# Synthesis and Chiroptical Properties of Enantiomerically Pure Bis- and Trisadducts of $C_{60}$ with an Inherent Chiral Addition Pattern

**Francis Djojo and Andreas Hirsch***

**Abstract:** In this paper we describe facile access to enantiomerically pure bis- and trisadducts of $C_{60}$ with four different inherent chiral addition patterns, namely $^{f}C$- and $^{f}A$-I,II* (*trans-2*), $^{f}C$- and $^{f}A$-I,III* (*trans-3*), $^{f}C$- and $^{f}A$-I,III*,III* (*trans-3,trans-3,trans-3*) and $^{f}C$- and $^{f}A$-I,eI,eII (*e,e,e*), obtained by cyclopropanation of [6,6] double bonds with $C_2$-symmetrical bisoxazolines and subsequent chromatographic separation of the corresponding diastereomers on achiral stationary phases. The CD spectra of the related pairs of diastereomers, whose addition patterns represent pairs of enantiomers, reveal pronounced Cotton effects and mirror-image behavior. It is the chiral arrangement of the conjugated π-electron system within the fullerene core itself that predominantly determines the chiroptical properties. We show that the magnitude of the Cotton effects strongly depends on the extent of chiral distortion of the π-electron system within the fullerene cage.

**Keywords:** fullerenes · chirality · chiral auxiliaries · circular dichroism

## Introduction

The $I_h$ symmetry of $C_{60}$ is reduced if one or several addends are connected to the cage, for example, by cycloadditions to [6,6] bonds.[1] The addition pattern of the resulting adducts always corresponds to a subgroup of the $I_h$ point group. Among the possible subgroups of $I_h$ several, for example the $D_3$, $C_3$, $C_2$, and $C_1$ point groups, are chiral. An addition pattern of a $C_{60}$ adduct is inherently chiral[2,3] if it belongs to one of these point groups (Figure 1). When we investigated the regioselectivity of multiple nucleophilic cyclopropanations of $C_{60}$[3–8] we isolated the chiral adducts **1**–**5**, with the inherent chiral addition patterns **A**–**E** (Figure 1) as racemic mixtures. For the following reasons it is challenging to look for methods that allow synthesis and isolation of enantiomerically pure adducts of $C_{60}$ with an inherent chiral addition pattern: 1) The $C_{60}$ core is a unique tecton for the construction of fascinating new molecular structures including dendrimers[8] and novel carbon allotropes[9] and the use of core units with an addition pattern related to those shown in Figure 1 would provide axial chirality as an additional architecture principle. 2) The chiroptical properties of fullerene derivatives with an inherent chiral addition pattern, which are expected to depend on the structure of the conjugated π system (addition pattern), should be remarkable and comparable to those of helicenes, since the conjugated chromophore itself is responsible for the chirality. 3) Such bulky building blocks with axial chirality could find applications as new auxiliaries in enantioselective synthesis.

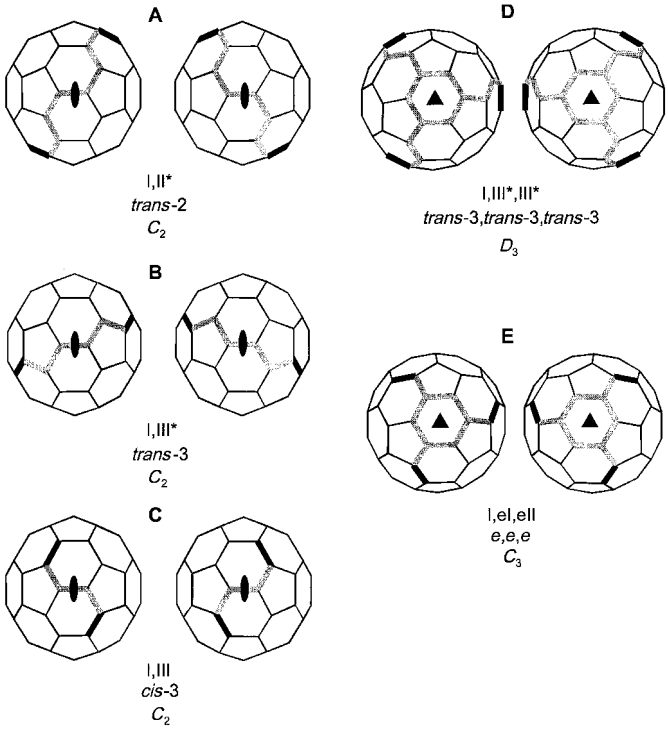


Figure 1. Schematic representations of inherent chiral addition patterns within bisadducts and trisadducts of $C_{60}$ as pairs of enantiomers. The bold black lines denote the [6,6] bonds carrying addends and the grey motifs represent $C_2$- or $C_3$-symmetrical substructures with the $C_2$ and $C_3$ axes as symmetry elements.

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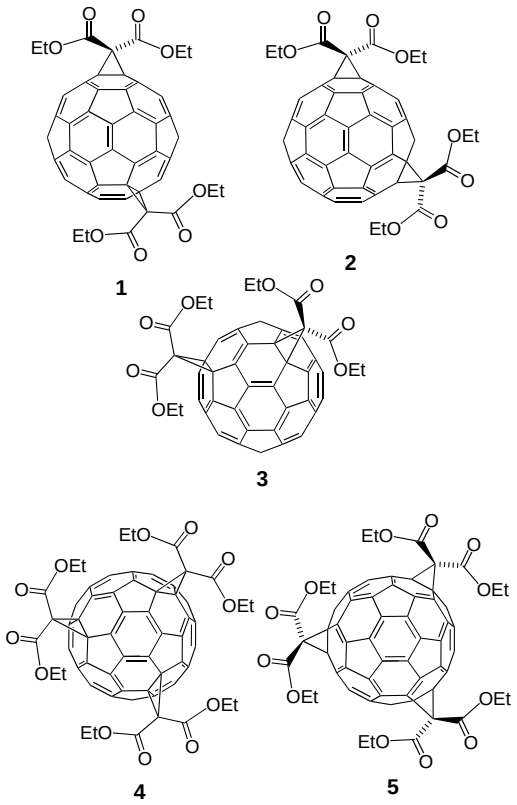
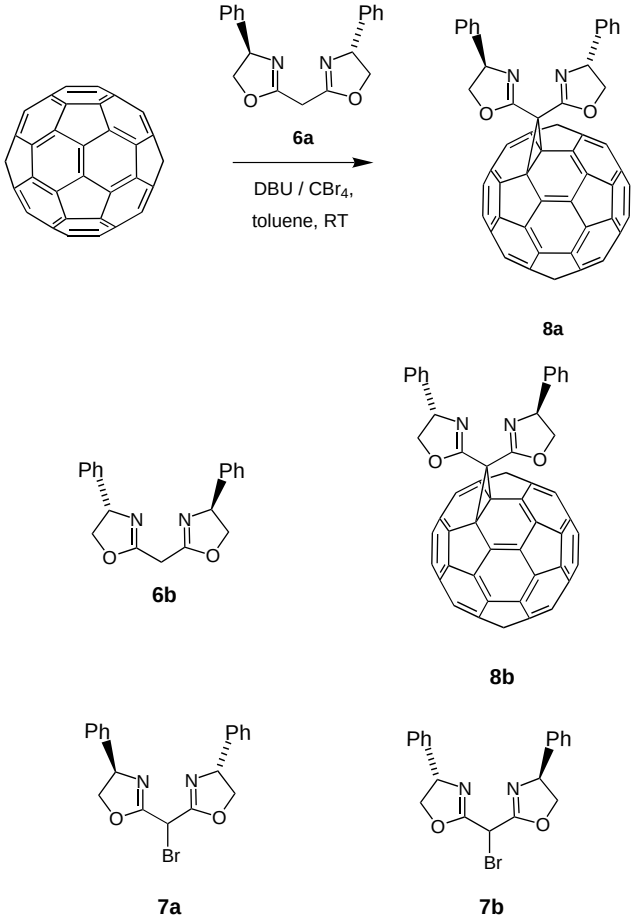
First efforts in this direction by the groups of Diederich[10] and Nakamura[11] provided access to enantiomerically pure adducts with the $C_2$ symmetrical addition pattern **C** (Figure 1) by diastereoselective tether-controlled bisadditions. Enantiomerically pure adducts of $C_{70}$ with inherent chiral addition patterns were isolated by Diederich and coworkers[12] by the addition of chiral addends and the subsequent separation of the diastereomeric adducts. Recently, we succeeded in enantiomer separation of **3–5** and other chiral $C_{60}$ adducts




by HPLC using the chiral Welk-O1 phase on a semipreparative scale.[13] In this work we describe the facile access to bis- and trisadducts with the inherent chiral addition patterns **A, B, D** and **E** (Figure 1) as well as to other enantiomerically pure $C_{60}$ derivatives by cyclopropanation with $C_2$-symmetrical bisoxazolines[14] and subsequent chromatographic separation on achiral stationary phases, for example silica gel and alumina. We show that the magnitude of the Cotton effects strongly depends on the extent of chiral distortion of the π-electron system within the fullerene cage.

## Results and Discussion

If one considers chiral addends connected to $C_{60}$, one can see that the stereoisomers of an adduct with an inherent chiral addition pattern are not a pair of enantiomers but a pair of diastereomers.[15] It should thus be possible to isolate enantiomerically pure compounds cheaply and easily in large quantities, since chromatography on conventional stationary phases could be used. However, this is only guaranteed if the corresponding addition reaction proceeds in comparatively good yields and the diastereomeric adducts separate well because of their structure and polarity. After surveying various types of reactions and addends, including cyclopropanations with optically active bromopropanedioates used by Diederich et al. to isolate chiral $C_{70}$[12] and $C_{76}$[16] derivatives, we found that the best results were obtained for nucleophilic cyclopropanations with the $C_2$-symmetrical bisoxazolines **6** (Scheme 1). The bisoxazolines, which are easily accessible

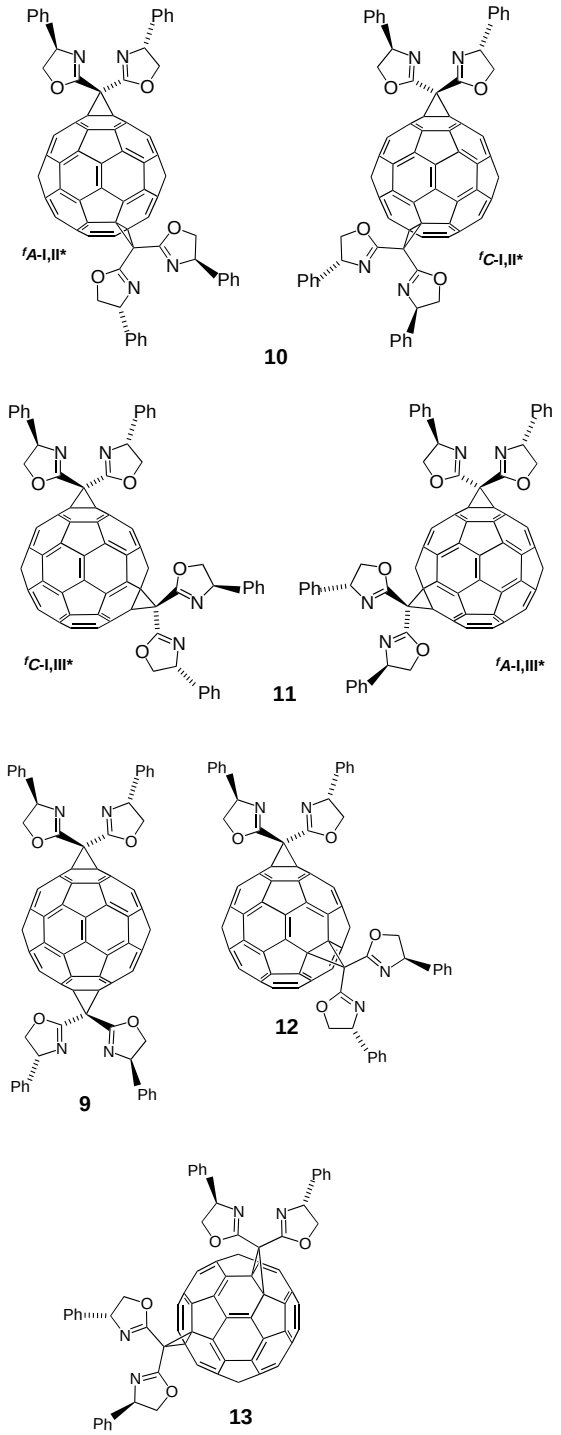



Scheme 1. Cyclopropanation of $C_{60}$ with $C_2$-symmetrical bisoxazolines.

from the corresponding amino acids,[14] are masked malonates and can therefore be used analogously for cyclopropanations of the strained [6,6] double bonds of $C_{60}$. As we have already shown for a variety of cyclopropanation reactions,[17] it is not necessary to isolate the bromomalonates[18] prior to the reaction with $C_{60}$. One-pot reactions in which the bromomalonates are prepared in situ from the corresponding unsubstituted malonates proceed in at least the same yield and avoid a time-consuming separation step. The in situ generation of **7** with $CBr_4$/DBU and the subsequent DBU-promoted deprotonation/cyclopropanation in one step allows the isolation of **8a** and **8b** with *R,R* and *S,S* configuration of the two stereogenic centers in 50% yield, respectively (Scheme 1). Starting from **7** instead of **6** does not lead to an enhancement of the yield of **8**.

