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A circular dichroism–DFT method for conformational study of flexible molecules: the case of 1- and 2-naphthyl diesters

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Dedicated to Prof. Jacek Młochowski on the occasion of his 80th anniversary

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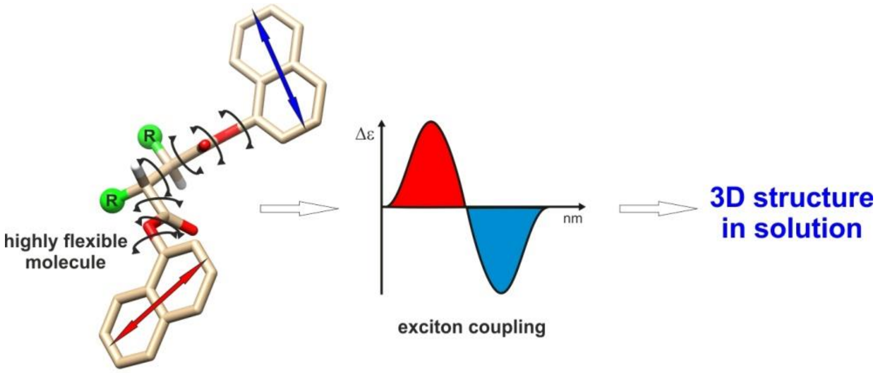
Abstract

The two chromophores, 1- or 2-naphthyl, have been introduced into chiral dicarboxylic acids molecules via the ester bond, in order to experimentally determine/prove the absolute stereochemistry of the molecule. The 1-naphthyl chromophore is considered to be a better CD chromophoric derivative for a hydroxy group. Di-1-naphthyl- and di-2-naphthyl esters of (1*S*,2*S*)-cyclopropane-1,2-dicarboxylic acid constitute the first examples of cyclopropane diaryl esters for which the crystal structures have been determined.



Keywords: 1- and 2-Naphthol, chiral dicarboxylic acids, circular dichroism, X-ray, conformation, DFT

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Introduction

One of the great achievements of computational chemistry is the possibility to predict the stereostructures and spectra of organic molecules. These results can then be correlated with the experimental spectroscopic data.[1,2] In the case of electronic circular dichroism (ECD) spectroscopy a breakthrough was achieved with the implementation of density functional theory (DFT) for such calculations.[3-5] In the past twenty years, empirical correlations between the ECD spectra and structures (absolute configuration, conformation) of chiral molecules became obsolescent and were gradually replaced by a much more reliable experiment – computation confrontation protocols.[6] While the level of accuracy for predicting molecular structures by computation steadily has increased over the years, challenges still remain for molecules having a relatively large number of atoms as well as for flexible molecules characterized by a large number of conformers accessible at ambient temperatures, particularly if the conformer populations are dependent on the effect of the medium (e.g. solvent polarity).

Chiral aliphatic dicarboxylic acids and their derivatives are among flexible molecules that can be studied by ECD if the molecules contain a suitable chromophore. Naphthalene is a particularly suitable UV and CD chromophore due to the high intensity of its electronic transition located at ca. 220 nm.[7] 1- and 2-Naphthyl esters are therefore of interest for ECD studies since naphthyl diesters can give rise to strong and distinct exciton type Cotton effects. Recently we observed such a behavior for the naphthyl diesters of ʟ-tartaric acid.[8] Exciton type Cotton effects were also recorded for axially chiral molecules bearing the benzylidene and 2-naphthyl chromophores.[9] The 2-naphthyl group was used as a powerful chromophore for configurational assignment of carboxylic acids, however the number of cases studied was limited.[10,11]

Naphthyl esters are of importance in organic chemistry and provide a way to introduce a planar group into a molecule to study intramolecular interactions. Diederich et al. used 2-naphthyl esters in a study of dipolar interactions between organic fluorine and amide groups.[12] Rebek[13,14] and Deslongchamps[15] employed these esters for the study of stacking interactions in mimicking these in nucleic base pairs. Naphthyl esters are suitable for HPLC detection[16] and for these and other reasons have been frequently used in syntheses, including electrocyclic ring-opening reactions,[17] asymmetric thermal cycloadditions,[18] stereoselective Baylis-Hillmann reactions,[19,20] asymmetric aza-Baylis-Hillmann reactions,[21] asymmetric alkylations of enolates,[22] and photo-Fries reactions.[23-25] In addition, 1- and 2-naphthols were used for studying the interactions with bovine serum albumin, emploing UV/ECD spectroscopy.[26]

With these facts in mind we anticipated that the combined use of ECD spectroscopy and TD-DFT calculations would provide appropriate grounds for determining the stereostructures of a series of naphthyl esters of highly flexible chiral dicarboxylic acids. In addition, it would determine the limits for the sensitivity of ECD spectroscopy for structural studies of naphthyl esters as well as the advantages of using naphthol derivatives as chromophoric probes.

Results and Discussion

We have investigated a series of 1- and 2-naphthyl esters of the chiral dicarboxylic acids **1**-**10** shown in Figure 1. The diesters have either a carbon or a heteroatom substituent (O, N) at the stereogenic center(s). They are either acyclic (**1**–**5**) or cyclic (**6**–**10**) and the ester groups are separated either by two, three, or four carbon atoms. Note that diesters **3**–**5** as well as **6**–**8** were obtained as enantiomers of the structures shown in Figure

1, however the experimental CD data reported in this article refer to the absolute configurations shown in Figure 1.

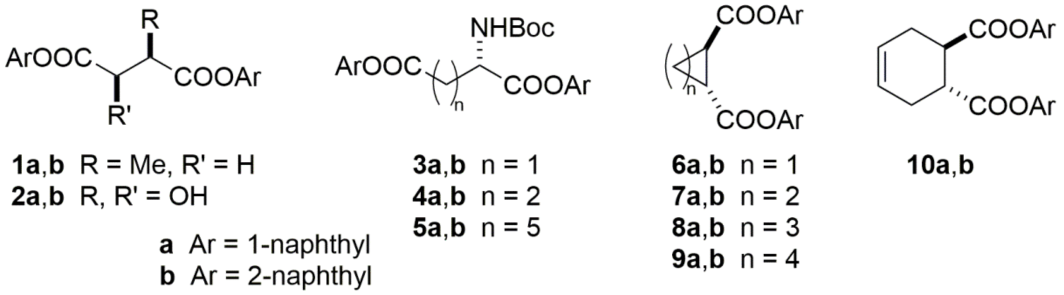


Figure 1. Structures of dinaphthyl esters of dicarboxylic acids.

Despite their flexible nature, in most cases these naphthyl diesters display very distinct and intense Cotton effects in their CD spectra, associated with the intense electronic transition at 223 nm polarized along the long axis of the naphthalene chromophore (Table 1).

