Dimerization of Dimethyl 2-(Naphthalen-1-yl)cyclopropane-1,1-dicarboxylate in the Presence of $GaCl_3$ to [3 + 2], [3 + 3], [3 + 4], and Spiroannulation Products

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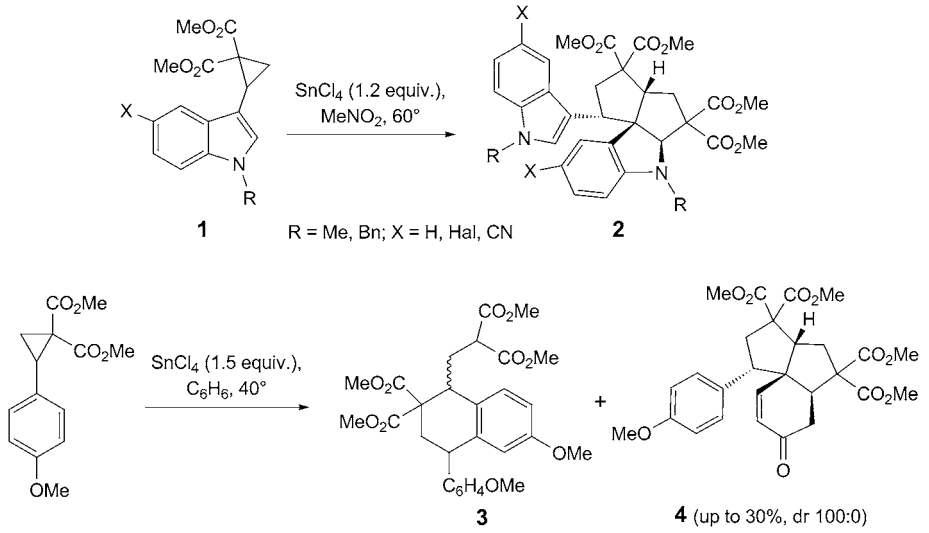
In the presence of a catalytic amount of $GaCl_3$, dimethyl 2-(naphthalen-1-yl)cyclopropane-1,1-dicarboxylate **5** undergoes selective [3 + 2]-annulation-type dimerization to give a polysubstituted cyclopentane containing two naphthalenyl substituents in the vicinal position (*Scheme 2*). Treatment of the same cyclopropane with an equimolar amount of $GaCl_3 \cdot THF$ results in dimerization with electrophilic attack on each of the benzene rings to give [3 + 3] and [3 + 4] annulation products. The latter represent a new type of dimerization of donor–acceptor cyclopropanes. Finally, under conditions of double catalysis with $GaCl_3$, 3,3,5,5-tetrasubstituted 4,5-dihydropyrazole, this cyclopropane-dicarboxylate undergoes stereospecific dimerization as a result of electrophilic *ipso*-attack to give a tetracyclic pentaleno[6a,1-*a*]naphthalene derivative (*Scheme 5*). Possible reaction mechanisms are proposed.

Introduction. – The exploitation of strain release in small rings as a driving force to trigger synthetic transformations has received increased attention over the last decade. In this context, various catalyzed ring openings of cyclopropane derivatives have been investigated (for recent reviews, see [1]). Among them, donor-substituted cyclopropane-1,1-dicarboxylates have attracted particular attention; they can be considered to be synthetic equivalents to 1,3-zwitterionic synthons. As such, they have been widely used in [3 + 2] annulation with generic double bonds (X=Y; for reviews, see [2]) or [3 + 4] annulation with dienes [3].

Recently [4–7], it has been shown that esters of 2-arylcyclopropane-1,1-dicarboxylic acids (usually referred to as donor–acceptor cyclopropanes) can undergo dimerization on treatment with *Lewis* acids in the absence of unsaturated substrates, other compounds which can trap the 1,3-dipoles generated. In this case, depending on the conditions and the nature of the aryl substituent, these reactions lead to compounds of various classes containing four ester groups in the molecule, *viz.*, diarylhexenes [4][5], cyclopentanes [5][6], cyclohexanes [4], aryl-1,2,3,4-tetrahydronaphthalenes, 9,10-dihydroanthracenes [4][6]. A special type of dimerization of donor–acceptor cyclopropanes was identified on heating of (indole-3-yl)cyclopropanedicarboxylates **1** in $MeNO_2$ in the presence of $SnCl_4$ [7]. In this case, coupling of the electrophilic and nucleophilic centers of two molecules of the activated cyclopropane, followed by electrophilic *ipso*-attack, gave pentaleno[1,6a-*b*]indole derivatives **2** (*Scheme 1*) as the major isolable compounds; unlike some other dimers, this polycyclic structure was formed as a single diastereoisomer. A similar process was found to occur in the case of

arylcyclopropane-1,1-dicarboxylates containing a strong electron-donating MeO group in the *para*-position of the benzene ring [4]. In this case (if 1.5 equiv. of $SnCl_4$ in benzene are used), along with *ortho*-substitution resulting in substituted tetrahydronaphthalene **3**, up to 30% of compound **4** containing an angularly fused 1*H*-cyclopenta[*c*]indene scaffold (*Scheme 1*) was obtained after hydrolysis. The competition between *ortho*- and *ipso*-attack was explained by a balance of steric and electronic factors. The strong electron-donating group makes an electrophilic attack at the *ipso*-position more preferable; conversely, higher steric repulsions for an *ipso*-attack render an *ortho*-attack more preferable [4].

Scheme 1. *Dimerization of Donor–Acceptor Cyclopropanes:* ipso-*Attack Route* (spiroannulation, 1,5-cyclization)

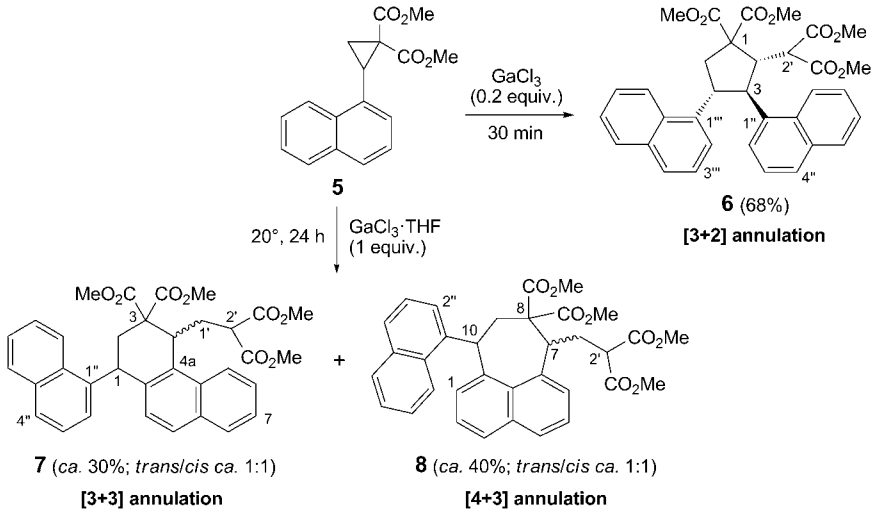


In this work, we studied the possibility of dimerization of dimethyl 2-(naphthalen-1-yl)cyclopropane-1,1-dicarboxylate (**5**; *cf. Scheme 2*). On the one hand, this compound has a binuclear aromatic ring, thus it might be converted on treatment with *Lewis* acids similarly to indolylcyclopropanes **1**; on the other hand, it manifests strong steric hindrance that might steer electrophilic substitution to other positions of the aromatic system. Isomerization of **5** to dimethyl 2-(naphthalen-1-yl)ethenylmalonate on treatment with trimethylsilyl trifluoromethanesulfonate in PhCl under reflux conditions in the presence of 4-Å molecular sieves was reported [8], but attempts of its dimerization failed until now.