The subsequent cyclopropanation of **8a** with **6a** under the same reaction conditions afforded a mixture of the I,I*

bisadduct **9,** the bisadducts **(+)-10** and **(−)-10** (inherent chiral $^{f}C$-I,II*- and $^{f}A$-I,II*-addition pattern), the bisadducts **(+)-11** and **(−)-11** (inherent chiral $^{f}C$-I,III*- and $^{f}A$-I,III*-addition pattern), the I,IV* bisadduct **12**, and the I,eI bisadduct **13** with




the relative positional relationships *trans-1*, *trans-2*, *trans-3*, *trans-4*, and *e* of the addends, respectively.[19] Next to **9 – 13**, three additional, more polar bisadducts, presumably those with the addition patterns I,IV, $^{f}C$-I,III, and $^{f}A$-I,III were formed in traces (analytical HPLC on silica gel; toluene/ethyl acetate/triethylamine (95:4.8:0.2)). The order of elution with increasing polarity of the bisadducts is **9, (−)-10, (+)-10, 13, (+)-11, (−)-11, 12**, showing that the equatorial adduct **13** has an $R_f$ value between those of the *trans-2* and *trans-3* adducts. The same retention behavior was observed for the *e′* adduct in the series of mixed bisadducts $C_{62}(anisyl)_2(COOEt)_2$.[7] Isolation of **9 – 13** from the reaction mixture was achieved by flash chromatography on silica gel with toluene/ethyl acetate/triethylamine (95:4.8:0.2) (preseparation of four fractions consisting of **9**, **(−)-10**, **(+)-10**, of pure **13**, of pure **(+)-11** and of **(−)-11**, **12**, respectively) followed by preparative HPLC. The relative yield of the *trans-1*, *trans-2*, *trans-3*, *trans-4*, and *e* isomers **9 – 13** is 3.7:12.5:23.5:13.0:47.2, demonstrating the typical regioselective preference for additions to *e*- and *trans-3* bonds (Figure 2). The formation of the bisadducts **10** and **11** is only weakly diastereoselective with *de* values of 9.2 % and 5.4 % (Figure 2).

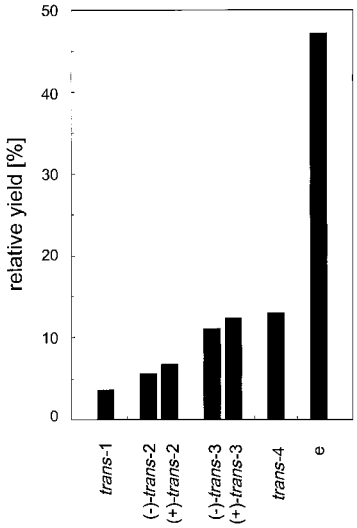



Figure 2. Relative yields of the isolated regioisomeric and diastereoisomeric bisadducts **9** (*trans-1*), **10** (*trans-2*), **11** (*trans-3*), **12** (*trans-4*), and **13** (*e*).

The $D_3$-symmetrical $^{f}C$-I,III*,III* and $^{f}A$-I,III*,III* trisadducts **14** were obtained by another cyclopropanation of **(+)-11** and **(−)-11**. Since in each precursor molecule **(+)-11** and **(−)-11** only one [6,6] double bond in the *trans-3* position relative to both the I and III* bonds is available, $^{f}C$-I,III*,III* can be formed only out of $^{f}C$-I,III* and $^{f}A$-I,III*,III* only out $^{f}A$-I,III*. Products **(+)-14** and **(−)-14** elute as the second product fraction on silica gel with toluene/ethyl acetate/triethylamine (86:13.8:0.2) as eluent. Their isolation was achieved by preparative HPLC. The relative yield of **(+)-14** and **(−)-14** is 17 % demonstrating the expected regioselective preference of an attack into a *trans-3* position relative to the addends already bound.[3,4,7]

Cyclopropanation of **13** with **7a** yielded the $C_3$-symmetrical diastereomeric trisadducts **(+)-15** and **(−)-15** with $^{f}C$- and $^{f}A$-I,eI,eII addition patterns. The combined relative yield of **(+)-15** and **(−)-15** is 41.2 %, which shows that the regioselectivity of their formation is even higher than that of **14** from **11**. This regioselectivity is comparable to that already observed for the corresponding diethoxycarbonylmethylene adducts.[3] The



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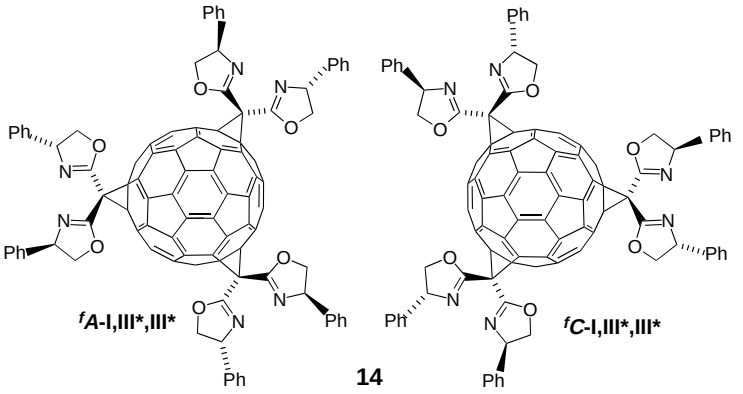
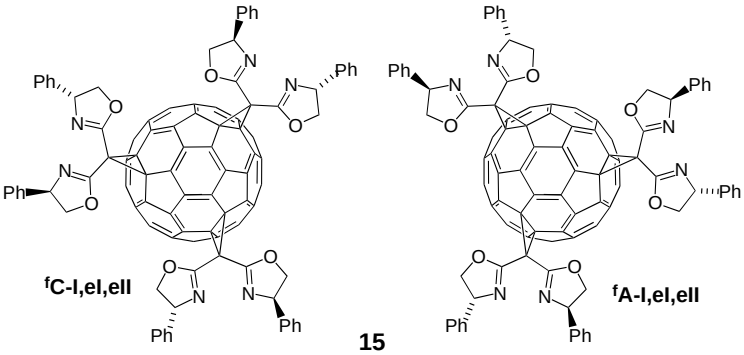


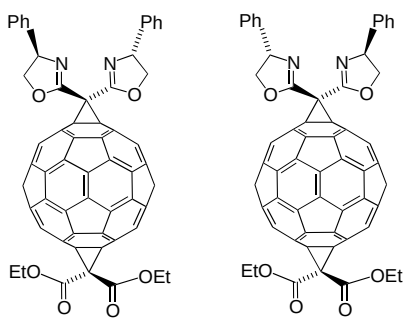

**14**




**15**

diastereomers **(+)-15** and **(−)-15** elute as the two least polar product fractions from silica gel.[3,4,7] Their isolation was achieved by preparative HPLC on silica gel with a mixture of toluene, ethyl acetate, and triethylamine in the ratio of 93:6.8:0.2 as eluent. Interestingly, both **(+)-15** and **(−)-15** are less polar than the two diastereomers of **14**. This is in contrast to the behavior of **4** and **5**, where the bisadducts **5** are the less polar compounds.[3]

In order to investigate the influence of the nature of the addend on the chiroptical properties and to gain access to isolated pairs of enantiomers, we synthesized a series of mixed I,eI,eII trisadducts, which contain one chiral bisoxazoline as well as two achiral malonate addends. For this purpose **8a** and **8b** were first monocyclopropanated with diethyl bromomalonate in the presence of NaH. Among the various optically active bisadducts (*R,R*)-I,I* (**16**), (*S,S*)-I,I* (**17**), (*R,R*)-I,eI (**18**), (*S,S*)-I,eI (**19**), (*R,R*)-I,eII (**20**), and (*S,S*)-I,eII (**21**) could be isolated by preparative HPLC. (*R*) and (*S*) species with the same addition pattern represent pairs of enantiomers. The subsequent cyclopropanation of **18** or **20** yielded the diastereomers **(+)-22** and **(−)-23** and that of **19** or **21** the diastereomers **(−)-22** and **(+)-23** (Scheme 2). Since each reaction mixture contained a pair of chromatographically separable diastereomers (Figure 3) with an inherent chiral I,eI,eII addition pattern, all of the four stereoisomers **22** and **23** were obtained in an enantiomerically pure form. Derivatives **(+)-22** and **(−)-22** as well as **(+)-23** and **(−)-23** are pairs of isolated enantiomers.



**16** **17**

All the new compounds **8–23** were characterized by $^1$H NMR, $^{13}$C NMR, FT-IR, and UV/Vis spectroscopy and by mass spectrometry. The addition pattern of each compound could be unambiguously assigned on the basis of 1) the symmetry deduced from the NMR spectra (Tables 1 and 2), 2) the number of diastereomers (one for adducts with an achiral addition pattern and two for adducts with a chiral addition pattern), 3) the UV/Vis spectra, which are characteristic for an addition pattern and independent of the nature of the substituents on the methylene bridges (Figure 4),[7] and 4) the order of elution. Moreover, the nature of follow-up products provides another proof for the correct structure assignment, since, for example, $D_3$-symmetrical **(+)-14** and **(−)-14,** which represent the only possible addition pattern of trisadducts with $D_3$ symmetry, can only be formed out of **(+)-11** and **(−)-11**.

In the $^1$H NMR spectra (Figure 5) of the monoadducts **8a,b** two doublets of doublets ($J = 8.8$ and 10.2 Hz) at $\delta = 5.6$ and 5.0 appear for the H$^a$ and H$^c$ protons, one pseudotriplet ($J =$ 8.8 Hz) at 4.5 for the H$^b$ protons and one multiplet at $\delta = 7.4$ for the corresponding phenyl protons. The assignment of the peaks was confirmed by the analysis of the corresponding NOESY spectra. The $^{13}$C NMR spectra of **8** show 18 resolved lines for the sp$^2$ fullerene C atoms between $\delta = 146.5$ and 138.8 and one signal at $\delta = 72$ for the sp$^3$ cage atoms. This small number of signals (30 signals expected for the depicted $C_2$ symmetry) reflects the local $C_{2v}$ symmetry within the cage

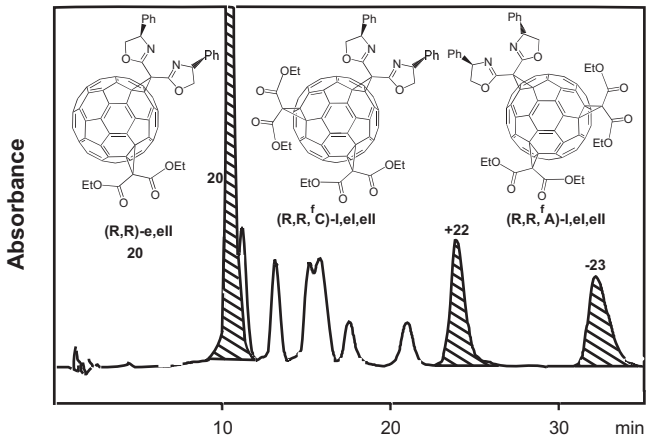
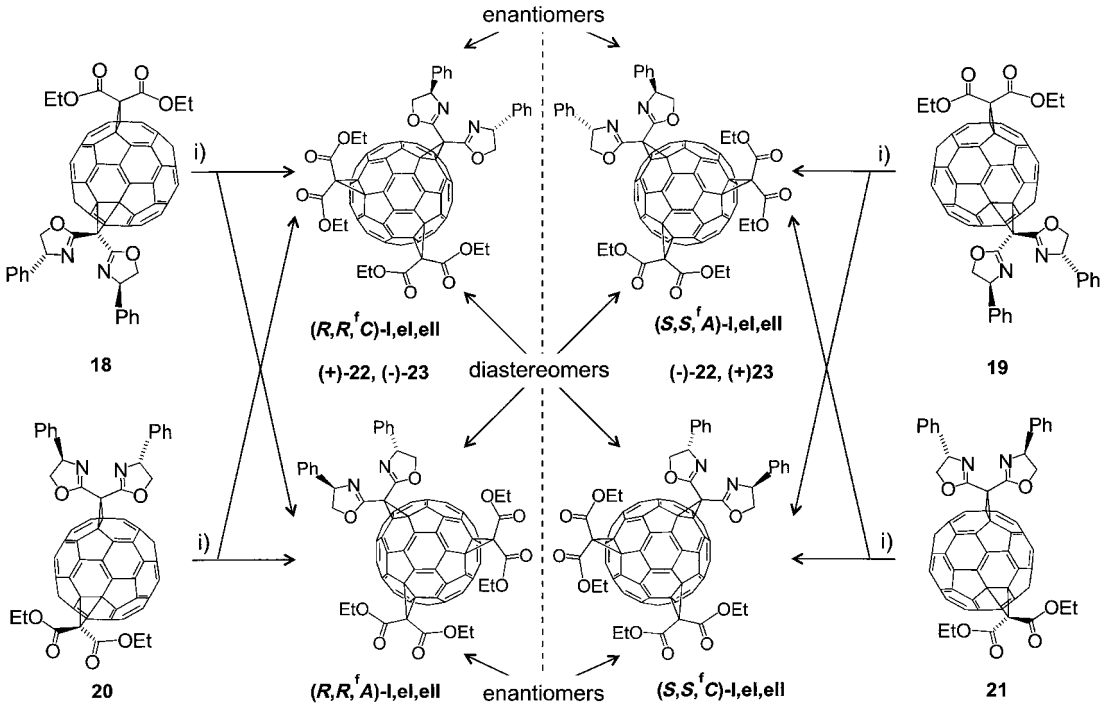



Figure 3. HPLC profile of the separation of the optically active trisadducts **(+)-22** and **(−)-23** obtained by reaction of **20** with diethyl malonate in the presence of DBU. Conditions: $SiO_2$, toluene/ethyl acetate/triethylamine (96:3.8:0.2), flow rate 18 mL min$^{-1}$, detection at $\lambda = 340$ nm.




Scheme 2. Cyclopropanation of the *equatorial* mixed bisadducts **18**–**21** to give the enantiomerically pure mixed trisadducts **(+)-22**, **(−)-22**, **(+)-23**, and **(−)-23**. i) Diethyl bromomalonate, NaH, toluene, RT, 24 h.