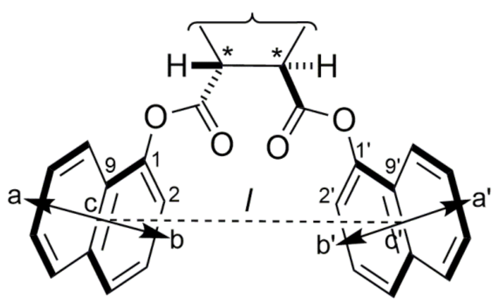
Table 1. Experimental UV and CD data of esters **1**-**10** (see Figure 1 for structures) measured in hexane solution containing 5% (v/v) of 1,2-dichloroethane

Ester	UV[a]	CD[a]		A[b]
	$\varepsilon / \lambda_{max}$	$\Delta\varepsilon / \lambda_{max}$		
1a	145 700 (223)	+67.6 (226)	-39.6 (217)	+107.2
1b	133 300 (223)	-43.0 (227)	+29.3 (217)	+72.3
2a	136 600 (220)	-153.4 (223)	+75.2 (215)	-228.6
2b	143 600 (223)	-34.8 (226)	+22.7 (215)	-57.6
3a	161 000 (223)	+160.4 (225)	-96.1 (216)	+256.5
3b	147 400 (223)	-59.6 (227)	+49.5 (218)	-109.1
4a	155 700 (223)	+24.0 (225)	-6.9 (220)	+30.9
4b	137 000 (223)	+7.2 (228)	-9.2 (217)	+16.4
5a	146 500 (223)	+5.6 (225)	-1.4 (219)	+7.0
5b	147 200 (223)	+3.9 (232)	-5.1 (221)	+9.0
6a	155 800 (223)	-135.1 (225)	+54.7 (216)	-189.8
6b	132 000 (223)	-87.5 (227)	+48.1 (218)	-135.6
7a	143 200 (223)	+47.7 (226)	-40.4 (214)	+88.1
7b	142 300 (223)	-75.3 (228)	+50.7 (218)	-126.0
8a	139 100 (223)	+72 8 (225)	-43.3 (215)	+116.1
8b	146 700 (223)	-41.0 (227)	+30.0 (218)	-71.0
9a	140 700 (223)	+237.0 (226)	-135.6 (216)	+372.6
9b	137 200 (223)	-129.1 (227)	+95.7 (218)	-224.8
10a[c]	138 300 (223)	+139.8 (226)	-72.7 (215)	+212.5
10b[c]	134 400 (223)	-62.8 (227)	+44.2 (217)	-107.0

[a] $M^{-1}\ cm^{-1}$ / nm; [b] amplitude of the exciton Cotton effect; [c] CD data corrected to 100% e.e.

These Cotton effects are predominantly of exciton type and therefore reflect the relative spatial positions of the naphthalene chromophores in each molecule. This means that if the absolute configuration of the molecule is known, the CD spectra reflect predominant conformation(s) of the diester molecules.

It is of interest to note that the amplitudes of the exciton Cotton effects are in the majority of cases lower for 2-naphthyl esters compared to the 1-naphthyl esters. We also note that diester **9b** has been reported earlier,[7] however, its exciton Cotton effects were of lower magnitude than those reported here. In the cases of **1**, **3**, **7**-**10** exciton Cotton effects due to 1- and 2-naphthyl diesters are of opposite sign for the same dicarboxylic acid molecule. This means that at least in some conformers the relative orientation of the naphthalene chromophores in the 1- and 2-naphthyl esters is of opposite helicity. The flexible nature of these diester molecules is evidenced by a number of conformers which differ in the values of torsion angles α–δ–α' along the chain of the carbon and oxygen atoms, starting from the ester group, as defined in Figure 2.



α,α' = C9(C9')-C1(C1')-O-C(=O)
β,β' = C1(C1')-O-C(=O)-C*
γ,γ' = O-C(=O)-C*-C*
δ = (O=)C-C*-C*-C(=O)
ω = a-c-c'-a' *or* a-c-c'-b
or b-c-c'-a' *or* b-c-c'-b'
assuming that 0° < $|\omega|$ < 180°
$l = |c\text{-}c'|$

Figure 2. Definition of torsion angles *α*, *α'*, *β*, *β'*, *γ*, *γ*', *δ* and *ω* that characterize molecular conformation, and the distance *l* between the midpoints of electric dipole transition moments polarized along the long axes of the naphthalene chromophores.

Figure 2 also defines the dihedral angle ω and the distance *l* between the electric dipole transition moments for the most intense naphthalene electronic transition at around 220 nm. These two parameters define the sign and the amplitude of the exciton Cotton effects located in the spectral region 215 to 230 nm. It would be useful to show that the sign (and to a limited extent the magnitude) of dihedral angle ω ($|\omega|<90°$) is qualitatively related to the torsion angles α, β, γ, δ, γ', β' , α' , i. e. to the conformation of the molecule.

In order to obtain an insight into the origin of the exciton Cotton effects of the dinaphthyl esters we carried out a computational analysis of the conformer structures and populations for diesters of dicarboxylic acids **1**, **2**, **6**–**10**.

We employed a protocol that includes initial systematic conformational search at the molecular mechanics level (MM3 force field)[27] and pre-optimization of all minimum-energy structures at the PBE0/6-31G(d) level followed by optimization of all stable conformers at the higher DFT level. Among the methods tested (see Computational Details in Supporting Information), the long-range corrected modification of PBE functional, called LC-wPBE[28] together with enhanced triple-ζ basis set 6-311++G(d,p) gave the best results (*vide infra*) and the further discussion will be limited to the structural results obtained with this particular combination of methods.[29] Total and free energy values have been calculated and used to obtain the Boltzmann population of the real minimum-energy conformers at 298.15 K. Only the results for conformers that differ from the most stable one by less than 2 kcal mol^{-1} have been taken into account for further calculations. A full list of calculated structures is given in the Supporting Information, Tables A1–G4, while the structures of the conformers are summarized in Figures B1−B7. On the basis of these structural data the CD spectra of individual conformers were calculated, using the TD-DFT method, employing several hybrid functionals and 6-311++G(2d,2p) basis set. After Boltzmann averaging over the contributions of participating conformers, the calculated CD spectra of the dinaphthyl esters were compared with those obtained experimentaly (see Figures C1–C7 in SI). In general, a good agreement between the calculated and the experimental UV/CD spectra was observed regardless of the method used for structure-spectra calculations, however the best results were obtained using the above mentioned LC-wPBE/6-311++G(d,p) level for structure refining and Δ*G*-based conformer distributions and TD-B2LYP/6-311++G(2d,2p) method[30,31] for calculations of CD spectra. The very good match obtained for the calculated and experimental spectra provided a solid ground for using the computational method as a reliable tool for conformational analysis of flexible diester molecules. Examples of the calculated CD spectra are shown in Figure 3.

