# Cascade dimerization of 2-styryl-1,1-cyclopropanedicarboxylate upon treatment with gallium trichloride*

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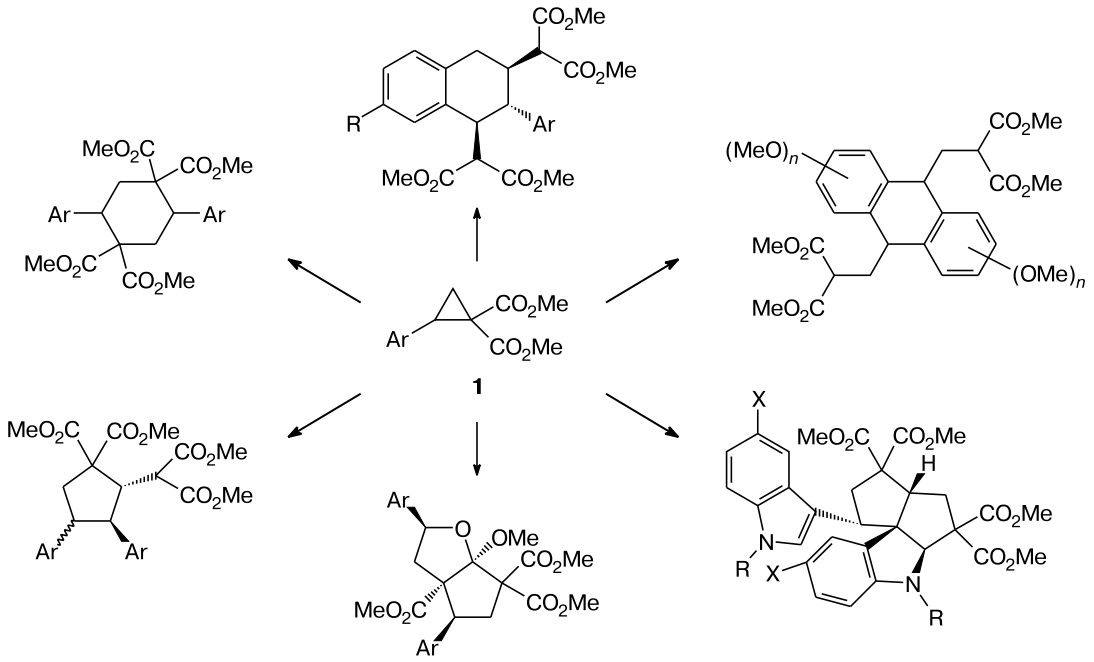
2-Styrylcyclopropane-1,1-dicarboxylate treated with anhydrous gallium trichloride undergoes dimerization with the cyclopropane ring opening and the styryl substituent double bond involvement, leading to the formation of polysubstituted cyclic and bicyclic structures with the predominance of the former or the latter depending on the reaction conditions. Most compounds are formed with very high diastereoselectivity. Thirteen major and minor dimeric structures were isolated and reliably characterized, two of which were found to additionally include a chlorine atom. A rare for the reactions of donor-acceptor cyclopropanes example of the formation of a product with the fused cyclobutane ring was effected at −80 °C. Plausible mechanisms of observed processes were discussed.

**Key words:** 2-styryl-1,1-cyclopropanedicarboxylate, gallium trichloride, cascade dimerization, diastereoselectivity.

Cyclopropanes with the vicinal donor and acceptor substituents (donor-acceptor cyclopropanes, DAC) are regarded as building blocks and are widely used in modern organic synthesis for construction of various carbo- and heterocyclic systems.[1—9] The most frequently DAC are used as the sources of 1,3-zwitterions[1—9] involving in the reactions with a wide scope of substrates.

In the absence of substrates, DAC can undergo isomerization or be involved in the dimerization reactions (Scheme 1).[9—17] These reactions are interesting from the

**Scheme 1**




* Dedicated to Academician of the Russian Academy of Sciences O. M. Nefedov on the occasion of his 85th birthday.