Table 1. Number of addends, addition patterns, symmetries, and expected and experimentally observed numbers of magnetically equivalent sets of $H^a$, $H^b$, and $H^c$ protons of the adducts **8**–**23**.

| Adduct | No. of addends | Addition pattern[a] | No. of different addends | Symmetry | $N$ [b] | $N_{exp}$ [c] |
|---|---|---|---|---|---|---|
| **8a** | 1 | (*R*)-I (*mono*) | 0 | $C_2$ | 1 | 1 |
| **8b** | 1 | (*S*)-I (*mono*) | 0 | $C_2$ | 1 | 1 |
| **9** | 2 | (*R*)-I,I* (*trans-1*)[d] | 0 | $D_2$ | 1 | 1 |
| **(+)-10** | 2 | (*R*)-I,II* (*trans-2*)[d] | 0 | $C_2$ | 2 | 2 |
| **(−)-10** | 2 | (*R*)-I,II* (*trans-2*)[d] | 0 | $C_2$ | 2 | 2 |
| **(+)-11** | 2 | (*R*)-I,III* (*trans-3*)[d] | 0 | $C_2$ | 2 | 2 |
| **(−)-11** | 2 | (*R*)-I,III* (*trans-3*)[d] | 0 | $C_2$ | 2 | 2 |
| **12** | 2 | (*R*)-I,IV* (*trans-4*)[d] | 0 | $C_1$ | 4 | 4 |
| **13** | 2 | (*R*)-I,eI (*e*)[d] | 0 | $C_1$ | 4 | 4 |
| **(+)-14** | 3 | (*R*)-I,III*,III* (*trans-3*, *trans-3*, *trans-3*)[d] | 0 | $D_3$ | 1 | 1 |
| **(−)-14** | 3 | (*R*)-I,III*,III* (*trans-3*, *trans-3*, *trans-3*)[d] | 0 | $D_3$ | 1 | 1 |
| **(+)-15** | 3 | (*R*)-I,eI,eII (*e*,*e*,*e*)[d] | 0 | $C_3$ | 2 | 2 |
| **(−)-15** | 3 | (*R*)-I,eI,eII (*e*,*e*,*e*)[d] | 0 | $C_3$ | 2 | 2 |
| **16** | 2 | (*R*)-I,I* (*trans-1*)[d] | 1 | $C_2$ | 1 | 1 |
| **17** | 2 | (*S*)-I,I* (*trans-1*)[d] | 1 | $C_2$ | 1 | 1 |
| **18** | 2 | (*R*)-I,eI (*e′*)[d] | 1 | $C_1$ | 2 | 2 |
| **19** | 2 | (*S*)-I,eI (*e′*)[d] | 1 | $C_1$ | 2 | 2 |
| **20** | 2 | (*R*)-I,eII (*e″*)[d] | 1 | $C_1$ | 2 | 2 |
| **21** | 2 | (*S*)-I,eII (*e″*)[d] | 1 | $C_1$ | 2 | 2 |
| **(+)-22** | 3 | (*R*)-I,eI,eII (*e*,*e*,*e*)[d] | 1 | $C_1$ | 2 | 2 |
| **(−)-22** | 3 | (*S*)-I,eI,eII (*e*,*e*,*e*)[d] | 1 | $C_1$ | 2 | 2 |
| **(−)-23** | 3 | (*R*)-I,eI,eII (*e*,*e*,*e*)[d] | 1 | $C_1$ | 2 | 2 |
| **(+)-23** | 3 | (*S*)-I,eI,eII (*e*,*e*,*e*)[d] | 1 | $C_1$ | 2 | 2 |

[a] *R* or *S* denote the absolute configuration of each stereogenic center within the bisoxazoline addends. [b] Expected number of magnetically equivalent sets of $H^a$, $H^b$, and $H^c$ protons. [c] Experimentally observed number of multiplets for $H^a$, $H^b$, $H^c$ protons. [d] Relative positional relationship.

of **8**. Also, only one doublet of doublets for the $H^a$, $H^c$ and one pseudotriplet for the $H^c$ protons of the bisoxazoline addends appear in the $^1$H NMR spectra of $D_2$-**9**, $D_3$-**(+)-14** (Figure 5c), $C_2$-**16**, and $C_2$-**17**. In all other cases the $H^a$, $H^b$, and $H^c$ protons of the corresponding oxazoline subunits are no longer magnetically equivalent. For example, two multiplets each appear for the two sets of protons $H^a$, $H^b$, and $H^c$ in $C_2$-**(+)-11** (Figure 5b) and $C_2$-**(−)-11** or $C_3$-**(+)-15** and $C_3$-**(−)-15** (Figure 5a) and a complex multiplet for the four different sets of such protons in the spectrum of **12** (Figure 5f) and **13** (Figure 5d). The same symmetry considerations are true for the phenyl protons of the oxazoline rings. The dependence of the number



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Table 2. Symmetry and expected as well as experimentally observed ($^{13}$C NMR) numbers of sp$^2$ C atoms, sp$^3$ C atoms, and CN groups of the adducts **8** and **10**–**23**.

| Adduct | Symmetry | | sp$^2$ C atoms[a] | | sp$^3$ C atoms[b] | | -CN groups[c] | |
|---|---|---|---|---|---|---|---|---|
| | molecule | addition pattern | expected | observed | expected | observed | expected | observed |
| **8a** | $C_2$ | $C_{2v}$ | 29 | 18 | 1 | 1 | 1 | 1 |
| **8b** | $C_2$ | $C_{2v}$ | 29 | 18 | 1 | 1 | 1 | 1 |
| **(+)-10** | $C_2$ | $C_2$ | 28 | 24 | 2 | 2 | 2 | 2 |
| **(−)-10** | $C_2$ | $C_2$ | 28 | 26 | 2 | 2 | 2 | 2 |
| **(+)-11** | $C_2$ | $C_2$ | 28 | 27 | 2 | 2 | 2 | 2 |
| **(−)-11** | $C_2$ | $C_2$ | 28 | 28 | 2 | 2 | 2 | 2 |
| **12** | $C_1$ | $C_s$ | 56 | 36 | 4 | 4 | 4 | 3 |
| **13** | $C_1$ | $C_s$ | 56 | 37 | 4 | 3 | 4 | 3 |
| **(+)-14** | $D_3$ | $D_3$ | 9 | 9 | 1 | 1 | 1 | 1 |
| **(+)-15** | $C_3$ | $C_3$ | 18 | 15 | 2 | 2 | 2 | 2 |
| **(−)-15** | $C_3$ | $C_3$ | 18 | 18 | 2 | 2 | 2 | 2 |
| **16** | $C_2$ | $D_{2h}$ | 28 | 14 | 2 | 2 | 1 | 1 |
| **17** | $C_2$ | $D_{2h}$ | 28 | 14 | 2 | 2 | 1 | 1 |
| **18** | $C_1$ | $C_s$ | 56 | 36 | 4 | 3 | 2 | 2 |
| **19** | $C_1$ | $C_s$ | 56 | 35 | 4 | 3 | 2 | 2 |
| **20** | $C_1$ | $C_s$ | 56 | 38 | 4 | 3 | 2 | 1 |
| **21** | $C_1$ | $C_s$ | 56 | 38 | 4 | 3 | 2 | 1 |
| **(+)-22** | $C_1$ | $C_3$ | 54 | 38 | 6 | 5 | 2 | 2 |
| **(−)-22** | $C_1$ | $C_3$ | 54 | 38 | 6 | 5 | 2 | 2 |
| **(−)-23** | $C_1$ | $C_3$ | 54 | 39 | 6 | 6 | 2 | 2 |
| **(+)-23** | $C_1$ | $C_3$ | 54 | 39 | 6 | 6 | 2 | 2 |

[a] Number of magnetically inequivalent sp$^2$ C atoms of the fullerene cage. [b] Number of magnetically inequivalent sp$^3$ C atoms of the fullerene cage. [c] Number of magnetically inequivalent C atoms within the -C=N moieties of the addend.

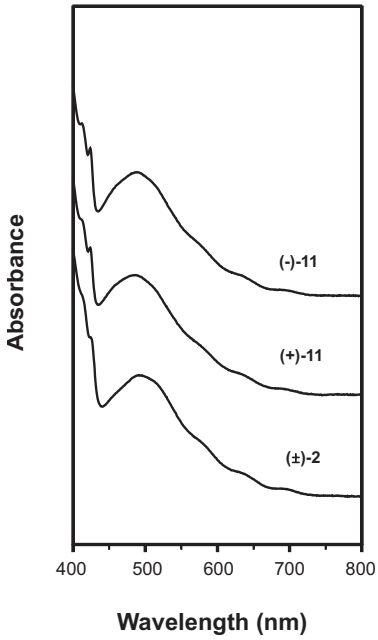


Figure 4. Comparable electronic absorption spectra ($CH_2Cl_2$) of the diastereomers **(−)-11** and **(+)-11** as well as of the racemic mixture of **2**.

of multiplets due to the protons H$^a$, H$^b$ and H$^c$ on the number of addends, the addition pattern, and the depicted symmetry is listed in Table 1.

Another important source of information concerning the local cage symmetry of the adducts **8**–**23** is provided by $^{13}$C NMR spectroscopy (Figure 6, Table 2). In many cases, the number of resolved signals for the sp$^2$ and sp$^3$ C atoms of the fullerene cage is lower than expected for the depicted symmetry. For example, 56 signals between $\delta = 138 - 148$ are expected for $C_1$-symmetrical **18** but only 35 are resolved, and three signals at $\delta = 70.44$, 71.57 and 72.47 appear for the sp$^3$ C atoms. This reveals a local pseudo-$C_s$ symmetry of the cage associated with the I,eI-addition pattern. A pseudo-$C_{2v}$ instead of a $C_2$ symmetry emerges for **16** and **17**, since only 14 sharp signals for fullerene sp$^2$ C atoms are resolved between $\delta = 139$ and 146. The $^{13}$C NMR spectra of the most symmetrical adducts **14** (with a I,III*,III*-addition pattern, $D_3$ symmetry) shows the expected number of only 9 signals for the sp$^2$ cage atoms and one signal at $\delta = 72.29$ for the six magnetically equivalent sp$^3$ cage atoms (Figure 6). Also only one set of signals appears for the three magnetically equivalent bisoxazoline addends. In the diastereomers **14** the local cage symmetry is identical with the depicted symmetry of the whole molecule. This is always the case for adducts with $C_2$-symetrical addends and an inherent chiral addition pattern. The close stereochemical relationship within pairs of diastereomers like **(+)-10**/**(−)-10**, **(+)-11**/**(−)-11**, **(+)-14**/**(−)-14**, **(+)-15**/**(−)-15**, **(+)-22**/**(−)-23**, and **(−)-22**/**(+)-23**, in which the corresponding addition pattern represent pairs of enantiomers, is nicely reflected by the similarity of the $^{13}$C NMR spectra. For example, the $^{13}$C NMR spectra of **(+)-11** and **(−)-11** are almost identical expect for the narrow region between $\delta = 146.5$ and 147.5 (Figure 6). It is reasonable to assume that the signals in this region are due to resonances of sp$^2$ C atoms located in close proximity to the bound addends. The UV/Vis spectra of all newly synthesized adducts **9**–**23** are always almost identical with those of the corresponding regioisomers within related series of adducts like $C_{62}(COOEt)_4$, $C_{63}(COOEt)_4$ or $C_{62}(anisyl)_2(COOEt)_2$ that we synthesized and characterized previously.[3,4,7] This again demonstrates that the electronic properties of a given regioisomer depend mostly on the addition pattern itself and not on the nature of the addend.

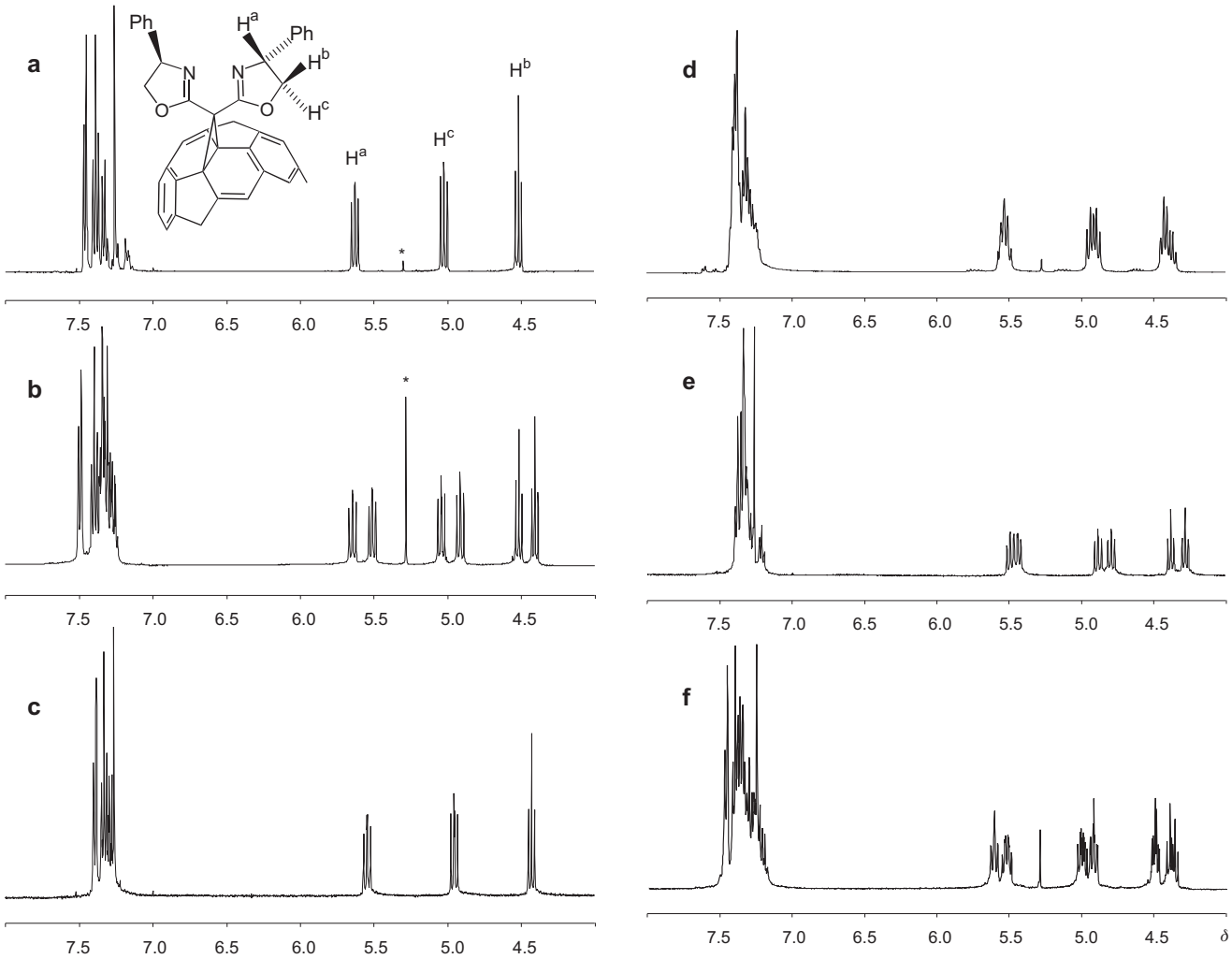


Figure 5. $^1$H NMR spectra (400 MHz, $CDCl_3$) of a) **8a**, b) **(+)-11**, c) **(+)-14**, d) **13**, e) **(−)-15**, and f) **12**. The peaks marked with an asterisk are due to a $CH_2Cl_2$ impurity.