Results and Discussion. – *Transformation of Dimethyl 2-(Naphthalen-1-yl)cyclopropane-1,1-dicarboxylate* (**5**) *to [3+2], [3+3], [3+4] Annulation Products.* Anhydrous gallium trichloride ($GaCl_3$) is an efficient *Lewis* acid, which causes opening of the three-membered ring in dimethyl 2-arylcyclopropane-1,1-dicarboxylates (donor–acceptor cyclopropanes). In this case, even minor changes of the reaction conditions (*e.g.*, increase in temperature or addition of tetrahydrofuran (THF),

tetrasubstituted 1-pyrazolines) change the reaction route considerably [6][9][10]. We have found that in the presence of 20 mol-% $GaCl_3$, naphthylcyclopropanedicarboxylate **5**, similarly to its phenyl analogue [6], can also be converted to a bis-naphthylcyclopentane **6** (*Scheme 2*), in which both naphthyl substituents are in vicinal position. However, unlike other 2-arylcyclopropane-1,1-dicarboxylates, due to steric effects, only one diastereoisomer with transoid arrangement of the naphthyl substituents at the five-membered ring is formed in this case.

Scheme 2. *Cyclodimerizations of (Naphthalen-1-yl)cyclopropane* **5** *in the Presence of* $GaCl_3$ *or* $GaCl_3 \cdot$ *THF*



The reaction behavior changes abruptly, if the $GaCl_3$ activity is decreased by complexation with THF. In this case, the amount of isomeric bis(naphthalen-1-yl)cyclopentanes **6** decreases abruptly, products of electrophilic substitution at the aromatic ring, *i.e.*, compounds **7** and **8**, which also have dimeric structures (*Scheme 2*), become the major compounds. For the reaction to occur successfully in this case, it is required that equimolar amounts of **5** and $GaCl_3 \cdot$ THF complex have to be used, and the reaction time has to be changed from 30 min to 20–24 h.

Unlike substituted cyclopentane **6**, compounds **7** and **8** are formed as a mixture of two diastereoisomers with an approximately equal amount of each. The structures of the resulting compounds were determined using 1D- and 2D-DEPT, COSY, TOCSY, NOESY, HSQC, HMBC, and ^{1}H-, ^{13}C-NMR spectra (*Fig. 1*). Due to the hindered rotation of the naphthalen-1-yl substituent, each isomer exists as various rotamers; this is observed as strong broadenings of certain signals in the NMR spectra, considerably complicating the determination of their relative configurations. The principal difference between the structural dimers **7** and **8** is manifested most distinctly in the COSY, TOCSY spectra: compound **7** is characterized by the presence of an isolated aromatic moiety CH=CH, whereas a characteristic feature of the more symmetric regioisomer **8** is that it has two similar three-spin systems CH=CH–CH.

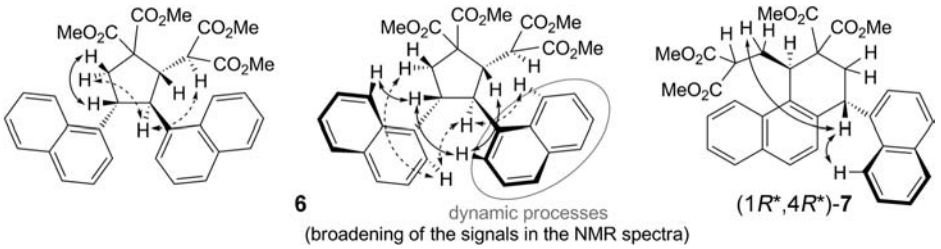
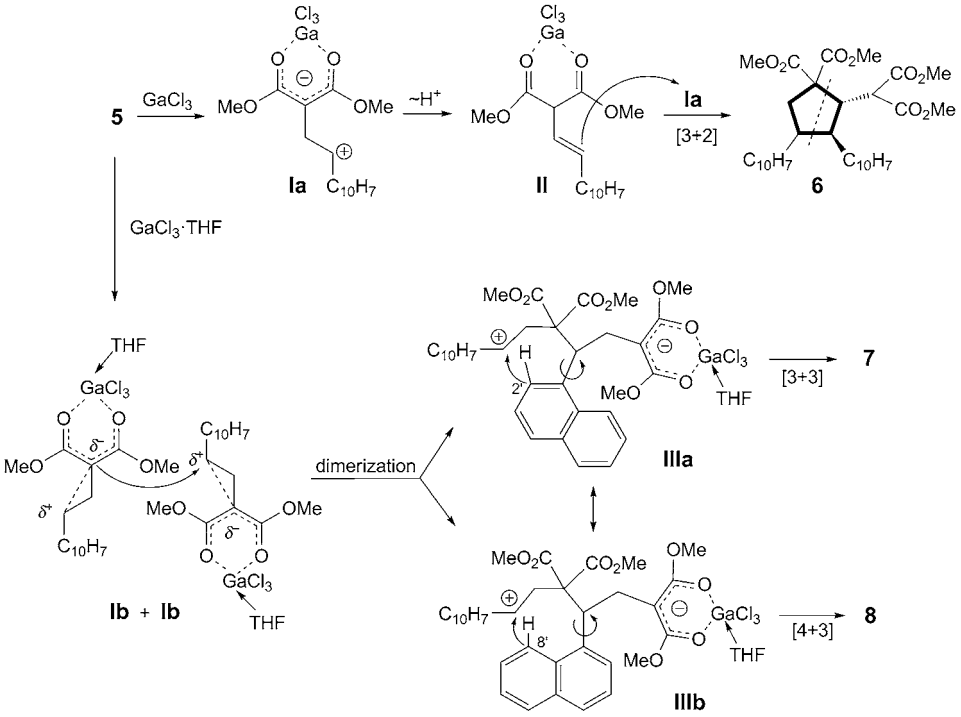


Fig. 1. *Key cross-peaks* (H↔H) *in 2D-*^{1}*H-NOESY spectra of compounds* **6** *and (1*R**,4*R**)-***7** *for determination of configuration.* Full and dashed arrows correspond to correlations above and below the plane, respectively.

