{f}*C*)-**20** in 32% yield, the highest yield obtained so far in a regio- and diastereoselective bis-functionalization of the C-sphere (*Scheme 7*).

Scheme 7. *Regio- and Diastereoselective* Bingel *Macrocyclization of C_{60} with Bis-malonate (*R,R*)-***19***.



(*R*,*R*)-**19** (*R*,*R*,^{f}*C*)-**20**

a) I_2, DBU, PhMe, 20°, 2 h; 32%.

The high diastereoselectivity was demonstrated by HPLC and NMR (^{1}H,^{13}C) spectroscopy. The CD spectra of (*R*,*R*,^{f}*C*)-**16** and (*R*,*R*,^{f}*C*)-**20** are essentially identical, which allowed the assignment of the absolute configuration of the *cis-3* addition pattern in the latter as (^{f}*C*) (*Fig. 3*). Again, any CD effects that result from the difference of the addends are so weak compared to the *Cotton* effects produced by the inherently chiral addition pattern that they cannot be detected.

In theory, the *trans*-cyclohexane-1,2-diol tether in bis-malonate (*R*,*R*)-**19** (and the intermediately formed mono-adduct) could also adopt the energetically less favorable 1,2-diaxial conformation during the reaction with C_{60}. To exclude this possibility, we prepared bis-malonate (α,D)-**21**, containing a tether derived from methyl 4,6-*O*,*O*-benzylidene-α-D-glucopyranoside, in which the two malonate residues are locked in the diequatorial position (*Scheme 8*). As the steric arrangement of the alkyl and malonate residues corresponds to that in (*S*,*S*)-cyclohexane-1,2-diol, we expected to produce regioselectively the (^{f}*A*)-configured *cis-3* bis-adduct. This expectation was confirmed in the subsequent *Bingel* macrocyclization that provided regio- and diastereoselectively (α,D,^{f}*A*)-**22** in 13% yield, together with 7% of the bis-fullerene derivative (α,D)-**23**. The reduced yield of bis-adduct (as compared to 36% yield in the reaction with the *trans*-cyclohexane-1,2-diol derivative (*R*,*R*)-**19**) and the formation of side-product (α,D)-**23** are readily explained by the additional steric hindrance in the transition state(s) of the macrocyclization, resulting from the bulky and conformationally locked protected glucose unit.

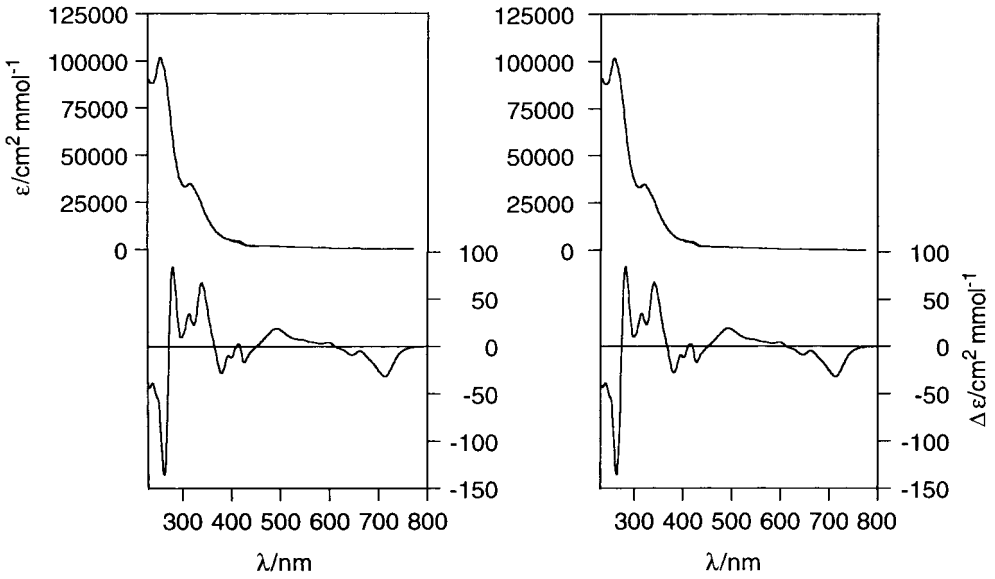
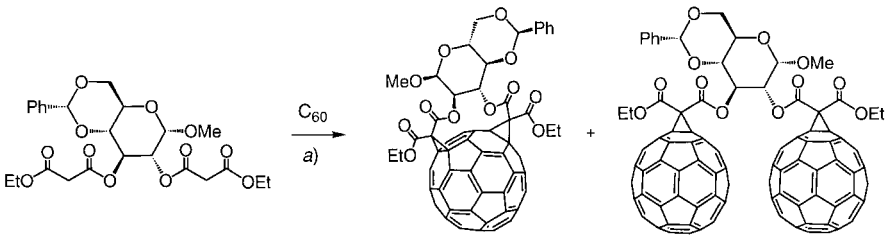


Fig. 3. *Experimental UV/VIS and CD spectra* (CH_2Cl_2) *of the* cis-3 *bis-adducts (*R,R,^{f}C*)*-**16** (left) *and (*R,R,^{f}C*)*-**20** (right)

Scheme 8. *Regio- and Diastereoselective* Bingel *Macrocyclization of* C_{60} *with Bis-malonate* (α,D)-**21**



(α,D)-**21** (α,D,^{f}*A*)-**22** (13%) (α,D)-**23** (7%)

a) I_2, DBU, PhMe, 20°, 2 h.

The absolute configuration of the *cis-3* addition pattern in (α,D,^{f}*A*)-**22** was readily assigned by comparison of its CD spectrum with that of (*S*,*S*,^{f}*A*)-**16** (*Fig. 4*). Thus, the computational prediction, that both the two alkyl groups and the two malonate groups in bis-malonates bridged by 1,2-dialkylated glycol-derived tethers adopt a *gauche* alignment during *Bingel* reaction with C_{60}, was confirmed in an impressive way. In fact, the reaction does not tolerate significant deviations from the *gauche* angles, as shown by the failure of the *exo-cis-* and the *trans*-norbornane-2,3-diyl-tethered bis-malonates **13** and (±)-**14** (*Scheme 5*) to undergo macrocyclization. Similarly, the reaction of C_{60} with bis-malonate (±)-**24** (*Scheme 9*) containing a (±)-*trans*-cyclopentane-1,2-diol tether gave racemic *cis-3* bis-adduct (±)-**25** in only 2% yield, in addition to several structurally unassigned side products.

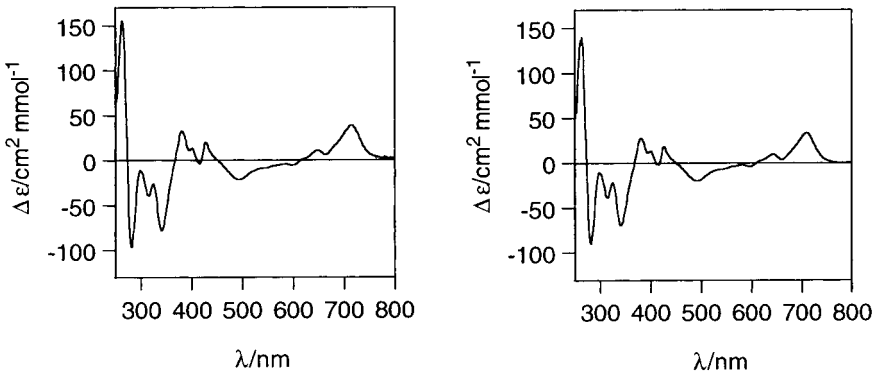
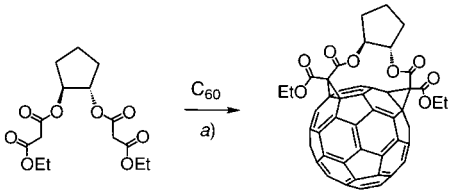


Fig. 4. *Experimental CD spectra (*CH_2Cl_2*) of the* cis-3 *bis-adducts (*S,S,^{f}A*)*-**16** (left) *and (*α,D,^{f}A*)*-**22** (right)

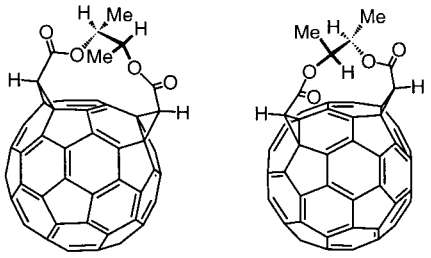
Scheme 9. Bingel *Macrocyclization of* C_{60} *with Bis-malonate (±)*-**24**



(±)-**24** (±)-**25**

a) I_2, DBU, 20°, 12 h; 2%.

2.4. *Determination of the Absolute Configuration of* cis-*3-Addition Patterns by* ^{1}*H-NMR Spectroscopy.* The computer modeling (*Sect. 2.2*) had provided good evidence that the more-favorable diastereoisomer (*R*,*R*,^{f}*C*)-**18** (*Fig. 2*) contains the two Me groups in a *gauche* relationship, whereas, in the less-favorable diastereoisomer (*R*,*R*,^{f}*A*)-**17**, they adopt an *ap* geometry. In (*R*,*R*,^{f}*C*)-**18**, the two vicinal H-atoms in the glycol fragment adopt an *ap* relationship, whereas in (*R*,*R*,^{f}*A*)-**17**, they are *gauche* (*Fig. 5*; *cf.* also *Fig. 2* for (*R*,*R*,^{f}*C*)-**18** and (*S*,*S*,^{f}*C*)-**17**). This should be readily checked



(*R*,*R*,^{f}*A*)-**17** (*R*,*R*,^{f}*C*)-**18**

Fig. 5. *Geometrical relationship of the H-atoms on C(2) and C(3) of the (*R,R*)-butane-2,3-diol-derived tether in (*R,R,^{f}C*)*-**18** *(*right*) and (*R,R,^{f}C*)*-**17** (left)

by ^{1}H-NMR spectroscopy, using the *Karplus* equation [27]. According to this equation, vicinal H-atoms in an *ap* relationship feature a coupling constant of *ca.* 7–10 Hz, whereas those in a *gauche* array are only coupled by *ca.* 1–3 Hz.

The experimentally determined vicinal coupling constant $^3J(H,H) = 7.9$ Hz provided strong support for the *ap* relationship between the two protons in (*R*,*R*,^{f}*C*)-**16** (*Scheme 6*) (and its enantiomer (*S*,*S*,^{f}*A*)-**16**). Thus, the combination of a computational conformational analysis, together with the experimental NMR data, provides a new way of determining the absolute configuration of the *cis-3* addition pattern, which is independent of the previous assignment of the absolute configuration by comparison of calculated and experimental CD spectra. Both methods are in agreement, strongly enhancing the level of confidence for the configurational assignments made.

2.5. *Chiral Exciton Coupling between Appended Chromophores in* cis-3-*Bis-adducts of* C_{60}. In previous work, we used the comparison of calculated and experimental CD spectra to assign the absolute configuration of [CD(−)488]-(^{f}*A*)-**3** and [CD(+)490]-(^{f}*C*)-**3** [9]. The CD band at *ca.* 490 nm was chosen to characterize the two enantiomeric addition patterns [12]: if a *cis-3* bis-adduct shows a negative *Cotton* effect around 490 nm [CD(−)490], the absolute configuration is (^{f}*A*), whereas a positive *Cotton* effect [CD(+)490] is indicative of the opposite (^{f}*C*) configuration. Thus, for the new derivatives with an (^{f}*C*)-configured *cis-3* addition pattern ((*R*,*R*,^{f}*C*)-**16** and (*R*,*R*,^{f}*C*)-**20**; *Schemes 6* and *7*) positive *Cotton* effects around 490 nm were observed, whereas (*S*,*S*,^{f}*A*)-**16** and (α,D,^{f}*A*)-**22** (*Schemes 6* and *8*) featured negative *Cotton* effects at this wavelength.

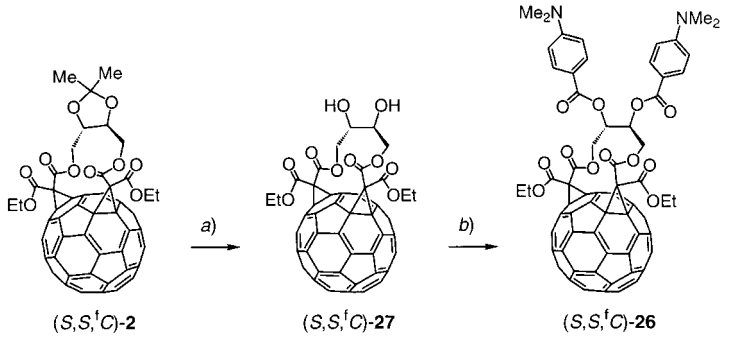
Another method for determining absolute configurations from CD data relies on the computer-assisted evaluation of chiral exciton coupling, resulting from the geometry-dependent interaction between two chromophores in a chiral environment. This method has been used extensively to determine the absolute configuration of chiral vicinal diols [13][14]. For this purpose, the glycols were transformed into diesters of 4-(dimethylamino)benzoic acid, and their CD spectra, displaying band splitting due to exciton coupling between the benzoate chromophores, were recorded. Comparison between experimental and calculated CD spectra subsequently allowed the determination of the absolute configuration. The 4-(dimethylamino)benzoate chromophores feature a number of properties that are advantageous to the applicability of the exciton chirality method, such as high symmetry and a strong charge-transfer transition in the UV/VIS spectrum with known directionality of the electric and magnetic transition dipole moments.

To explore experimentally chiral exciton coupling in fullerene chemistry, we prepared diester (*S*,*S*,^{f}*C*)-**26**, starting from the known *cis-3* bis-adduct (*S*,*S*,^{f}*C*)-**2** (*Scheme 10*) [5]. Acid-catalyzed acetal cleavage afforded diol (*S*,*S*,^{f}*C*)-**27** [28], which was esterified to give the bis[4-(dimethylamino)benzoate] in good yield.

A comparison of the CD spectra of (*S*,*S*,^{f}*C*)-**2** and (*S*,*S*,^{f}*C*)-**26** shows, at first view, a high degree of similarity with dominating chiroptical contributions from the chiral fullerence chromophore (*Fig. 6*, *a* and *b*). However, a closer examination of the region around 300 nm reveals small but significant differences.