The fact that compounds **(+)-10/(−)-10**, **(+)-11/(−)-11**, **(+)-14/(−)-14**, **(+)-15/(−)-15**, **(+)-22/(−)-23**, and **(−)-22/(+)-23** form pairs of diastereomers whose inherently chiral addition patterns have an enantiomeric relationship is clearly demonstrated in their circular dichroism (CD) spectra (Figure 7). The $[\alpha]_D$ values lie in the range between $\pm 1200$ and $\pm 3500$. The CD spectra of each pair of diastereomers closely resemble those expected for enantiomers, since almost perfect mirror-image behavior is observed. This shows that the chiral bisoxazoline addends do not significantly contribute to the chiroptical properties, which are essentially due to the distorted π system of the $C_{60}$ adducts with the inherently chiral addition patterns I,II*, I,III*, I,III*,III* and I,eI,eII. This is also clearly demonstrated by the fact that all three isolated pairs of diastereomers **(+)-15/(−)-15**, **(+)-22/(−)-23**, and **(−)-22/(+)-23** having a I,eI,eII addition pattern but different combinations of addends give rise to the same mirror-image CD spectra. Moreover, the CD spectra of **(+)-15/(−)-15** are identical to those of **(+)-4/(−)-4** with I,eI,eII addition patterns and the same is true for the two pairs of diastereomers **(+)-14/(−)-14** and **(+)-5/(−)-5** with I,III*,III* addition patterns.[13] A comparable situation was observed by Diederich and coworkers[12] for pairs of diastereomers of $C_{70}$ derivatives with an inherent chiral addition pattern. It is interesting to note that the Cotton effects of the $C_2$-symmetrical bisadducts **10** and **11** are significantly larger than those of the $C_3$-symmetrical trisadducts **15** and the $D_3$-symmetrical trisadducts **14** (Figure 7, p. 352) but are comparable to those of the $C_2$-symmetrical bisadduct **3** measured by Diederich and coworkers.[10] We explain this behavior with the higher symmetry of the trisadducts, which cause a less pronounced distortion of the conjugated π system within the $C_{60}$ chromophore. This explanation is also corroborated by the fact that the maximum $\Delta\varepsilon$ values for enantiomerically pure $C_{76}$ derivatives are up to twice as large as those for **10** and **11**.[16] $D_2$-$C_{76}$ is an inherently chiral fullerene, whose π-electron system is arranged within a double helical structure motif, similar to that of helicenes. In comparison with this helical arrangement, the chiral distortion of the π-electron system within $C_{60}$ derivatives with an inherent chiral addition pattern is less pronounced and the distortion decreases with increasing



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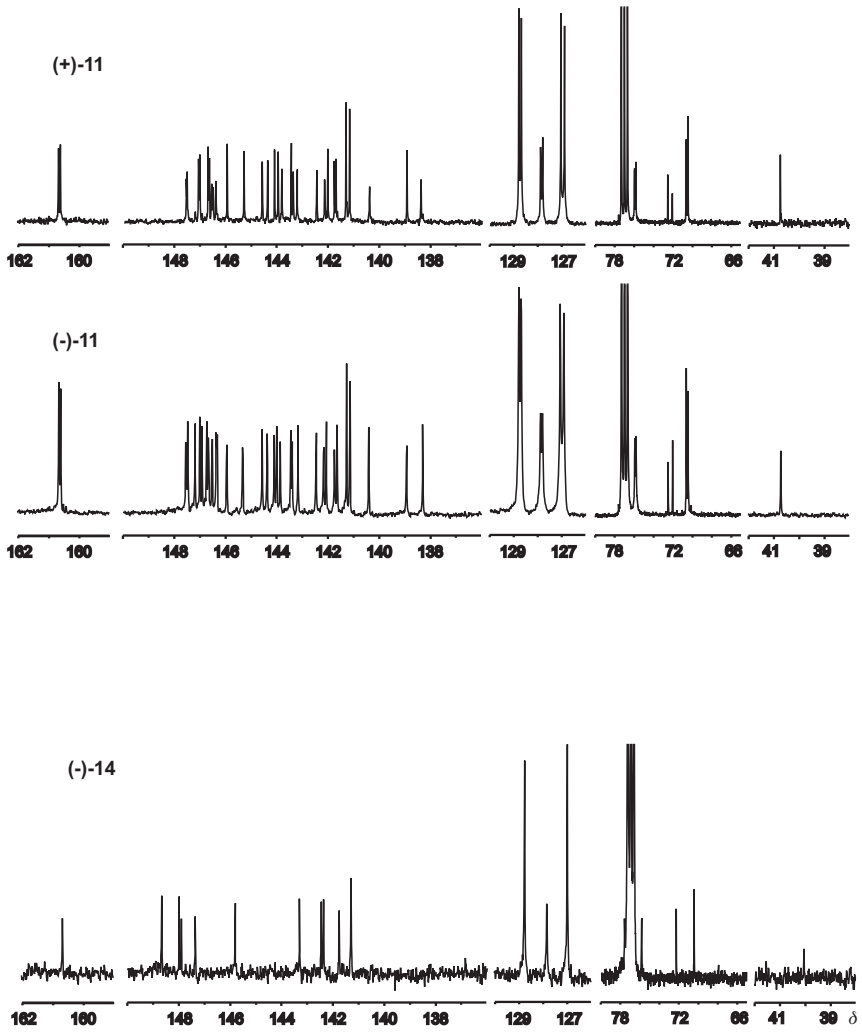
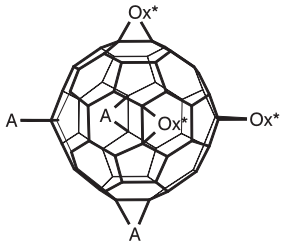



Figure 6. $^{13}C$ NMR spectra (100 MHz, $CDCl_3$) of **(+)-11**, **(−)-11**, and **(+)-14**.

symmetry of the addition pattern, for example, going from $C_2$ to $C_3$ or $D_3$.

## Conclusion and Outlook

Multiple additions of chiral $C_2$-symmetrical bisoxazolines to [6,6] bonds of the fullerene cage by nucleophilic cyclopropanation provide facile access to enantiomerically pure bis- and trisadducts of $C_{60}$ with the inherent chiral addition patterns $C_2$-I,II*, $C_2$-I,III*, $D_3$-I,III*,III*, and $C_3$-I,eI,eII. The investigations reported here complement our previous studies on the synthesis and isolation of stereochemically defined multiple adducts of $C_{60}$.[3–8] The CD spectra of the corresponding pairs of diastereomers, whose addition patterns are pairs of enantiomers, reveal pronounced Cotton effects and mirror-image behavior. It is therefore predominantly the chiral arrangement of the conjugated π-electron system within the fullerene core itself which determines the chiroptical properties. Adducts with a $C_2$-symmetrical addition pattern show significantly larger Cotton effects than those with more symmetrical addition patterns ($C_3$, $D_3$). Besides derivatives with identical addends we have shown that mixed adducts are also easily accessible. In this respect, mixed $C_3$-symmetrical hexaadducts like **24**, for example, are interesting




**24**

synthetic targets. Such compounds should be easily accessible in high yields from precursor adducts with an incomplete octahedral addition pattern by our template-mediation method.[5] Such hexaadducts, whose remaining [6,6] double bonds are comparatively inert towards further addition reactions, could be interesting catalysts for all those enantioselective reactions that are catalyzed by bisoxazolines themselves,[20–28] since in addition to the local $C_2$ symmetry of the chiral addends their screw-like $C_3$-symmetrical arrangement within **24** provides a further effective scenario for chiral discrimination. Next to their role as protecting groups for the fullerene surface against addition reactions the addends A, which could be long-chain molecules,[17] dendrimer[8] or peptide derivatives,[29] can also be used to modify the solubility properties of **24** or to direct the substrate to the chiral regions of new types of potential chemzymes. Investigations with this aim are currently underway.

## Experimental Procedure

$^1H$ and $^{13}C$ NMR: JEOL JNM EX 400 and JEOL JNM GX 400; MS: Micromass ZabSpec (FAB); IR: Bruker Vektor 22; UV/Vis: Shimadzu UV 3102 PC; HPLC preparative: Shimadzu SIL 10 A, SPD 10 A, CBM 10 A, LC 8 A, FRC 10 A (Grom-Sil 100 Si, NP 1, 5 μm, 25 m × 4.6 mm), TLC (Riedel–de Haën, silica gel $F_{254}$ and Macherey–Nagel, aluminum oxide N/$UV_{254}$), CD: JASCO J-710. Reagents were prepared according to common procedures. Materials and solvents were obtained from commercial suppliers and were used without further purification. All reactions were carried out under nitrogen. Products were isolated where possible by flash column chromatography (silica gel 60, particle size 0.04–0.063 nm, Merck or aluminum oxide activated, neutral, Brockmann I, STD grade, ca. 150 mesh, 58 Å, Aldrich). $[\alpha]_D$ values were measured at 25°C.

**Adducts 8**: To a solution of $C_{60}$ (1 g, 1.39 mmol) in dry toluene (600 mL), bisoxazoline **6** (511 mg, 1.2 equiv) in dry methylene chloride (100 mL) was added through a dropping funnel. Subsequently, under vigorous stirring first $CBr_4$ (553 mg, 1.2 equiv) in $CH_2Cl_2$ (25 mL) and then DBU (498 μL,

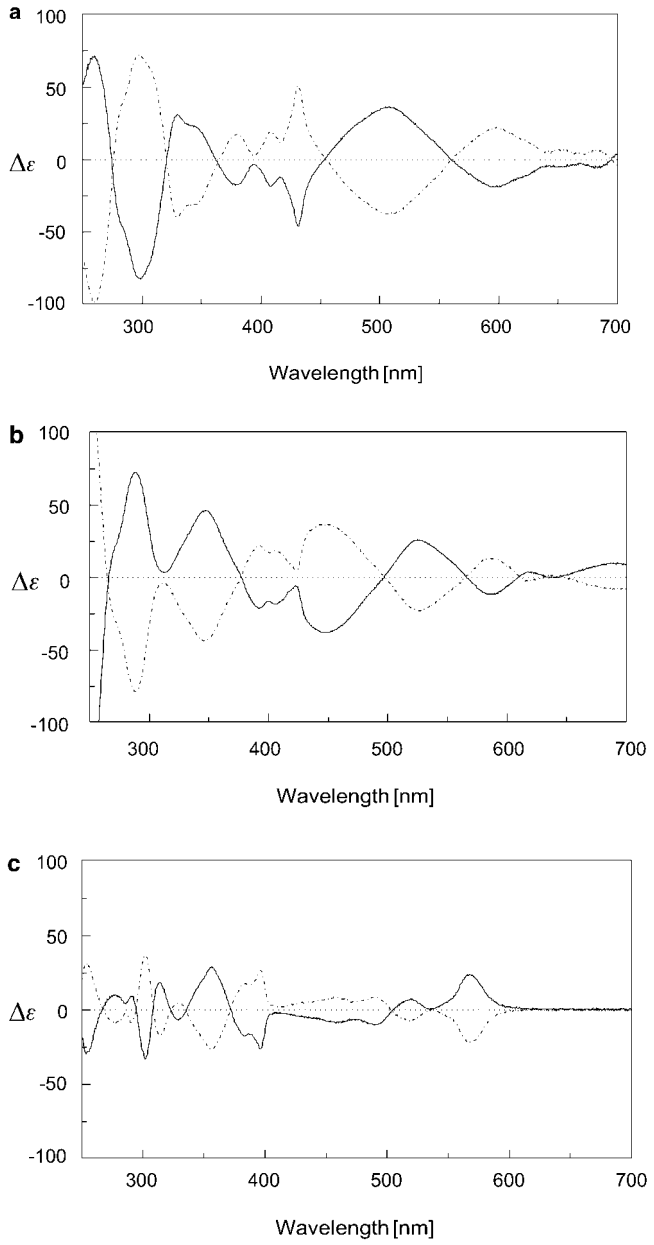



Figure 7. CD spectra ($CH_2Cl_2$) of the pairs of diastereomers of a) **(−)-10** (—), **(+)-10** (- · - · -), b) **(−)-11** (—), **(+)-11** (- · - · -), and c) **(+)-15**(—), **(−)-15** (- · - · -).

2.4 equiv) were added to the solution. After 24 h the solution was concentrated at room temperature and fractionated by column chromatography ($SiO_2$, toluene/ethyl acetate/triethylamine 95:4.8:0.2). Yield: 711 mg (50 %).

**Monoadduct 8a**: $R_f$ ($SiO_2$, toluene/ethyl acetate/triethylamine 95:4.8:0.2:0.39; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 4.52$ (dd, $J$(H,H) = 8.8 Hz, 2H, Oxaz $CH_2$), 5.02 (dd, $J$(H,H) = 10.2 Hz, 8.8 Hz, 2H, Oxaz $CH_2$), 5.63 (dd, $J$(H,H) = 10.2 Hz, 8.8 Hz, 2H, Oxaz CH), 7.1 – 7.5 (m, 10H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 41.46$ (1C, methylene C), 70.60 (2C, Oxaz CH), 72.43 (2C, $sp^3$), 75.94 (2C, Oxaz $CH_2$), 127.03 (4C, Ph C), 127.94 (2C, Ph C), 128.84 (4C, Ph C), 137.32 (2C, Ph C), 138.85, 138.89, 140.90, 141.26, 142.01, 142.07, 142.18, 142.98, 143.04, 143.89, 144.70, 144.88, 145.23, 145.30, 145.45, 145.48, 146.31, 146.43, 160.67 (2C, CN); IR (KBr): $\tilde{\nu} = 3024$, 2949, 2890, 1744, 1646 (C=N), 1492, 1467, 1453, 1360, 1268, 1235, 752, 696, 584, 560, 525 $cm^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 258 (81000), 327 (25100), 428 (1500), 490 (900), 532 (700) nm; MS (FAB/3-NBA): $m/z$ = 1025 ([$M^+$+H], 45 %), 720 ($C_{60}^+$, 100 %), $^{12}C_{79}H_{16}N_2O_2$ calcd 1024.1.