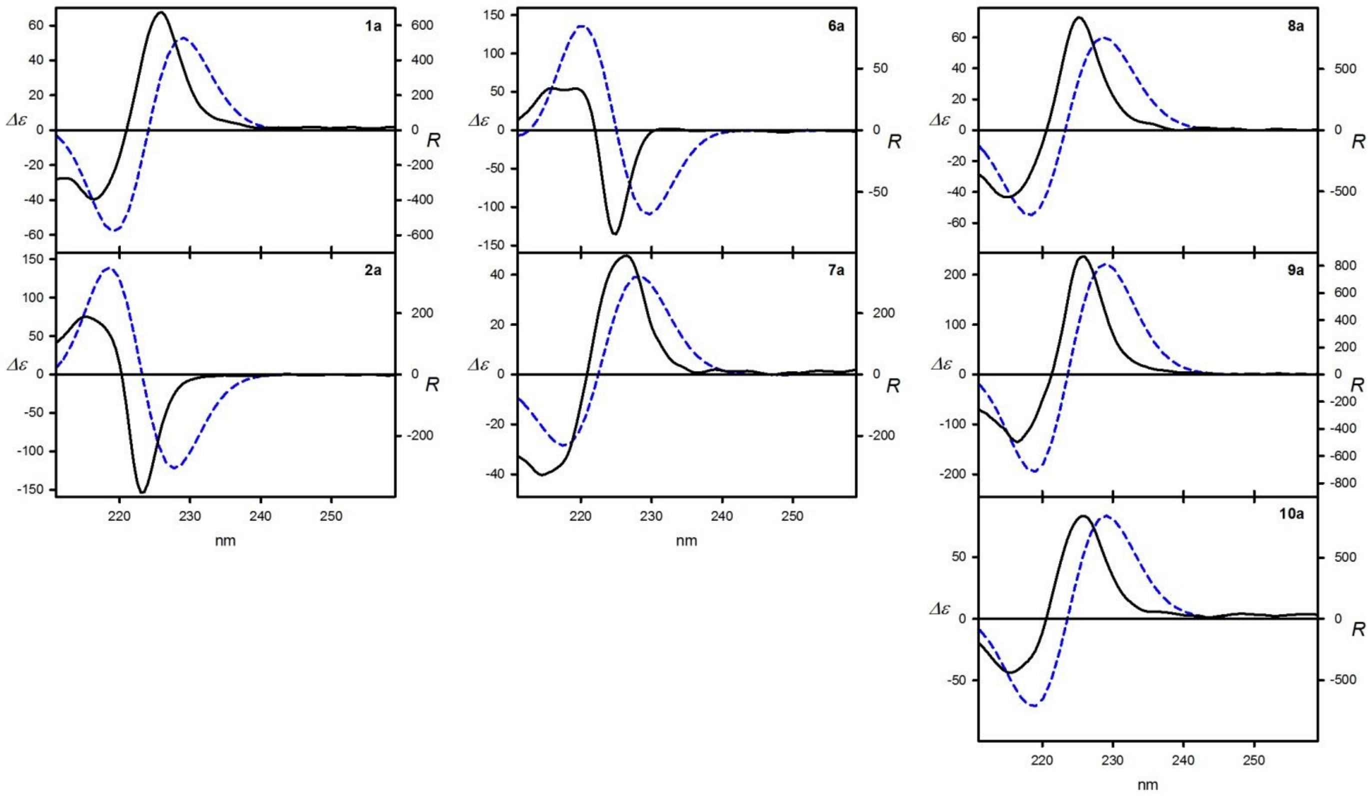


Figure 3. ECD spectra of representative dinaphthyl esters **1a**, **2a**, **6a**-**10a**, measured in hexane-1,2-dichloroethane solutions (solid black lines) and calculated at the TD-B2LYP/6-311++G(2d,2p) level and ΔG_{DFT}-based Boltzmann averaged (dashed blue lines). All calculated spectra were wavelength corrected to match the experimental UV spectra.

Note, the 2-naphthyl esters are more flexible, a larger number of conformers were obtained by calculation within the assumed 2 kcal mol^{-1} energy window, compared to 1-naphthyl esters. As a result, 2-naphthyl esters produce weaker Cotton effects and further discussion will be limited to 1-naphthyl diesters.

There are quite substantial changes in the conformer populations due to the calculation method used, therefore the list of conformers to be discussed for each diester is limited to those being populated over 9%, using the Δ*G* values. The calculated structural data for representative 1-naphthyl diesters are collected in Tables H1 and H2 in SI and the structures of individual, lowest energy conformers of **1a**, **2a**, **6a**-**10a** are shown in Figure 4. Table H2 additionally gives the values of calculated exciton Cotton effects and their amplitudes (A), using the TD-B2LYP/6-311++G(2d,2p) method.

Calculated structures of low energy conformers of 1-naphthyl diesters (Table 2) are characterized by non-coplanarity of the carboxy group and of the naphthalene ring, i.e. angles α, α' are *anticlinal,* in the range 81-

120° (absolute values). This is rather unexpected result since there are two extreme planar conformations characterized by direct C=O···H-C$_{ar}$ interactions. From the theoretical results obtained for model *O*-acetyl-1-naphthol it appears, that the minimum energy conformers are characterized by the value of α angle ±125°.

Table 2. Structural parameters (torsion angles *α*, *β*, *γ*, *δ*, dihedral angle *ω* and distance *l*) calculated at the LC-wPBE/6-311G(d,p) level and found in the crystal, and amplitudes (A) of the exciton Cotton effects of individual conformers of 1-naphthyl esters **1a**, **2a**, **6a**-**10a**[a,b]

Diester[c]		*α*	*α*'	*β*	*β*'	*γ*	*γ*'	*δ*	*ω*	*l*	A[d]
1a	25	*-ac*	*ac*	*-ap*	*ap*	*ap*	*ap*	*-ac*	*ac*	8.754	+++
	26	*ac*	*-ac*	*-ap*	*-ap*	*ap*	*ap*	*-ac*	*ac*	8.447	+++
	28	*-ac*	*-ac*	*-ap*	*-ap*	*ap*	*ap*	*-ac*	*sc*	10.203	++
2a	1[e]	*ac*		*ap*		*sc*		*ap*	*-ac*	10.424	–
	2	*-ac*	*ac*	*-ap*	*ap*	*ac*	*sc*	*ap*	*-ac*	10.468	–
6a	18[e]	*ac*		*-ap*		*ac*		*-ac*	*sc*	9.193	++
	22	*ac*	*-ac*	*-ap*	*ap*	*ac*	*ac*	*-ac*	*-ac*	10.368	–
	24	*-ac*	*ac*	*ap*	*ap*	*ac*	*ac*	*-ac*	*-sc*	10.673	–
6a[f]		*-ac*	*sc*	*-ap*	*-ap*	*-ap*	*-ac*	*ac*	*sc*	10.510	
		ac	*-ac*	*-ap*	*-ap*	*-ac*	*-ac*	*ac*	*sc*	10.690	
7a	3	*ac*	*-ac*	*ap*	*ap*	*ap*	*ap*	*-ac*	*sc*	10.983	+
	7	*ac*	*ac*	*ap*	*-ap*	*-ap*	*ap*	*-ac*	*ac*	9.491	++
	26	*ac*	*ac*	*ap*	*ap*	*ap*	*-ap*	*-ac*	*ac*	9.667	++
8a	2[e]	*ac*		*-ap*		*ap*		*-ac*	*ac*	6.966	+++
	4	*-ac*	*ac*	*-ap*	*ap*	*ap*	*sc*	*-ac*	*sc*	7.667	+++
	6	*ac*	*-ac*	*-ap*	*-ap*	*ap*	*ap*	*-ac*	*sc*	8.987	+++
9a	2[e]	*ac*		*ap*		*ap*		*-ac*	*ac*	6.647	+++
	11	*-ac*	*ac*	*-ap*	*ap*	*ap*	*ap*	*-sc*	*ac*	8.311	+++
10a	1[e]	*ac*		*ap*		*ap*		*-sc*	*ac*	6.605	+++
	6	*ac*	*-ac*	*ap*	*-ap*	*ap*	*ap*	*-sc*	*ac*	8.240	+++

[a] optimized at the LC-wPBE0/6-311G(d,p) level; [b] only conformers with population ≥ 9% (based on ΔG_{DFT} values) are listed in the Table; [c] conformers are numbered according to their appearance during conformational search; [d] + or - |A| < 500; ++ or -- |A| 500÷1000; +++ or --- |A| > 1000; [e] conformer of C_2 symmetry; [f] X-ray data for two independent molecules of (*S*,*S*)-**6a**.

The *antiplanar* conformer has higher energy by 1.2 kcal mol^{-1} then the *anticlinal* conformer, whereas the second planar conformer, characterized by the value of angle α equal 0°, is energetically much less favored. The relatively high energy (11.9 kcal mol^{-1}) calculated for this conformer resulted from significant deformation of C-C-O and C-O-C valence angles, whereas the *anticlinal* conformation typified by the α, α' angles forms the basis for attractive interactions between the oxygen lone pairs and positively charged protons connected to the C2, C2', C8 and C8' carbon atoms.