For a better analysis of these differences, the CD difference spectrum was calculated by computationally subtracting the CD spectrum of (*S*,*S*,^{f}*C*)-**2** from that of (*S*,*S*,^{f}*C*)-**26** (*Fig. 6*, *c*), thereby removing the (dominant) chiroptical contributions,

Scheme 10. *Synthesis of Bis[4-(dimethylamino)benzoate]* (S,S,^{f}C)-**26**



(*S*,*S*,^{f}*C*)-**2** (*S*,*S*,^{f}*C*)-**27** (*S*,*S*,^{f}*C*)-**26**

a) CF_3COOH, CH_2Cl_2, H_2O, 20°, 3 d; 70%. *b*) 4-(Dimethylamino)benzoyl chloride, DMAP, CH_2Cl_2, 20°, 4 h; 65%.

resulting from the inherently chiral fullerene-addition pattern. This difference spectrum shows a clear splitting of the band around 300 nm, typical of chiral exciton coupling. A negative first *Cotton* effect (at longer wavelength) is followed by a positive second *Cotton* effect (at shorter wavelength), with the zero intercept at *ca.* 310 nm. This wavelength corresponds to the absorption maximum of the 4-(dimethylamino)benzoate chromophore and is readily revealed in the UV/VIS difference spectrum obtained by subtracting the UV/VIS spectrum of (*S*,*S*,^{f}*C*)-**2** from that of (*S*,*S*,^{f}*C*)-**26** (*Fig. 6, d*). The relationship between the two chiral exciton couplets in (*S*,*S*,^{f}*C*)-**26** corresponds to negative exciton chirality (*Fig. 6*) [13]. Calculation of signs and magnitudes of the CD bands in the spectrum, featuring the chiral exciton coupling, should in the future allow conclusions on the geometric arrangement of the 4-(dimethylamino)benzoate chromophores and, therefore, provide another independent determination of the absolute configuration of the addition pattern in (*S*,*S*,^{f}*C*)-**26**.

Suitable chromophores for the determination of absolute configurations by the exciton-chirality method possess high symmetry and a narrow absorption band with a high molar extinction coefficient. These requirements are nicely met by *meso*-tetraphenylporphyrin chromophores [29]. Thus, we prepared the optically active fullerene-bis-porphyrin conjugate (*R*,*R*,^{f}*C*)-**28** (*Scheme 11*). The synthesis of (*R*,*R*,^{f}*C*)-**28** started from bis-malonate (*R*,*R*)-**29**, which underwent the double *Bingel* cyclopropanation to give (*R*,*R*,^{f}*C*)-**30**. Acid-catalyzed cleavage of the *tert*-butyl esters provided the dicarboxylic acid (*R*,*R*,^{f}*C*)-**31**, which was transformed into the bis(acyl halide) and esterified with (hydroxyphenyl)porphyrin **32** [30] to give the target compound.

The UV/VIS spectrum of (*R*,*R*,^{f}*C*)-**28** displays the characteristic *Soret* band of the two porphyrins as the dominant absorption at 430 nm (*Fig. 7, a*). To detect any chiral exciton coupling between the two porphyrin chromophores in the CD spectrum of (*R*,*R*,^{f}*C*)-**28** (*Fig. 7, a*), the spectrum of (*R*,*R*,^{f}*C*)-**2** was subtracted, to provide the CD difference spectrum shown in *Fig. 7, b*. Although the subtraction did not completely remove the much stronger *Cotton* effect contributions of the inherently chiral fullerene chromophore (*cf.* also *Fig. 6, c*), a sharp split band around 430 nm, corresponding to the

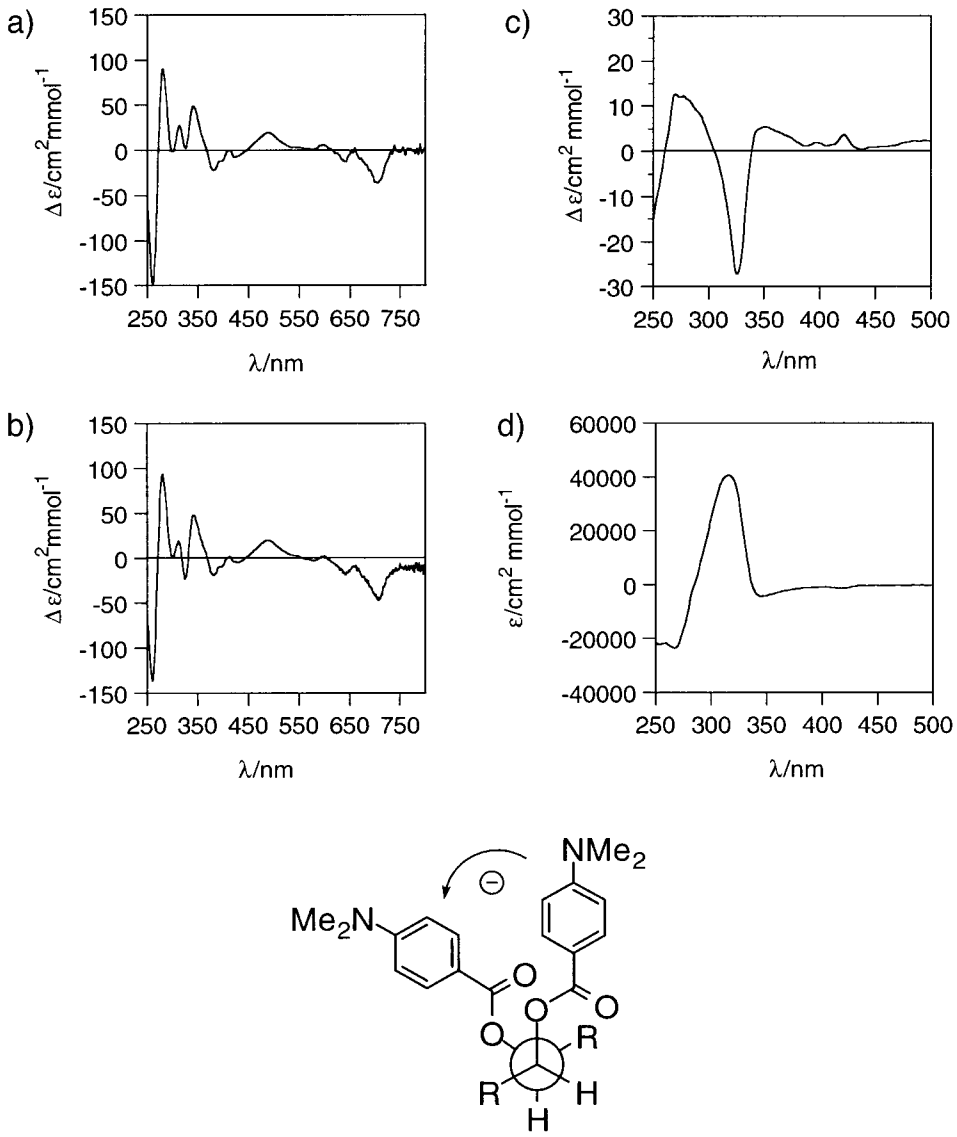
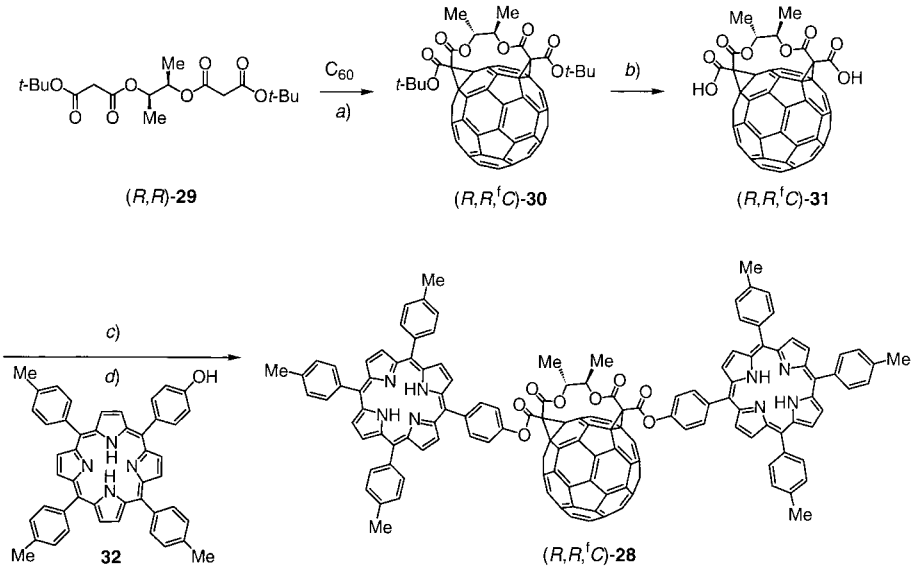


Fig. 6. *CD Spectra* (CH_2Cl_2) of a) *(*S,S,^{f}C*)*-**2** *and* b) *(*S,S,^{f}C*)*-**26**, *and* c) *CD and* d) *UV/VIS difference spectra obtained by subtraction of the spectra of (*S,S,^{f}C*)*-**2** *from those of (*S,S,^{f}C*)*-**26**. Also shown is the relationship between the two chiral exciton couplets, which corresponds to negative chirality [13].

maximum of the *Soret* band, became clearly visible in the difference spectrum. It displays a positive first *Cotton* effect together with a negative second *Cotton* effect.

For future determinations of the absolute configuration of the fullerene-addition pattern from the CD spectrum of (*R*,*R*,^{f}*C*)-**28**, it was of interest to calibrate the chiral exciton coupling of the two porphyrin chromophores using a chiral 'spacer' of known absolute configuration [29]. Therefore, we prepared the bis-porphyrin derivative (*R*)-

Scheme 11. *Synthesis of the Chiral Fullerene-Porphyrin Conjugate (*R,R,*f*C)-**28**



a) I_2, DBU, PhMe, 20°, 2 h; 12%. *b*) $TsOH \cdot H_2O$, PhMe/MeCN, 20° (14 h), Δ (11 h); 85%. *c*) $(COCl)_2$, THF, 20°, 12 h. *d*) DMAP, CH_2Cl_2, 20°, 4 h; 30% (from (*R,R,*t*C*)-**31**).

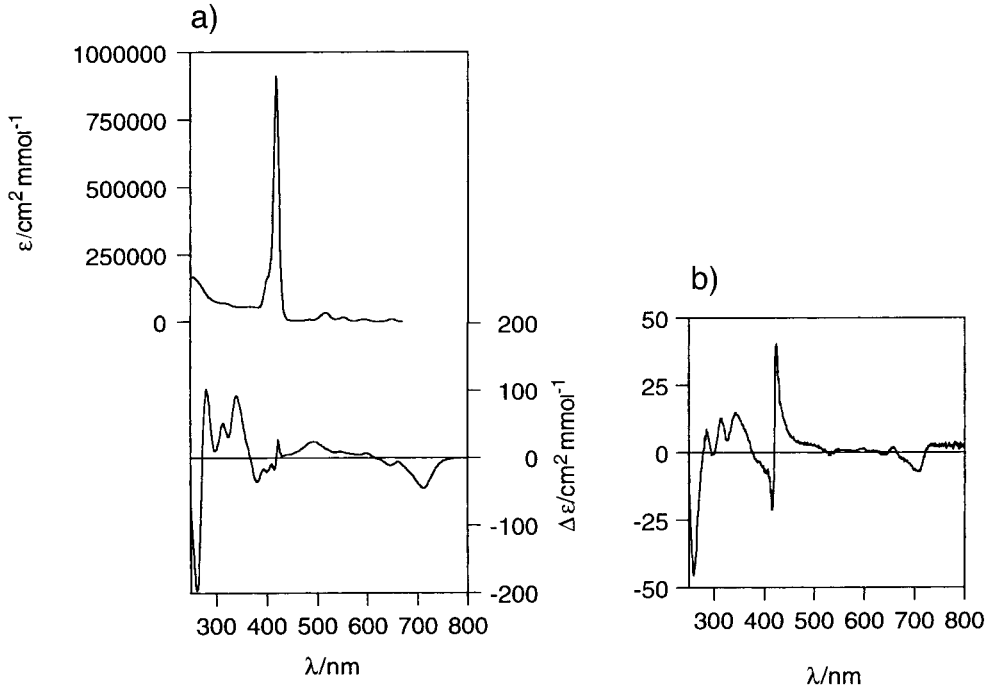
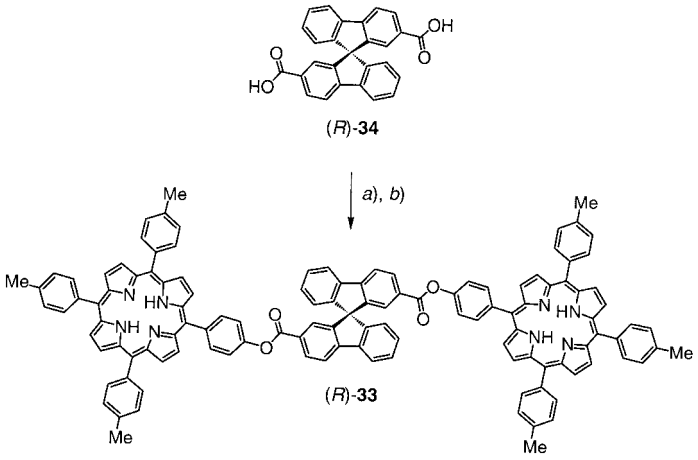


Fig. 7. *UV/VIS and CD spectra* (CH_2Cl_2) *of* a) (R,R,*f*C)-**28** *and* b) *CD difference spectrum obtained by subtraction of the spectrum of (*R,R,*f*C)-**16** *from that of (*R,R,*f*C)-**28**

Scheme 12. *Synthesis of Bis-porphyrin (*R*)-***33***



a) $(COCl)_2$, DMF (cat.), THF, 20°, 4 h. *b*) **32**, Pyridine, DMAP, CH_2Cl_2, 20°, 4 h; 46% (from (*R*)-**34**).