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point of view that allows one to assemble quite complex carbo- and heterocyclic skeletons, including polyannulated, in one step from one simple substrate. In most cases, these reactions proceed with high regio- and diastereoselectivity, and the formed compounds can be used as synthons in subsequent chemical transformations and for the synthesis of analogs of biologically active and natural compounds. Apart from that, mechanistic aspects of the observed transformations are very interesting. At the present time, it is known that dimerization of DAC can follow a large variety of directions, and the studies of these transformation continue.[9—17]

Due to a possibility of the wide variation of reactivity of DAC, it seemed interesting to study the behavior of more complex carbon synthons, retaining however the cyclopropane ring and the principle of spacing of donor and acceptor substituents in the molecule. One of the most simple representatives described earlier[1—8,18—21] is 2-styrylcyclopropane-1,1-dicarboxylate (**2**), for which, however, no other types of transformations were known apart from those characteristic of the most DAC of type **1**, which proceed with the generation of 1,3-zwitterion. In this cases, the styryl substituent served exclusively as a donor substituent and was not directly involved in the transformations.[18—21] Suprisingly, but even simple and obvious vinylcyclopropane-cyclopentene rearrangment is not known for DAC **2**, and the corresponding cyclopentene **3** is not still described.[22—26] In the present work, we realized the concept of "extended" reactivity of **2** with the involvement of its double bond in different transformations and in detail studied transformations of cyclopropane **2** upon treatment with different Lewis acids, first of all, in dimerization processes.


**2**

## Results and Discussion

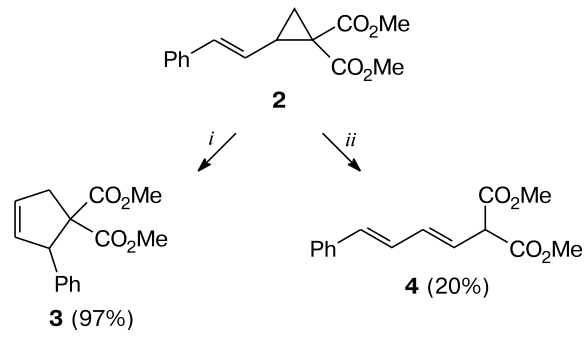
Styrylcyclopropanedicarboxylate **2** was synthesized from *trans*-cinnamic aldehyde according to a well working two-step procedure which includes Knoevenagel condensation and Corey—Chaykovsky cyclopropanation.[27,28]

Already first experiments on the transformations of DAC **2** upon treatment with different Lewis acids showed that actually no dimeric products were formed. In a number of cases, there were no reactions at all, in other cases the reactions led exclusively to vinylcyclopropane-cyclopentene rearrangement[22—26] with the formation of 2-phenylcyclopent-3-ene-1,1-dicarboxylate (**3**). In some cases oligomerization occurred, especially when more drastic conditions were used. We unsuccessfully tested all the available arsenal of Lewis acids commonly used in DAC chemistry: $SnCl_4$, $TiCl_4$, $AlCl_3$, $EtAlCl_2$, $BF_3 \cdot Et_2O$, $ZnCl_2$, $InCl_3$, TMSOTf, $Sn(OTf)_2$, $Cu(OTf)_2$, $Sc(OTf)_3$, $Yb(OTf)_3$, $In(OTf)_3$, $Ni(ClO_4)_2$, $MgI_2$. The introduction into the reaction of different additional substrates did not change much, and the reactions followed the usual for DAC pathways without involvement of the styryl substituent.[1—9,18—21]

The situation was changed when a specific Lewis acid, anhydrous gallium trichloride, was used, the application of which in the reactions of DAC have been intensively studied by our research group. In fact, $GaCl_3$ under certain conditions turned out to be the only Lewis acid capable of involving into the chemical transformations of both the cyclopropane ring and the double bond in DAC **2** with the formation of identifiable compounds.