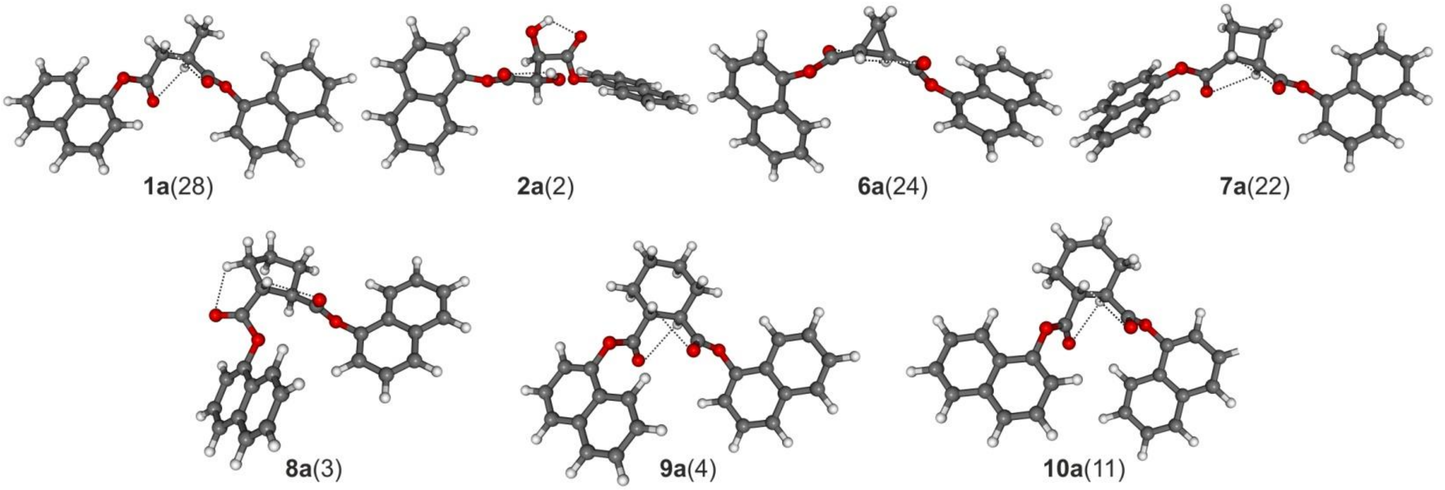


Figure 4. Structures of ΔG_{DFT}-based lowest-energy conformers of dinaphthyl esters **1a**, **2a**, **6a**-**10a**, calculated at the LC-wPBE0/6-311++G(d,p) level. Dashed lines show possible C=O···H-C or C=O···H-O attractive interactions.

Without exception, angles β, β' describe the *antiperiplanar* conformation. The attractive 1,3-dipole-dipole interactions between carbonyl groups and C-H bonds are the consequence of an extended conformation of the C1-O-C(=O)-C* chains in dinaphthyl esters. Therefore, the 1,3-dipole-dipole interactions determine the conformation around the γ, γ' angles.[32] The exception is the lowest energy conformer of **2a**, where the overall molecular structure is affected by the formation of a set of intramolecular hydrogen bonds between carbonyl oxygen atoms and α-hydroxyl groups. For this structure the conformation around both γ and γ' angles is *synclinal*.

The value of the δ angle is determined by the carbon skeleton of a given diester. Acyclic derivatives **1a** and **2a** are characterized either by *anticlinal* or *antiperiplanar* conformations. In the case of cyclic derivatives, conformational diversity of the δ angle is limited. Rigid, three- and four-membered-ring derivatives as well as the more flexible cyclopentane derivative are characterized by an *anticlinal* conformation defined by the δ angle. A *synclinal* conformation around the δ angles is observed for cyclohexane derivatives **9a** and **10a**. This is a result of a strong preference for the equatorial conformation of substituents attached to a cyclohexane or cyclohexene ring.

This kind of structure analysis would not be complete without specifying the relationship between interacting electric transition dipole moments responsible for the observed exciton Cotton effects. There are at least two important parameters that characterize the spatial arrangement of the electric transition dipole moments. The first of them – responsible for the sign of the generated exciton Cotton effect – is the dihedral angle ω defined in Figure 2. The second parameter is the distance *l* between electric transition dipole midpoints that controls the magnitude of observed and calculated exciton Cotton effects. In the case of the 1-naphthyl chromophore, the electric dipole transition moment for the most intense electronic transition is polarized almost parallel to the long axis of the chromophore, and is identical to the C_2 symmetry axis generated by two perpendicular symmetry planes. Thus, the midpoint of the dipole is identical with the midpoint of C9-C10 bond in the naphthalene skeleton. Going back to the analysis, we do not observe any exception to the exciton chirality, in general. Thus, for a given conformer the positive value of the dihedral angle ω corresponds to a positive sign of the exciton Cotton effect. Amplitudes of the Cotton effects depend strongly on the distance between chromophores. Two dipoles interacting at a distance less than 9 Å generate the highest magnitude of exciton Cotton effects (measured as the amplitude) within the whole series of diesters analyzed. The distance *l* ranging between 9 and 10.2 Å caused a decrease of the amplitude. For the cases where the distance between midpoints exceeds 10.2 Å, the amplitudes are low.

Our attempts to crystallize dinaphthyl esters **1**-**10** resulted in only partial success. Among the compounds tested, only 1- and 2-napthyl esters of (1*S*,2*S*)-cyclopropanedicarboxylic acid gave crystals suitable for X-ray diffraction study (calculations and analysis of the CD data were performed for compounds of opposite absolute configuration). We briefly comment on the structure of **6a** in relation to the computational data, whereas the discussion of the crystal structure of **6b** can be fond in the SI. Both (*S*,*S*)-**6a** and (*S*,*S*)-**6b** constitute the first examples of cyclopropane diaryl esters for which the crystal structures has been determined. The structures have been deposited at the Cambridge Crystallographic Data Center with deposition numbers 1496470 and 1496471**.** The atomic displacement ellipsoid plot for two symmetry independent molecules of **6a** is shown in Figure 5.

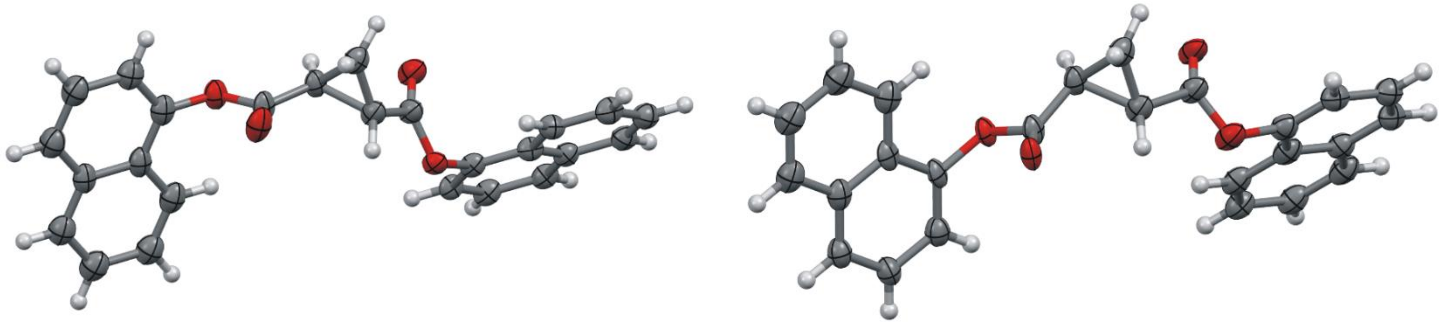


Figure 5. Perspective view of two independent molecules of **6a** that occupy the same site in crystal. The occupancy factors for the two sites refined to 0.54 and 0.46.