**Monoadduct 8b**: $R_f$ ($SiO_2$, toluene/ethyl acetate/triethylamine 95:4.8:0.2): 0.39; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 4.52$ (dd, $J$(H,H) = 8.8 Hz, 2H, Oxaz $CH_2$), 5.02 (dd, $J$(H,H) = 10.2 Hz, 8.8 Hz, 2H, Oxaz $CH_2$), 5.63 (dd, $J$(H,H) = 10.2 Hz, 8.8 Hz, 2H, Oxaz CH), 7.1 – 7.5 (m, 10H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 41.46$ (1C, methylene C), 70.60 (2C, Oxaz CH), 72.43 (2C, $sp^3$), 75.94 (2C, Oxaz $CH_2$), 127.03 (4C, Ph C), 127.94 (2C, Ph C), 128.84 (4C, Ph C), 137.32 (2C, Ph C), 138.85, 138.89, 140.90, 141.26, 142.01, 142.07, 142.18, 142.98, 143.04, 143.89, 144.70, 144.88, 145.23, 145.30, 145.45, 145.48, 146.31, 146.43, 160.67 (2C, CN); IR (KBr): $\tilde{\nu} = 3024$, 2949, 2890, 1744, 1646 (C=N), 1492, 1467, 1453, 1360, 1268, 1235, 752, 696, 584, 560, 525 $cm^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 258 (81000), 327 (25100), 428 (1500), 490 (900), 532 (700) nm; MS (FAB/3-NBA): $m/z$ = 1025 ([$M^+$+H], 43 %), 720 ($C_{60}^+$, 100 %), $^{12}C_{79}H_{16}N_2O_2$ calcd 1024.1.

**Adducts 9 – 13**: Bisoxazoline **6a** (447 mg, 1.5 equiv) in dry methylene chloride (100 mL), $CBr_4$ (485 mg, 1.5 equiv) in dry methylene chloride (50 mL), and DBU (437 μL, 3 equiv) were added to a solution of **8a** (1 g, 0.976 mmol) in dry toluene (400 mL). After being stirred for 24 h the solvent was evaporated and fractionated by column chromatography ($SiO_2$, toluene/ethyl acetate/triethylamine 95:4.8:0.2). Fractions containing pure recovered **8a**, a mixture of **9**, **(−)-10** and **(+)-10**, pure **13**, pure **(+)-11**, and a mixture of **(−)-11** and **12** were obtained. A final separation of **9**, **(−)-10** and **(+)-10** was achieved by preparative HPLC (toluene/ethyl acetate/triethylamine 95:4.8:0.2). Compounds **(−)-11** and **12** were isolated by chromatography on alumina as stationary phase (toluene/ethyl acetate 95:5). The relative yields (HPLC) of the bisadducts are: **9** (3.7 %), **(−)-10** (5.7 %), **(+)-10** (6.8 %), **13** (47.2 %), **(+)-11** (12.4 %), **(−)-11** (11.1 %), **12** (13.0 %).

**Bisadduct 9**: $R_f$ ($SiO_2$, toluene/ethyl acetate/triethylamine 95:4.8:0.2):0.20; $k'$ ($SiO_2$, toluene/ethyl acetate/triethylamine 95:4.8:0.2): 4.10; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 4.52$ (dd, $J$(H,H) = 8.6 Hz, 4H, Oxaz $CH_2$), 5.03 (dd, $J$(H,H) = 10 Hz, 8.6 Hz, 4H, Oxaz $CH_2$), 5.63 (dd, $J$(H,H) = 10 Hz, 8.6 Hz, 4H, Oxaz CH), 7.2 – 7.5 (m, 20H, Ph); IR (KBr): $\tilde{\nu} = 3057$, 3027, 2958, 2895, 1745, 1660 (CN), 1492, 1452, 1429, 1351, 1271, 1235, 1094, 736, 698, 592, 520 $cm^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 262 (82000), 324 (40000), 412 (6000), 440 (4200), 472 (5000); MS (FAB/3-NBA): $m/z$ = 1328 ($M^+$, 30 %), 720 ($C_{60}^+$, 100 %), $^{12}C_{98}H_{32}N_4O_4$ calcd 1328.2.

**Bisadduct (−)-10**: $R_f$ ($SiO_2$, toluene/ethyl acetate/triethylamine 95:4.8:0.2):0.19; $k'$ ($SiO_2$, toluene/ethyl acetate/triethylamine 95:4.8:0.2): 9.57; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 4.47$ (dd, $J$(H,H) = 8.5 Hz, 2H, Oxaz $CH_2$), 4.67 (dd, $J$(H,H) = 8.6 Hz, 2H, Oxaz $CH_2$), 4.98 (dd, $J$(H,H) = 10 Hz, 8.8 Hz, 2H, Oxaz $CH_2$), 5.16 (dd, $J$(H,H) = 10.3 Hz, 8.3 Hz, 2H, Oxaz $CH_2$), 5.58 (dd, $J$(H,H) = 10.2 Hz, 8.3 Hz, 2H, Oxaz CH), 5.78 (dd, $J$(H,H) = 10 Hz, 8.8 Hz, 2H, Oxaz CH), 7.1 – 7.7 (m, 20H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 39.09$ (2C, methylene C), 70.50 (2C, Oxaz CH), 70.73 (2C, Oxaz CH), 71.69 (2 $sp^3$ C), 72.28 (2 $sp^3$ C), 75.85 (2C, Oxaz $CH_2$), 76.06 (2C, Oxaz $CH_2$), 126.96 (4C, Ph C), 127.14 (4C, Ph C), 127.96 (2C, Ph C), 127.85 (2C, Ph C), 128.74 (4C, Ph C), 128.87 (4C, Ph C), 137.31 (2C, Ph C), 137.46 (2C, Ph C), 140.04, 140.59, 141.21, 141.40, 141.70, 141.94, 142.06, 142.25, 142.38, 142.64, 143.19, 143.70, 143.90, 144.01, 144.23, 144.42, 144.98, 145.15, 145.30, 145.48, 145.69, 146.06, 146.24, 146.41, 147.23, 149.09, 160.95 (2C, CN), 160.69 (2C, CN); IR (KBr): $\tilde{\nu} = 3058$, 3026, 2958, 2895, 1744, 1660 (CN), 1492, 1420, 1452, 1427, 1350, 1271, 1235, 1191, 754, 698, 592, 526 $cm^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 234 (79000), 262 (78900), 320 (27900), 382 (6700), 405 (3500), 432 (2500), 491 (1400), 634 (400), 700 (200) nm; CD ($CH_3OH$) = 260 ($\Delta\varepsilon = 70$), 299 (−83), 329 (30), 343 (22), 381 (−17), 408 (−19), 432 (−47), 507 (36), 599 (−20), 650 (−6), 682 (−6), 708 (7) nm; $[\alpha]_D$ ($c$ = 2 mg/100 mL, $CH_3Cl$) = −3500°; MS (FAB/3-NBA): $m/z$ = 1328 ($M^+$, 32 %), 720 ($C_{60}^+$, 100 %), $^{12}C_{98}H_{32}N_4O_4$ calcd 1328.2.

**Bisadduct (+)-10**: $R_f$ ($SiO_2$, toluene/ethyl acetate/triethylamine 95:4.8:0.2): 0.18; $k'$ ($SiO_2$, toluene/ethyl acetate/triethylamine 95:4.8:0.2): 11.1; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 4.46$ (dd, $J$(H,H) = 8.8 Hz, 2H, Oxaz $CH_2$), 4.65 (dd, $J$(H,H) = 8.8 Hz, 2H, Oxaz $CH_2$), 4.98 (dd, $J$(H,H) = 10.3 Hz, 8.3 Hz, 2H, Oxaz $CH_2$), 5.17 (dd, $J$(H,H) = 10.3 Hz, 8.8 Hz, 2H, Oxaz $CH_2$), 5.58 (dd, $J$(H,H) = 10.2 Hz, 8.8 Hz, 2H, Oxaz CH), 5.78 (dd, $J$(H,H) = 10.3 Hz, 8.3 Hz, 2H, Oxaz CH), 7.2 – 7.7 (m, 20H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 39.14$ (2C, methylene C), 70.57 (2C, Oxaz CH), 70.79 (2C, Oxaz CH), 71.70 (2C, $sp^3$ C), 72.29 (2C, $sp^3$ C), 75.89 (2C, Oxaz $CH_2$), 79.09 (2C, Oxaz $CH_2$), 127.00 (4C, Ph C), 127.19 (4C, Ph C), 127.88 (2C, Ph C), 128.00 (2C, Ph C), 128.77 (4C, Ph C), 128.91 (4C, Ph C), 137.38 (2C, Ph C), 137.47 (2C, Ph C), 140.13, 140.60, 141.25, 141.43, 141.75, 142.09, 142.25, 142.46, 142.59. 143.73, 144.09, 144.27, 144.47, 144.89, 145.18, 145.35, 145.50, 145.76, 146.06, 146.30, 146.52, 147.26, 149.00, 160.74 (2C,



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CN), 160.98 (2C, CN); IR (KBr): $\tilde{\nu}$ = 3058, 3026, 2957, 2921, 2897, 2851, 1716, 1661 (CN), 1492, 1453, 1348, 1262, 1189, 753, 698, 593, 526 cm$^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 234 (70800), 262 (66500), 320 (25200), 383 (6400), 405 (3600), 431 (2600), 492 (1500), 634 (300), 700 (180) nm; CD ($CH_3OH$) = 260 ($\Delta\varepsilon$ = −100), 297 (72), 329 (−40), 347 (−30), 381 (17), 408 (19), 432 (51), 510 (−38), 597 (21), 682 (6), 710 (−8) nm; $[\alpha]_D$ (*c* = 2 mg/100 mL, $CH_2Cl_2$) = +3150°; MS (FAB/3-NBA): *m*/*z* = 1328 ($M^+$, 25%), 720 ($C_{60}^+$, 100%), $^{12}C_{98}H_{32}N_4O_4$ calcd 1328.2.

**Bisadduct (+)-11**: $R_f$ ($SiO_2$, toluene/ethyl acetate/triethylamine 95:4.8:0.2): 0.06; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 4.41 (dd, *J*(H,H) = 8.3 Hz, 2H, Oxaz $CH_2$), 4.52 (dd, *J*(H,H) = 8.8 Hz, 2H, Oxaz $CH_2$), 4.92 (dd, *J*(H,H) = 8.8 Hz, 8.4 Hz, 2H, Oxaz $CH_2$), 5.05 (dd, *J*(H,H) = 8.3 Hz, 8.3 Hz, 2H, Oxaz $CH_2$), 5.52 (dd, *J*(H,H) = 8.8 Hz, 8.3 Hz, 2H, Oxaz CH), 5.68 (dd, *J*(H,H) = 10 Hz, 8.3 Hz, 2H, Oxaz CH), 7.1–7.7 (m, 20H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta$ = 40.76 (2C, methylene C), 70.41 (2C, Oxaz CH), 70.61 (2C, Oxaz CH), 72.04 (2C, sp$^3$ C), 72.51 (2C, sp$^3$ C), 75.82 (2C, Oxaz $CH_2$), 75.95 (2C, Oxaz $CH_2$), 126.91 (4C, Ph C), 127.07 (4C, Ph C), 127.82 (2C, Ph C), 127.92 (2C, Ph C), 128.72 (4C, Ph C), 128.83 (4C, Ph C), 138.41 (2C, Ph C), 138.95 (2C, Ph C), 140.41, 141.20, 141.34, 141.73, 141.79, 142.05, 142.17, 142.47, 143.25, 143.40, 143.48, 143.84, 143.99, 144.13, 144.40, 144.61, 145.33, 145.98, 146.42, 146.54, 146.59, 146.98, 146.72, 147.04, 147.09, 147.56, 147.57, 160.66 (2C, CN), 160.60 (2C, CN); IR (KBr): $\tilde{\nu}$ = 3059, 3026, 2958, 2896, 1661 (C=N), 1492, 1470, 1452, 1429, 1351, 1267, 1224, 754, 698, 586, 570, 528 cm$^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 248 (90000), 318 (29000), 380 (7500), 412 (3300), 425 (2700), 484 (2200), 576 (990), 633 (400); CD ($CH_3OH$) = 289 ($\Delta\varepsilon$ = −79), 347 (−44), 393 (21), 497 (18), 447 (36), 525 (−23), 590 (13), 637 (1), 694 (9) nm; $[\alpha]_D$ (*c* = 2 mg/100 mL, $CH_3Cl$) = +1250°; MS (FAB/3 – NBA): *m*/*z* = 1328 ($M^+$, 64%), 720 ($C_{60}^+$, 100%), $^{12}C_{98}H_{32}N_4O_4$ calcd 1328.2.

**Bisadduct (−)-11**: $R_f$ ($SiO_2$, toluene/ethyl acetate/triethylamine 95:4.8:0.2): 0.05; $R_f$ ($Al_2O_3$, toluene/ethyl acetate 95:5): 0.26; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 4.42 (dd, *J*(H,H) = 8.5 Hz, 2H, $CH_2$), 4.55 (dd, *J*(H,H) = 8.2 Hz, 2H, $CH_2$), 4.93 (dd, *J*(H,H) = 8.8 Hz, 8.9 Hz, 2H, $CH_2$), 5.05 (dd, *J*(H,H) = 8.6 Hz, 10.4 Hz, 2H, CH), 5.53 (dd, *J*(H,H) = 10.1 Hz, 8.3 Hz, 2H, CH), 7.2 – 7.7 (m, 20H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta$ = 40.73 (2C, methyleneC), 70.44 (2C, Oxaz CH), 70.62 (2C, Oxaz CH), 72.04 (2C, sp$^3$ C), 72.51 (2C, sp$^3$ C), 75.82 (2C, Oxaz $CH_2$), 75.94 (2C, Oxaz $CH_2$), 126.94 (4C, Ph C), 127.10 (4C, Ph C), 127.84 (2C, Ph C), 127.92 (2C, Ph C), 128.74 (4C, Ph C), 128.83 (4C, Ph C), 138.33 (2C, Ph C), 138.95 (2C, Ph C), 140.44, 141.17, 141.30, 141.67, 141.78, 142.09, 142.20, 142.49, 143.20, 143.43, 143.49, 143.89, 144.04, 144.13, 144.42, 144.60, 145.37, 145.98, 146.36, 146.41, 146.56, 146.71, 146.77, 146.95, 147.04, 147.23, 147.51, 147.59, 160.61 (2C, CN), 160.68 (2C, CN); IR (KBr): $\tilde{\nu}$ = 3058, 3026, 2958, 2895, 1801, 1660 (C=N), 1492, 1470, 1452, 1429, 1351, 1267, 1224, 754, 698, 586, 570, 528 cm$^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 248 (76000), 319 (23000), 380 (6100), 413 (2600), 414 (2500), 424 (2200), 483 (1800), 577 (700), 634 (300); CD ($CH_3OH$) = 289 ($\Delta\varepsilon$ = 72), 348 (46), 393 (−22), 406 (−19), 447 (−38), 525 (25), 584 (−12), 618 (3), 693 (9) nm; $[\alpha]_D$ (*c* = 2 mg/100 mL, $CH_2Cl_2$) = −1400°; MS (FAB/3-NBA): *m*/*z* = 1328 ($M^+$, 67%), 720 ($C_{60}^+$, 100%), $^{12}C_{98}H_{32}N_4O_4$ calcd 1328.2.