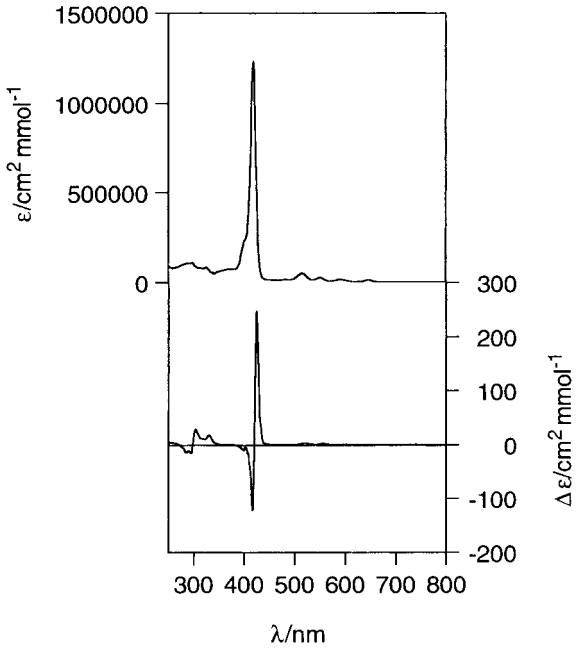
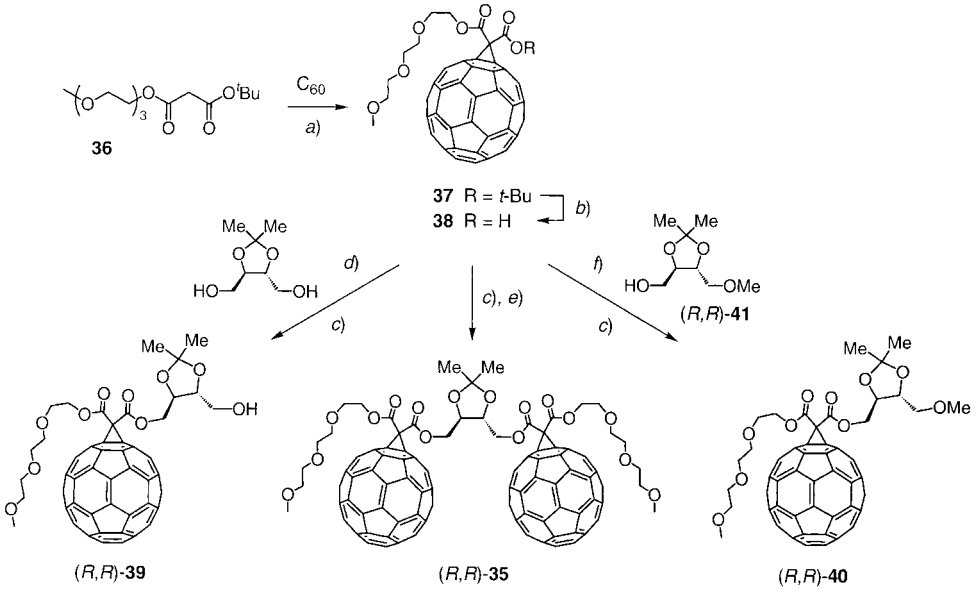


Fig. 8. *UV/VIS* (top) *and CD* (bottom) *spectra of (*R*)-***33** *in* CH_2Cl_2

33 starting from 9,9′-spirobifluorene-2,2′-dicarboxylic acid (*R*)-**34** of known absolute configuration (*Scheme 12*) [31]. The CD spectrum of (*R*)-**33** showed a strong chiral exciton coupling with a positive first *Cotton* effect and a negative second *Cotton* effect, and the zero-intercept point of the exciton couplet corresponds to the maximum of the *Soret* band (*Fig. 8*).

2.6. *Chiral Exciton Coupling between Fullerene Chromophores.* Investigations of the chiral exciton coupling between two fullerene chromophores required the consideration that the amplitide of the CD band splitting shows a linear dependence on the molar extinction coefficient ε and, most importantly, an inverse-square dependence on the distance between the chromophores [13]. Therefore, it was mandatory to design a chiral molecule in which the two fullerene moieties are located in closest possible proximity. Accordingly, we prepared bis-fullerene (*R*,*R*)-**35** (*Scheme 13*) with a short threitol-derived spacer. *Bingel* addition of malonate **36** to C_{60} provided mono-adduct **37**, which was deprotected to give carboxylic acid **38** (*Scheme 13*). Transformation into the acyl halide and esterification with an excess of (*R*,*R*)-(2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(methanol) afforded (*R*,*R*)-**39**, which was reacted with the acyl halide, prepared from **38**, to give the target compound (*R*,*R*)-**35**. Its enantiomer (*S*,*S*)-**35** was also prepared and, for comparison, mono-fullerene derivative (*R*,*R*)-**40** (from **38** and (*R*,*R*)-**41**; *Scheme 13*) as well. With their triethyleneglycol monomethyl ether residues, all three compounds showed high solubility in CH_2Cl_2 and could also be dissolved to a satisfying extent in THF.

Scheme 13. *Synthesis of Bis-fullerene* (R,R)-**35**



a) I_2, DBU, PhMe, 20°, 2 h; 44%. *b*) TsOH · H_2O, PhMe, Δ, 4 h; 94%. *c*) $(COCl)_2$, CH_2Cl_2, 20°, 12 h. *d*) Pyridine, CH_2Cl_2, 20°, 12 h; 65% (from **38**). *e*) (*R*,*R*)-**39**, pyridine, CH_2Cl_2, 20°, 12 h; 14% (from (*R*,*R*)-**39**). *f*) DMAP, CH_2Cl_2, 20°, 2 h; 51% (from **38**).

In all three compounds (*R*,*R*)-**35**, (*S*,*S*)-**35**, and (*R*,*R*)-**40**, chirality resides only in the chiral addends and, correspondingly, only weak *Cotton* effects are observed in their CD spectra (*Fig. 9*) [4a][5a][18]. The spectrum of bis-fullerene (*R*,*R*)-**35** displays two split bands resulting from chiral exciton coupling, with zero-intercept points at 424 and 325 nm. These bands appear unsplit in the control spectrum of (*R*,*R*)-**40**, which, in

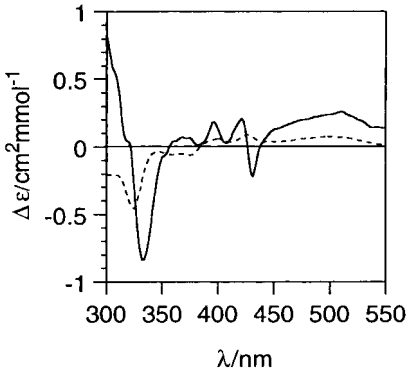
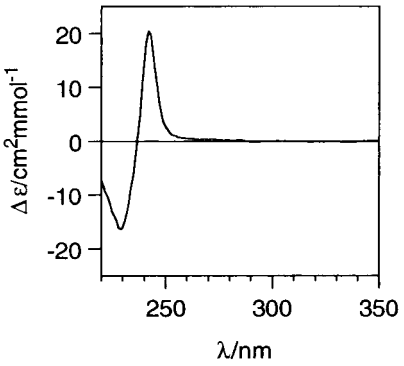
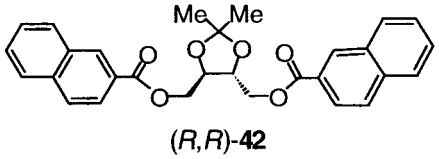


Fig. 9. *CD Spectra* (CH_2Cl_2) *of (*R,R*)*-**35** (—) *and (*R,R*)*-**40** (- - - -)

contrast, features extrema at 427 and 325 nm. In support of the chiral exciton coupling, the zero-intercept points are located at wavelengths corresponding to absorption maxima in the UV/VIS spectrum of (*R*,*R*)-**35** ($\lambda_{max} = 426$ nm ($\varepsilon = 5300$ cm^2 mmol^{-1}) and $\lambda_{max} = 325$ nm ($\varepsilon = 67500$ cm^2 mmol^{-1})). This is the first observation of chiral exciton coupling between fullerene chromophores; however, the effects are only weak.

To become calibrated the amplitude of the coupling between other chromophores separated by the same threitol spacer, we also prepared (*R*,*R*)-**42** featuring two 2-naphthoate chromophores (*Fig. 10*). Its CD spectrum displayed a strong chiral exciton coupling with a peak at 242, a trough at 229 nm, and an amplitude of 36 cm^2 mmol^{-1}. The position of the zero-intercept point corresponds again to the absorption maximum in the UV/VIS spectrum at $\lambda_{max} = 237$ nm ($\varepsilon = 114800$ cm^2 mmol^{-1}). As mentioned above, ideal chromophores for chiral exciton coupling should feature high symmetry and a strong electronic absorption (with a high electrical-transition dipole moment). This is the case for both (*R*,*R*)-**42** ($\lambda_{max} = 237$ nm ($\varepsilon = 114800$ cm^2 mmol^{-1})) and (*R*,*R*)-**35** ($\lambda_{max} = 325$ nm ($\varepsilon = 67500$ cm^2 mmol^{-1})). Nevertheless, the chromophoric coupling in the fullerene is much weaker. This could be a result of a large spatial separation of the transition dipole moments of the two fullerene chromophores, due to their localization in the interior of the C-sphere (for an example of a large electronic





(*R*,*R*)-**42**

Fig. 10. *CD Spectrum* (CH_2Cl_2) *of (*R,R*)*-**42**

coupling between two fullerene chromophores in a rigid bis-fullerene derivative, see [32]).

3. Conclusions. – The absolute configuration of optically active fullerene derivatives with a chiral *cis-3* addition pattern is now firmly established. Following initial configurational assignments made for (^{f}A)-**3** and (^{f}C)-**3** (*Scheme 1*) by comparison of experimental and calculated CD spectra, this study provides a second assignment of the absolute configuration by a combined computational-experimental (^{1}H-NMR-spectroscopic) approach. There is full agreement between the two independent configurational assignments. A series of optically active *cis-3* bis-adducts was obtained regio- and diastereoselectively by *Bingel* macrocyclization of C_{60} with bis-malonates, which contain optically active 1,2-dialkylated 1,2-diol-derived tethers. With the semiempirical AM1 and OM2 methods, geometries and heats of formation were calculated for the diastereoisomers that can form when bis-malonates with an (*R*,*R*)- or (*S*,*S*)-configured butane-2,3-diol-derived tether react with C_{60} under exclusive formation of an *out-out cis-3* bis adduct with the absolute configuration (^{f}C) or (^{f}A), respectively. According to the computer-assisted calculations, the substituents at the glycolic fragment in the two diastereoisomeric *out-out cis-3* bis-adducts that can possibly form are fully staggered, and the two ester linkers to the fullerene always adopt a *gauche* conformation. In the most stable diastereoisomer (*e.g.,* (*R*,*R*,^{f}C)-**16**), calculations predicted a *gauche* orientation of the two Me groups in the tether, whereas the two glycolic H-atoms are in an *ap* array. In contrast, in the calculated less favorable diastereoisomer, the Me groups adopt an *ap* and the two H-atoms a *gauche* orientation. Also the OM2 calculations revealed an excellent geometric fit between the free tethered bis-malonate and the corresponding fragment in the formed C_{60} bis-adduct, provided that both Me groups and the ester linkers adopt the *gauche* orientation in the fully staggered tether. Such a good fit can also be assumed for the intermediate C_{60} mono-adduct that undergoes the macrocyclization step determining the regio- and diastereoselectivity. Evaluation of the vicinal coupling constants by ^{1}H-NMR spectroscopy clearly showed that the glycolic H-atoms in the experimentally formed *cis-3* bis-adducts (*R*,*R*,^{f}C)-**16** and (*S*,*S*,^{f}A)-**16** adopt an *ap* orientation (^{3}J(H,H) = 7.9 Hz), which allowed assignment of the (^{f}C)- or (^{f}A)-configuration to the inherently chiral addition patterns. This conformational analysis was further supported by the regio- and diastereoselective synthesis of bis-adducts using cyclic glycol-derived tethers with a fixed *gauche* conformation of the alkyl residues at the glycolic unit ((*R*,*R*,^{f}C)-**20**, (α,D,^{f}A)-**22**). If the geometry between the alkyl groups R at the glycolic C-atoms deviates from a *gauche* relationship, as in the case of tethers derived from *exo-cis*- and *trans*-norbornane-2,3-diol, or *trans*-cyclopentane-1,2-diol, hardly any macrocyclic product is formed. The absolute configurations of the various optically active *cis-3* bis-adducts were also assigned by comparison of their CD spectra, which are dominated by the chiroptical contributions from the inherently chiral addition pattern.

This paper also presents the first comprehensive investigation of chiral exciton coupling in fullerene chemistry. A strong chromophoric coupling was observed for optically active macrocyclic *cis-3* bis-adducts of C_{60} with two appended 4-(dimethylamino)benzoate ((*S*,*S*,^{f}C)-**26**) or *meso*-tetraphenylporphyrin ((*R*,*R*,^{f}C)-**28**) chromophores. Future determinations of signs and amplitudes of the split CD bands in the

spectra that display exciton coupling should provide yet another method to determine the absolute configuration of the chiral addition pattern. Chiral exciton coupling between two fullerene chromophores was observed for the first time in the CD spectrum of the threitol-bridged bis-fullerene (*R*,*R*)-**35**, which suggests that this method can be used as a sensorial tool to probe the proximity and orientation of two fullerene derivatives in a chiral environment. This paper provides another impressive demonstration of the various avenues of interest associated with fullerene chirality.

We thank the *Swiss National Science Foundation* for generous support of this work. We also thank Prof. *Walter Thiel* (*Max-Planck-Institut für Kohleforschung*, Mülheim) for allowing to perform the semiempirical calculations with his MNDO97 program including the new OM2 implementation.