A possible mechanism for the formation of the observed products involves $GaCl_3$-induced cyclopropane ring opening with formation of 1,3-zwitterion **Ia**, its transformation to 2-(naphthalen-1-yl)ethenylmalonate **II**. The interaction of **II** with the electrophilic center of another intermediate **Ia** leads cyclopentane **6**, a [3+2] annulation product (*Scheme 3*).

Scheme 3. *Possible Routes of Cyclodimerization of Cyclopropane* **5**

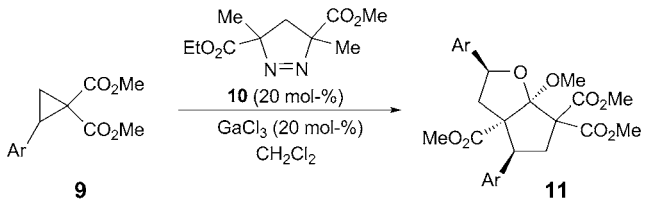


Ring opening of cyclopropane **5** on treatment with the $GaCl_3 \cdot THF$ also involves the generation of the 1,3-dipole **Ib**, additionally stabilized by a THF molecule. However,

because of the strong decrease in $GaCl_3$ acidity due to complexation with THF, this process occurs much more slowly and requires equimolar amounts of the reagents. As a result, coupling of electrophilic and nucleophilic centers of two intermediates **Ia** yields dimeric zwitterionic intermediate **III**, which offers more than one possibility for further transformations. Electrophilic substitutions in the benzene ring appear to be the most obvious route. Attack at C(2′) (*Scheme 3*; intermediate **IIIa**), by analogy with the formation of compound **3** (see *Scheme 1*), corresponds to [3 + 3] annulation to give stereoisomeric 1,2-dihydrophenanthrene-3,3(4*H*)-dicarboxylates **7**. However, in the case of a naphthalenyl substituent, attack at C(8′), *i.e.*, [3 + 4] annulation (intermediate **IIIb**), also becomes possible; it results in a dimer of a new type, 9,10-dihydrocyclohepta[*de*]naphthalene-8,8(7*H*)-dicarboxylate **8**. It should be noted that both processes, which result in compounds **7** and **8**, need prototropic shifts during the formation of the malonyl moiety, whereas the reactions themselves occur much more slowly (*ca.* 24 h) in comparison with the formation of dimer **6**.

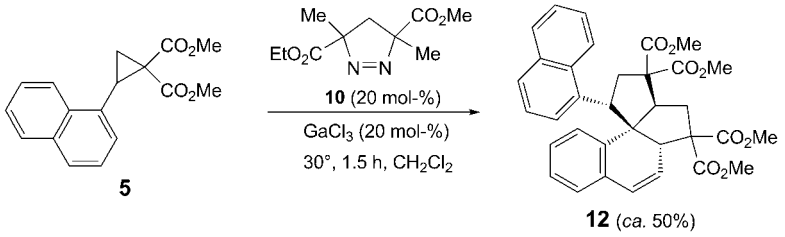
Dimerization of 2-(Naphthalen-1-yl)cyclopropane-1,1-dicarboxylate **5** *to the Pentaleno[1*-a*]naphthalene.* Using dimethyl 2-arylcyclopropane-1,1-dicarboxylates **9** as an example, we recently discovered a new type of dimerization of donor–acceptor cyclopropanes involving an ester group of one molecule of **9** under double catalysis conditions in the presence of a *Lewis* acid and organocatalyst **10** (*trans*/*cis*) to give substituted 2-oxabicyclooctanes **11** (*Scheme 4*) [11]. We used tetrasubstituted 4,5-dihydro-3*H*-pyrazole **10** as the organocatalyst; it was found to be an original catalyst system, only this system was found to work in this reaction.

Scheme 4. *Organocatalyzed Dimerization of Donor–Acceptor Cyclopropanes to 2-Oxabicyclo[3.3.0]octanes*



It was found that cyclopropane **5** did not undergo dimerization to 2-oxabicyclooctane **11** (Ar = naphthalen-1-yl) under these conditions but gave dimer **12** containing a 2,3,3a,4,5,5a-hexahydro-1*H*-pentaleno[6a,1-*a*]naphthalene moiety as the major product (*Scheme 5*). In essence, this route was found to be the same as in dimerization of indolylcyclopropanes **1** (see *Scheme 1*), but **5** did not undergo dimerization and to form even traces of compound **12** under the conditions reported for indolylcyclopropanes **1**. In the case of dimerization of cyclopropanes **1**, the attack is preferably directed at the *ipso*-position due to the electron-donating property of C(3) of the indole moiety. In contrast, in the dimerization of **5**, the attack at the *ipso*-position becomes unfavorable in comparison with electrophilic substitution at the aromatic ring. Thus, the addition of dihydropyrazol **10** is the key approach, which allows electrophilic center to attack at the *ipso*-position.

Scheme 5. *Dimerization of Cyclopropane* **5** *to Pentalenonaphthalene* **12** *in the Presence of $GaCl_3$ and 4,5-Dihydropyrazole* **10**



Upon treatment of cyclopropane **5** with $GaCl_3$ and **10** in a molar ratio of 1:1:5, the total amount of dimers **7** and **8** decreased to 20–25%, tetracyclic compound **12** became the major reaction product (*Scheme 5*). It was found that, in this case, **10** itself remained unchanged and could can be re-isolated almost quantitatively, *i.e.*, it acted as a catalyst. We were the first to discover this reaction for a cyclopropanedicarboxylate containing a naphthalenyl substituent. The complex (1*R**,5a*R**,11b*R**)-2,3,3a,4,5,5a-hexahydro-1*H*-pentaleno[6a,1-*a*]naphthalene skeleton was assembled stereoselectively in one step using a rather simple method.

4,5-Dihydro-3*H*-pyrazoles **10** were used as the catalysts. They were obtained quantitatively as mixtures of *trans*/*cis*-isomers in a 3.5:1 ratio by 1,3-dipolar cycloadditions of methyl or ethyl diazopropanoates to methyl methacrylate [12]. The isomers can be easily separated by column chromatography on silica gel; however, they can be used as catalysts without separation of isomers, even without additional purification of the resulting reaction mixture. It should be noted that polycyclic compound **12** was not formed in the presence of other N-containing compounds, *e.g.*, azobenzene, pyridine, or Et_3N.