**Bisadduct 12**: $R_f$ ($SiO_2$, toluene/ethyl acetate/triethylamine 95:4.8:0.2): 0.04; $R_f$ ($Al_2O_3$, toluene/ethyl acetate 95:5): 0.14; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 4.38 (m, 2H, Oxaz $CH_2$), 4.50 (m, 2H, Oxaz $CH_2$), 4.93 (m, 2H, Oxaz $CH_2$), 5.01 (m, 2H, Oxaz $CH_2$), 5.53 (m, 2H, Oxaz CH), 5.61 (m, 2H, Oxaz CH), 7.1–7.6 (m, 20H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta$ = 39.35 (1C, methylene C), 39.44 (1C, methylene C), 70.41 (2C, Oxaz CH), 70.53 (2C, Oxaz CH), 71.49 (1C, sp$^3$ C), 71.53 (1C, sp$^3$ C), 71.90 (1C, sp$^3$ C), 71.98 (1C, sp$^3$ C), 75.87 (2C, Oxaz $CH_2$), 75.88 (2C, Oxaz $CH_2$), 126.87 (2C, Ph C), 126.91 (2C, Ph C), 127.05 (4C, Ph C), 127.78 (1C, Ph C), 127.79 (1C, Ph C), 127.90 (2C, Ph C), 128.69 (2C, Ph C), 128.75 (2C, Ph C), 128.83 (4C, Ph C), 135.40 (1C, Ph C), 135.65 (1C, Ph C), 138.28 (2C, Ph C), 138.75, 138.86, 140.29, 140.55, 140.94, 141.32, 141.53, 141.65, 141.99, 142.03, 142.19, 142.22, 142.75, 142.96, 143.09, 143.10, 143.28, 143.67, 143.81, 144.22, 144.95, 144.96, 145.07, 145.28, 145.37, 145.38, 145.60, 145.69, 145.74, 146.09, 146.12, 146.31, 146.38, 146.60, 147.06, 148.29, 160.77 (2C, CN), 160.96 (1C, CN), 161.07 (1C, CN); IR (KBr): $\tilde{\nu}$ = 3059, 3026, 2959, 2921, 2899, 2852, 1661 (C=N), 1492, 1453, 1350, 1262, 1183, 754, 697, 590, 528 cm$^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 240 (97000), 268 (77000), 321 (35000), 477 (2200), 637 (400) nm; MS (FAB/3-NBA): *m*/*z* = 1328 ($M^+$, 63%), 720 ($C_{60}^+$, 100%), $^{12}C_{98}H_{32}N_4O_4$ calcd 1328.2.

**Bisadduct 13**: $R_f$ ($SiO_2$, toluene/ethyl acetate/triethylamine 95:4.8:0.2): 0.15; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 4.3–4.5 (m, 4H, Oxaz $CH_2$), 4.8–5.0 (m, 4H, Oxaz $CH_2$), 5.4–5.6 (m, 4H, Oxaz CH), 7.2–7.5 (m, 20H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta$ = 40.41 (2C, methylene), 70.26 (1C, Oxaz CH), 70.49 (2C, Oxaz CH), 70.52 (1C, Oxaz CH), 72.40 (2C, sp$^3$ C), 72.43 (1C, sp$^3$ C), 72.52 (1C, sp$^3$ C), 75.72 (1C, Oxaz $CH_2$), 75.80 (1C, Oxaz $CH_2$), 75.85 (1C, Oxaz $CH_2$), 76.04 (1C, Oxaz $CH_2$), 126.91 (2C, Ph C), 126.99 (6C, Ph C), 127.79 (1C, Ph C), 127.85 (2C, Ph C), 127.89 (1C, Ph C), 128.78 (4C, Ph C), 128.81 (2C, Ph C), 128.84 (2C, Ph C), 138.69 (2C, Ph C), 138.78 (1C, Ph C), 138.82 (1C, Ph C), 141.23, 141.30, 141.35, 141.56, 141.61, 141.68, 141.73, 141.78, 141.81, 142.26, 142.29, 142.87, 143.02, 143.40, 143.64, 143.67, 143.90, 143.93, 143.99, 144.33, 144.37, 144.54, 144.72, 144.75, 144.98, 145.33, 145.36, 145.40, 145.46, 145.51, 145.60, 146.10, 146.34, 146.39, 146.54, 147.33, 148.61, 160.40 (1C, CN), 160.49 (2C, CN), 160.58 (1C, CN); IR (KBr): $\tilde{\nu}$ = 3059, 3027, 2958, 2897, 1662 (C=N), 1493, 1471, 1453, 1425, 1351, 1271, 1227, 755, 698, 591, 542, 525 cm$^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 254 (57000), 313 (22000), 362 (8000), 401 (2000), 423 (1300), 483 (1600) nm; MS (FAB/3-NBA): *m*/*z* = 1328 ($M^+$, 20%), 720 ($C_{60}^+$, 100%), $^{12}C_{98}H_{32}N_4O_4$ calcd 1328.2.

**Trisadduct (+)-14**: Bisoxazoline **6a** (17 mg, 1.5 equiv) in dry $CH_2Cl_2$ (25 mL) was added through a dropping funnel to a solution of **(+)-11** (60 mg, 0.037 mmol) in dry toluene (50 mL). Under vigorous stirring $CBr_4$ (18 mg, 1.5 equiv) in dry $CH_2Cl_2$ (10 mL) and DBU (16 μL, 3 equiv) were added to the reaction mixture. After stirring for 24 h the reaction mixture was concentrated and fractionated by preparative HPLC ($SiO_2$, toluene/ethyl acetate/triethylamine 86:13.8:0.2). Relative yield: 17%. $k'$ ($SiO_2$, toluene/ethyl acetate/triethylamine 86:13.8:0.2): 8.73; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 4.43 (dd, *J*(H,H) = 8.6 Hz, 6H, Oxaz $CH_2$), 4.95 (dd, *J*(H,H) = 10 Hz, 8.5 Hz, 6H, Oxaz $CH_2$), 5.55 (dd, *J*(H,H) = 10 Hz, 8.2 Hz, Oxaz CH), 7.2–7.5 (m, 30H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta$ = 40.05 (3C, methylene C), 70.44 (6C, Oxaz CH), 72.29 (6C, sp$^3$ C), 75.88 (6C, Oxaz C), 126.99 (12C, Ph C), 127.84 (6C, Ph C), 128.75 (12C, Ph C), 141.32 (6C, Ph C), 141.78, 142.38, 142.47, 143.32, 145.83, 147.38, 147.92, 148.00, 148.68, 160.68 (6C, CN); IR (KBr): $\tilde{\nu}$ = 3058, 3027, 2958, 2895, 1801, 1661 (CN), 1493, 1470, 1452, 1429, 1351, 1267, 1223, 750, 696, 586, 570, 528 cm$^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 242 (62000), 296 (27000), 326 (15000), 372 (4400), 487 (2100), 573 (900) nm; CD ($CH_3OH$) = 245 ($\Delta\varepsilon$ = 30), 289 (−13), 304 (−4), 346 (−10), 398 (3), 468 (8), 528 (−4), 618 (−2) nm; $[\alpha]_D$ (*c* = 0.7 mg/14 mL, $CH_3Cl$) = +100°; MS (FAB/3-NBA): *m*/*z* = 1634 ([$M^+$+H], 13%), 720 ($C_{60}^+$, 100%), $^{12}C_{116}{}^{13}CH_{48}N_6O_6$ calcd 1633.4.

**Adducts 15**: Bisoxazoline **6a** (75 mg, 1.2 equiv) in dry $CH_2Cl_2$ (100 mL) solution was added to a solution of **13** (270 mg, 0.204 mmol) in dry toluene (200 mL) through a dropping funnel. Under vigorous stirring $CBr_4$ (84 mg, 1.2 equiv) in dry $CH_2Cl_2$ (20 mL) and DBU (77.4 μL, 2.4 equiv) were added successively to the solution. After 24 h at RT the mixture was concentrated and separated by preparative HPLC ($SiO_2$, toluene/ethyl acetate/triethylamine = 93:6.8:0.2). Relative yield (HPLC): **(+)-15** (21.9%) and **(−)-15** (19.2%).

**Trisadduct (+)-15**: $R_f$ ($SiO_2$, toluene/ethyl acetate/triethylamine 95:4.8:0.2): 0.25; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 4.30 (dd, *J*(H,H) = 8.3 Hz, 3H, Oxaz $CH_2$), 4.35 (dd, *J*(H,H) = 8.3 Hz, 3H, Oxaz $CH_2$), 4.82 (dd, *J*(H,H) = 10.2 Hz, 8.8 Hz, 3H, Oxaz $CH_2$), 4.84 (dd, *J*(H,H) = 10.3 Hz, 8.3 Hz, 3H, Oxaz $CH_2$), 5.43 (dd, *J*(H,H) = 10.2 Hz, 8.3 Hz, 3H, Oxaz CH), 5.49 (dd, *J*(H,H) = 10.3 Hz, 8.8 Hz, 3H, Oxaz CH), 7.2–7.5 (m, 30H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta$ = 42.12 (3C, methylene C), 70.24 (3C, Oxaz CH), 70.44 (3C, Oxaz CH), 71.06 (3C, sp$^3$ C), 71.77 (3C, sp$^3$ C), 75.65 (3C, Oxaz $CH_2$), 75.89 (3C, Oxaz $CH_2$), 126.94 (6C, Ph C), 127.01 (6C, Ph C), 127.72 (3C, Ph C), 127.85 (3C, Ph C), 128.78 (12C, Ph C), 140.99 (6C, Ph C), 141.34, 141.37, 141.90, 142.34, 143.07, 143.62, 143.95, 144.22, 144.73, 144.81, 145.63, 146.74, 146.65, 146.89, 146.93, 160.28 (3C, CN), 160.61 (3C, CN); IR (KBr): $\tilde{\nu}$ = 3059, 3027, 2958, 2898, 1661 (CN), 1493, 1471, 1453, 1454, 1263, 1229, 1189, 753, 698, 589, 526 cm$^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 252 (60500), 283 (40300), 353 (8700), 380 (3700), 483 (2900) nm; CD ($CH_3OH$) = 254 ($\Delta\varepsilon$ = −32), 277 (4), 291 (4), 301 (−39), 314 (13), 329 (−7), 357 (24), 383 (−18), 396 (−26), 459 (−9), 488 (−9), 517 (6), 569 (20) nm; $[\alpha]_D$ (*c* = 1 mg/10 mL, $CH_3Cl$) = +1180°; MS (FAB/3-NBA): *m*/*z* = 1634 ([$M^+$+H], 15%), 720 ($C_{60}^+$, 100%), $^{12}C_{116}{}^{13}CH_{48}N_6O_6$ calcd 1633.4.

**Trisadduct (−)-15**: $R_f$ ($SiO_2$, toluene/ethyl acetate/triethylamine 95:4.8:0.2): 0.21; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 4.28 (dd, *J*(H,H) = 8.2 Hz, 3H, Oxaz $CH_2$), 4.38 (dd, *J*(H,H) = 8.3 Hz, 3H, Oxaz $CH_2$), 4.79 (dd, *J*(H,H) = 9.9 Hz, 8.3 Hz, 3H, Oxaz $CH_2$), 4.89 (dd, *J*(H,H) = 9.9 Hz, 8.3 Hz, 3H, Oxaz $CH_2$), 5.44 (dd, *J*(H,H) = 9.9 Hz,

8.8 Hz, 3H, Oxaz CH), 5.49 (dd, $J$(H,H) = 9.9 Hz, 8.8 Hz, 3H, Oxaz CH), 7.2–7.5 (m, 30H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta$ = 42.15 (3C, methylene C), 70.15 (3C, Oxaz CH), 70.46 (3C, Oxaz CH), 71.08 (3C, $sp^3$ C), 71.64 (3C, $sp^3$ C), 75.72 (3C, Oxaz $CH_2$), 75.83 (3C, Oxaz $CH_2$), 126.91 (6C, Ph C), 127.02 (6C, Ph C), 127.72 (3C, Ph C), 127.84 (3C, Ph C), 128.75 (6C, Ph C), 128.81 (6C, Ph C), 141.03 (6C, Ph C), 141.32, 141.41, 141.75, 142.41, 142.97, 143.58, 143.98, 144.25, 144.66, 144.98, 145.63, 146.28, 146.53, 146.62, 146.68, 146.75, 146.86, 148.29, 160.55 (3C, CN), 160.48 (3C, CN); IR (KBr): $\tilde{\nu}$ = 3059, 3027, 2958, 2898, 1661, 1493, 1471, 1453, 1454, 1263, 1229, 1189, 753, 698, 589, 526 cm$^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 252 (62000), 283 (42500), 353 (8500), 381 (4200), 483 (4000) nm; CD ($CH_3OH$) = 254 ($\Delta\varepsilon$ = 22), 276 (−12), 291 (−13), 302 (22), 313 (−20), 330 (3), 356 (−26), 382 (14), 396 (21), 461 (6), 491 (7), 520 (−7), 567 (−22) nm; $[\alpha]_D$ ($c$ = 1 mg/10 mL, $CH_3Cl$) = −520°; MS (FAB/3-NBA): $m/z$ = 1634 ([$M^+$+H], 14%), 720 ($C_{60}^+$, 100%), $^{12}C_{116}{}^{13}CH_{48}N_6O_6$ calcd 1633.4.

**Adducts 16–21**: Diethyl bromomalonate (95 mg, 1.2 equiv) and NaH (79.2 mg, 10 equiv) were added to a solution of (340 mg, 0.33 mmol) **8a** in dry toluene (200 mL). After stirring for 24 h at RT the remaining NaH was destroyed by the addition of $H_2SO_4$ (5 mL, 2N). The reaction mixture was concentrated and separated with preparative HPLC ($SiO_2$, toluene/ethyl acetate = 97:3). The relative yields (HPLC) of the bisadducts are: **16** or **17** 1.70%, **18** or **19** 14.23%, **20** or **21** 14.64%.