Experimental Part

General. All reactions were carried out under N_2. Solvents and reagents were reagent-grade and commercially available, and used without further purification unless otherwise stated. C_{60} was obtained from *Southern Chemical Group LLC*, Stone Mountain, GA 30087, USA and from *Materials, Technologies, Research-MTR Ltd.*, Cleveland, OH 44124, USA. Compounds (*S*,*S*,^{t}*C*)-**2** [5], **11** [17], (±)-**12** [17], **32** [30], and (*R*)-(+)-**34** [31] were prepared according to literature procedures. THF was freshly distilled from sodium benzophenone ketyl and CH_2Cl_2 over CaH_2. Evaporation *in vacuo* was conducted at H_2O-aspirator pressure. For anal. and spectroscopic characterization, compounds were dried at 10^{-2} Torr. Column chromatography (CC): SiO_2-*60* (230–400 mesh, 0.040–0.063 mm) from *E. Merck*, SiO_2 (70–230 mesh, 0.05–0.2 mm) from *Macherey-Nagel*, or SiO_2-*H* (0.005–0.040 mm) from *Fluka*, using 0.3 bar of air pressure. Anal. HPLC: *Macherey-Nagel Nucleosil 100-7* SiO_2 (7 μm) column (250 × 4.6 mm); *Knauer HPLC 64* high-pressure gradient pumps, flow rate 1 ml min^{-1}; the probe was injected in CH_2Cl_2/hexane (varying ratio, 20 μl volume), solvents from *Biosolve*. *Variable Wavelength Monitor* UV/VIS detector from *Knauer*, with detector wavelength fixed at $\lambda = 310$ nm. Determination of ee values: chiral stationary phase (CSP) (*S*,*S*)-*Whelk-01* (5 μm, 250 mm × 4.6 mm) column from *Regis Chemical Company*, Morton Grove, IL, USA. TLC: Glass sheets coated with SiO_2 *60* F_{254} from *E. Merck*; visualization by UV light or coloring with a 'mostain' soln. (400 ml of 10% aq. H_2SO_4, 20 g of $(NH_4)_6Mo_7O_{24}\cdot 6\,H_2O$, 0.6 g of $Ce(SO_4)_2$). M.p.: *Büchi 510* or *Büchi B-540*; uncorrected. Optical rotation: *Perkin-Elmer-241* polarimeter, 10-cm cuvette, at 25 ± 2°; conc. given in g of solute per 100 ml of solvent. UV/VIS Spectra: *Varian-CARY-5* spectrometer; ε [l mol^{-1} cm^{-1}]. CD Spectra: *Jasco J-710* spectropolarimeter; $\Delta\varepsilon$ [cm^2 mmol^{-1}], 293 K. IR Spectra [cm^{-1}]: *Perkin-Elmer 1600-FT-IR*. NMR Spectra: *Bruker AMX 500*, and *Varian Gemini 300* or *200* at 293 K, with solvent peak as reference. MS (*m*/*z* (%)): EI-MS: *VG TRIBRID* spectrometer at 70 eV; FAB-MS: *VG ZAB2-SEQ* spectrometer with 3-nitrobenzyl alcohol (NOBA) as matrix. MALDI-TOF-MS: *Bruker REFLEX* spectrometer; matrices: 2,4,6-trihydroxyacetophenone (0.5M in EtOH); diammonium citrate (0.1M in H_2O); negative-ion mode at −20 kV acceleration voltage, reflector mode. ESI-MS: *Finnigan TSQ 7000*. Elemental analyses were performed by the Mikrolabor of the Laboratorium für Organische Chemie, ETH-Zürich.

General Procedure 1 (*GP 1*) *for the Preparation of Tethered Bis-malonates*. Ethyl 2-(chlorocarbonyl)acetate (3 equiv.) and pyridine (3 equiv.) were added at 0° under N_2 to the 1,2-diol (1 equiv.) in CH_2Cl_2/THF or pure CH_2Cl_2. After stirring for 12 h at 20°, the mixture was evaporated *in vacuo*. The crystalline precipitate was isolated by filtration and the filtrate washed with H_2O. The org. phase was dried ($MgSO_4$) and evaporated *in vacuo*, and the crude product purified by CC (SiO_2).

General Procedure 2 (*GP 2*) *for the* Bingel *Macrocyclization*. Bis-malonate (1.2 equiv.), I_2 (2.5 equiv.), and DBU (6 equiv.) were added at 20° under N_2 to C_{60} (300 mg, 0.416 mmol, 1 equiv.) in PhMe, and the soln. was stirred for 12 h. The mixture was poured onto SiO_2, and the crude product was isolated by extracting with CH_2Cl_2. CC (SiO_2) and precipitation from CH_2Cl_2/hexane provided the pure bis-adduct. Samples for elemental analysis were dried for 8 h at 80°/10^{-2} Torr.

1,1′-(Ethane-1,2-diyl) 3,3′-Diethyl Bis(malonate) (**4**). According to the *GP 1*, ethane-1,2-diol (250 mg, 4.03 mmol), ethyl 2-(chlorocarbonyl)acetate (1.8 g, 12.1 mmol), and pyridine (0.96 g, 12.1 mmol) were reacted in CH_2Cl_2/THF (60 ml/10 ml), and CC (SiO_2; CH_2Cl_2/AcOEt 3:1) gave **4** (1.013 g, 87%) as colorless oil. IR (neat): 2985*m*, 1754*s*, 1733*s*, 1446*m*, 1410*m*, 1328*m*, 1271*m*, 1189*s*, 1151*s*, 1035*s*, 979*m*, 867*w*, 841*w*, 787*w*, 681*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.31 (*s*, 4 H); 4.14 (*q*, *J* = 7.5, 4 H); 3.34 (*s*, 4 H); 1.22 (*t*, *J* = 7.5, 6 H). ^{13}C-NMR

(50 MHz, $CDCl_3$): 165.90; 165.77; 62.28; 61.11; 40.82; 13.55. EI-MS: 291 (MH^+). Anal. calc. for $C_{12}H_{18}O_8$ (290.27): C 49.65, H 6.25; found: C 49.42, H 6.03.

(±)-61,62-(Ethane-1,2-diyl) out,out-*61,62-Diethyl 1,2:16,17-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* ((±)-**5**) *and 2-[2-(Ethoxycarbonyl)acetoxy]ethyl Ethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate* (**6**). According to the *GP 2*, C_{60} (1.08 g, 1.5 mmol), **4** (550 mg, 1.85 mmol), I_2 (476 mg, 3.75 mmol), and DBU (1.3 ml) were reacted in PhMe (1.9 l), and CC (SiO_2; CH_2Cl_2/hexane 2:1) afforded first (±)-**5** (223 mg, 12%), then **6** (242 mg, 13%).

Data of (±)-**5**: M.p. >250°. UV/VIS (CH_2Cl_2): 699 (260), 634 (sh, 480), 459 (2140), 314 (34700), 253 (99300). IR (neat): 2967*m*, 1745*s*, 1439*m*, 1362*m*, 1230*s*, 1097*m*, 1050*m*, 751*w*, 525*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.27 (br. *d*, *J* = 11.2, 2 H); 4.52 (*q*, *J* = 7.1, 4 H); 4.26 (br. *d*, *J* = 11.2, 2 H); 1.47 (*t*, *J* = 7.1, 6 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 163.91; 163.24; 146.71; 146.58; 145.58; 145.56; 145.55; 145.50; 145.43; 145.13; 144.96; 144.90; 144.56; 144.41; 144.14; 143.91; 143.65; 143.36; 142.49; 142.46; 142.45; 141.96; 141.07; 141.06; 140.87; 140.83; 140.55; 135.31; 128.75; 71.80; 68.56; 63.93; 63.57; 49.80; 14.22. FAB-MS: 1006 (75, M^+), 720 (100, C_{60}^+).

Data of **6**: Rusty-brown solid. M.p. >250°. UV/VIS (CH_2Cl_2): 687 (221), 486 (2000), 425 (2800), 325 (41000), 261 (140000). IR (KBr): 2966*w*, 1746*s*, 1233*s*, 1027*w*, 526*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.73–4.71 (*m*, 2 H); 4.57 (*q*, *J* = 7.1, 2 H); 4.54 (*m*, 2 H); 4.22 (*q*, *J* = 7.1, 2 H); 3.41 (*s*, 2 H); 1.56–1.55 (*t*, *J* = 7.1, 3 H); 1.30 (*t*, *J* = 7.1, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 166.36; 166.10; 163.47; 163.29; 145.20 (2×); 145.13; 145.10; 145.02; 144.92; 144.83; 144.70; 144.69; 144.65; 144.58; 143.90; 143.87; 145.29; 145.21; 143.10; 143.10; 143.04; 143.03; 142.96; 142.21; 142.19; 141.88; 141.86; 140.97; 140.97; 138.81; 138.71; 71.38; 64.39; 63.58; 62.69; 61.73; 51.84; 41.28; 14.22; 14.11. Anal. calc. for $C_{72}H_{16}O_8$ (1008.91): C 85.72, H 1.60; found: C 85.49, H 1.47.

*1,1′-[(*R,R*)-1,2-Bis(ethoxycarbonyl)ethane-1,2-diyl] 3,3′-Diethyl Bis(malonate)* ((*R*,*R*)-**7a**). *GP 1*, starting from diethyl (*R*,*R*)-tartrate (1.5 g, 7.2 mmol) afforded, after CC (SiO_2; CH_2Cl_2/AcOEt 5:1), (*R*,*R*)-**7a** (3.28 g, 95%). Yellow oil. $[\alpha]_D^{25} = 4.8$ (*c* = 1.45, CH_2Cl_2). IR (neat): 2985*m*, 1764*s*, 1741*s*, 1467*w*, 1371*m*, 1271*m*, 1137*m*, 1066*m*, 1031*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.78 (*s*, 2 H); 4.25 (*dd*, *J* = 7.0, 1.3, 4 H); 4.20 (*q*, *J* = 7.0, 4 H); 3.48 (*d*, *J* = 1.3, 4 H); 1.27 (*t*, *J* = 7.0, 12 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 163.31; 162.99; 162.64; 71.16; 68.85; 60.09; 59.29; 38.31; 11.43. EI-MS: 435 (M^+). Anal. calc. for $C_{18}H_{26}O_{12}$ (434.40): C 49.77, H 6.03; found: C 48.99, H 6.09.

Hydrogen 2-[2-(2-Methoxyethoxy)ethoxy]ethyl Malonate (**8**). A mixture of triethyleneglycol (2.849 g, 17.349 mmol) and 2,2-dimethyl-1,3-dioxane-4,6-dione (2.5 g, 17.349 mmol) was heated for 4 h to 110° (heating above 120° is to be avoided since the product shows an increased tendency to decay at higher temp.), which produced **8** (4.25 g, 17.3 mmol, 98%). Pale-yellow oil. IR (neat): 3458*m*, 3165*m*, 1735*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 9.46 (br. *s*, 1 H); 4.27 (*t*, *J* = 4.6, 2 H); 3.67 (*t*, *J* = 4.6, 2 H); 3.64–3.50 (*m*, 8 H); 3.38 (*s*, 2 H); 3.35 (*s*, 3 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 168.72; 166.47; 71.39; 70.09; 69.96; 69.77; 68.22; 64.12; 58.37; 40.66. FAB-MS: 251 (100, MH^+). Anal. calc. for $C_{10}H_{18}O_7$ (250.10): C 46.33, H 7.39; found: C 46.07, H 7.13.

*1,1′-[(*R,R*)-1,2-Bis(ethoxycarbonyl)ethane-1,2-diyl] 3,3′-[2-[2-(2-Methoxyethoxy)ethoxy]ethyl] Bis(malonate)* ((*R*,*R*)-**7b**). Diethyl (*R*,*R*)-tartrate (7.5 g, 30 mmol), **8** (3.09 g, 15.0 mmol), and DCC (6.80 g, 33.0 mmol) were dissolved at 0° in THF (150 ml). DMAP (0.733 g, 6.0 mmol) was added, and the mixture was stirred for 12 h at 20°. The crystals formed were removed by filtration, a small amount of PhMe was added to the filtrate, and the soln. was cooled to −20°. A second batch of crystals was removed by filtration, the filtrate was evaporated *in vacuo*, and the residue purified by CC (SiO_2; CH_2Cl_2/MeOH 98:2) to give (*R*,*R*)-**7b** (6.03 g, 60%). Colorless oil. $[\alpha]_D^{25} = -2.4$ (*c* = 0.836, CH_2Cl_2). IR (neat): 2944*m*, 2878*m*, 1761*s*, 1739*s*, 1451*w*, 1369*m*, 1353*m*, 1280*s*, 1205*s*, 1138*s*, 1061*m*, 1031*m*, 986*w*, 857*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.76 (*s*, 2 H); 4.24 (*q*, *J* = 7.1, 4 H); 4.28 (*m*, 4 H); 3.72–3.61 (*m*, 16 H); 3.55–3.51 (*m*, 8 H); 3.37 (*s*, 6 H); 1.27 (*t*, *J* = 7.1, 6 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 165.26; 164.76; 164.53; 71.45; 70.88; 70.15; 68.34; 64.28; 62.19; 58.57; 40.15; 13.52. FAB-MS: 671 (MH^+). Anal. calc. for $C_{28}H_{46}O_{18}$ (670.26): C 50.15, H 6.91; found: C 50.17, H 6.95.

2-[2-(2-Methoxyethoxy)ethoxy]ethyl 1,2-Methano[60]fullerene-61-carboxylate (**9**). *GP 2*, starting from (*R*,*R*)-**7b** (334 mg, 0.5 mmol) and C_{60} (300 mg, 0.416 mmol), followed by CC (SiO_2, CH_2Cl_2/AcOEt 30:1) yielded **9** (62 mg, 16%). Brownish-red solid. M.p. >250°. UV/VIS (CH_2Cl_2): 688 (350), 479 (2570), 427 (3370), 413 (sh, 3280), 401 (sh, 4460), 326 (36400), 258 (117300). IR (KBr): 2856*m*, 1733*s*, 1422*w*, 1233*s*, 1104*s*, 1100*s*, 1027*m*, 700*w*, 661*w*, 572*w*, 525*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.84 (*s*, 1 H); 4.63–4.61 (*m*, 2 H); 3.95–3.92 (*m*, 2 H); 3.79–3.69 (*m*, 6 H); 3.67–3.56 (*m*, 2 H); 3.40 (*s*, 3 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 166.73; 148.55; 146.54; 145.90; 145.57; 145.39; 144.99; 144.73; 144.04; 143.56; 143.30; 143.11; 142.73; 142.37; 141.22; 140.91; 136.69; 119.40; 111.20; 72.11; 70.90; 70.81; 69.16; 65.49; 59.23; 38.92. FAB-MS: 925 (35, MH^+), 720 (100, C_{60}^+).