Despite the similarity of the polycyclic structures that are formed upon dimerization of 2-(indol-3-yl)cyclopropanedicarboxylates **1** on treatment with $SnCl_4$ in $MeNO_2$ [7], and of 2-(naphthalen-1-yl)cyclopropanedicarboxylates **5** on treatment with $GaCl_3$ in the presence of **10**, the structures of formed dimers **4** and **12** differed considerably. Dimerization of indolylcyclopropanes gave compound **4** containing an indolyl substituent at C(1) in *trans*-position relative to the dihydroindole core [7], whereas we identified a *cisoid*-arrangement of naphthalene moieties in compound **12**. Undoubtedly, the presence of **10** in the latter case plays an important role as a specific organocatalyst in the step determining the relative configuration of the products, since compound **12** was not formed at all in the absence of **10**.

The structure of polycyclic compound **12** was determined by 1D- and 2D-DEPT, COSY, TOCSY, NOESY, HSQC, HMBC, and ^1H- and ^{13}C-NMR spectra. The spectra of this compound displayed a distinct set of signals suggesting that it exists as a single diastereoisomer. The molecular asymmetry was characterized by the presence of four different COOMe groups, two different isolated spin systems CH–CH_2, one CH=CH–CH moiety, two naphthalenyl groups one of which became formally partially hydrogenated. The presence of numerous interactions in the ^1H,^{13}C-HMBC spectrum of **12** indicated that the molecule of this polycyclic compound (*Fig. 2*, *a*) was densely packed.

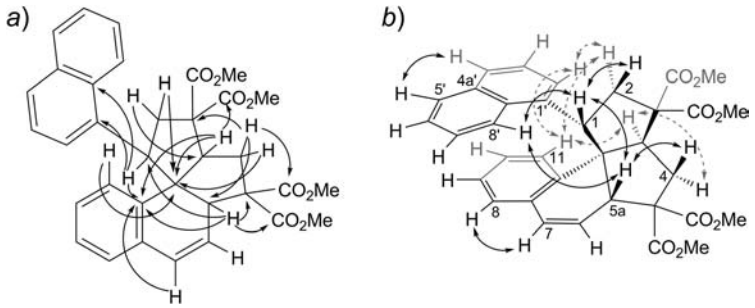
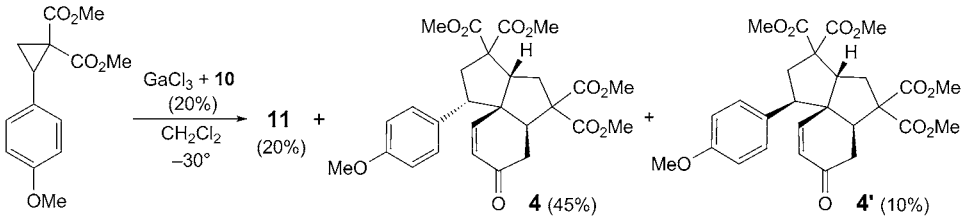


Fig. 2. a) *Selected interactions in the* $^{1}H,^{13}C$*-HMBC spectra* (H → C) *of compound* **12** *for confirmation of the ring system.* b) *Key cross-peaks* (H ↔ H) *in 2D-*^{1}H*-NOESY spectra of compound* **12** *for determination of configuration.* Full and dashed arrows correspond to correlations above and below the plane, respectively.

The relative configuration of compound **12** was unambiguously determined from the 2D-^{1}H-NOESY NMR spectrum (*Fig. 2*, *b*), displaying intense cross-peaks between the H–C(1) and H–C(5a), which is only possible if they are arranged in a *syn*-orientation. The cross-peaks between H–C(5a), H–C(8′), H–C(11), and H–C(2′) of different 'naphthalene' rings indicates that the planes of the rings are arranged above, close to each other to form a helical-like structure. In this configuration, the naphthalenyl substituent almost lacks free rotation around the C(1)–C(1′) bond; this situation is characterized by the presence of narrow signals in the spectra and distinct cross-peaks in NOESY experiments.

The essential role of the organocatalyst in the formation of spiroannulated structures in the course of the transformation of the donor–acceptor cyclopropanes is also documented by the catalytic dimerization of dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate. In this case, in contrast to the previously described dimerization of cyclopropane under $SnCl_4$ (see *Scheme 1*) [4], the application of the catalytic system $GaCl_3$–organocatalyst provided almost twofold increase in the yield of spiroannulated products. Furthermore, the presence of organocatalyst changed the stereoselectivity of the reaction, leading to the formation of stereoisomer **4′** (*Scheme 6*), corresponding to the structure of the naphthalenyl derivative **12**, which distinguished in principle the dimerization process of donor–acceptor cyclopropanes in the presence of 4,5-dihydro-3*H*-pyrazole-3,5-dicarboxylates **10** as organocatalyst.

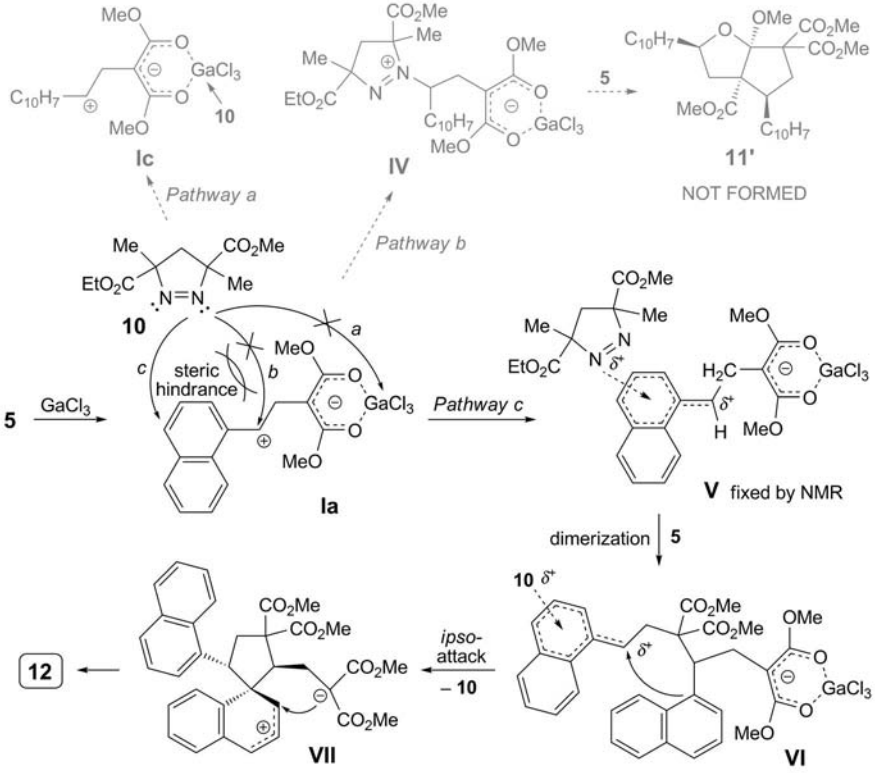
Scheme 6. *Dimerization of 2-(4-Methoxyphenyl)cyclopropane-1,1-dicarboxylate to Isomeric Spiroannulated Compounds* **4** *and* **4′**