**Bisadduct 16**: $k'$ ($SiO_2$, toluene/ethyl acetate 97:3): 13.21; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.57 (t, $J$(H,H) = 7.4 Hz, 6H, $CH_3$), 4.61 (dd, $J$(H,H) = 8.4 Hz, 2H, Oxaz $CH_2$), 4.67 (q, $J$(H,H) = 7.4 Hz, 4H, $CH_2$), 5.12 (dd, $J$(H,H) = 10.3 Hz, 8.3 Hz, 2H, Oxaz $CH_2$), 5.72 (dd, $J$(H,H) = 10.3 Hz, 8.3 Hz, 2H, Oxaz CH), 7.2–7.6 (m, 10H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta$ = 14.32 (2C, $CH_3$), 35.25 (1C, Oxaz methylene C), 53.41 (1C, methylene C), 63.47 (2C, $CH_2$), 70.17 (2C, $sp^3$ C), 70.72 (2C, Oxaz CH), 70.82 (2C, Oxaz $sp^3$ C), 76.04 (2C, Oxaz $CH_2$), 127.11 (4C, Ph C), 127.96 (2C, Ph C), 128.86 (4C, Ph C), 139.03 (2C, Ph C), 139.07, 139.16, 141.24, 141.38, 143.42, 143.69, 143.70, 144.34, 144.48, 144.89, 145.27, 145.42, 145.54, 145.57, 161.19 (2C, CN), 164.18 (2C, CO); IR (KBr): $\tilde{\nu}$ = 3059, 3026, 2975, 2925, 2896, 1743 (C=O), 1660 (C=N), 1492, 1451, 1365, 1242, 1094, 737, 697, 580, 551, 525 cm$^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 262 (180000), 324 (72000), 412 (9500), 440 (6600), 472 (8100) nm; MS (FAB/3-NBA): $m/z$ = 1183 ([$M^+$+H], 47%), 720 ($C_{60}^+$, 100%), $^{12}C_{86}H_{26}N_2O_6$ calcd 1182.2.

**Bisadduct 17**: $k'$ (HPLC, toluene/ethyl acetate 97:3): 13.21; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.57 (t, $J$(H,H) = 7.4 Hz, 6H, $CH_3$), 4.61 (dd, $J$(H,H) = 8.4 Hz, 2H, Oxaz $CH_2$), 4.67 (q, $J$(H,H) = 7.4 Hz, 4H, $CH_2$), 5.12 (dd, $J$(H,H) = 10.3 Hz, 8.3 Hz, 2H, Oxaz $CH_2$), 5.72 (dd, $J$(H,H) = 10.3 Hz, 8.3 Hz, 2H, Oxaz CH), 7.2–7.6 (m, 10H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta$ = 14.32 (2C, $CH_3$), 35.25 (1C, Oxaz methylene C), 53.41 (1C, methylene C), 63.47 (2C, $CH_2$), 70.17 (2C, $sp^3$ C), 70.72 (2C, Oxaz CH), 70.82 (2C, Oxaz $sp^3$ C), 76.04 (2C, Oxaz $CH_2$), 127.11 (4C, Ph C), 127.96 (2C, Ph C), 128.86 (4C, Ph C), 139.03 (2C, Ph C), 139.07, 139.16, 141.24, 141.38, 143.42, 143.69, 143.75, 144.34, 144.48, 144.89, 145.27, 145.31, 145.42, 145.54, 145.57, 161.19 (2C, CN), 164.18 (2C, CO); IR (KBr): $\tilde{\nu}$ = 3059, 3026, 2975, 2925, 2896, 1743 (C=O), 1660 (C=N), 1492, 1451, 1365, 1242, 1094, 737, 697, 580, 551, 525 cm$^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 262 (180000), 324 (72000), 412 (9500), 440 (6600), 472 (8100) nm; MS (FAB/3-NBA): $m/z$ = 1183 ([$M^+$+H], 45%), 720 ($C_{60}^+$, 100%), $^{12}C_{86}H_{26}N_2O_6$ calcd 1182.2.

**Bisadduct 18**: $k'$ ($SiO_2$, toluene/ethyl acetate 97:3): 22.71; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.43 (tt, $J$(H,H) = 7.8 Hz, 6H, $CH_3$), 4.35–4.55 (m, 6H, Oxaz $CH_2$ and $CH_2$), 4.91 (dd, $J$(H,H) = 10.2 Hz, 8.8 Hz, 1H, Oxaz $CH_2$), 4.95 (dd, $J$(H,H) = 10.2 Hz, 8.8 Hz, 1H, Oxaz $CH_2$), 5.53 (dd, $J$(H,H) = 10.2 Hz, 8.3 Hz, 1H, Oxaz CH), 5.56 (dd, $J$(H,H) = 10.2 Hz, 8.8 Hz, 1H, Oxaz CH), 7.2–7.5 (m, 10H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta$ = 14.20 (2C, $CH_3$), 42.70 (1C, Oxaz methylene C), 51.25 (1C, methylene C), 63.24 (2C, $CH_2$), 70.33 (1C, Oxaz CH), 70.44 (2C, $sp^3$ C), 70.50 (1C, Oxaz CH), 71.57 (1C, Oxaz $sp^3$ C), 72.47 (1C, Oxaz $sp^3$ C), 75.79 (2C, Oxaz $CH_2$), 126.99 (2C, Ph C), 127.03 (2C, Ph C), 127.80 (1C, Ph C), 127.89 (1C, Ph C), 128.75 (2C, Ph C), 128.80 (2C, Ph C), 138.58 (1C, Ph C), 138.60 (1C, Ph C), 138.83, 138.91, 141.30, 141.54, 141.63, 141.77, 142.25, 142.43, 142.65, 142.78, 142.89, 143.24, 143.42, 143.66, 143.82, 143.88, 143.95, 144.00, 144.41, 144.57, 144.68, 144.94, 145.21, 145.32, 145.41, 145.48, 145.54, 145.59, 146.09, 146.12, 146.51, 146.54, 146.76, 147.27, 147.55, 160.52 (1C, CN), 160.67 (1C, CN), 163.45 (2C, CO); IR (KBr): $\tilde{\nu}$ = 3085, 3060, 3027, 2976, 2958, 2931, 2931, 1745 (C=O), 1663 (C=N), 1493, 1454, 1366, 1296, 1235, 1098, 755, 699, 590, 543, 526 cm$^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 252 (85000), 311 (32000), 359 (12000), 421 (2100), 482 (2500) nm; MS (FAB/3-NBA): $m/z$ = 1183 ([$M^+$+H], 90%), 720 ($C_{60}^+$, 100%), $^{12}C_{86}H_{26}N_2O_6$ calcd 1182.2.

**Bisadduct 19**: $k'$ ($SiO_2$, toluene/ethyl acetate 97:3): 22.71; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.43 (tt, $J$(H,H) = 7.8 Hz, 6H, $CH_3$), 4.35–4.55 (m, 6H, Oxaz $CH_2$ and $CH_2$), 4.91 (dd, $J$(H,H) = 10.2 Hz, 8.8 Hz, 1H, Oxaz $CH_2$), 4.95 (dd, $J$(H,H) = 10.2 Hz, 8.8 Hz, 1H, Oxaz $CH_2$), 5.53 (dd, $J$(H,H) = 10.2 Hz, 8.3 Hz, 1H, Oxaz CH), 5.56 (dd, $J$(H,H) = 10.2 Hz, 8.8 Hz, 1H, Oxaz CH), 7.2–7.5 (m, 10H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta$ = 14.20 (2C, $CH_3$), 42.70 (1C, Oxaz methylene C), 51.25 (1C, methylene C), 63.24 (2C, $CH_2$), 70.33 (1C, Oxaz CH), 70.44 (2C, $sp^3$ C), 70.50 (1C, Oxaz CH), 71.57 (1C, Oxaz $sp^3$ C), 72.47 (1C, Oxaz $sp^3$ C), 75.79 (2C, Oxaz $CH_2$), 126.99 (2C, Ph C), 127.03 (2C, Ph C), 127.80 (1C, Ph C), 127.89 (1C, Ph C), 128.75 (2C, Ph C), 128.80 (2C, Ph C), 138.58 (1C, Ph C), 138.60 (1C, Ph C), 138.83, 138.91, 141.30, 141.54, 141.63, 141.77, 142.25, 142.43, 142.65, 142.78, 142.89, 143.24, 143.42, 143.66, 143.82, 143.88, 143.95, 144.00, 144.41, 144.57, 144.68, 144.94, 145.21, 145.32, 145.41, 145.48, 145.54, 145.59, 146.09, 146.12, 146.51, 146.54, 146.76, 147.27, 147.55, 160.52 (1C, CN), 160.67 (1C, CN), 163.45 (2C, CO); IR (KBr): $\tilde{\nu}$ = 3085, 3060, 3027, 2976, 2958, 2931, 2931, 1745 (C=O), 1663 (C=N), 1493, 1454, 1366, 1296, 1235, 1098, 755, 699, 590, 543, 526 cm$^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 252 (85000), 311 (32000), 359 (12000), 421 (2100), 482 (2500) nm; MS (FAB/3-NBA): $m/z$ = 1183 ([$M^+$+H], 70%), 720 ($C_{60}^+$, 100%), $^{12}C_{86}H_{26}N_2O_6$ calcd 1182.2.

**Bisadduct 20**: $k'$ (HPLC, toluene/ethyl acetate 97:3): 31.89; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.39 (t, $J$(H,H) = 7.4 Hz, 3H, $CH_3$), 1.43 (t, $J$(H,H) = 7.4 Hz, 3H, $CH_3$), 4.40–4.56 (m, 6H, Oxaz $CH_2$ and $CH_2$), 4.91 (dd, $J$(H,H) = 4.4 Hz, 8.3 Hz, 1H, Oxaz $CH_2$), 4.94 (dd, $J$(H,H) = 4.4 Hz, 8.3 Hz, 1H, Oxaz $CH_2$), 5.54 (dd, $J$(H,H) = 9.8 Hz, 8.8 Hz, 2H, Oxaz CH), 7.2–7.5 (m, 10H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta$ = 14.07 (1C, $CH_3$), 14.16 (1C, $CH_3$), 40.51 (1C, Oxaz methylene C), 53.41 (1C, methylene C), 63.17 (1C, $CH_2$), 63.20 (1C, $CH_2$), 70.50 (2C, $sp^3$ C), 71.19 (2C, Oxaz CH), 71.63 (1C, Oxaz $sp^3$ C), 72.40 (1C, Oxaz $sp^3$ C), 75.79 (2C, Oxaz $CH_2$), 126.99 (4C, Ph C), 127.83 (2C, Ph C), 128.75 (4C, Ph C), 138.74 (2C, Ph C), 138.80, 138.92, 141.21, 141.26, 141.56, 141.59, 141.70, 141.76, 141.87, 141.90, 142.25, 142.30, 142.87, 143.27, 143.36, 143.73, 143.82, 144.04, 144.13, 144.17, 144.22, 144.33, 144.57, 144.77, 144.81, 145.03, 145.17, 145.36, 145.41, 145.56, 146.09, 146.40, 146.43, 146.47, 146.54, 147.29, 148.65, 148.72, 160.49 (2C, CN), 163.23 (1C, CO), 163.61 (1C,CO); IR (KBr): $\tilde{\nu}$ = 3060, 3027, 2975, 2925, 2899, 1743 (C=O), 1660 (C=N), 1493, 1452, 1366, 1296, 1238, 1094, 756, 740, 698, 582, 542, 524 cm$^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 251 (79000), 311 (30000), 356 (11000), 399 (3200), 423 (1900), 481 (2300) nm; MS (FAB/3-NBA): $m/z$ = 1183 ([$M^+$+H], 47%), 720 ($C_{60}^+$, 100%), $^{12}C_{86}H_{26}N_2O_6$ calcd 1182.2.

**Bisadduct 21**: $k'$ (HPLC, toluene/ethyl acetate 97:3): 31.89; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.39 (t, $J$(H,H) = 7.4 Hz, 3H, $CH_3$), 1.43 (t, $J$(H,H) = 7.4 Hz, 3H, $CH_3$), 4.40–4.56 (m, 6H, Oxaz $CH_2$ and $CH_2$), 4.91 (dd, $J$(H,H) = 4.4 Hz, 8.3 Hz, 1H, Oxaz $CH_2$), 4.94 (dd, $J$(H,H) = 4.4 Hz, 8.3 Hz, 1H, Oxaz $CH_2$), 5.54 (dd, $J$(H,H) = 9.8 Hz, 8.8 Hz, 2H, Oxaz CH), 7.2–7.5 (m, 10H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta$ = 14.07 (1C, $CH_3$), 14.16 (1C, $CH_3$), 40.51 (1C, Oxaz methylene C), 53.41 (1C, methylene C), 63.17 (1C, $CH_2$), 63.20 (1C, $CH_2$), 70.50 (2C, $sp^3$ C), 71.19 (2C, Oxaz CH), 71.63 (1C, Oxaz $sp^3$ C), 72.40 (1C, Oxaz $sp^3$ C), 75.79 (2C, Oxaz $CH_2$), 126.99 (4C, Ph C), 127.83 (2C, Ph C), 128.75 (4C, Ph C), 138.74 (2C, Ph C), 138.80, 138.92, 141.21, 141.26, 141.56, 141.59, 141.70, 141.76, 141.87, 141.90, 142.25, 142.30, 142.87, 143.27, 143.36, 143.73, 143.82, 144.04, 144.13, 144.17, 144.22, 144.33, 144.57, 144.77, 144.81, 145.03, 145.17, 145.36, 145.41, 145.56, 146.09, 146.40, 146.43, 146.47, 146.54, 147.29, 148.65, 148.72, 160.49 (2C, CN), 163.23 (1C, CO), 163.61 (1C, CO); IR (KBr): $\tilde{\nu}$ = 3060, 3027, 2975, 2925, 2899, 1743 (C=O), 1660 (C=N), 1493, 1452, 1366, 1296, 1238, 1094, 756, 740, 698, 582, 542, 524 cm$^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 251 (79000), 311 (30000), 356 (11000), 399 (3200), 423 (1900), 481 (2300) nm; MS (FAB/3-NBA): $m/z$ = 1183 ([$M^+$+H], 67%), 720 ($C_{60}^+$, 100%), $^{12}C_{86}H_{26}N_2O_6$ calcd 1182.2.