*1,1′-((*S,S*)-1,2-Diphenylethane-1,2-diyl) 3,3′-Diethyl Bis(malonate)* ((*S*,*S*)-**10**). According to *GP 1*, (*S*,*S*)-diphenylethane-1,2-diol (100 mg, 0.47 mmol), ethyl 2-(chlorocarbonyl)acetate (0.15 ml, 1.17 mmol), and pyridine (0.09 ml, 1.17 mmol) were stirred in THF/CH_2Cl_2 (10 ml/5 ml). A yellow solid formed rapidly, and,

after 15 min, additional THF (15 ml) was added, and the mixture was stirred for 12 h at 20°. Workup and CC (SiO_2; hexane/AcOEt 4:1) provided (*S,S*)-**10** (89 mg, 43%). Colorless oil. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.27–7.11 (*m*, 10 H); 6.11 (*s*, 2 H); 4.18 (*q*, *J* = 7.1, 4 H); 3.44 (*s*, 4 H); 1.23 (*t*, *J* = 7.1, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 165.83; 165.10; 134.81; 128.24; 127.87; 127.23; 75.96; 61.14; 41.16; 13.58.

*1,1′-(*exo,exo-*Bicyclo[2.2.1]heptane-2,3-diyl) 3,3′-Diethyl Bis(malonate)* (**13**). According to *GP 1*, **11** (600 mg, 5 mmol) provided, after CC (SiO_2; CH_2Cl_2/AcOEt 95:5), **13** (250 mg, 15%). Colorless oil. IR (neat): 2976*m*, 2878*w*, 1750*s*, 1735*s*, 1449*w*, 1411*m*, 1371*m*, 1333*s*, 1267*s*, 1183*s*, 1147*s*, 1037*m*, 955*w*, 919*w*, 850*w*, 733*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.75 (*d*, *J* = 1.6, 2 H); 4.17 (*q*, *J* = 7.1, 4 H); 3.35 (*s*, 4 H); 2.30 (br. *s*, 2 H); 1.81–1.75 (*m*, 1 H); 1.57–1.49 (*m*, 2 H); 1.26 (*t*, *J* = 7.1, 6 H); 1.22–1.15 (*m*, 3 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 166.77; 166.10; 77.41; 61.54; 41.42; 40.98; 33.50; 24.14; 14.08. EI-MS: 357 (M^+), 311 ([$M - C_2H_5OH$]$^+$). Anal. calc. for $C_{17}H_{24}O_8$ (356.38): C 57.30, H 6.79; found: C 57.21, H 6.52.

*(±)-1,1′-(*endo,exo-*Bicyclo[2.2.1]heptane-2,3-diyl) 3,3′-Diethyl Bis(malonate)* ((±)-**14**). According to *GP 1*, (±)-**12** (200 mg, 1.56 mmol) gave, after CC (SiO_2; $CH_2Cl_2 \rightarrow CH_2Cl_2$/AcOEt 95:5), (±)-**14** (360 mg, 65%). Colorless oil. IR (neat): 2978*m*, 2877*w*, 1751*s*, 1733*s*, 1458*w*, 1404*w*, 1371*m*, 1369*m*, 1328*s*, 1267*s*, 1187*s*, 1151*s*, 1035*s*, 1002*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.86 (*d*, *J* = 3.3, 1 H); 4.45 (br. *s*, 1 H); 4.16 (*q*, *J* = 7.3, 4 H); 3.35 (*s*, 2 H); 3.33 (*s*, 2 H); 2.57 (br. *s*, 1 H); 2.28 (br. *d*, *J* = 4.6, 1 H); 2.02–1.50 (*m*, 4 H); 1.24 (*t*, *J* = 7.3, 6 H); 1.22–1.15 (*m*, 2 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 164.07; 164.00; 163.59; 163.46; 79.63; 79.48; 59.07; 39.13; 36.94; 31.74; 22.06; 17.48; 11.52. EI-MS: 357 (M^+). Anal. calc. for $C_{17}H_{24}O_8$ (356.38): C 57.30, H 6.79; found: C 57.11, H 6.88.

*1,1′-[(*R,R*)-Butane-2,3-diyl] 3,3′-Diethyl Bis(malonate)* ((*R,R*)-**15**). According to *GP 1*, (2*R*,3*R*)-butane-2,3-diol (0.5 ml, 5.6 mmol), ethyl 2-(chlorocarbonyl)acetate (1.5 ml, 12.3 mmol), and pyridine (0.94 ml, 12.3 mmol) were reacted in CH_2Cl_2 (30 ml), and CC (SiO_2; hexane/AcOEt 4:1) gave (*R,R*)-**15** (1.12 g, 63%). Colorless oil. $[\alpha]_D^{25} = -13.6$ (*c* = 1.68, CH_2Cl_2). IR (neat): 2974*m*, 1748*s*, 1735*s*, 1448*m*, 1409*m*, 1370*s*, 1322*s*, 1266*s*, 1189*s*, 1153*s*, 1086*m*, 1031*s*, 964*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.00 (*m*, 2 H); 4.15 (*q*, *J* = 7.1, 4 H); 3.34 (*s*, 4 H); 1.24 (*t*, *J* = 7.1, 6 H); 1.21 (*d*, *J* = 6.2, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 165.99; 165.52; 71.96; 61.04; 41.17; 15.42; 13.55. EI-MS: 319 (*M*H$^+$). Anal. calc. for $C_{14}H_{22}O_8$ (318.33): C 52.82, H 6.97; found: C 53.01, H 7.02.

*1,1′-[(*S,S*)-Butane-2,3-diyl] 3,3′-Diethyl Bis(malonate)* ((*S,S*)-**15**). According to *GP 1*, (2*S*,3*S*)-butane-2,3-diol (992 mg, 11 mmol), ethyl 2-(chlorocarbonyl)acetate (3.5 ml, 27.5 mmol), and pyridine (2.17 ml, 27.5 mmol) were reacted in CH_2Cl_2 (40 ml) to give, after CC (SiO_2; hexane/AcOEt 3:1), (*S,S*)-**15** (2.39 g, 68%). $[\alpha]_D^{25} = 14.1$ (*c* = 0.262, CH_2Cl_2). Anal. calc. for $C_{14}H_{22}O_8$ (318.33): C 52.82, H 6.97; found: C 52.83, H 7.02.

*61,62-[(*R,R*)-Butane-2,3-diyl]* out-out-*61,62-Diethyl (*^{f}*C)-1,2:16,17-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* ((*R,R,*^{f}*C*)-**16**). According to *GP 2*, C_{60} (154 mg, 0.214 mmol), (*R,R*)-**15** (68 mg, 0.214 mmol), I_2 (113 mg, 0.445 mmol), and DBU (0.17 ml) were reacted in PhMe (270 ml) for 1.5 h to give, after CC (SiO_2; CH_2Cl_2/hexane 1:1), (*R,R,*^{f}*C*)-**16** (52 mg, 24%). Rusty-brown solid. M.p. >250°. UV/VIS (CH_2Cl_2): 708 (120), 645 (300), 450 (1890), 320 (37600), 255 (110500). CD (CH_2Cl_2): 712 (−28), 660 (0.2), 644 (−4.4), 595 (9), 551 (8), 491 (24), 427 (−16), 415 (6), 400 (−10), 395 (−9), 380 (−28), 342 (50), 324 (2), 312 (27), 301 (0), 281 (92), 260 (−148), 242 (−41). IR (KBr): 2966*w*, 2922*w*, 1750*s*, 1238*s*, 1050*w*, 526*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.21–5.15 (*m*, *J* = 7.9, 6.1, 2 H); 4.53–4.34 (*m*, 4 H); 1.46 (*d*, *J* = 6.1, 6 H); 1.44 (*t*, *J* = 7.1, 6 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 164.02; 162.84; 146.62; 146.52; 145.52; 145.51; 145.45; 145.36; 145.33; 145.04; 144.92; 144.81; 144.44; 144.39; 143.98; 143.82; 143.55; 143.19; 142.59; 142.44; 142.42; 141.98; 141.72; 141.18; 140.99; 140.78; 140.72; 140.70; 135.16; 129.27; 75.26; 71.55; 68.44; 63.32; 49.71; 16.41; 14.17. FAB-MS: 1035 (100, *M*H$^+$), 720 (86, C_{60}^+).

*61,62-[(*S,S*)-Butane-2,3-diyl]* out,out-*61,62-Diethyl (*^{f}A*)-1,2:16,17-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* ((*S,S,*^{f}*A*)-**16**). According to *GP 2*, C_{60} (500 mg, 0.69 mmol), (*S,S*)-**15** (260 mg, 0.81 mmol), I_2 (440 mg, 1.73 mmol), and DBU (0.6 ml) were reacted in PhMe for 1.5 h to give, after CC (SiO_2; CH_2Cl_2/hexane 1:1); (*S,S,*^{f}*A*)-**16** (70 mg, 8%). HPLC Analysis (*Nucleosil 100-7*, flow rate 2.0 ml min^{-1}, hexane/AcOEt 6:1; t_R ((*S,S,*^{f}*A*)-**16**) 23.2 min) showed complete absence of the second (*S,S,*^{f}*C*)-diastereoisomer. HPLC with CH_2Cl_2/hexane 3:2 of the product, which had not been purified by CC, provided an additional peak (4% of the integral intensity of the main product), which presumably corresponded to the *cis-2* bis-adduct. CD (CH_2Cl_2): 711 (26), 662 (−0.2), 642 (4), 595 (−9), 551 (−8), 490 (−23), 427 (16), 416 (−7), 400 (11), 396 (9), 380 (28), 342 (−52), 323 (−2), 313 (−27), 303 (0), 281 (−92), 261 (148), 243 (41).

*1,1′-[(*R,R*)-Cyclohexane-1,2-diyl] 3,3′-Diethyl Bis(malonate)* ((*R,R*)-**19**). (*R,R*)-Cyclohexane-1,2-diol (150 mg, 1.39 mmol), ethyl 2-(chlorocarbonyl)acetate (0.65 ml, 5.17 mmol), and DMAP (631 mg, 5.17 mmol) were dissolved at 0° in CH_2Cl_2 (20 ml), and the mixture was stirred for 12 h at 20°. The soln. was washed with H_2O (2×) and sat. aq. NH_4Cl soln., then dried ($MgSO_4$). CC (SiO_2; CH_2Cl_2/AcOEt 95:5) provided (*R,R*)-**19**

(120 mg, 25%). Colorless oil. $[\alpha]_D^{25} = -27.5$ ($c = 0.2$, CH_2Cl_2). IR (neat): 2944*m*, 1750*s*, 1734*s*, 1455*m*, 1370*s*, 1333*s*, 1267*s*, 1189*s*, 1143*s*, 1035*s*, 844*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.89–4.86 (*m*, 2 H); 4.19 (*q*, $J = 7.5$, 4 H); 3.36 (*s*, 4 H); 2.11–2.02 (*m*, 2 H); 1.79–1.68 (*m*, 2 H); 1.45–1.32 (*m*, 4 H); 1.28 (*t*, $J = 7.5$, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 166.15; 165.67; 73.99; 61.04; 41.20; 29.46; 22.82; 13.65. CI-MS: 345 (M^+). Anal. calc. for $C_{16}H_{24}O_8$ (344.36): C 55.81, H 6.55; found: C 55.62, H 6.75.

*61,62-[(*R,R*)-Cyclohexane-1,2-diyl]* out,out-*61,62-Diethyl (*^{f}*C)-1,2 :16,17-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* ((*R*,*R*,^{f}*C*)-**20**). According to *GP 2*, C_{60} (174 mg, 0.24 mmol), (*R*,*R*)-**19** (100 mg, 0.29 mmol), I_2 (152 mg, 0.6 mmol), and DBU (0.22 ml) were reacted in PhMe (600 ml) for 2 h to give, after CC (SiO_2; CH_2Cl_2), (*R*,*R*,^{f}*C*)-**20** (80 mg, 32%). HPLC Analysis (SiO_2; PhMe, flow rate: 1 ml min^{-1}) showed traces of a side product, presumably corresponding to a bis-fullerene derivative resulting from mono-addition of the bis-malonate to two C-spheres. Rusty-brown solid. M.p. >250°. UV/VIS (CH_2Cl_2): 703 (290), 641 (490), 454 (1800), 409 (sh, 4200), 316 (35000), 255 (101800). CD (CH_2Cl_2): 712 (−28), 660 (−4.4), 644 (−10), 595 (9), 551 (8), 493 (28), 427 (−16), 415 (6), 411 (−9), 400 (−8), 380 (−28), 342 (50), 324 (12), 312 (27), 301 (10), 281 (82), 260 (−138). IR (KBr): 2922*w*, 1747*s*, 1261*s*, 1233*s*, 1200*m*, 1094*w*, 1050*w*, 1011*w*, 526*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.29–5.06 (*m*, 2 H); 4.54–4.45 (*m*, 4 H); 2.42–2.40 (*m*, 2 H); 1.90–1.89 (*m*, 2 H); 1.57–1.43 (*m*, 4 H); 1.45 (*t*, $J = 7.2$, 6 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 164.06; 162.90; 146.68; 146.59; 145.63; 145.57; 145.51; 145.44; 145.40; 145.10; 144.99; 144.88; 144.52; 144.46; 144.06; 143.92; 143.63; 143.27; 142.56; 142.48 (2×); 142.03; 141.18 (2×); 141.06; 140.83; 140.78; 140.75; 135.30; 129.48; 75.54; 71.69; 68.60; 63.34; 49.85; 30.41; 23.59; 14.17. FAB-MS: 1061 (100, MH$^+$), 720 (75, C_{60}^+).