The processes in these transformations can be separated in two types, namely, proceeding at reduced and elevated temperatures. Thus, the processes of isomerization of cyclopropane **2** predominantly take place at the temperatures above 20 °C (Scheme 2), which mainly give the product of vinylcyclopropane-cyclopentene rearrangement, cyclopentene **3**, independent of the amount of $GaCl_3$. Since this reaction is a sigmatropic rearrangement and does not require the formation of complex intermediates, it proceeds especially readily; gallium chloride activates it through the coordination at the ester groups. At room temperature and with an equimolar amount of $GaCl_3$, cyclopentene **3** is formed almost in quantitative yield. When a catalytic amount of $GaCl_3$ is used, another isomer, diene **4**, is also formed together with cyclopentene **3**, but only in 20% yield (Scheme 2).

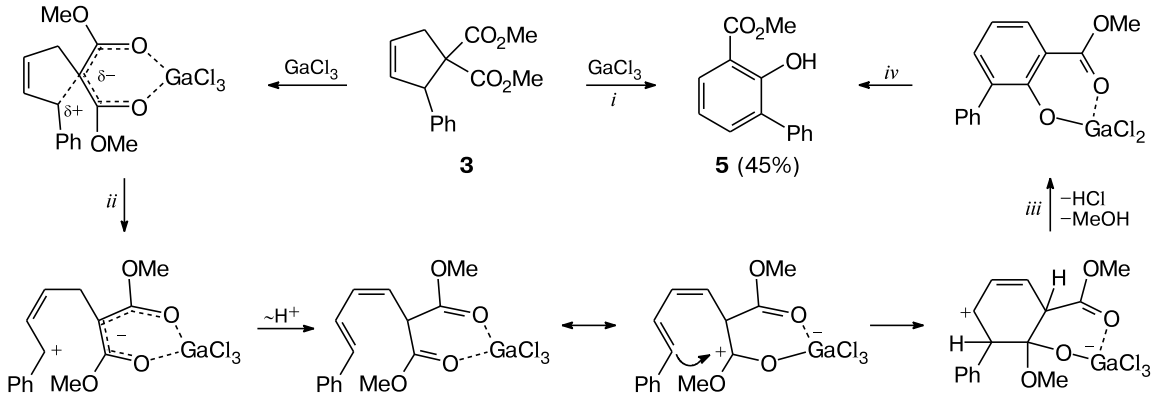
**Scheme 2**




**Reagents and conditions:** *i*. $GaCl_3$ (100 mol.%), 25 °C, 1 h, $CH_2Cl_2$; *ii*. $GaCl_3$ (20 mol.%), 25 °C, 1 h, $CH_2Cl_2$.

The deeper process occured upon reflux of **2** in *ortho*-dichlorobenzene (180 °C). In this case, substituted phenol **5** was isolated as the major product, the yield of which was only ~45% because of a large amount of oligomers. It turned out that initially cyclopropane **2** isomerizes to cyclopentene **3**, which at high temperature undergoes transformation to phenol **5** (Scheme 3). In fact, subjecting cyclopentene **3** to similar conditions we obtained the

**Scheme 3**




*i*. $GaCl_3$ (100 mol.%), 180 °C, 8 h, *o*-DCB; *ii*. Ring opening; *iii*. Aromatization; *iv*. Hydrolysis.

same result as with cyclopropane **2**, *i.e.*, the five-membered ring in cyclopentenedicarboxylate **3** treated with $GaCl_3$ can undergo opening, that is a very rare example of the "donor-acceptor cyclopentane". A plausible mechanism of transformation of **3** to phenol **5** is given in Scheme 3.