As mentioned above, dihydropyrazole **10** played the key role in the formation of compound **12**, similarly to the formation of oxabicyclooctanes **11**. The addition of molecule **10** to the benzyl cationoid C-atom in intermediate **Ia** generated by ring opening of the original cyclopropane with $GaCl_3$ might be the key step required for the formation of oxabicyclooctane **11′** (*Scheme 7*, *Pathway b*) [11]. If this were the case, by analogy with arylcyclopropanedicarboxylates **9**, one would expect the formation of diastereoisomeric intermediates **IV** with a characteristic set of *triplet*s for methine H-atoms in the range of δ(H) *ca.* 6.1 – 6.5 in ^{1}H-NMR spectra. In reality, when the reaction of cyclopropane **5** with $GaCl_3$ and **10b** was carried out in an NMR tube, a set of signals in the region of δ(H) *ca.* 7.1 – 7.4 for the CH moiety in the ^{1}H,^{1}H-COSY spectrum was recorded, which disappeared once the reaction was completed (*Fig. 3*).

These signals do not belong to intermediate **IV**, since they were observed in a lower-field region of the spectrum. Furthermore, they cannot belong to intermediate **Ia**, for which the chemical shift of the benzyl H-atom would be observed at δ(H) 10 – 11 [13]. Apparently, the signal in question still belongs to the benzyl cation in which the positive charge is partially compensated by the external nucleophile, *viz.*, **10** (*Scheme 7*, *Pathway c*).

Scheme 7. *Proposed Mechanism for the Formation of Pentalenonaphthalene* **12**



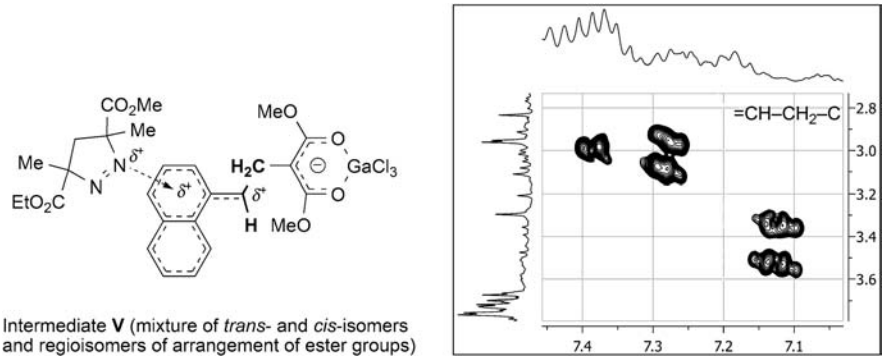


Fig. 3. *Structure of intermediate* **V** *and its key signals in 2D-*^{1}*H,*^{1}*H-COSY spectrum* (mixture of diastereoisomers)

Thus, complex **V** (a mixture of diastereoisomers) rather than betaine **IV** was the key intermediate in this case; the dihydropyrazole moiety in **V** was somehow bound to the naphthalenyl ring, thus withdrawing a fraction of positive charge and decreasing the electrophilicity of the benzyl C-atom. This intermediate reacts with a second naphthylcyclopropane molecule to give intermediate **VI**. Essentially, both of these intermediates, **V** and **VI**, contain a similar specifically bound naphthalenyl moiety, the properties of which replicate those of the indolyl substituent in cyclopropanes **1**. The reason for the unusual behavior of naphthalenylcyclopropanedicarboxylate **5** is that the naphthalenyl substituent creates a considerable steric hindrance against the approach of **10** to the carbocation site of intermediate **Ia** in comparison with other arylcyclopropanes, thus excluding *Route b*. Furthermore, intermediate **Ia** almost does not coordinate **10** to the Ga atom (*Scheme 7*, *Pathway a*), which, unlike THF, decreases abruptly the probability of the formation of dimers **7** and **8**.

In comparison with intermediates **IIIa** and **IIIb** (*Scheme 3*), intermediate **VI** is sterically congested more heavily, while the benzyl C-atom is less electrophilic, since it additionally contains the dihydropyrazole moiety. All these factors favor the attack to the *ipso*-position of the naphthalenyl substituent to give intermediate **VII**, which then undergoes 1,5-cyclization to furnish the final product **12**. During the *ipso*-attack, both naphthalene moieties do not move away from each other as is the case of indolyl-substituted cyclopropanedicarboxylates **1** [7], but get closer instead, which is apparently facilitated by the presence of molecule **10** on the rear side of the electron-deficient naphthalene moiety. This process results in a stereoisomer in which both 'naphthalenyl' rings are oriented in the same direction, thus forming a helical-like structure.

Conclusions. – In summary, we were the first to study the cyclodimerization reactions of 2-(naphthalen-1-yl)cyclopropane-1,1-dicarboxylate in the presence of $GaCl_3$. It has been found that this cyclopropanedicarboxylate undergoes selective dimerization in the presence of catalytic amounts of $GaCl_3$ to give polysubstituted cyclopentane **6**, a [2 + 3]-annulation product. In the presence of an equimolar amount of the $GaCl_3 \cdot THF$ complex, the same cyclopropanedicarboxylate undergoes dimeri-

zation through electrophilic attack at the naphthalene ring to give [3 + 3], [3 + 4] annulation products **7** and **8**, respectively. The [3 + 4] annulation represents a new dimerization type for donor–acceptor cyclopropanes. Under double catalysis conditions on treatment with $GaCl_3$, an organocatalyst (tetrasubstituted 4,5-dihydro-3*H*-pyrazole), 2-(naphthalen-1-yl)cyclopropane-1,1-dicarboxylate undergoes stereospecific dimerization to a tetracyclic pentaleno[6a,1-*a*]naphthalene derivative **12** as a result of electrophilic *ipso*-attack. Thus, we have introduced new methods for the synthesis of some polycyclic compounds, including such compounds which are difficult to obtain by other methods.

Experimental Part

General. All reagents and solvents used were of commercial grade without additional purification. All operations with $GaCl_3$ (from *Aldrich*) were carried out under dry Ar. Prep. column chromatography (CC): silica gel *60* (0.040 – 0.063 mm; *Merck*). TLC: *Silufol* chromatographic plates (*Merck*). IR Spectra: *Specord M80-2* spectrometer in $CHCl_3$ soln. (1%). ^{1}H- and ^{13}C-NMR spectra: *Bruker AMX-400* (400.1 and 100.6 MHz, resp.) spectrometer in $CDCl_3$ containing 0.05% Me_4Si as the internal standard; assignments of ^{1}H- and ^{13}C-signals with the aid of 2D-COSY, TOCSY, NOESY, HSQC, and HMBC spectra; monitoring of the reactions in an NMR tube conducted in CD_2Cl_2 soln. containing 0.05% Me_4Si as the internal standard; δ in ppm, J in Hz. MS: *Finnigan MAT INCOS-50* instrument (EI, 70 eV, direct inlet probe); *m*/*z* (rel. int.). High-resolution (HR) MS: *micrOTOF* instrument; *m*/*z*.