*Methyl 4,6-*O,O*-Benzylidene-2,3-*O,O*-bis[(ethoxycarbonyl)acetyl]-α-*D*-glucopyranoside* ((α,D)-**21**). Methyl 4,6-*O*,*O*-benzylidene-α-D-glucopyranoside (1 g, 3.5 mmol), ethyl 2-(chlorocarbonyl)acetate (1.11 ml, 8.8 mmol), and DMAP (1.07 g, 8.8 mmol) were dissolved at 0° in CH_2Cl_2, and the soln. was stirred for 12 h at 20°. The mixture was extracted with H_2O (2×), then sat. aq. NH_4Cl soln., and dried ($MgSO_4$). Evaporation and CC (SiO_2; hexane/AcOEt 3:1) afforded (α,D)-**21** (100 mg, 6%). Colorless oil. $[\alpha]_D^{25} = +345$ ($c = 0.058$, CH_2Cl_2). IR (neat): 2983*m*, 2933*m*, 1761*s*, 1732*s*, 1455*m*, 1367*s*, 1327*s*, 1267*s*, 1189*s*, 1147*s*, 1035*s*, 922*w*, 752*m*, 701*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.45–7.43 (*m*, 2 H); 7.34–7.31 (*m*, 3 H); 5.62 (*dd*, $J = 9.9$, 9.9, 1 H); 5.50 (*s*, 1 H); 4.97 (*dd*, $J = 9.9$, 3.7, 1 H); 4.94 (*d*, $J = 3.7$, 1 H); 4.30 (*dd*, $J = 9.9$, 4.9, 1 H); 4.19 (*dq*, $J = 7.5$, 0.4, 2 H); 4.12–4.07 (*m*, 2 H); 3.93 (*ddd*, $J = 9.9$, 9.9, 4.9, 1 H); 3.77 (*dd*, $J = 9.9$, 9.9, 1 H); 3.67 (*dd*, $J = 9.9$, 9.9, 1 H); 3.45 (*d*, $J = 1.3$, 2 H); 3.41 (*s*, 3 H); 3.38 (*d*, $J = 3.3$, 2 H); 1.27 (*t*, $J = 7.1$, 3 H); 1.17 (*t*, $J = 7.1$, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 166.19 (2×); 166.16; 166.35; 136.79; 129.00; 128.12 (2×); 126.11 (2×); 101.52; 97.45; 78.92; 71.92; 69.56; 68.73; 62.32; 61.54; 61.40; 55.46; 41.42; 41.05; 13.98; 13.91. CI-MS: 511 (M^+). Anal. calc. for $C_{24}H_{30}O_{12}$ (510.50): C 56.47, H 5.92; found: C 56.65, H 5.70.

*Methyl 4,6-*O,O*-Benzylidene-2,3-*O,O*-[(*^{f}A)-out,out-*61,62-bis(ethoxycarbonyl)-1,2 :16,17-bis(methano)[60]fullerene-61,62-dicarbonyl]-α-*D*-glucopyranoside ((α,D,*^{f}*A*)-**22**) and Methyl 4,6-*O,O*-Benzylidene-2,3-*O,O*-bis[61-(ethoxycarbonyl)-1,2-methano[60]fullerene-61-carbonyl]-α-*D*-glucopyranoside* ((α,D)-**23**). According to *GP 2*, the reaction of C_{60} (250 mg, 0.33 mmol), (α,D)-**21** (200 mg, 0.39 mmol), I_2 (219 mg, 0.86 mmol), and DBU (0.33 ml) in PhMe (600 ml) for 2 h, followed by CC (SiO_2; CH_2Cl_2), afforded (α,D)-**23** (20 mg, 0.011 mmol 7%), followed by (α,D,^{f}*A*)-**22** (53 mg, 0.043 mmol, 13%).

*Data of (*α,D,^{f}*A*)-**22**. Rusty-brown solid. M.p. >250°. UV/VIS (CH_2Cl_2): 699 (330), 634 (520), 454 (1940), 316 (35000), 255 (110000). CD (CH_2Cl_2): 711 (33), 662 (3.8), 643 (10), 597 (−4), 492 (−20), 426 (18), 415 (−2), 401 (14), 395 (12), 381 (28), 341 (−69), 323 (−3), 326 (−22), 315 (−38), 299 (−10), 281 (−90), 263 (142). IR (KBr): 2978*w*, 2922*w*, 1748*s*, 1366*w*, 1234*s*, 1200*m*, 1097*m*, 1054*m*, 994*w*, 526*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.58–7.57 (*m*, 2 H); 7.41–7.35 (*m*, 3 H); 5.86–5.82 (*m*, 1 H); 5.64 (*s*, 1 H); 5.02 (*d*, $J = 3.7$, 1 H); 5.01 (*dd*, $J = 9.9$, 3.7, 1 H); 4.55–4.49 (*m*, 2 H); 4.40 (*dd*, $J = 9.9$, 4.9, 1 H); 4.28–4.17 (*m*, 2 H); 4.09 (*ddd*, $J = 9.9$, 9.9, 4.9, 1 H); 3.89 (*dd*, $J = 9.9$, 9.9, 1 H); 3.83 (*dd*, $J = 9.9$, 9.9, 1 H); 3.58 (*s*, 3 H); 1.49 (*t*, $J = 7.1$, 3 H); 1.03 (*t*, $J = 7.1$, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 163.82; 163.79; 163.27; 162.05; 146.74; 146.70; 146.59 (2×); 145.64; 145.56; 145.55 (2×); 145.52; 145.49; 145.47; 145.46; 145.41 (2×); 145.14; 145.11; 145.01; 144.94; 144.91; 144.88; 144.60; 144.48; 144.45; 144.32; 122.12; 122.10; 143.91; 143.85; 143.68; 143.63; 143.39; 143.35; 142.55; 142.53; 142.51; 142.48; 142.45; 142.41; 142.00; 141.98; 141.31; 141.23; 141.12; 141.05; 141.02; 140.99; 140.97; 140.93; 140.91; 140.90; 140.49; 140.47; 136.79; 135.46; 135.11; 129.59; 129.31; 129.18; 128.30 (2×); 126.07 (2×); 101.42; 97.36; 79.71; 73.34; 71.80; 71.51; 68.82; 68.46; 68.30; 63.55; 63.35; 62.10; 55.77; 49.66; 49.27; 14.27; 13.90.

*Data of (*α,D)-**23**. Rusty-brown solid. M.p. >250°. IR (KBr): 2956*w*, 2866*w*, 1747*s*, 1366*w*, 1233*s*, 1085*s*, 526*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.44–7.42 (*m*, 2 H); 7.28–7.20 (*m*, 3 H); 6.15 (*dd*, $J = 9.9$, 9.9, 1 H); 5.61 (*s*, 1 H); 5.52 (*dd*, $J = 9.9$, 3.7, 1 H); 5.29 (*d*, $J = 3.7$, 1 H); 4.75–4.65 (*m*, 2 H); 4.60 (*dq*, $J = 7.1$, 1.3, 2 H); 4.44 (*dd*, $J = 9.9$, 4.9, 1 H); 4.13 (*ddd*, $J = 9.9$, 9.9, 4.9, 1 H); 3.96 (*dd*, $J = 9.9$, 9.9, 1 H); 3.89 (*dd*, $J = 9.9$, 9.9, 1 H); 3.49 (*s*, 3 H); 1.55 (*t*, $J = 7.1$, 3 H); 1.44 (*t*, $J = 7.1$, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 163.77; 163.24; 163.08; 162.49;

145.88; 145.78; 145.71; 145.30; 145.28; 145.22; 145.19; 145.12; 145.09; 145.00; 144.94; 144.90; 144.87; 144.83; 144.79; 144.73; 144.66; 144.57; 144.54; 144.46; 144.30; 143.91; 143.86; 143.81; 143.11 (2×); 143.05; 142.95; 142.92; 142.84; 142.80; 142.74; 142.24; 142.20; 141.93; 141.76; 141.75; 141.68; 141.67; 141.15; 140.97; 140.87; 140.82; 140.77; 140.58; 140.27; 140.08; 140.06; 139.83; 138.52; 138.51; 138.08; 138.07; 136.58; 129.17; 128.31; 126.18; 101.84; 97.40; 79.37; 75.18; 74.99; 73.40; 71.82; 71.61; 71.43; 71.29; 70.99; 70.85; 70.75; 70.58; 68.80; 68.53; 63.86; 63.69; 62.39; 55.76; 14.50; 14.43.

(±)-1,1′-(Cyclopentane-1,2-diyl) 3,3′-Diethyl Bis(malonate) ((±)-**24**). According to *GP 1*, the reaction of (±)-*trans*-cyclopentane-1,2-diol (200 mg, 1.96 mmol), followed by CC (SiO_2; CH_2Cl_2/AcOEt 2:1), provided (±)-**24** (388 mg, 60%). Colorless oil. IR (Film): 2983*s*, 1750*s*, 1732*s*, 1447*w*, 1411*w*, 1369*m*, 1327*s*, 1266*s*, 1148*s*, 1083*s*, 1034*s*, 983*w*, 865*w*, 783*w*, 672*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.14–5.12 (*m*, 2 H); 4.16 (*q*, *J* = 7.2, 4 H); 3.21 (*s*, 4 H); 2.14–2.01 (*m*, 2 H); 1.82–1.62 (*m*, 4 H); 1.25 (*t*, *J* = 7.2, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 165.90; 165.36; 79.32; 61.14; 41.17; 29.74; 21.04; 13.58. EI-MS: 331 (3, MH^+), 199 (100, $[M - EtO_2CCH_2CO_2]^+$). Anal. calc. for $C_{15}H_{22}O_8$ (330.34): C 54.54, H 6.71; found: C 54.60, H 6.72.

(±)-61,62-(Cyclopentane-1,2-diyl) out,out-*61,62-Diethyl 1,2:16,17-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* ((±)-**25**). According to *GP 2*, the reaction of (±)-**24** (165 mg, 0.5 mmol) with C_{60} (300 mg, 0.416 mmol), followed by CC (SiO_2; CH_2Cl_2/AcOEt 1:1), afforded (±)-**25** (7 mg, 2%). Brown solid. M.p. >250°. UV/VIS (CH_2Cl_2): 700 (280), 635 (sh, 490), 460 (2200), 314 (35000), 252 (100000). ^{1}H-NMR (200 MHz, $CDCl_3$): 5.41 (*m*, 2 H); 4.54 (*q*, *J* = 7.2, 2 H); 4.53 (*q*, *J* = 7.2, 2 H); 2.42–2.41 (*m*, 2 H); 1.99–1.96 (*m*, 2 H); 1.82–1.75 (*m*, 2 H); 1.47 (*t*, *J* = 7.2, 3 H); 1.45 (*t*, *J* = 7.2, 3 H). FAB-MS: 1047 (72, M^+), 720 (100, C_{60}^+).

out,out-*61,62-Diethyl 61,62-[(*S,S*)-2,3-Dihydroxybutane-1,4-diyl] (^{f}C)-1,2:16,17-bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* ((*S,S,*^{f}*C*)-**27**). Compound (*S,S,*^{f}*C*)-**2** (92 mg, 0.083 mmol) was dissolved in CH_2Cl_2 (30 ml), and a layer of H_2O (15 ml) was added. After addition of CF_3CO_2H (1 ml), the mixture was stirred for 3 d at 20°. The separated org. phase was washed with sat. aq. $NaHCO_3$ soln. and H_2O, then dried ($MgSO_4$). Evaporation *in vacuo* and CC (SiO_2; $CH_2Cl_2 \rightarrow CH_2Cl_2$/MeOH 10:1) yielded (*S,S,*^{f}*C*)-**27** (19 mg, 21%). Brownish-red solid of sufficient purity to be directly used for the next conversion.

*61,62-((*S,S*)-2,3-Bis{[4-(dimethylamino)benzoyl]oxy}butane-1,4-diyl)* out,out-*61,62-Diethyl (^{f}C)-1,2:16,17-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* ((*S,S,*^{f}*C*)-**26**). DMAP (20 mg, 0.16 mmol) and 4-(dimethylamino)benzoyl chloride [13a] (22 mg, 0.12 mmol) were added to (*S,S,*^{f}*C*)-**27** (20 mg, 0.02 mmol), and the mixture was stirred for 4 d at 20°. CC (SiO_2; CH_2Cl_2) provided (*S,S,*^{f}*C*)-**26** (18 mg, 65%). Brown-red solid. M.p. >250°. UV/VIS (CH_2Cl_2): 696 (250), 631 (430), 452 (1600), 316 (78400), 255 (86400). CD (CH_2Cl_2): 702 (−40), 658 (−3), 642 (−15), 600 (2), 579 (−3), 488 (20), 429 (−5), 412 (2), 382 (−19), 342 (48), 325 (−22), 312 (19), 301 (2), 281 (94), 261 (−137). IR (KBr): 2967*w*, 1744*m*, 1717*m*, 1607*s*, 1263*s*, 1233*s*, 1183*s*, 1088*s*, 522*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.01 (*d*, *J* = 9.1, 4 H); 6.68 (*d*, *J* = 9.1, 4 H); 5.56 (*dd*, *J* = 9.7, 2.8, 2 H); 4.96 (*dd*, *J* = 9.7, 2.8, 2 H); 4.40–4.47 (*m*, 4 H); 4.30 (*t*, *J* = 9.7, 2 H); 3.07 (*s*, 12 H); 1.35 (*t*, *J* = 7.1, 6 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 163.37; 163.35; 162.61; 153.71; 146.68; 146.52; 145.61; 145.61; 145.29; 145.20; 144.97; 144.93; 144.86; 144.69; 144.61; 144.38; 144.31; 143.69; 143.63; 142.38; 142.26; 142.17; 141.53; 141.31; 141.00; 140.98; 140.92; 139.61; 139.10; 136.26; 131.76; 130.05; 115.72; 110.82; 71.63; 69.07; 67.46; 63.45; 40.07; 14.07. FAB-MS: 1361 (M^+), 720 (C_{60}^+).

*3,3′-[(*R,R*)-Butane-2,3-diyl] 1,1′-Di(*tert*-butyl) Bis(malonate)* ((*R,R*)-**29**). *tert*-Butyl malonate (2.24 g, 13.98 mmol) was added to (*R,R*)-butane-2,3-diol (0.42 mg, 4.6 mmol) in CH_2Cl_2 (60 ml), and the soln. was cooled to 0°. Solns. of DCC (2.88 g, 13.98 mmol) in CH_2Cl_2 (10 ml) and DMAP (227 mg, 1.8 mmol) in CH_2Cl_2 (10 ml) were added, and the mixture was stirred for 14 h at 20°. Filtration and evaporation of the filtrate *in vacuo* provided a residue, which was purified by CC (SiO_2; hexane/AcOEt 3:1) to give (*R,R*)-**29** (860 mg, 49%). Colorless oil. $[\alpha]_D^{25} = +13.8$ (*c* = 0.58, CH_2Cl_2). IR (neat): 2982*m*, 1750*s*, 1731*s*, 1458*m*, 1369*s*, 1327*s*, 1277*s*, 1281*s*, 1144*s*, 1086*m*, 1022*m*, 968*w*, 840*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.09–5.00 (*m*, 2 H); 3.32 (*s*, 4 H); 1.48 (*s*, 18 H); 1.27 (*d*, *J* = 5.8, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 164.04; 163.31; 79.70; 69.77; 40.50; 25.45; 13.43. EI-MS: 375 (MH^+). Anal. calc. for $C_{18}H_{30}O_8$ (374.43): C 57.74, H 8.08; found: C 57.76, H 7.94.