The second, more interesting group of transformations of cyclopropane **2** treated with gallium trichloride is the dimerization reactions, which can be successfully carried out only at reduced temperatures. The reaction result considerably depends on conditions of the process and sometimes considerably changes even at their insignificant variations. Many of these processes proceed as complicated cascade reactions with the formation of bicyclic structures with many stereocenters, which, nonetheless, are formed with exclusively high diastereoselectivity. Unfortunately, the complicated character of proceeding processes plays also a considerable negative role, since they are interfered by a number of side processes. The most frequent of them is the readily proceeding vinylcyclopropane-cyclopentene rearrangement to cyclopentene **3**, always present in the reaction mixtures. Another dominating side process is oligomerization and polymerization reactions proceeding even at quite low temperatures. This results in the formation of a mixture of compounds and difficulties with their isolation, that, nonetheless, is largely compensated by the high complexity of assembling structures and very high diastereoselectivity (up to the formation of a single diastereomer at a simultaneous formation of six stereocenters in one process). The main directions of the transformation of DAC **2** (disregarding the side processes) and conditions required for them to proceed are given in Scheme 4.

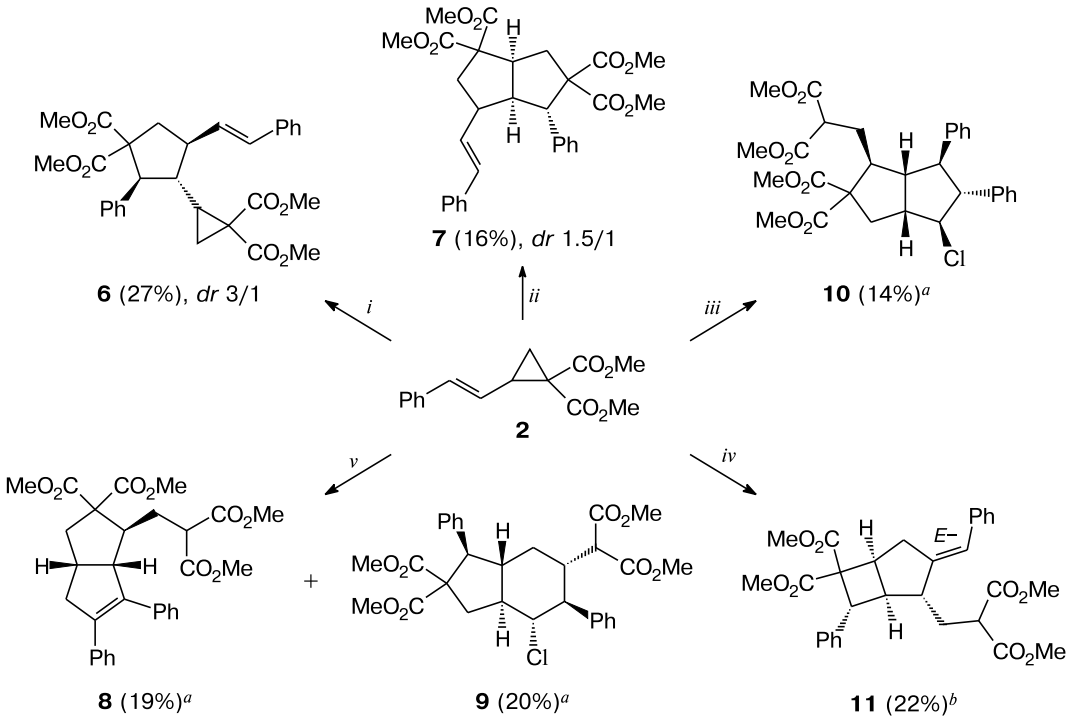
Let us consider these processes in more details. Two quite routine dimerization processes predominantly proceed in the temperature range from –30 °C to 0 °C when using 20 mol.% of $GaCl_3$: a formal [3+2] cycloaddition reaction of one molecule of DAC **2** as a classic 1,3-zwitterion to the double bond of the second molecule of cyclopropane **2** or of the formed from it cyclopentene **3**. This leads to polysubstituted cyclopentane **6** and bicyclo[3.3.0]octane **7** (with an equimolar amount of $GaCl_3$, the reaction stops in the step of the formation of cyclopentene **3**). Since these reactions are quite simple and do not require many steps, compounds **6** and **7** are formed as mixtures of diastereomers, with cyclopentane **6**, depending on the conditions, being obtained as a mixture of from two to four diastereomers (from eight possible), which can be successfully separated. Bicyclooctane **7** is formed more selectively as a mixture of only two diastereomers in the ratio of ~1.5 : 1.