Ester (*S*,*S*)-**6a** forms merohedrally twinned crystals in highly symmetrical space group $P3_2$. The molecules in the crystal are disordered over two partially occupied sites, with occupancy ratio 0.54:0.46, and adopt the asymmetrical C_1 conformation typified by a set of significantly different values of the torsion angles α and α' as illustrated in Figure 5 (for definition of the α and α' angles see Figure 2). The two angles, measure in the crystal -97.2(12) and 82.3(12)° in molecule 1, and 89.7(13)° and -104.3(16)° in molecule 2 in agreement with results found for structures "*in silico*" for conformers 36 and 22, respectively (compare Tables H1 and I2 in SI). The two molecules that occupy the same crystallographic site have the same *S* absolute configuration at the stereogenic centers but opposite relative helicities of the two naphthyl chromophores. The two naphthyl groups in each of the two independent molecules of **6a** are inclined at angles of 41.3 and 40.0°. In all crystallographically characterized molecules one can distinguish several pairs of either C=O or C–O bonds that lie nearly parallel to the C–H dipoles situated in relative 1,3-positions, which suggest the presence of stabilizing local CO/CH dipole/dipole interactions, therefore confirming the theoretical results.

Conclusions

Here we have shown the high predictive power of computed CD – DFT method, versus expeeroimental, for structural study of flexible molecules. For a series of 1-naphthyl esters of chiral acyclic and cyclic dicarboxylic acids careful conformational analysis allowed determination of structural parameters that affect the conformation of a given molecule. Among them the most important are 1,3 dipole-dipole interactions between C=O and C-H bonds and attractive interactions between "phenolic" oxygen lone pairs and protons at the C2 and C8 positions in naphthalene rings. These interactions are responsible for an almost perpendicular arrangement of carboxylic groups and naphthalene rings.

Of the two chromophores, 1- or 2-naphthyl, the former provides a more reliable way for absolute configuration determination, based on the CD exciton chirality method. It is considered to be more conformationally restricted compared to its 2-naphthyl isomer and hence it is better suited as a CD chromophoric derivative for a hydroxy group in flexible molecules.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VNMR-S 400 MHz instrument. Chemical shifts (δ) are reported in ppm relative to $SiMe_4$ and coupling constants (*J*) are expressed in Hz. HR-MS spectra were obtained with a Bruker 320 MS spectrometer or on a AB Sciex TripleTOF® 5600+ System. UV and ECD spectra were recorded in spectroscopic grade hexane (containing 5% of 1,2-dichloroethane) and acetonitrile solution using a JASCO J-810 instrument. Due to the similarity between spectra measured in non-polar and polar environments, only those measured in hexane-1,2-dichloroethane were taken into considerations. FT-IR spectra were measured on a Bruker FT-IR IFS 66/s in KBr pellets. A PerkinElmer 341 polarimeter was used for optical rotation ($[\alpha]_D$) measurements (ca. 20 °C). Flash column chromatography was performed on Merck Kieselgel type 60 (250 - 400 mesh). Merck Kieselgel type $60F_{254}$ analytical plates were employed for TLC. Melting points were measured on a Büchi Melting Point B-545 and uncorrected. All reagents were used as purchased from commercial suppliers. All solvents were provided by a local supplier and were purified by conventional methods prior to use. 1- and 2-Napthyl esters of (*R*,*R*)-tartaric acid (**2a** and **2b**) were prepared according to a previously published procedure.[8]

(*R*)-Methylsuccinic acid dinaphthyl esters (1a,1b). These compounds were prepared from the disodium salt of (*R*)-methylsuccinic acid. The salt was prepared by hydrolysis of dimethyl (*R*)-methylsuccinate (1 g, 6.2 mmol) by the addition of a hot EtOH solution of NaOH (0.5 g in 20 mL) and stirring the mixture overnight at rt, followed by concentration *in vacuo*. The oily white residue was then triturated with dry Et_2O and stirred in an ice bath. The crystalline product was filtered off, washed with cold dry Et_2O and dried in vacuum (yield: 1.06 g, 96%). ^{1}H NMR (400 MHz, D_2O) *δ* 2.68 - 2.63 (m, 2H), 2.55 (d, *J* 5.1 Hz, 1H), 2.52 (d, *J* 5.1 Hz, 1H), 2.13 (dd, *J* 10.1, 14.2 Hz, 1H), 1.09 (d, *J* 7 Hz, 6H).

To a suspension of (*R*)-methylsuccinic acid disodium salt (0.2 g, 1.1 mmol) in dry toluene (2 mL) containing one drop of DMF was added dropwise $SOCl_2$ (0.35 mL) at 2-3 °C. After the reaction subsided, the mixture was gently heated at 50 °C for 2 h and then stirred overnight at rt. After evaporation of excess $SOCl_2$ and the organic solvent under reduced pressure, the dichloride was obtained and immediately used for diester preparation without further purification.

To a solution of dichloride in dry CH_2Cl_2 (5 mL) 2 equivalents (0.34 g, 2.2 mmol) of 1- or 2 naphthol were added, followed by dropwise addition of pyridine (0.3 mL) in dry CH_2Cl_2 (2 mL). After overnight stirring the reaction mixture was extracted with 2N HCl, the organic layer was separated and washed twice with water then dried over Na_2SO_4. After filtration the solvent was evaporated and the residue purified by radial chromatography on silica gel plates (2 mm thickness), using CH_2Cl_2 /MeOH mixtures as moving phase.

(*R*)-Methylsuccinic acid di-1-naphthyl ester (1a). Yield 212 mg (48%), colorless oil; $[\alpha]_D^{20}$ +13.6 (*c* 0.5, Me_2CO); IR (solid, KBr, ν_{max}, cm^{-1}): 3056, 3011, 2976, 2937, 2813, 1751, 1598, 1508, 1460, 1390, 1347, 1258, 1222, 1117, 1077, 1039, 1012, 793, 768; ^{1}H NMR (400 MHz, CD_3COCD_3) *δ* 8.01-7.93 (m, 4H), 7.82 (dd, *J* 4.6, 8.3 Hz, 2H), 7.54-7.48 (m, 4H), 7.43 (m, 2H), 7.33-7.27 (m, 2H), 3.63-3.56 (m, 1H), 3.44-3.37 (dd, *J* 9, 17.2 Hz, 1H), 3.25 (dd, *J* 5, 17.2 Hz, 1H), 1.65 (d, *J* 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 174.55, 171.37, 147.77, 147.69, 135.54, 135.52, 128.75, 128.73, 127.87 , 127.80, 127.28, 127.27, 126.80, 126.75, 126.34, 126.31, 122.17, 122.12, 119.14, 119.03, 37.93, 36.91, 17.47; HRMS (*m/z*) 407.1282 |M + Na]$^+$ ($C_{25}H_{20}O_4Na$, calcd 407.1279).

(*R*)-Methylsuccinic acid di-2-naphthyl ester (1b). Yield 264 mg (60%), white crystals, mp 125-128 °C (Et_2O/hexane); $[\alpha]_D^{20}$ –45.0 (*c* 0.5, Me_2CO); IR (solid, KBr, $\nu_{max,}$ cm^{-1}): 3056, 3025, 2991, 2942, 1742, 1629, 1599, 1509, 1467, 1303, 1244, 1211, 1160, 1142, 1057, 962, 895, 822, 738; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.81 (m, 4H), 7.78-7.75 (m, 2H), 7.57 (t, *J* 2.6 Hz, 2H), 7.49-7.42 (m, 4H), 7.23 (dd, *J* 2.3, 8.9 Hz, 2H), 3.41-3.32 (m, 1H), 3.18 (dd, *J* 8.7, 16.8 Hz, 1H), 2.90 (dd, *J* 5.4, 16.8 Hz, 1H), 1.53 (d, *J* 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.90, 170.50, 148.36, 148.18, 133.73, 131.51, 129.48, 129.45, 127.76, 127.65, 127.64, 126.59, 126.55, 125.76, 125.71, 121.02, 118.53, 118.48, 37.81, 36.1, 17.06; HRMS (*m/z*) 407.1254 [M + Na]$^+$ ($C_{25}H_{20}O_4Na$, calcd 407.1259).