*61,62-[(*R,R*)-Butane-2,3-diyl]* out,out-*61,62-Di(*tert*-butyl) (^{f}C)-1,2:16,17-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* ((*R,R,*^{f}*C*)-**30**). According to *GP 2*, reaction of C_{60} (500 mg, 0.69 mmol), (*R,R*)-**29** (312 mg, 0.83 mmol), I_2 (440 mg, 1.73 mmol), and DBU (6.5 ml) in PhMe (1 l) for 2 h, followed by CC (SiO_2; CH_2Cl_2/hexane 2:1), gave (*R,R,*^{f}*C*)-**30** (90 mg, 12%). HPLC (SiO_2; PhMe, flow rate 1 ml min^{-1}) of the crude product showed that traces of another regioisomer had also formed. The UV/VIS analysis of a small isolated quantity (1 mg) indicated that this minor side product is an *e* isomer. Rusty-brown solid. M.p. >250°. UV/VIS (CH_2Cl_2): 709 (150), 645 (290), 451 (1890), 320 (37000), 255 (110000). CD (CH_2Cl_2): 712 (−27), 661 (0.3), 644 (−4.4), 595 (10), 551 (8), 491 (24), 427 (−16), 414 (5), 401 (−11), 395 (−8), 379 (−29), 342 (50), 324 (2), 312 (26), 301 (0), 281 (92), 262 (−152), 242 (−43). IR (KBr): 2967*w*, 2922*w*, 1741*s*, 1261*s*, 1246*s*, 1151*s*, 526*m*.

^{1}H-NMR (200 MHz, $CDCl_3$): 5.21–5.17 (*m*, 2 H); 1.67 (*s*, 18 H); 1.51 (*d*, *J* = 6.0, 6 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 163.28; 162.81; 146.42; 146.61; 145.81; 145.51; 145.41; 145.39; 145.34; 145.07; 144.97; 144.83; 144.68; 144.53; 144.49; 144.00; 143.92; 143.61; 143.22; 143.02; 142.55; 142.49; 142.38; 142.09; 141.87; 141.27; 141.23; 141.06; 141.00; 140.71; 140.70; 135.22; 129.35; 85.57; 75.13; 71.66; 68.69; 50.78; 28.16; 16.50. FAB-MS: 1090 (100, M^+), 720 (78, C_{60}^+).

*61,62-[(*R,R*)-Butane-2,3-diyl]* out,out-*61,62-Dihydrogen (*^{f}*C)-1,2 :16,17-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* ((*R*,*R*,^{f}*C*)-**31**). A soln. of (*R*,*R*,^{f}*C*)-**30** (70 mg, 0.064 mmol) and $TsOH \cdot H_2O$ (244 mg, 1.2 mmol) in PhMe/MeCN (100 ml/100 ml) was heated to reflux for 4 h. Since TLC analysis (SiO_2; CH_2Cl_2) revealed remaining starting material, CF_3CO_2H (1 ml) was added, and the mixture was stirred for 14 h at 20°. The conversion was still not complete, and additional CF_3CO_2H (2 ml) was added, and the mixture was heated to reflux for 7 h. After addition of CH_2Cl_2 (200 ml), the soln. was washed with H_2O (5×) and dried ($MgSO_4$). Evaporaton *in vacuo* provided a residue, which was re-precipitated from THF/hexane to give crude (*R*,*R*,^{f}*C*)-**31** (53 mg, 85%), which was used in the next reaction without further purification. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.52–5.43 (*m*, 2 H); 1.51 (*d*, *J* = 5.8, 6 H).

*61,62-[(*R,R*)-Butane-2,3-diyl]* out,out-*61,62-Bis{4-[10,15,20-tris(4-methylphenyl)porphyrin-5-yl]phenyl}(*^{f}*C)-1,2 :16,17-Bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate* ((*R*,*R*,^{f}*C*)-**28**). $(COCl)_2$ (20 ml) was added to (*R*,*R*,^{f}*C*)-**31** (53 mg, 0.054 mmol) in THF (20 ml), and the mixture was stirred for 12 h at 20°. Evaporation *in vacuo* provided a residue, which was dried for 1 h at 20°/10^{-2} Torr. The crude bis(acyl halide) was dissolved in CH_2Cl_2 (200 ml), and **32** (200 mg, 0.3 mmol) and DMAP (36 mg, 0.3 mmol) were added. After stirring for 4 h at 20°, CC (SiO_2; CH_2Cl_2) and reprecipitation (CH_2Cl_2/hexane) yielded (*R*,*R*,^{f}*C*)-**28** (40 mg, 30%). Brown solid. M.p. >250°. UV/VIS (CH_2Cl_2): 699 (250), 647 (11000), 592 (11100), 551 (19400), 515 (36900), 486 (sh, 8900), 419 (911000), 402 (sh, 166000), 313 (sh, 72100), 255 (167000). CD (CH_2Cl_2): 712 (–33), 661 (–4.4), 645 (–8.6), 598 (5.2), 551 (8), 492 (18), 423 (20), 416 (–13), 409 (–7.7), 400 (–15), 394 (–12), 382 (–26), 341 (69), 325 (23), 315 (39), 298 (7.6), 282 (75), 262 (–147). Zero-intercept point of exciton couplet: 420 nm. IR (KBr): 2922*w*, 1744*s*, 1222*s*, 1199*s*, 1161*s*, 961*m*, 800*s*, 526*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.89–8.84 (*m*, 16 H); 8.34–8.31 (*m*, 4 H); 8.12–8.10 (*m*, 12 H); 7.75–7.72 (*m*, 4 H); 7.59–7.56 (*m*, 12 H); 5.43–5.40 (*m*, 2 H); 2.72 (*s*, 6 H); 2.71 (*s*, 12 H); 1.70–1.69 (*m*, 6 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 163.01; 162.72; 149.98; 145.82; 145.79; 145.73; 145.19; 145.14; 145.10; 144.85; 144.74; 144.71; 144.53; 144.48; 144.37; 144.28; 144.19; 143.90; 143.83; 143.43; 143.37; 143.30; 143.02; 142.93; 142.72; 142.67; 142.62; 142.39; 142.28; 141.89; 141.75; 141.57; 141.13; 140.57; 140.45; 140.41; 140.03; 139.95; 139.27; 139.22; 137.41; 135.52; 134.53; 127.49; 127.46; 120.42; 119.56; 118.08; 75.81; 71.46; 68.35; 49.46; 28.16; 21.54; 16.83.

*Bis{4-[10,15,20-tris(4-methylphenyl)porphyrin-5-yl]phenyl}(*R*)-9,9′-Spirobifluorene-2,2′-dicarboxylate* ((*R*)-**33**). $(COCl)_2$ (50 ml) was added to (+)-(*R*)-**34** (200 mg, 0.5 mmol) in abs. THF (100 ml), followed by addition of one drop of DMF. After stirring for 4 h at 20°, the mixture was evaporated *in vacuo*, and the residue was dried for 1 h at 20°/10^{-2} Torr. The crude bis(acyl halide) was dissolved in CH_2Cl_2 (200 ml), and **32** (733 mg, 1.1 mmol), C_5H_5N (3 ml) and DMAP (122 mg, 0.94 mmol) were added. After stirring for 4 h at 20°, CC (SiO_2, CH_2Cl_2) yielded (*R*)-**33** (339 mg, 46%). Violet crystals. M.p. >250°. UV/VIS (CH_2Cl_2): 647 (12900), 592 (14200), 551 (24900), 516 (48500), 484 (sh, 9600), 418 (1216000), 401 (sh, 228000), 325 (72200), 313 (sh, 68100), 298 (96800), 291 (sh, 88900). CD (CH_2Cl_2): 425 (250), 416 (–130), 378 (22), 342 (15), 309 (33), 301 (–14), 293 (–8), 285 (–13), 240 (15). Zero-intercept point of exciton couplet: 420 nm. IR (KBr): 3311*w*, 3022*w*, 2911*w*, 1736*s*, 1500*m*, 1469*m*, 1250*s*, 1195*s*, 1161*s*, 961*s*, 799*s*, 730*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.92–8.87 (*m*, 16 H); 8.54 (*dd*, *J* = 8.3, 1.3, 2 H); 8.27–8.24 (*m*, 4 H); 8.12 (*d*, *J* = 7.7, 2 H); 8.11 (*d*, *J* = 7.7, 12 H); 8.07 (*d*, *J* = 7.7, 4 H); 7.84 (*s*, 2 H); 7.59–7.55 (*m*, 4 H); 7.55 (*d*, *J* = 7.7, 12 H); 7.53 (*dd*, *J* = 7.5, 7.5, 2 H); 7.36 (*dd*, *J* = 7.5, 7.5, 2 H); 6.97 (*d*, *J* = 7.5, 2 H); 2.75 (*s*, 18 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 165.13; 150.77; 149.16; 148.32; 147.47; 140.56; 139.87; 139.26; 139.22; 137.33; 135.32; 134.49; 131.00; 129.58; 129.06; 128.48; 127.41; 127.39; 126.03; 124.31; 121.42; 120.43; 120.35; 120.24; 119.95; 118.64; 65.94; 21.49. FAB-MS: 1714 (100, M^+).

tert-*Butyl 2-[2-(2-Methoxyethoxy)ethoxy]ethyl Malonate* (**36**). Solns. of DCC (2.0 g, 9.6 mmol) in CH_2Cl_2 (10 ml) and DMAP (350 mg, 3 mmol) in CH_2Cl_2 (10 ml) were added at 0° to **8** (2.0 g, 8.0 mmol) and *t*-BuOH (720 mg, 9.6 mmol) in CH_2Cl_2 (100 ml), and the mixture was stirred for 12 h at 20°. The formed crystals were removed by filtration, and the filtrate was evaporated *in vacuo* to give a residue, which was purified by CC (SiO_2; AcOEt/hexane 3 :1) to yield **36** (2.0 g, 80%). Colorless oil. IR (neat): 2878*m*, 1744*s*, 1728*s*, 1450*w*, 1369*m*, 1327*m*, 1283*m*, 1250*m*, 1143*s*, 1033*m*, 966*w*, 851*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.71–3.70 (*m*, 2 H); 3.69–3.68 (*m*, 2 H); 3.63–3.59 (*m*, 6 H); 3.54–3.49 (*m*, 2 H); 3.34 (*s*, 3 H); 3.28 (*s*, 2 H); 1.44 (*s*, 9 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 166.56; 165.2; 81.58; 71.49; 70.15 (3×); 68.47; 63.93; 58.57; 42.31; 27.45. ESI-MS: 324 (100, $[M + NH_4]^+$), 329 (55, $[M + Na]^+$). Anal. calc. for $C_{14}H_{26}O_7$ (306.36): C 54.89, H 8.55; found: C 54.77, H 8.44.

tert-*Butyl 2-[2-(2-Methoxyethoxy)ethoxy]ethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate* (**37**). According to *GP 2*, reaction of C_{60} (552 mg, 0.75 mmol), **36** (1.0 g, 0.81 mmol), I_2 (456 mg, 1.75 mmol), and DBU (0.9 ml) for 2 h, followed by CC (SiO_2; CH_2Cl_2/MeOH 40:1), afforded **37** (338 mg, 44%). Red-brown solid. M.p. >250°. UV/VIS (CH_2Cl_2): 689 (200), 483 (2100), 424 (2700), 325 (41000), 262 (142000). IR (KBr): 3439*m*, 2875*m*, 1746*s*, 1422*w*, 1372*w*, 1260*s*, 1231*s*, 1199*m*, 1096*s*, 802*m*, 526*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.65–4.63 (*m*, 2 H); 3.90–3.88 (*m*, 2 H); 3.73–3.70 (*m*, 2 H); 3.68–3.64 (*m*, 4 H); 3.57–3.54 (*m*, 2 H); 3.38 (*s*, 3 H); 1.69 (*s*, 9 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 163.97; 162.17; 145.60; 145.43; 145.28; 145.24; 145.22; 145.16; 145.15; 144.84; 144.71; 144.68; 144.66; 144.56; 143.88; 143.08; 143.07; 143.00; 142.98; 142.96; 142.22; 142.20; 141.91; 141.89; 140.93; 140.88; 139.08; 138.94; 85.18; 71.94; 71.84; 70.67; 70.66; 70.64; 68.83; 66.06; 59.07; 53.08; 28.03. FAB-MS: 1024 (45, M^+), 720 (100, C_{60}^+). Anal. calc. for $C_{74}H_{24}O_7$ (1025.00): C 86.71, H 2.36; found: C 86.65, H 2.44.

Hydrogen 2-[2-(2-Methoxyethoxy)ethoxy]ethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate (**38**). A mixture of **37** (1.2 g, 1.17 mmol) and $TsOH \cdot H_2O$ (1.14 g, 5.99 mmol) in PhMe (600 ml) was heated to reflux for 4 h. The soln. was washed with H_2O (5 × 200 ml), and the org. phase was dried and evaporated *in vacuo*. Re-precipitation (CH_2Cl_2/hexane) provided **38** (1.063 g, 94%). Red-brown solid. M.p. >250°. UV/VIS (CH_2Cl_2): 686 (200), 485 (2100), 425 (2900), 324 (40000), 260 (142000). IR (KBr): 3422*s*, 2867*m*, 1742*s*, 1427*w*, 1232*s*, 1089*m*, 526*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.68–4.67 (*m*, 2 H); 3.94–3.92 (*m*, 2 H); 3.81–3.79 (*m*, 6 H); 3.76–3.73 (*m*, 2 H); 3.58 (*s*, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 164.01; 163.77; 145.60; 145.44; 145.33; 145.30; 145.21; 145.12; 145.14; 145.12; 144.83; 144.75; 144.68; 144.66; 144.55; 144.53; 143.89; 143.86; 143.04; 143.03; 142.97 (2×); 142.94; 142.22; 142.21; 141.99; 141.97; 140.92; 140.90; 139.42; 138.80; 72.22; 71.84; 70.91; 70.32; 69.64; 68.25; 66.00; 58.74; 52.38. FAB-MS: 969 (50, M^+), 720 (100, C_{60}^+). Anal. calc. for $C_{70}H_{16}O_7$ (968.89): C 86.78, H 1.66; found: C 86.59, H 1.70.