At a temperature near –80 °C and with an equimolar amount of $GaCl_3$, bicyclic structures **8** and **9** are formed, with the latter containing a chlorine atom in the six-membered ring (see Scheme 4). The reaction reached completion within 9 h and leads to the formation of compounds **8** and **9** approximately in the equal ratio, which can be easily separated by chromatography on $SiO_2$. Different amounts of cyclopentene **3** and isomeric dimers **6** were also isolated together with these compounds.

When using non-optimal conditions, the reaction leads, apart from compounds **8** and **9**, to a quite selective formation of chlorine-containing bicyclo[3.3.0]octane **10** or dimer **11** with the structure rarely encountered in this-type processes which contains a cyclobutane ring and an exocyclic double bond (see Scheme 4). Both compounds are obtained only in very narrow range of conditions. Thus, especially low temperature (–95 °C) is required for the formation of chloride **10**, while dimer **11** is formed at –80 °C, but when 50 mol.% of $GaCl_3$ is used.

Note that compounds **8**—**11** are formed as a result of complex multi-step and not very obvious processes, and all of them are formed as the only regio- and diastereomer despite the fact that up to six stereocenters are simultaneously generated in one process. Apart from that, compounds **9** and **10** together with the fragments of cyclopropanes **2** additionally have a chlorine atom borrowed from the Lewis acid, that is also quite unusual for the

**Scheme 4**

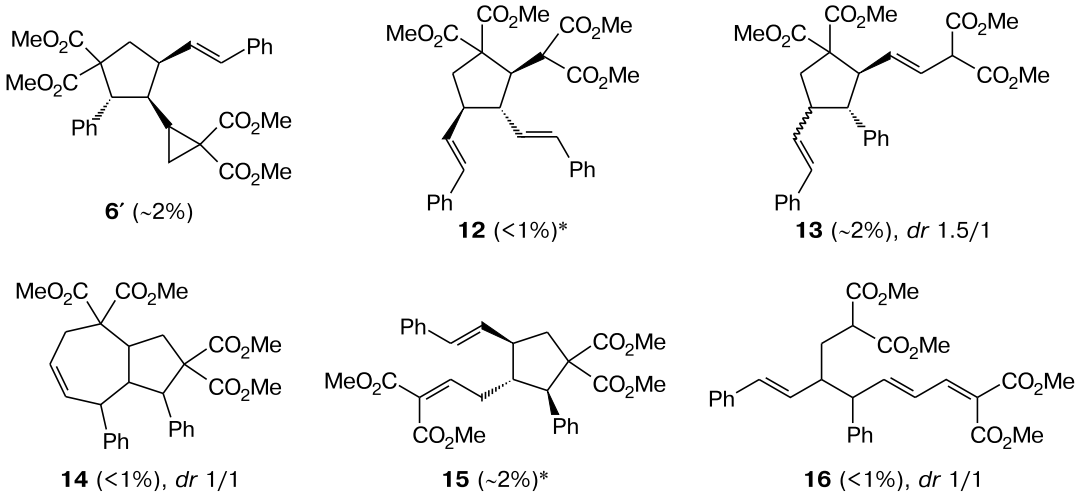



**Reagents and conditions:** *i*. $GaCl_3$ (20 mol.%), −30 °C, 1 h, $CH_2Cl_2$; *ii*. $GaCl_3$ (20 mol.%), 0 °C, 1 h, $CH_2Cl_2$; *iii*. $GaCl_3$ (100 mol.%), −95 °C, 8 h, $CH_2Cl_2$; *iv*. $GaCl_3$ (50 mol.%), −80 °C, 8 h, $CH_2Cl_2$; *v*. $GaCl_3$ (100 mol.%), −80 °C, 9 h, $CH_2Cl_2$.