***N*-(*tert*-Butoxycarbonyl)-L-amino acids dinaphthyl esters 3-6.** Dinaphthyl esters of *N*-Boc protected amino acids were prepared by a general procedure starting from *N*-(*tert*-butoxycarbonyl)-L-amino acids.

N,N'-Dicyclohexylcarbodiimide (0.42 g, 2 mmol) dissolved in dry hexane/EtOAc (1:1) mixture was added dropwise over 15 min to a stirred suspension of *N*-Boc-L-amino acid (1 mmol) in dry hexane/EtOAc (1:1) mixture at 5 °C. To the reaction mixture 1- or 2-naphthol (0.29 g, 2 mmol) and a catalytic amount of 4-(dimethylamino)pyridine dissolved in dry hexane/EtOAc (1:1) mixture was added dropwise over 1 h. The mixture was stirred at 5 °C over 4 h and then concentrated. The residue was stirred in Et_2O (10 mL) and oxalic acid (0.3 g, 3.3 mmol) was introduced in portions to decompose excess DCC and precipitate DMAP. The mixture was filtered and evaporated under reduced pressure leaving oil, which was purified using radial chromatography on silica gel plates (2 mm thickness), using hexanes/EtOAc as moving phase.

***N*-(*tert*-Butoxycarbonyl)-L-aspartic acid di-1-naphthyl ester (3a).** Yield 176 mg (42%), small white microcrystals, mp 143–145 °C (Et_2O/hexane); $[\alpha]_D^{20}$ –6.6 (*c* 0.5, Me_2CO); IR (solid, KBr, $\nu_{max,}$ cm^{-1}): 3370, 3064, 2983, 2940, 1769, 1746, 1686, 1599, 1508, 1441, 1385, 1368, 1256, 1224, 1205, 1136, 1048, 776, 761; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93-7.84 (m, 4H), 7.75 (t, *J* 8.5 Hz, 2H), 7.52-7.38 (m, 6H), 7.28-7.23 (m, 2H), 5.81 (d, *J* 8.5 Hz, 1H), 5.18 (m, 1H), 3.73 (dd, *J* 4.4, 17.3 Hz, 1H), 3.51 (dd, *J* 4.8, 17.3 Hz, 1H), 1.51 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.20, 169.82, 155.64, 146.50, 146.36, 134.71, 134.65, 128.08, 127.96, 126.74, 126.70, 126.60, 126.57, 126.49, 126.41, 125.36, 121.21, 121.13, 118.06, 117.93, 80.68, 50.54, 37.05, 28.36; HRMS (*m/z*) 508.1731 [M + Na]$^+$ ($C_{29}H_{27}NO_6Na$, calcd 508.1736).

***N*-(*tert*-Butoxycarbonyl)-L-aspartic acid di-2-naphthyl ester (3b).** Yield 192 mg (46%), white crystals, mp 133–135 °C (hexane/EtOAc); $[\alpha]_D^{20}$ –16.4 (*c* 0.5, Me_2CO); IR (solid, KBr, $\nu_{max,}$ cm^{-1}): 3380, 3061, 3022, 2983, 2926, 1747, 1695, 1519, 1420, 1370, 1323, 1271, 1240, 1207, 1146, 1116, 1058, 963,931, 898, 861, 811, 773; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.76 (m, 6H), 7.59 (dd, *J* 2.2, 10 Hz, 2H), 7.52-7.44 (m, 4H), 7.27-7.23 (m, 2H), 5.71 (d, *J* 8.1 Hz, 1H), 5.03 (m, 1H), 3.51 (dd, *J* 4.4, 17.0 Hz, 1H), 3.32 (dd, *J* 4.7, 17.0 Hz, 1H), 1.51 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.89, 155.44, 148.15, 147.95, 133.68, 131.65, 131.60, 129.61, 129.57, 127.79, 127.69, 126.70, 126.66, 125.90, 120.79, 120.66, 118.52, 118.45, 80.61, 50.41, 37.42, 28.31; HRMS (*m/z*) 508.1734 [M + Na]$^+$ ($C_{29}H_{27}NO_6Na$, calcd 508.1736).

***N*-(*tert*-Butoxycarbonyl)-L-glutamic acid di-1-naphthyl ester (4a).** Yield 197 mg (49%), white powder, mp 123–125 °C (EtOAc/hexane); $[\alpha]_D^{20}$ –21.8 (*c* 0.5, Me_2CO); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.86 (m, 4H), 7.75 (d, *J* 8.2 Hz, 2H), 7.53-7.43 (m, 6H), 7.30-7.25 (m, 2H), 5.35 (d, *J* 7.8 Hz, 1H), 4.90 (d, 1H), 3.12-2.98 (m, 2H), 2.77-2.72 (m, 1H), 2.48-2.39 (m, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.39, 171.05, 155.70, 146.48, 146.26, 134.65, 128.04, 126.74, 126.60, 126.55, 126.48, 126.42, 126.15, 125.37, 125.31, 121.11, 118.09, 117.85, 80.56, 53.37, 30.54, 28.35, 27.81; HRMS (*m/z*) 522.1881 [M+Na]$^+$ ($C_{30}H_{29}NO_6Na$, calcd 522.1893).

***N*-(*tert*-Butoxycarbonyl)-L-glutamic acid dinaphthalen-2-yl ester (4b).** Yield 216 mg (54%), white powder, mp 115–117 °C (EtOAc/hexane); $[\alpha]_D^{20}$ – 21.0 (*c* 0.5, Me_2CO); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.84-7.73 (m, 6H), 7.57 (dd, *J* 2.2, 13.7 Hz, 2H), 7.49-7.44 (m, 4H), 7.26-7.23 (m, 2H), 5.33 (d, *J* 8.2 Hz, 1H), 4.75 (m, 1H), 2.92-2.82 (m, 2H), 2.60-2.55 (m, 1H), 2.37-2.28 (m, 1H), 1.50 (s, 9H); ^{13}C NMR (75MHz, $CDCl_3$) *δ* 171.48, 171.05, 155.5l, 148.22, 147.96, 133.69, 133.63, 131.58, 131.47, 129.55, 129.38, 127.73, 127.68, 127.63, 126.65, 126.53, 125.88, 125.71, 121.03, 120.64, 118.51, 118.42, 80.43, 53.19, 30.49, 28.30, 27.60 HRMS (*m/z*) 522.5890 [M + Na]$^+$ ($C_{30}H_{29}NO_6Na$, calcd 522.1893).

***N*-(*tert*-Butoxycarbonyl)-L-2-aminosuberic acid di-1-naphthyl ester (5a).** Yield 60 mg (64%), colorless oil; $[\alpha]_D^{20}$ +14.6 (*c* 0.5, Me_2CO); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.92-7.84 (m, 4H), 7.73 (dd, *J* 4.4, 8.3 Hz, 2H), 7.53-7.42 (m, 6H), 7.24 (dd, *J* 1.1, 7.8 Hz, 2H), 5.18 (d, *J* 8.3 Hz, 1H), 4.73 (q, *J* 5.1, 7.7, 7.9 Hz, 1H), 2.77 (t, *J* 7.5 Hz, 2H), 2.18-2.14 (m, 1H), 1.99-1.88 (m, 3H), 1.70-1.59 (m, 4H), 1.49 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 171.98, 171.68, 155.56, 146.57, 146.39, 134.63, 128.99, 128.19, 128.01, 127.96, 126.80, 126.59, 126.51, 126.40, 126.38, 126.24, 125.90, 125.37, 125.28, 121.13, 121.05, 118.04, 117.77, 80.19, 53.81, 34.15, 32.50, 28.76, 28.30, 25.26, 24.81; HRMS (*m/z*) 564.2369 [M + Na]$^+$ ($C_{33}H_{35}NO_6Na$, calcd 564.2362).