*(*R,R*)-[[5-(Hydroxymethyl)-2,2-dimethyl-1,3-dioxolan-4-yl]methyl] 2-[2-(2-Methoxyethoxy)ethoxy]ethyl 1,2-Methano[60]fullerene-61,61-dicarboxylate* ((*R,R*)-**39**). A mixture of **38** (215 mg, 0.123 mmol) and $(COCl)_2$ (25 ml) in CH_2Cl_2 (15 ml) was stirred at 20° for 12 h. Evaporation *in vacuo* afforded crude acyl chloride, which was dissolved in CH_2Cl_2 (10 ml). (*R,R*)-(2,2-dimethyl-1,3-dioxolan-4,5-diyl)bis(methanol) (108 mg, 0.666 mmol) and pyridine (0.04 ml, 0.5 mmol) were added, and the mixture was stirred for 12 h, then washed with sat. aq. NH_4Cl soln., and dried ($MgSO_4$). CC (SiO_2; CH_2Cl_2/MeOH 40:1) gave (*R,R*)-**39** (160 mg, 65%), which was re-precipitated (CH_2Cl_2/hexane) for elemental analysis. Red-brown solid. M.p. >250°. UV/VIS (CH_2Cl_2): 688 (200), 483 (2100), 425 (2700), 325 (41300), 262 (141500). IR (KBr): 3431*s*, 2867*m*, 1746*s*, 1372*w*, 1232*s*, 1097*s*, 526*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.68 (*dd*, *J* = 10.6, 4.7, 1 H); 4.67–4.64 (*m*, 2 H); 4.62 (*dd*, *J* = 10.6, 4.7, 1 H); 4.34–4.30 (*dt*, *J* = 8.1, 4.7, 1 H); 4.14–4.11 (*dt*, *J* = 8.1, 4.3, 1 H); 3.91–3.88 (*m*, 2 H); 3.90–3.86 (*m*, 1 H); 3.83–3.76 (*m*, 1 H); 3.73–3.70 (*m*, 2 H); 3.68–3.62 (*m*, 4 H); 3.56–3.54 (*m*, 2 H); 3.38 (*s*, 3 H); 2.43 (*t*, *J* = 6.7, 1 H); 1.49 (*s*, 3 H); 1.48 (*s*, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 163.41; 163.27; 145.29; 145.21; 145.19; 145.10 (3×); 145.09; 144.97; 144.93; 144.66 (2×); 144.69; 144.64; 144.63; 144.59; 143.90; 143.88; 143.09; 143.03 (2×); 142.98; 142.20 (2×); 141.91; 141.87; 141.86; 140.98; 140.96; 139.23; 139.04; 139.03; 109.99; 78.31; 75.13; 71.92; 71.32; 70.62; 70.56; 68.78; 66.41; 66.28; 66.15; 62.11; 61.98; 59.03; 51.76; 27.13; 27.05. FAB-MS: 1112 (30, M^+), 720 (100, C_{60}^+). Anal. calc. for $C_{77}H_{28}O_{10}$ (1113.06): C 83.09, H 2.54; found: C 82.90, H 2.30.

(*S,S*)-**39** (166 mg, 67%) was prepared in the same way starting from **38** (215 mg, 0.222 mmol) and (*S,S*)-(2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(methanol) (108 mg, 0.67 mmol).

*61,61′-Bis{2-[2-(2-Methoxyethoxy)ethoxy]ethyl} 61,61′-(*R,R*)-(2,2-Dimethyl-1,3-dioxolane-4,5-diyl)bis-(methylene) Bis(1,2-methano[60]fullerene-61,61-dicarboxylate)* ((*R,R*)-**35**). A mixture of **38** (410 mg, 0.424 mmol) and $(COCl)_2$ in CH_2Cl_2 (45 ml) was stirred for 12 h at 20°, then evaporated *in vacuo* to give a crude acyl chloride, which was dried for 1 h at 20°/10^{-2} Torr, then dissolved in CH_2Cl_2. Fullerene derivative (*R,R*)-**39** (150 mg, 0.153 mmol) and pyridine (0.015 ml, 0.2 mmol) were added, followed by a second addition of pyridine (0.1 ml) after 1 h. After stirring for 12 h at 20°, CC (SiO_2; CH_2Cl_2/MeOH 50:1) yielded (*R,R*)-**35** (43 mg, 14%), which was re-precipitated (CH_2Cl_2/hexane) and dried at 20°/10^{-2} Torr. Red-brown powder. M.p. >250°. UV/VIS (CH_2Cl_2): 686 (379), 601 (sh, 1030), 548 (sh, 1900), 481 (2900), 426 (5300), 412 (sh, 5700), 325 (67500), 262 (270000). CD (CH_2Cl_2): 509 (0.26), 432 (−0.16), 419 (0.21), 407 (0.02), 396 (0.16), 385 (0.01), 372 (0.07), 333 (−0.8). Zero-intercept points of exciton couplets: 426 and 320 nm. IR (KBr): 2870*m*, 1747*s*, 1230*s*, 1110*s*, 526*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.76–4.69 (*m*, 4 H); 4.68–4.66 (*m*, 4 H); 4.41–4.40 (*m*, 2 H); 3.89–3.87 (*m*, 4 H); 3.71–3.69 (*m*, 4 H); 3.66–3.63 (*m*, 8 H); 3.56–3.54 (*m*, 4 H); 3.37 (*s*, 6 H); 1.51 (*s*, 6 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 163.40; 163.27; 145.22 (2×); 145.10 (2×); 145.14 (2×); 145.11; 145.07; 145.05; 144.94; 144.71 (2×); 144.66; 144.63; 144.61; 143.90; 143.11; 143.05; 143.04; 143.01 (2×); 142.21 (2×); 141.93; 141.88; 141.85; 141.00; 140.95; 139.22; 139.10; 110.77; 75.61; 71.95; 71.32; 70.68; 70.63; 68.77; 66.33; 66.17; 59.07; 59.07; 51.86; 27.16. FAB-MS: 2063 (100, M^+), 720 (40, C_{60}^+).

(*S*,*S*)-**35** (52 mg, 21%) was prepared in the same way starting from **38** (380 mg, 0.393 mmol) and (*S*,*S*)-**39** (136 mg, 0.122 mmol). CD (CH_2Cl_2): 510 (−0.24), 430 (0.30), 422 (0.1), 406 (0.1), 397 (−0.05), 386 (0.01), 371 (−0.05), 332 (0.7). Zero-intercept points of exciton couplets: 424 and 318 nm.

*(*R,R*)-[5-(Methoxymethyl)-2,2-dimethyl-1,3-dioxolan-4-yl]methanol* ((*R*,*R*)-**41**). (*R*,*R*)-(2,2-Dimethyl-1,3-dioxolane-4,5-diyl)bis(methanol) (500 mg, 3.06 mmol) and MeI (438 mg, 3.06 mmol) were dissolved in THF (20 ml), and NaH (55% suspension in mineral oil; 134 mg, 3.06 mmol) was added. After stirring for 5 h, MeOH was added, and the mixture was filtered over a plug (SiO_2; AcOEt). CC (SiO_2; AcOEt/hexane 2:1) gave (*R*,*R*)-**41** (140 mg, 26%). Colorless oil. $[\alpha]_D^{25} = -3.0$ ($c = 0.166$, CH_2Cl_2). IR (neat): 3446*s*, 2987*s*, 2934*s*, 2878*s*, 1457*m*, 1372*m*, 1250*s*, 1216*s*, 1161*s*, 1082*s*, 1050*s*, 987*w*, 894*w*, 846*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.99 (*ddd*, $J = 8.3$, 5.3, 5.3, 1 H); 3.86 (*ddd*, $J = 8.3$, 5.0, 5.0, 1 H); 3.78–3.61 (*m*, 2 H); 3.55 (*dd*, $J = 10.0$, 5.3, 1 H); 3.45 (*dd*, $J = 10.0$, 5.0; 1 H); 3.37 (*s*, 3 H); 2.55 (br. *s*, 1 H); 1.38 (*s*, 6 H). ^{13}C-NMR (200 MHz, $CDCl_3$): 107.03; 76.97; 74.08; 70.68; 59.95; 57.01; 24.43. CI-MS: 177 (15, M^+), 119 (100, $[M - OC(Me)_2]^+$). Anal. calc. for $C_8H_{16}O_4$ (176.21): C 54.53, H 9.15; found: C 54.20, H 8.86.

*2-[2-(2-Methoxyethoxy)ethoxy]ethyl (*R,R*)-[5-(Methoxymethyl)-2,2-dimethyl-1,3-dioxolan-4-yl]methyl 1,2-Methano[60]fullerene-61,61-dicarboxylate* ((*R*,*R*)-**40**). A mixture of **38** (200 mg, 0.21 mmol) and $(COCl)_2$ (30 ml) in CH_2Cl_2 (30 ml) was stirred for 12 h at 20°. Evaporation *in vacuo* and drying (20°/10^{-2} Torr, 1 h) provided crude acyl chloride, which was dissolved in CH_2Cl_2 (30 ml). After addition of (*R*,*R*)-**41** (90 mg, 0.51 mmol) and DMAP (61 mg, 0.5 mmol), the mixture was stirred for 2 h at 20°. Filtration through a plug (SiO_2; CH_2Cl_2/MeOH 9:1) and CC (SiO_2; CH_2Cl_2/MeOH 80:1) yielded (*R*,*R*)-**40** (120 mg, 51%), which was re-precipitated (CH_2Cl_2/hexane) and dried at 20°/10^{-2} Torr. Red-brown powder. M.p. >250°. UV/VIS (CH_2Cl_2): 690 (210), 485 (2000), 424 (2700), 324 (42000), 262 (150000). CD (CH_2Cl_2): 687 (−0.06), 661 (−0.02), 616 (−0.06), 504 (0.08), 441 (0.04), 427 (0.11), 409 (0.02), 402 (0.07), 383 (−0.01), 351 (0.08), 325 (−0.38). IR (KBr): 2867*m*, 1743*s*, 1227*s*, 1094*s*, 838*w*, 526*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.69 (*dd*, $J = 11.7$, 3.6, 1 H); 4.66–4.64 (*m*, 2 H); 4.55 (*dd*, $J = 11.7$, 5.5, 1 H); 4.20 (*ddd*, $J = 8.2$, 5.5, 3.6, 1 H); 4.13 (*ddd*, $J = 8.2$, 5.0, 5.0, 1 H); 3.88–3.86 (*m*, 2 H); 3.71–3.68 (*m*, 2 H); 3.65–3.62 (*m*, 4 H); 3.62–3.57 (*m*, 2 H); 3.55–3.53 (*m*, 2 H); 3.43 (*s*, 3 H); 3.37 (*s*, 3 H); 1.48 (*s*, 3 H); 1.44 (*s*, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 163.39; 163.29; 145.28; 145.23; 145.20; 145.18; 145.14; 145.13; 145.13; 145.10; 144.99; 144.97; 144.92; 144.69; 144.65; 144.64; 144.63; 144.59; 143.89; 143.88; 143.20; 143.02; 142.97; 142.09; 141.89; 141.86; 140.95 (2×); 139.29; 138.99; 110.20; 76.15; 72.96; 71.92; 71.34; 70.69; 70.65; 70.61; 68.72; 66.55; 66.24; 59.61; 59.05; 51.86; 27.06; 27.00. FAB-MS: 1127 (40, M^+), 720 (50, C_{60}^+).

*(*R,R*)-(2,2-Dimethyl-1,3-dioxolan-4,5-diyl)bis(methylene) Bis(2-naphthoate)* ((*R*,*R*)-**42**). Solns. of DCC (522 mg, 2.53 mmol) in CH_2Cl_2 (10 ml) and DMAP (56 mg, 0.5 mmol) in CH_2Cl_2 (10 ml) were added at 0° to (*R*,*R*)-(2,2-dimethyl-1,3-dioxolan-4,5-diyl)dimethanol (187 mg, 1.15 mmol) and 2-naphthoic acid (516 mg, 3.0 mmol) in CH_2Cl_2 (100 ml), and the mixture was stirred for 12 h at 20°. Precipitated crystals were removed by filtration, and the filtrate was evaporated *in vacuo* to give a residue, which was purified by CC (SiO_2; hexane/AcOEt 3:1) to give (*R*,*R*)-**42** (335 mg, 62%). Colorless crystals. M.p. 153°. UV (CH_2Cl_2): 338 (2300), 321 (2900), 293 (9600), 283 (11700), 273 (15000), 237 (114000). CD (CH_2Cl_2): 242 (20), 229 (−16). Zero-intercept point of exciton couplet: 237 nm. IR (KBr): 2981*m*, 2932*m*, 1709*s*, 1463*w*, 1383*m*, 1352*s*, 1288*s*, 1228*s*, 1197*s*, 1168*m*, 1128*s*, 1088*s*, 970*m*, 879*m*, 847*m*, 783*s*, 769*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.67 (*d*, $J = 1.6$, 2 H); 8.08 (*dd*, $J = 8.2$, 1.6, 2 H); 7.97–7.85 (*m*, 6 H); 7.61–7.53 (*m*, 4 H); 4.68–4.63 (*m*, 4 H); 4.45–4.43 (*m*, 2 H); 1.54 (*s*, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 166.06; 135.26; 132.06; 131.01; 129.04; 128.03; 127.89; 127.36; 126.32; 126.31; 124.78; 110.12; 75.99; 64.03; 26.76. ESI-MS: 488 ($[M + NH_4]^+$).

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Received June 30, 2000