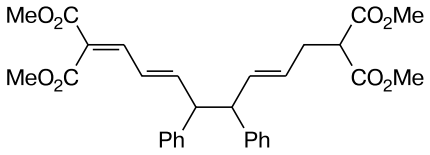
*Notes*. [a] One diastereomer. [b] One isomer.

reactions of DAC with gallium chloride. Note that the chlorine atom in the product also has a strictly fixed configuration. Unfortunately, the yields of the dimeric compounds **8**—**11** are not very high, but this is fully compensated by a certain complexity of the structures obtained from simple and available cyclopropanedicarboxylate **2**.

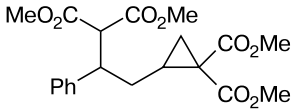
Apart from that major products of DAC **2** transformation, in the temperature range from −40 to +10 °C we also isolated and characterized a number of minor dimers **12**—**18** in the yields about 1.5—2%. The processes of their formation are simpler than the cascade reactions described above, while structurally they are either acyclic dimers, or different products of formal [3+2] cycloaddition of 1,3-zwitterion to different double bonds. Thus, compounds **12** and **13** correspond to a formal addition of the 1,3-zwitterion generated from one molecule of cyclopropane **2** to differ-




* One diastereomer.



**17** (~2%), *dr* 1/1



**18** (~5%), *dr* 1/1

ent double bonds of (4-phenylbuta-1,3-dienyl)malonate formed from another cyclopropane **2** molecule. Bicyclic compound **14** is an analog of dimer **7** formed by the formal [5+2] cycloaddition reaction. Compounds **15**—**17** are distinguished by the formation of an alkylidenemalonate fragment, that is quite characteristic of the three-membered ring opening in type **1** DAC upon treatment with $GaCl_3$ (see Refs 9, 16, 17, and 29—32).

Note that none of the isolated compounds contained fragments, in which the phenyl substituent would have been involved, *i.e.*, the electrophilic substitution left it intact, though for arylcyclopropanedicarboxylates this process occurs upon treatment with both $GaCl_3$[9,13,15—17,29,31] and other Lewis acids.[9—12]

The methods used for determination of structures of formed compounds should be discussed separately, since this turned out to be a nontrivial problem, taking into account their complicated character and nonobviousness of formation. Since all the dimeric compounds, despite of double purification by chromatography on $SiO_2$, were heavy oils without any hope for crystallization, it was impossible to use X-ray diffraction analysis. In this connection, the structures were analyzed based on the combination of $^1H$ and $^{13}C$ NMR spectra, using 2D experiments COSY, TOCSY, NOESY, HSQC, and HMBC. For the dimers isolated in small amounts, we used a long acquisition time, up to several days. Molecular formulas were confirmed by high resolution mass spectrometry.

We used the following strategy for establishing the structures. First, the COSY and TOCSY spectra were used to find all the proton spin systems and establish fragments of molecular skeleton consisting of the proton-containing C atoms. In the proton spectra, the $CH_2$ groups (in which both protons are always nonequivalent and usually have individual chemical shifts) was distinguished from the CH groups using the edited-HSQC or HSQC+DEPT-135. The signals of all overlapped protons were also distinguishable and were assigned using 2D spectra. In this case, the TOCSY spectra were found to be very useful, since the proton spin systems in the dimers are quite long and some interactions can be lost in the COSY spectra. Apart from that, TOCSY allows one to unambiguously distinguish the spin systems of separate components in the case of isolation of an unseparable mixture of diastereomers. Then, we used the HSQC spectra to completely assign all the protonated carbon atoms. The final and the most important step in the establishing entire carbon skeleton of the molecule was carried out using the HMBC spectra based on the analysis of remote C—H constants through two and three bonds. From the HMBC spectra, we extracted all the data on the presence of these constants and used them to build a graph from the atoms, which had an unambiguous solution for fitting of all the observed constants, since in the HMBC spectra a large amount of interactions is observed (due to the presence of a large number of different protons in the structures), which several times duplicate and verify each other. As a result, we obtained an unambiguous and well confirmed structure of the studied compound. This is the reason why the high-quality 2D spectra with a high signal/noise ratio were required.