***N*-(*tert*-Butoxycarbonyl)-L-2-aminosuberic acid di-2-naphthyl ester (5b).** Yield 60 mg (64%), white powder, mp 58–60 °C (Et_2O/hexane); $[\alpha]_D^{20}$+18.0 (*c* 0.5, Me_2CO); IR (solid, KBr, $\nu_{max,}$ cm^{-1}): 3390, 3071, 2986, 2900, 1749, 1697, 1549, 1430, 1370, 1323, 1271, 1240, 1207; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.85-7.77 (m, 6H), 7.55 (dd, *J* 2.2, 6.9 Hz, 2H), 7.49-7.43 (m, 4H), 7.24-7.20 (m, 2H), 5.14 (d, *J* 8.3 Hz, 1H), 4.61 (m, 1H), 2.64 (t, *J* 7.4 Hz, 2H), 2.10-2.02 (m, 1H), 1.91-1.81 (m, 3H), 1.64-1.57 (m, 4H), 1.49 (s, 9H); ^{13}C NMR (75MHz, $CDCl_3$) *δ* 172.18, 171.74, 155.46, 148.34, 148.08, 133.74, 133.67, 131.53, 131.40, 129.52, 129.35, 127.75, 127.72, 127.64, 127.60, 126.63, 126.50, 125.82, 125.63, 121.12, 120.71, 118.46, 118.36, 80.12, 53.63, 34.20, 32.50, 28.65, 28.30, 25.10, 24.66 HRMS (*m/z*) 564.2365 [M + Na]$^+$ ($C_{33}H_{35}NO_6Na$, calcd 564.2362).

Diesters 6-10. Compounds **6-10** were synthesized by the same procedure starting from either (1*S,*2*S*)-cyclopropane-1,2-dicarboxylic acid (**6a**,**6b**), (1*S,*2*S*)-cyclobutane-1,2-dicarboxylic acid (**7a**,**7b**), (1*S,*2*S*)-cyclopentane-1,2-dicarboxylic acid (**8a**,**8b**), (1*R*,2*R*)-*trans*-cyclohexane-1,2-dicarboxylic acid (**9a**,**9b**) and (1*R*,2*R*)-*trans*-cyclohex-4,5-ene-1,2-dicarboxylic acid (**10a**,**10b**).[33,34]

To a suspension of an appropriate diacid (1 mmol) in dry toluene (2 mL) containing one drop of DMF, $SOCl_2$ (0.6-1.0 mL) was added dropwise at 2-3 °C. After the reaction subsided, the mixture was gently refluxed at 65 °C for 2 h and then stirred overnight at rt. After evaporation of the excess $SOCl_2$ and the organic solvent under reduced pressure the dichloride was obtained and immediately used for diester preparation without further purification.

To a solution of dichloride in dry CH_2Cl_2 (5 mL) 2 equivalents of 1- or 2-naphthol were added, followed by dropwise addition of pyridine (0.5 mL) in dry CH_2Cl_2 (2 mL). After overnight stirring at rt, the reaction mixture was extracted with 2N HCl, the organic layer was separated and washed twice with water and dried over Na_2SO_4. After filtration, the solvent was evaporated and the residue purified by radial chromatography on silica gel plates (2 mm thickness), using mixtures of hexanes/EtOAc or CH_2Cl_2/MeOH as moving phases.

(1*S,*2*S*)-Cyclopropane-1,2-dicarboxylic acid di-1-naphthyl ester (6a). Yield 153 mg (51%); white needless, mp 176-177 °C (Et_2O/hexane); $[\alpha]_D^{20}$ +231 (*c* 1.03, $CHCl_3$); IR (solid, KBr, $\nu_{max,}$ cm^{-1}): 3058, 1736, 1631, 1599, 1581, 1506, 1464, 1328, 1230, 1209, 1148, 1058, 966, 950, 9101, 870, 810, 738, 479; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* 8.0 Hz, 1H), 7.89 (d, *J* 7.4 Hz, 1H), 7.77 (d, *J* 8.3 Hz, 1H), 7.59-7.48 (m, 3H), 7.33 (d, *J* 7.3 Hz, 1H), 2.86 (t, *J* 7.5, 7.3 Hz, 1H), 1.92 (t, *J* 7.5, 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.20, 146.35, 134.69, 128.14, 126.69, 126.59, 126.35, 125.39, 120.95, 117.98, 22.90, 16.74; HRMS (*m/z*) 405.1099 [M + Na]$^+$ ($C_{25}H_{18}O_4Na$, calcd 405.1103).

(1*S*,2*S*)-Cyclopropane-1,2-dicarboxylic acid di-2-naphthyl ester (6b). Yield 155 mg (53%); white crystals, mp 164-165 °C (Et_2O/hexane); $[\alpha]_D^{20}$ +272.5 (*c* 1.28, $CHCl_3$); IR (solid, KBr, $\nu_{max,}$ cm^{-1}): 3101, 3062, 1749, 1599, 1509, 1389, 1321, 1260, 1226, 1126, 1060, 1012, 935, 874, 793, 768, 720; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.81 (m, 3H), 7.62 (d, *J* 2.1 Hz, 1H), 7.52-7.45 (m, 2H), 7.29-7.27 (dd, *J* 2.3, *J* 8.8 Hz, 1H), 2.67 (t, *J* 7.5, 7.2 Hz, 1H), 1.81 (t, *J* 7.5, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.33, 148.13, 133.71, 131.56, 129.54, 127.80, 127.70, 126.69, 125.88, 120.80, 118.46, 23.05, 16.58; HRMS (*m/z*) 405.1100 $[M + Na]^+$ ($C_{25}H_{18}O_4Na$, calcd 405.1103).

(1*S*,2*S*)-Cyclobutane-1,2-dicarboxylic acid di-1-naphthyl ester (7a). Yield 75 mg (47%); colorless oil; $[\alpha]_D^{20}$ +43 (*c* 1, $CHCl_3$); IR (solid, KBr, $\nu_{max,}$ cm^{-1}): 3064, 3002, 2933, 2863, 1763, 1733, 1597, 1389, 1312, 1233, 1204, 1137, 1079, 1039, 1031, 961, 907, 798, 782; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.9 (d, *J* 8.3 Hz, 1H), 7.86 (d, *J* 7.8 Hz, 1H), 7.75 (d, *J* 8.1 Hz, 1H), 7.51-7.39 (m, 3H), 7.3 (dd, *J* 1.0 Hz, *J* 7.6 Hz, 1H), 4.15-4.07 (m, 1H), 2.68-2.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.83, 146.4, 134.67, 128.04, 126.71, 126.59, 126.48, 126.17, 125.37, 120.98, 117.99, 40.84, 22.29; HRMS (*m/z*) 396.1365 $[M^+]$ ($C_{26}H_{20}O_4$, calcd 396.1362).

(1*S*,2*S*)-Cyclobutane-1,2-dicarboxylic acid di-2-naphthyl ester (7b). Yield 95 mg (60%); white powder, mp 125-128 °C (Et_2O/hexane); $[\alpha]_D^{20}$ +95.7 (*c* 1.1, $CHCl_3$); IR (solid, KBr, $\nu_{max,}$ cm^{-1}): 3055, 3009, 2964, 2910, 1743, 1629, 1599, 1508, 1464, 1442, 1355, 1307, 1237, 1199, 1158, 979, 932, 887, 811; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.79 (m, 3H), 7.61 (d, *J* 2.2 Hz, 1H), 7.51-7.44 (m, 1H), 7.28-7.25 (dd, *J* 2.3 Hz, *J* 8.9 Hz,1H), 3.95-3.85 (m, 1H), 2.55-2.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.01, 148.24, 133.73, 131.50, 129.47, 127.78, 127.66, 126.62, 125.77, 120.93, 118.46, 40.54, 22.16; HRMS (*m/z*) 396.1352 $[M^+]$ ($C_{26}H_{20}O_4$, calcd 396.1362).