*Dimethyl (2*R**,3*R**,4*S**)-2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-3,4-di(naphthalen-1-yl)cyclopentane-1,1-dicarboxylate* (**6**). A soln. of $GaCl_3$ (25 mg, 0.14 mmol, 20 mol-%) in dry CH_2Cl_2 (0.5 ml) was added under Ar to a soln. of **5** (200 mg, 0.70 mmol) in CH_2Cl_2 (5 ml), and the mixture was stirred at r.t. for 30 min. Then, aq. HCl (5%) was added at 0°, until pH of 3 was attained, and the mixture was extracted with CH_2Cl_2 (3 × 10 ml). The org. layer was dried ($MgSO_4$), and the solvent was removed *in vacuo*. The residue was purified by CC (benzene/AcOEt 20 : 1) to afford **6** (135 mg, 68%). White powder. M.p. 123 – 125°. IR ($CHCl_3$): 3020, 2977, 2955, 2898, 1733 (br., C=O), 1598, 1515, 1476, 1436, 1323, 1265, 1224. ^{1}H-NMR ($CDCl_3$): 7.99 (br. *d*, ^3J = 6.4, H–C(2″)); 7.83 (*d*, ^3J = 7.2, H–C(2‴)); 7.76 (br. *d*, ^3J = 7.6, H–C(8″)); 7.61 (br. *d*, ^3J = 8.6, H–C(8‴)); 7.56 (br. *d*, ^3J = 8.3, H–C(5‴)); 7.54 (*m*, H–C(5″)); 7.52 (br. *d*, ^3J = 7.9, H–C(4″), H–C(4‴)); 7.44 (br. *dd*, ^3J = 7.9, 6.4, H–C(3″)); 7.36 (*dd*, ^3J = 7.9, 7.2, H–C(3‴)); 7.23 – 7.09 (*m*, H–C(6″), H–C(7″)); 7.19 (br. *dd*, ^3J = 8.3, 7.1, H–C(6‴)); 7.13 (*ddd*, ^3J = 8.6, 7.1, ^4J = 1.4, H–C(7‴)); 4.99 (br. *dd*, ^3J = 10.8, H–C(3)); 4.36 (*m*, H–C(2)); 4.22 (*m*, H–C(4)); 3.95 (br. *d*, ^3J = 5.6, H–C(2′)); 3.93, 3.75 (2*s*, 2 MeOCO–C(1)); 3.33, 2.97 (2*s*, 2 MeOCO–C(2′)); 3.19 (br. *dd*, ^2J = 13.0, ^3J = 13.2, H–C(5)); 2.79 (br. *dd*, ^2J = 13.0, ^3J = 6.6, H–C(5)). ^{13}C-NMR ($CDCl_3$): 173.4, 170.9 (2 C(1)–*C*OO); 168.8, 168.6 (2 C(2′)–*C*OO); 137.7 (br., C(1″)); 137.0 (C(1‴)); 133.6 (C(4a‴)); 133.5 (br., C(4a″)); 132.6 (br., C(8a″)); 132.3 (C(8a‴)); 128.5 (C(5‴)); 128.2 (br., C(5″)); 127.1 (br., C(4″)); 127.0 (C(4‴)); 125.6 (br., C(3″)); 125.5 (C(3‴)); 125.4 (C(7‴)); 125.2 (br., C(7″)); 125.0 (C(6′), C(6‴)); 124.5 (br., C(2″)); 123.6 (C(2‴)); 123.4 (br., C(8′)); 122.7 (C(8‴)); 61.5 (C(1)); 53.5, 52.8 (2 MeOCO–C(1)); 52.0 (2 MeOCO–C(2′)); 51.9 (C(2)); 51.7 (C(2′)); 47.5 (C(3), C(4)); 43.3 (C(5)). MS: 567 (4, $[M^+ - H]$), 436 (7), 253 (7), 223 (18), 165 (100), 153 (53), 141 (31), 128 (22), 113 (13), 100 (12), 59 (88), 32 (21). HR-ESI-MS: 569.2163 ($[M + H]^+$, $C_{34}H_{33}O_8^+$; calc. 569.2170), 591.1987 ($[M + Na]^+$, $C_{34}H_{32}NaO_8^+$; calc. 591.1989).

Synthesis of Compounds **7** *and* **8**. A soln. of $GaCl_3 \cdot THF$ in CH_2Cl_2, which was prepared by mixing of equimolar amounts of solid $GaCl_3$ (125 mg, 0.70 mmol) and THF (50 mg, 0.70 mmol) in CH_2Cl_2, (1 ml) under Ar, was added to a soln. of **5** (200 mg, 0.70 mmol) in dry CH_2Cl_2 (5 ml), and the mixture was stirred at r.t. for 24 h. Then, aq. HCl (5%) was added at 0°, until pH 3 was achieved, and the mixture was extracted with CH_2Cl_2 (3 × 10 ml). The org. layer was dried ($MgSO_4$), and the solvent was removed *in vacuo*. The residue was separated by CC (benzene/AcOEt 20 : 1) to afford **7** (*ca.* 30%) and **8** (*ca.* 40%) (total 140 mg, both mixture of diastereoisomers in a *ca.* 1 : 1 ratio). The product obtained was additionally

separated on a *Silufol* chromatographic plate (hexane/acetone 2:1) to afford the pure diastereoisomer (1*R**,4*R**)-**7**.