For example, the CH group containing a phenyl substituent was unambiguously determined from two correlations in the HMBC: $HC_{aliph}$ — $HC_{o\text{-}Ph}$ (direct and reverse) and the interaction of the neighboring $HC_{aliph}$ with $C_{ipso\text{-}Ph}$. The CH at the ester groups and the points of their attachment (from the $HC_{aliph}$ — C=O correlations) were determined similarly. The quaternary C atoms, their assignment, and points of attachment were also determined from the set of correlations in the HMBC. The locations of the addition of chlorine atoms were determined in the final step from the incomplete skeleton of the molecule based on the combination of all the 2D experiments, while their introduction into the structure was unambiguously confirmed by the HRMS data.

The final step in the structural analysis was the assignment of configuration for all the stereocenters in the molecule. This was made using the 2D NOESY spectra by the analysis of the cross-peaks and identification of spatially close protons based on the NOE effect. The presence of a large number of protons in the structures, their rigid polycyclic structure, and, as a consequence, the presence of a large number of cross-peak in the NOESY made the configurational analysis very simple, nonproblematic, and accurate, which allowed us to unambiguously find relative configurations of all the stereocenters in the molecule. Apart from that, the NOESY data well enough double-check and verify the skeleton and the structure established previously.

As an example, Fig. 1 shows some key interactions in the NOESY and HMBC spectra for compounds **9**—**11**, which were used to establish carbon skeletons and configurations of substituents.

As to the possible mechanism of transformations, we should note that the "high-temperature" processes (above −30 °C) are mainly represented by a typical for DAC formal [3+2] cycloaddition[1—9,18—21] of 1,3-zwitterion **19** to the double bonds of the starting or formed compounds. Here, two principal processes are observed: the reaction of zwitterion **19** with the second molecule of the starting cyclopropane **2** or cyclopentene **3** formed from it (Scheme 5,