**Adducts 22–23**: Diethyl bromomalonate (40 μL, 1.1 equiv) and NaH (50 mg, 10 equiv) were added to a solution of **18** (or **19**, **20**, **21**; 250 mg, 0.21 mmol) in dry toluene (200 mL). After stirring for 24 h at RT the excess NaH was destroyed with $H_2SO_4$ (5 mL, 2N). The reaction mixture was concentrated and separated with preparative HPLC ($SiO_2$, toluene/ethyl acetate/triethylamine 96:3.8:0.2). Relative yield: **(+)-22** (22%), **(−)-23** (21%), **(−)-22** (21%), **(−)-23** (22%).



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**Trisadduct (+)-22**: $R_f$ ($SiO_2$, toluene/ethyl acetate/triethylamine 96:3.8:0.2): 23.84; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.3-1.4$ (m, 12H, $CH_3$), 4.25–4.45 (m, 10H, Oxaz $CH_2$ and $CH_2$), 4.82 (dd, $J$(H,H) = 10.3 Hz, 8.8 Hz, 1H, Oxaz $CH_2$), 4.86 (dd, $J$(H,H) = 10.3 Hz, 8.8 Hz, 1H, Oxaz $CH_2$), 5.44 (dd, $J$(H,H) = 10.3 Hz, 8.3 Hz, 1H, Oxaz CH), 5.48 (dd, $J$(H,H) = 10.2 Hz, 8.8 Hz, 1H, Oxaz CH), 7.2–7.4 (m, 10H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 14.02$ (1C, $CH_3$), 14.07 (2C, $CH_3$), 14.14 (1C, $CH_3$), 42.03 (1C, Oxaz methylene C), 52.75 (1C, methylene C), 52.90 (1C, methylene C), 63.02 (2C, $CH_2$), 63.06 (2C, $CH_2$), 70.07 (1C, $sp^3$ C), 70.15 (1C, $sp^3$ C), 70.24 (1C, Oxaz CH), 70.42 (1C, Oxaz CH), 70.82 (1C, Oxaz $sp^3$ C), 70.90 (2C, $sp^3$ C), 71.68 (1C, Oxaz $sp^3$ C), 75.67 (1C, Oxaz $CH_2$), 75.72 (1C, Oxaz $CH_2$), 126.99 (2C, Ph C), 127.03 (2C, Ph C), 127.71 (1C, Ph C), 127.81 (1C, Ph C), 128.67 (2C, Ph C), 128.73 (2C, Ph C), 140.81 (1C, Ph C), 140.92 (1C, Ph C), 140.95, 141.30, 141.67, 141.74, 141.88, 141.92, 142.25, 142.40, 142.47, 142.74, 142.93, 143.38, 143.44, 143.55, 143.91, 144.17, 144.22, 144.28, 144.53, 144.73, 144.94, 145.03, 145.16, 145.50, 145.56, 145.61, 146.18, 146.27, 146.38, 146.43, 146.51, 146.62, 146.65, 146.69, 146.78, 146.85, 147.02, 147.20, 160.38 (1C, CN), 160. 49 (1C, CN), 163.04 (1C, CO), 163.39 (2C, CO), 163.40 (1C, CO); IR (KBr): $\tilde{\nu} = 3060$, 3027, 2977, 2926, 2901, 1874, 1744 (C=O), 1661 (C=N), 1493, 1453, 1388, 1366, 1296, 1270, 1241, 1214, 1101, 742, 700, 527 $cm^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 252 (60000), 283 (42500), 352 (8750), 380 (3600), 483 (3100) nm; CD ($CH_3OH$) = 242 ($\Delta\varepsilon$ = 7), 251 (−19), 270 (6), 286 (−6), 300 (−34), 312 (11), 327 (−5), 354 (19), 381 (−16), 395 (−21), 457 (−6), 489 (−6), 516 (5), 564 (16) nm; $[\alpha]_D$ ($c$ = 1 mg/10 mL, $CH_3Cl$) = +1800°; MS (FAB/3-NBA): $m/z$ = 1340 ($M^+$, 100%), 720 ($C_{60}^+$, 100%), $^{12}C_{93}H_{36}N_2O_{10}$ calcd 1340.2.

**Trisadduct (−)-22**: $R_f$ ($SiO_2$, toluene/ethyl acetate/triethylamine 96:3.8:0.2): 23.84; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.3-1.4$ (m, 12H, $CH_3$), 4.25–4.45 (m, 10H, Oxaz $CH_2$ and $CH_2$), 4.82 (dd, $J$(H,H) = 10.3 Hz, 8.8 Hz, 1H, Oxaz $CH_2$), 4.86 (dd, $J$(H,H) = 10.3 Hz, 8.8 Hz, 1H, Oxaz $CH_2$), 5.44 (dd, $J$(H,H) = 10.3 Hz, 8.3 Hz, 1H, Oxaz CH), 5.48 (dd, $J$(H,H) = 10.2 Hz, 8.8 Hz, 1H, Oxaz CH), 7.2–7.4 (m, 10H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 14.02$ (1C, $CH_3$), 14.07 (2C, $CH_3$), 14.14 (1C, $CH_3$), 42.03 (1C, Oxaz methylene C), 52.75 (1C, methylene C), 52.90 (1C, methylene C), 63.02 (2C, $CH_2$), 63.06 (2C, $CH_2$), 70.07 (1C, $sp^3$ C), 70.15 (1C, $sp^3$ C), 70.24 (1C, Oxaz CH), 70.42 (1C, Oxaz CH), 70.82 (1C, Oxaz $sp^3$ C), 70.90 (2C, $sp^3$ C), 71.68 (1C, Oxaz $sp^3$ C), 75.67 (1C, Oxaz $CH_2$), 75.72 (1C, Oxaz $CH_2$), 126.99 (2C, Ph C), 127.03 (2C, Ph C), 127.71 (1C, Ph C), 127.81 (1C, Ph C), 128.67 (2C, Ph C), 128.73 (2C, Ph C), 140.81 (1C, Ph C), 140.92 (1C, Ph C), 140.95, 141.30, 141.67, 141.74, 141.88, 141.92, 142.25, 142.40, 142.47, 142.74, 142.93, 143.38, 143.44, 143.55, 143.91, 144.17, 144.22, 144.28, 144.53, 144.73, 144.94, 145.03, 145.16, 145.50, 145.56, 145.61, 146.18, 146.27, 146.38, 146.43, 146.51, 146.62, 146.65, 146.69, 146.78, 146.85, 147.02, 147.20, 160.38 (1C, CN), 160. 49 (1C, CN), 163.04 (1C, CO), 163.39 (2C, CO), 163.40 (1C, CO); IR (KBr): $\tilde{\nu} = 3060$, 3027, 2977, 2926, 2901, 1874, 1744 (C=O), 1661 (C=N), 1493, 1453, 1388, 1366, 1296, 1270, 1241, 1214, 1101, 742, 700, 527 $cm^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 252 (61000), 283 (43000), 352 (8900), 380 (3600), 483 (3000) nm; CD ($CH_3OH$) = 253 ($\Delta\varepsilon$ = 30), 278 (−9), 291 (−8), 302 (36), 314 (−17), 329 (4), 356 (−27), 383 (17), 397 (26), 458 (9), 490 (11), 518 (−8), 568 (−22) nm; $[\alpha]_D$ ($c$ = 4.16 mg/100 mL, $CH_2Cl_2$) = −1930°; MS (FAB/3-NBA): $m/z$ = 1340 ($M^-$, 90%), 720 ($C_{60}^+$, 100%), $^{12}C_{93}H_{36}N_2O_{10}$ calcd 1340.2.

**Trisadduct (+)-23**: $R_f$ ($SiO_2$, toluene/ethyl acetate/triethylamine 96:3.8:0.2): 32.162; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.33$ (tt, $J$(H,H) = 7.3 Hz, 6H, $CH_3$), 1.38 (tt, $J$(H,H) = 7.3 Hz, 6H, $CH_3$), 4.25–4.50 (m, 10H, Oxaz $CH_2$ and $CH_2$), 4.81 (dd, $J$(H,H) = 10.3 Hz, 8.8 Hz, 1H, Oxaz $CH_2$), 4.87 (dd, $J$(H,H) = 10.2 Hz, 8.3 Hz, 1H, Oxaz $CH_2$), 5.44 (dd, $J$(H,H) = 10.3 Hz, 8.8 Hz, 1H, Oxaz CH), 5.48 (dd, $J$(H,H) = 10.2 Hz, 8.8 Hz, 1H, Oxaz CH), 7.2–7.4 (m, 10H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 14.02$ (1C, $CH_3$), 14.07 (2C, $CH_3$), 14.14 (1C, $CH_3$), 42.01 (1C, Oxaz methylene C), 52.75 (1C, methylene C), 52.90 (1C, methylene C), 62.99 (2C, $CH_2$), 63.06 (2C, $CH_2$), 70.09 (1C, $sp^3$ C), 70.13 (1C, $sp^3$ C), 70.22 (1C, Oxaz CH), 70.44 (1C, Oxaz CH), 70.81 (1C, Oxaz $sp^3$ C), 70.86 (1C, $sp^3$ C), 70.92 (1C, $sp^3$ C), 71.65 (1C, Oxaz $sp^3$ C), 75.67 (2C, Oxaz $CH_2$), 127.01 (4C, Ph C), 127.71 (1C, Ph C), 127.81 (1C, Ph C), 128.67 (2C, Ph C), 128.73 (2C, Ph C), 140.84 (1C, Ph C), 140.92 (1C, Ph C), 141.24, 141.32, 141.63, 141.76, 141.85, 141.88, 142.41, 142.52, 142.82, 142.96, 143.09, 143.38, 143.49, 143.69, 144.17, 144.26, 144.31, 144.61, 144.83, 144.92, 144.99, 145.16, 145.47, 145.56, 145.58, 145.62, 145.65, 146.21, 146.27, 146.38, 146.49, 146.56. 146.62, 146.67, 146.76, 146.84, 146.93, 147.22, 148.33, 160.38 (1C, CN), 160.49 (1C, CN), 163.04 (1C, CO), 163.37 (1C, CO), 163.41(2C,CO); IR (KBr): $\tilde{\nu} = 33061$, 3028, 2960, 2924, 2853, 1744 (C=O), 1663 (C=N), 1493, 1454, 1367, 1243, 1215, 1100, 742, 700, 527 $cm^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 252 (60500), 283 (42700), 353 (9000), 381 (3800), 483 (3100) nm; CD ($CH_3OH$) = 254 ($\Delta\varepsilon$ = −29), 277 (10), 291 (9), 302 (−33), 314 (18), 329 (−7), 383 (−18), 397 (−27), 458 (−9), 490 (−11), 519 (−7), 568 (23) nm; $[\alpha]_D$ ($c$ = 4.16 mg/100 mL, $CH_2Cl_2$) = 2020°; MS (FAB/3-NBA): $m/z$ = 1340 ($M^+$, 80%), 720 ($C_{60}^+$, 100%), $^{12}C_{93}H_{36}N_2O_{10}$ calcd 1340.2.

**Trisadduct (−)-23**: $R_f$ ($SiO_2$, toluene/ethyl acetate/triethylamine 96:3.8:0.2): 32.162; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.33$ (tt, $J$(H,H) = 7.3 Hz, 6H, $CH_3$), 1.38 (tt, $J$(H,H) = 7.3 Hz, 6H, $CH_3$), 4.25–4.50 (m, 10H, Oxaz $CH_2$ and $CH_2$), 4.81 (dd, $J$(H,H) = 10.3 Hz, 8.8 Hz, 1H, Oxaz $CH_2$), 4.87 (dd, $J$(H,H) = 10.2 Hz, 8.3 Hz, 1H, Oxaz $CH_2$), 5.44 (dd, $J$(H,H) = 10.3 Hz, 8.8 Hz, 1H, Oxaz CH), 5.48 (dd, $J$(H,H) = 10.2 Hz, 8.8 Hz, 1H, Oxaz CH), 7.2–7.4 (m, 10H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 14.02$ (1C, $CH_3$), 14.07 (2C, $CH_3$), 14.14 (1C, $CH_3$), 42.01 (1C, Oxaz methylene C), 52.75 (1C, methylene C), 52.90 (1C, methylene C), 62.99 (2C, $CH_2$), 63.06 (2C, $CH_2$), 70.09 (1C, $sp^3$ C), 70.13 (1C, $sp^3$ C), 70.22 (1C, Oxaz CH), 70.44 (1C, Oxaz CH), 70.81 (1C, Oxaz $sp^3$ C), 70.86 (1C, $sp^3$ C), 70.92 (1C, $sp^3$ C), 71.65 (1C, Oxaz $sp^3$ C), 75.67 (2C, Oxaz $CH_2$), 127.01 (4C, Ph C), 127.71 (1C, Ph C), 127.81 (1C, Ph C), 128.67 (2C, Ph C), 128.73 (2C, Ph C), 140.84 (1C, Ph C), 140.92 (1C, Ph C), 141.24, 141.32, 141.63, 141.76, 141.85, 141.88, 142.41, 142.52, 142.82, 142.96, 143.09, 143.38, 143.49, 143.69, 144.17, 144.26, 144.31, 144.61, 144.83, 144.92, 144.99, 145.16, 145.47, 145.56, 145.58, 145.62, 145.65, 146.21, 146.27, 146.38, 146.49, 146.56. 146.62, 146.67, 146.76, 146.84, 146.93, 147.22, 148.33, 160.38 (1C, CN), 160.49 (1C, CN), 163.04 (1C, CO), 163.37 (1C, CO), 163.41 (2C, CO); IR (KBr): $\tilde{\nu} = 33061$, 3028, 2960, 2924, 2853, 1744 (C=O), 1663 (C=N), 1493, 1454, 1367, 1243, 1215, 1100, 742, 700, 527 $cm^{-1}$; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 252 (61000), 283 (42000), 353 (7500), 381 (3800), 483 (3400) nm; CD ($CH_3OH$) = 230 ($\Delta\varepsilon$ = 23), 242 (−16), 253 (28), 273 (−18), 289 (−9), 300 (39), 312 (−19), 327 (5), 354 (−32), 380 (17), 394 (27), 456 (8), 489 (8), 516 (−10), 564 (−25); $[\alpha]_D$ ($c$ = 1 mg/10 mL, $CH_3Cl$) = −2200°; MS (FAB/3-NBA): $m/z$ = 1340 ($M^+$, 75%), 720 ($C_{60}^+$, 100%), $^{12}C_{93}H_{36}N_2O_{10}$ calcd 1340.2.

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