*(1*R**,4*R**)-Dimethyl 4-[3-Methoxy-2-(methoxycarbonyl)-3-oxopropyl]-1-(naphthalen-1-yl)-1,4-dihydrophenanthrene-3,3(2*H*)-dicarboxylate* (1*R**,4*R**)-**7**). White powder. M.p. 190–192°. IR ($CHCl_3$): 3020, 2976, 2956, 2896, 2847, 1733 (br., C=O), 1598, 1512, 1436, 1397, 1324, 1224. ^{1}H-NMR ($CDCl_3$): 8.30 (br. *d*, ^3J = 9.4, H–C(8″)); 8.28 (br. *d*, ^3J = 9.6, H–C(5)); 7.89 (br. *d*, ^3J = 8.2, H–C(5′)); 7.81 (*dd*, ^3J = 8.1, ^4J = 1.0, H–C(8)); 7.65 (br. *d*, ^3J = 8.0, H–C(4″)); 7.64 (*ddd*, ^3J = 8.2, 7.0, ^4J = 1.4, H–C(6″)); 7.60 (*ddd*, ^3J = 8.1, 6.9, ^4J = 1.4, H–C(7)); 7.56 (*d*, ^3J = 8.5, H–C(9)); 7.54 (*ddd*, ^3J = 9.4, 7.0, ^4J = 1.1, H–C(7″)); 7.50 (*d*, H–C(6), ^3J = 9.6, 6.9, ^4J = 1.0); 7.17 (*dd*, ^3J = 8.0, 7.5, H–C(3″)); 6.94 (*d*, ^3J = 8.5, H–C(10)); 6.38 (br. *d*, ^3J = 7.5, H–C(2″)); 5.38 (*dd*, ^3J = 9.3, 1.3, H–C(1)); 4.71 (br. *dd*, ^3J = 8.7, 5.1, H–C(4)); 3.80 (*s*, MeOCO–C(3)); 3.68, 3.51 (2*s*, 2 MeOCO–C(2′)); 3.29 (*dd*, ^2J = 14.7, ^3J = 9.3, H_a–C(2)); 3.27 (*dd*, ^3J = 8.4, 6.1, H–C(2′)); 2.93 (*s*, MeOCO–C(3)); 2.79 (*ddd*, ^2J = 14.7, ^3J = 1.3, ^4J = 1.7, H_b–C(2)); 2.40 (*ddd*, ^2J = 14.2, ^3J = 8.4, 5.1, H_a–C(1′)); 2.17 (*ddd*, ^2J = 14.2, ^3J = 8.7, 6.1, H_b–C(1′)). ^{13}C-NMR ($CDCl_3$): 171.3, 170.7 (2 C(3)–*C*OO); 169.5, 169.4 (2 C(2′)–*C*OO); 142.5 (C(1″)); 135.1 (C(4a)); 134.1 (C(4a″)); 133.8 (C(10a)); 133.0 (C(8a)); 131.9 (C(4b)); 131.6 (C(8a″)); 129.18, 129.16 (C(10), C(5″)); 128.7 (C(8)); 127.1, 126.9, 126.8, 126.6, 126.5 (C(9), C(2″), C(4″), C(6″), C(7″)); 125.71, 125.67 (C(6), C(7)); 125.0 (C(3″)); 123.51, 123.48 (C(5), C(8″)); 56.6 (C(3)); 53.0 (*Me*OCO–C(3)); 52.7, 52.5 (2 *Me*OCO–C(2′)); 52.0 (*Me*OCO–C(3)); 49.5 (C(2′)); 37.3 (C(1)); 35.4 (C(4)); 32.6 (C(1′)); 30.5 (C(2)). MS: 567 (10, $[M-H]^+$), 536 (2, $[M-CH_3OH]^+$), 476 (6), 436 (8), 424 (28), 363 (45), 331 (92), 317 (46), 303 (100), 289 (57), 278 (41), 265 (17), 205 (12), 165 (13), 145 (15), 113 (17), 59 (38). HR-ESI-MS: 591.1983 ($[M+Na]^+$, $C_{34}H_{32}NaO_8^+$; calc. 591.1989).

*Mixture of Dimethyl (7*R**,10*R**)- and (7*R**,10*S**)-7-[3-Methoxy-2-(methoxycarbonyl)-3-oxopropyl]-10-(naphthalen-1-yl)-9,10-dihydrocyclohepta[*de*]naphthalene-8,8(7*H*)-dicarboxylate* ((7*R**,10*R**)-**8**/(7*R**,10*S**)-**8**)*, and (1*R**,4*S**)-**7** (ratio *ca.* 1:1:1). Colorless thick oil. IR ($CHCl_3$): 3020, 2976, 2956, 2896, 2847, 1733 (br., C=O), 1599, 1514, 1476, 1436, 1323, 1225. ^{1}H-NMR ($CDCl_3$): 8.34–6.83 (*m*, 39 arom. H); 5.38–5.23 (*m*, 1 H); 5.21–5.14 (*m*, 1 H); 5.01–4.90 (*m*, 2 H); 4.71 (br. *dd*, ^3J = 9.7, 4.8, 1 H); 4.36–4.27 (*m*, 4 H); 3.93, 3.91, 3.84, 3.82, 3.79, 3.75 (all *s*, 6 MeO); 3.55, 3.48 (2 br. *s*, 2 eO); 3.40–3.33 (*m*, 2 H); 3.33, 3.20, 3.17, 2.97 (all *s*, 4 MeO); 3.06–2.90 (*m*, 4 H); 2.51–2.29 (*m*, 2 H); 2.30–2.12 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 173.4, 172.3, 171.1, 170.9, 170.5, 170.4, 169.6, 169.5, 169.2, 169.0, 168.8, 168.6 (12 COO); 137.7, 137.6, 137.0, 136.8, 135.7, 135.3, 135.2, 134.9, 134.2, 134.1, 134.0, 133.6, 133.2, 133.1, 132.62, 132.60, 132.26, 132.23, 131.98, 131.95, 131.94 (21 arom. C); 129.1, 128.7, 128.5, 128.3, 127.8, 127.6, 127.1, 127.0, 126.0, 126.55, 126.50, 125.95, 125.85, 125.63, 125.57, 125.51, 125.47, 125.39, 125.35, 125.2, 125.03, 124.97, 124.7, 124.6, 124.5, 124.3, 124.2, 123.9, 123.8, 123.6, 123.4, 123.2, 122.7 (39 arom. C); 61.92, 61.91, 61.5 (3 C); 53.5, 53.2, 53.1, 52.9, 52.8, 52.7, 52.6, 52.22, 52.18, 52.0, 51.9, 51.7 (12 MeO); 49.7, 47.5 (br.), 43.9, 43.3, 43.1, 40.2, 39.4 (br.), 35.9, 33.9 (br.), 31.6 (br.). MS: 567 (5, $[M-H]^+$), 476 (1), 436 (11), 424 (7), 363 (11), 331 (20), 303 (22), 223 (16), 165 (72), 145 (41), 113 (22), 59 (100). HR-ESI-MS: 569.2161 ($[M+H]^+$, $C_{34}H_{33}O_8^+$; calc. 569.2170), 591.1984 ($[M+Na]^+$, $C_{34}H_{32}NaO_8^+$; calc. 591.1989).