(1*S*,2*S*)-Cyclopentane-1,2-dicarboxylic acid di-1-naphthyl ester (8a). Yield 100 mg (55%); colorless oil; $[\alpha]_D^{20}$ +28.4 (*c* 0.925, $CHCl_3$); IR (solid, KBr, $\nu_{max,}$ cm^{-1}): 3061, 2964, 2876, 1756, 1597, 1507, 1455, 1389, 1337, 1259, 1226, 1178, 1120, 1039, 1013, 930, 778, 762; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* 8.4 Hz, 1H), 7.86 (d, *J* 8.26 Hz, 1H), 7.74 (d, *J* 8.26 Hz, 1H), 7.40-7.36 (m, 3H), 7.27 (d, *J* 7.5 Hz, 1H), 3.85-3.78 (m, 1H), 2.53-2.43 (m, 1H), 2.31-2.22 (m, 1H), 2.06-1.99 (quintet, *J* 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.38, 146.59, 134.66, 128.01, 126.79, 126.57, 126.46, 126.14, 125.38, 121.10, 118.03, 47.69, 30.69, 25.57; HRMS (*m/z*) 433.1416 $[M + Na]^+$ ($C_{27}H_{22}O_4Na$, calcd 433.1416).

(1*S*,2*S*)-Cyclopentane-1,2-dicarboxylic acid di-2-naphthalyl ester (8b). Yield 116 mg (61%); white powder, mp 121-122 °C (Et_2O/hexane); $[\alpha]_D^{20}$ +144.5 (*c* 0.66, $CHCl_3$); IR (solid, KBr, $\nu_{max,}$ cm^{-1}): 3061, 2962, 2930, 2862, 1758, 1738, 1600,1508, 1464, 1242, 1210, 1134, 1117, 1078, 899, 813, 747; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.77 (m, 3H), 7.59 (d, *J* 2.15 Hz, 1H), 7.51 -7.44 (m, 2H), 7.27-7.24 (dd, *J* 7.26 Hz, *J* 2.3 Hz, 1H), 3.64-3.57 (m, 1H), 2.40-2.32 (m, 1H), 2.20-2.11 (m, 1H), 1.98-1.91 (quintet, *J* 7.25 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.51, 148.38, 133.75, 131.50, 129.47, 127.78, 127.66, 126.59, 125.74, 121.02, 118.49, 47.66, 30.44, 25.39; HRMS (*m/z*) 433.1413 $[M + Na]^+$ ($C_{27}H_{22}O_4Na$, calcd 433.1416).

(1*R*,2*R*)-Cyclohexane-1,2-dicarboxylic acid di-1-naphthyl ester (9a). Yield 127 mg (30%), white powder, mp 129–132 °C (CH_2Cl_2/hexane); $[\alpha]_D^{20}$ +92.8 (*c* 0.5, Me_2CO); IR (solid, KBr, $\nu_{max,}$ cm^{-1}): 3056, 2928, 2860, 1749, 1599, 1510, 1449, 1384, 1320, 1225, 1131, 1108, 1074, 1038, 1013, 774; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.86-7.83 (m, 2H), 7.72 (d, *J* 8.2 Hz, 1H), 7.47-7.31 (m, 3H), 7.17 (d, *J* 7.5 Hz, 1H), 3.30-3.22 (m, 1H), 2.58 (d, *J* 13.9 Hz, 1H), 2.03 (d, *J* 9.1 Hz, 1H), 1.83-1.75 (m, 1H), 1.61-1.53 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 173.75, 146.63, 134.61, 127.89, 126.90, 126.49, 126.37, 126.07, 125.36, 121.30, 118.06, 45.05, 29.34, 25.37; HRMS (*m/z*) 447.1573 $[M + Na]^+$ ($C_{28}H_{24}O_4Na$, calcd 447.1572).

(1*R*,2*R*)-Cyclohexane-1,2-dicarboxylic acid di-2-naphthyl ester (9b). Yield 159 mg (37%), white powder, mp 124–126 °C (CH_2Cl_2/hexane); $[\alpha]_D^{20}$ –106.8 (*c* 0.5, Me_2CO); IR (solid, KBr, $\nu_{max,}$ cm^{-1}): 3059, 2953, 2926, 2861, 1745, 1629, 1599, 1521, 1465, 1441, 1373, 1357, 1313, 1206, 1137, 970, 897, 875; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.83-7.74 (m, 3H), 7.54 (d, *J* 2.2 Hz, 1H), 7.48-7.42 (m, 2H), 7.21 (dd, *J* 2.3, 8.9 Hz, 1H), 3.10-3.02 (m, 1H), 2.42

(d, *J* 14.2 Hz, 1H), 1.96 (d, *J* 9 Hz, 1H), 1.71-1.63 (m, 1 H), 1.49-1.41 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.73, 148.36, 133.75, 131.50, 129.42, 127.75, 127.63, 126.51, 125.67, 121.11, 118.52, 45.09, 28.93, 25.23; HRMS (*m/z*) 447.1575 $[M + Na]^+$ ($C_{28}H_{24}O_4Na$, calcd 447.1572).

(1*R*,2*R*)-Cyclohex-4-ene-1,2-dicarboxylic acid di-1-naphthyl ester (10a). Yield 167 mg (39%), white powder, mp 87–90 °C (Et_2O/hexane); $[\alpha]_D^{20}$ –9.6 (*c* 0.5, Me_2CO); IR (solid, KBr, ν_{max}, cm^{-1}): 3058, 3034, 2921, 2845, 1749, 1599, 1509, 1463, 1435, 1387, 1301, 1260, 1218, 1155, 1123, 1076, 787, 767; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* 8.4 Hz, 1H), 7.82 (d, *J* 8.2 Hz, 1H), 7.71 (d, *J* 8.2 Hz, 1H), 7.45-7.32 (m, 3H), 7.19 (d, *J* 7.4 Hz, 1H), 5.88 (q, *J* 11.6, 13.4 Hz, 1H), 3.52-3.44 (m, 1H), 2.92-2.88 (m, 1H), 2.64-2.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.59, 146.51, 134.59, 127.90, 126.82, 126.50, 126.38, 126.11, 125.33, 124.98, 121.20, 118.04, 41.45, 28.33; HRMS (*m/z*) 445.1410 $[M + Na]^+$ ($C_{28}H_{22}O_4Na$, calcd 445.1416).

(1*R*,2*R*)-Cyclohex-4-ene-1,2-dicarboxylic acid di-2-naphthyl ester (10b). Yield 193 mg (46%), white microcrystals, mp 168-170 °C (Et_2O/hexane); $[\alpha]_D^{20}$ +50.4 (*c* 0.5, Me_2CO); IR (solid, KBr, ν_{max}, cm^{-1}): 3056, 3032, 2933, 2911, 2843, 1746, 1629, 1601, 1510, 1465, 1435, 1383, 1352, 1307, 1224, 1207, 1193, 1175, 1132, 1011, 970, 900, 861, 807, 739; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.86 (m, 3H), 7.68 (d, *J* 2.1 Hz, 1H), 7.61-7.55 (m, 2H), 7.35 (dd, *J* 2.l, 8.8 Hz, 1H), 5.97 (d, *J* 2.6 Hz, 1H), 3.45-3.42 (m, 1H), 2.92-2.87 (m, 1H), 2.67-2.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.58, 148.29, 133.74, 131.53, 129.46, 127.77, 127.65, 126.55, 125.72, 124.95, 121.04, 118.52, 41.55, 28.05; HRMS (*m/z*) 445.1415 $[M + Na]^+$ ($C_{28}H_{22}O_4Na$, calcd 445.1416).

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