*Tetramethyl (1*R**,3a*R**,5a*S**,11b*S**)-1-(Naphthalen-1-yl)-3a,4-dihydro-1*H*-pentaleno[6a,1-*a*]naphthalene-3,3,5,5(2*H*,5a*H*)-tetracarboxylate* (**12**). All operations were performed in dry Ar. A soln. of **5** (200 mg, 0.70 mmol) and **10** (32 mg, 0.14 mmol, 20 mol-%) in dry CH_2Cl_2 (5 ml) was cooled to −10°. Solid $GaCl_3$ (25 mg, 0.14 mmol, 20 mol-%) was then added in one portion at −10° with vigorous stirring, and the mixture was heated to 30° and stirred for 1.5 h. Then, aq. HCl (5%) was added at 0°, until pH 3 was achieved, and the mixture was extracted with CH_2Cl_2 (3 × 10 ml). The org. layer was dried ($MgSO_4$), and the solvent was removed *in vacuo*. The residue was separated by CC (benzene/AcOEt 20:1) to afford **12** (*ca.* 100 mg, 50%). White powder. M.p. 192–193°. IR ($CHCl_3$): 3020, 2955, 2929, 2847, 1730 (br., C=O), 1514, 1487, 1436, 1263, 1224. ^{1}H-NMR ($CDCl_3$): 8.24 (br. *d*, ^3J = 8.4, H–C(8′)); 7.70 (*dd*, ^3J = 8.0, ^4J = 1.3, H–C(5′)); 7.50 (*ddd*, ^3J = 8.4, 6.8, ^4J = 1.3, H–C(7′)); 7.43 (br. *d*, ^3J = 8.2, H–C(4′)); 7.39 (*ddd*, ^3J = 8.0, 6.8, ^4J = 1.0, H–C(6′)); 7.36 (br. *d*, ^3J = 7.6, H–C(11)); 7.23 (*ddd*, ^3J = 7.6, 7.4, ^4J = 1.3, H–C(10)); 6.96 (*ddd*, ^3J = 7.5, 7.4, ^4J = 1.1, H–C(9)); 6.80 (*dd*, ^3J = 8.2, 7.4, H–C(3′)); 6.46 (*dd*, ^3J = 7.5, ^4J = 1.3, H–C(8)); 6.25 (*dd*, ^3J = 7.4, ^4J = 1.0, H–C(2′)); 5.66 (*dd*, ^3J = 9.7, 5.8, H–C(6)); 5.55 (br. *d*, ^3J = 9.7, H–C(7)); 4.76 (*dd*, ^3J = 13.9, 5.4, H–C(1)); 4.58 (*dd*, ^3J = 9.9, 8.9, H–C(3a)); 3.90, 3.84 (2*s*, 2 MeOCO–C(3)); 3.79 (*dd*, ^3J = 5.8, ^4J = 0.5, H–C(5a)); 3.76, 2.97 (2*s*, 2 MeOCO–C(5)); 2.94 (*dd*, ^2J = 13.3 ^3J = 13.9, H_{syn}–C(2)); 2.73 (*dd*, ^2J = 12.9, ^3J = 8.9, H_{anti}–C(4)); 2.68 (*dd*, ^2J = 13.3, ^3J = 5.4,

H_{anti}–C(2)); 1.93 (*dd*, $^2J = 12.9$, $^3J = 9.9$, H_{syn}–C(4)). ^{13}C-NMR ($CDCl_3$): 172.4, 172.2 (2 C(3)–COO); 171.2, 169.7 (2 C(5)–COO); 137.7 (C(11a)); 134.4 (C(1′)); 133.4 (C(4a')); 133.1 (C(8a')); 132.9 (C(7a)); 128.6 (C(5′)); 128.4 (C(7)); 127.5 (C(10)); 126.58 (C(9)); 126.55 (C(4′)); 126.3 (C(8)); 126.2 (C(11)); 125.9 (C(7′)); 125.2 (C(6)); 125.0 (C(6′)); 124.6 (C(2′)); 124.0 (C(3′)); 123.7 (C(8′)); 69.0 (C(5)); 61.8 (C(3)); 58.8 (C(11b)); 57.0 (C(3a)); 54.1 (C(5a)); 53.1 (C(1), *Me*OCO–C(3)); 52.7 (*Me*OCO–C(5)); 52.6 (*Me*OCO–C(3)); 51.7 (*Me*OCO–C(5)); 44.5 (C(2)); 36.1 (C(4)). MS: 567 (2, $[M - H]^+$), 414 (13), 382 (16), 350 (5), 322 (6), 283 (36), 251 (48), 223 (81), 195 (29), 165 (100), 153 (68), 141 (35), 113 (16), 83 (21), 59 (65). HR-ESI-MS: 591.1980 ($[M + Na]^+$, $C_{34}H_{32}NaO_8^+$; calc. 591.1989).

*Tetramethyl (1*R*,3a*S*,5a*R*,9a*S*)- and (1*R*,3a*R*,5a*S*,9a*R*)-1-(4-Methoxyphenyl)-7-oxo-3a,4,6,7-tetrahydro-1*H*-cyclopenta[c]indene-3,3,5,5(2*H*,5a*H*)-tetracarboxylate* (**4** and **4′**, resp.). A soln. of 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (150 mg, 0.57 mmol) and **10** (26 mg, 0.11 mmol, 20 mol-%) in dry CH_2Cl_2 (3 ml) was cooled to $-45°$. Then, solid $GaCl_3$ (20 mg, 0.11 mmol, 20 mol-%) was added in one portion at $-45°$ under vigorous stirring, the temp. was raised to $-30°$, and the mixture was stirred for 1 h. After that, cold THF (0.7 ml) was added for the destruction of Ga complexes, and the solvent was evaporated under vacuum at $-20°$. The residue was separated immediately by CC (benzene/AcOEt 20:1) to afford starting cyclopropane (15 mg, 10%), **11** (30 mg, 20%), **4** (68 mg, 45%), **4′** (15 mg, 10%), and starting **10** (25 mg, 97%). The NMR spectrum of **4** was identical to the one described earlier [4].

Data of **4′**. Colorless thick oil. ^{1}H-NMR ($CDCl_3$, 300.1 MHz): 7.04–7.08 (*m*, 2 *o*-CH); 6.74–6.78 (*m*, 2 *m*-CH); 6.65 (*dd*, $^3J = 10.4$, $^4J = 1.4$, H–C(9)); 5.67 (*d*, $^3J = 10.4$, H–C(8)); 3.81 (*dd*, $^3J = 11.7$, 8.1, H–C(3a)); 3.80, 3.77, 3.76, 3.73, 3.51 (5*s*, 5 MeO); 3.67 (*dd*, $^3J = 13.2$, 5.5, H–C(1)); 3.28 (br. *d*, $^3J = 8.2$, H–C(5a)); 2.90 (*dd*, $^2J = 14.2$, $^3J = 5.5$, H_a–C(2)); 2.71 (br. *d*, $^2J = 18.0$, H_a–C(6)); 2.68 (*dd*, $^2J = 12.6$, $^3J = 8.1$, H_a–C(4)); 2.59 (*dd*, $^2J = 14.2$, $^3J = 13.2$, H_b–C(2)); 2.27 (*dd*, $^2J = 18.0$, $^3J = 8.2$, H_b–C(6)); 1.65 (*dd*, $^2J = 12.6$, $^3J = 11.7$, H_b–C(4)).

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