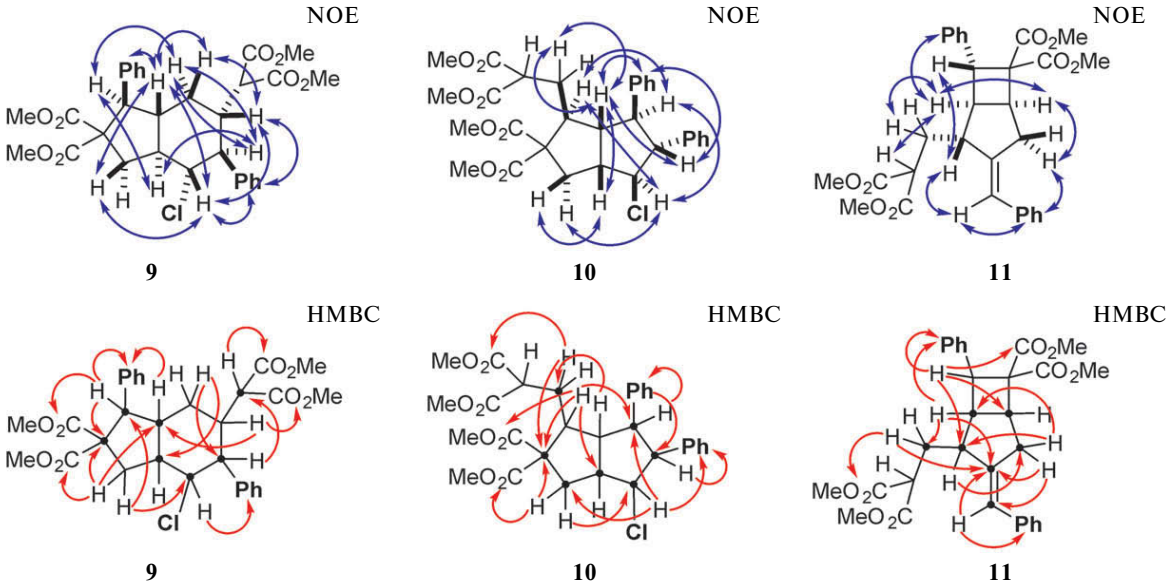
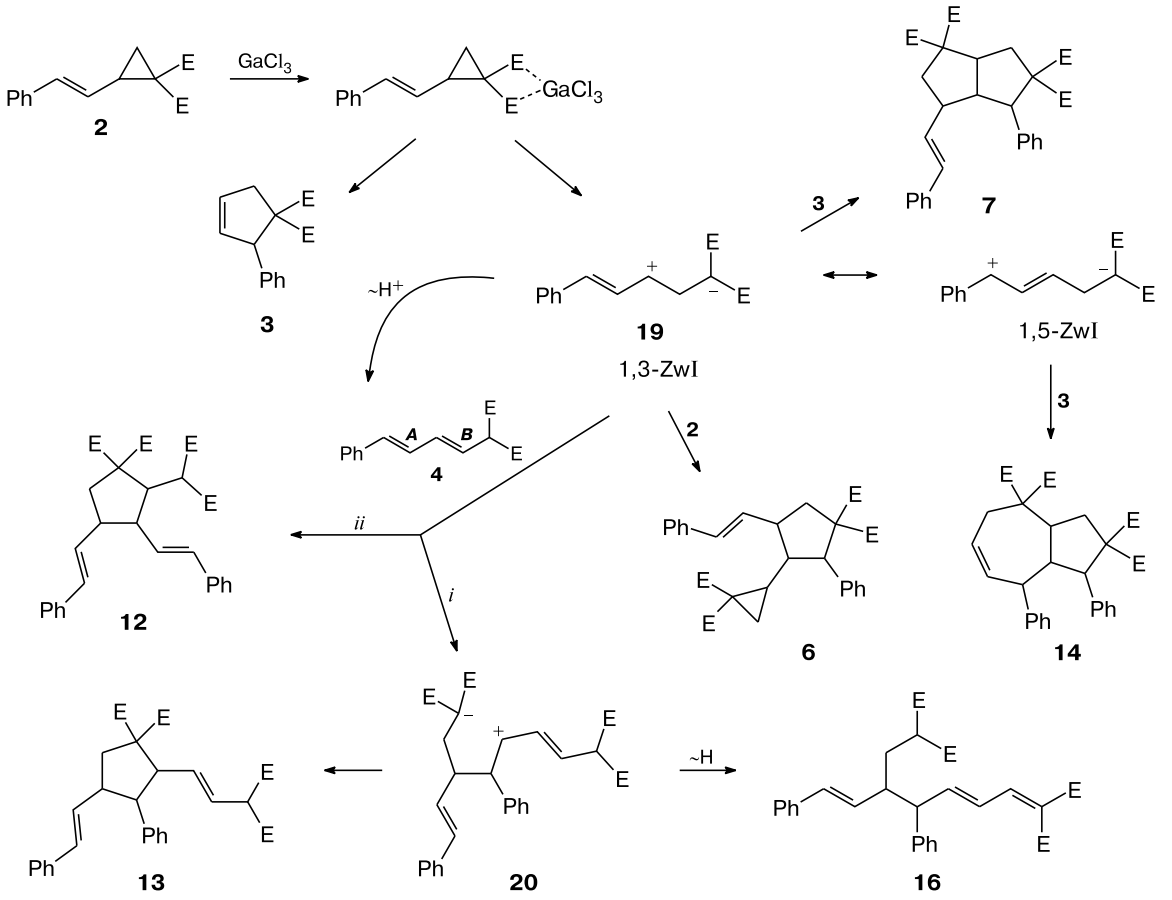



**Fig. 1.** Key interactions in the NOESY and HMBC spectra of compounds **9**—**11**.
*Note*. Fig. 1 is available in full color on the web page of the journal (http://www.linkspringer.com).

**Scheme 5**

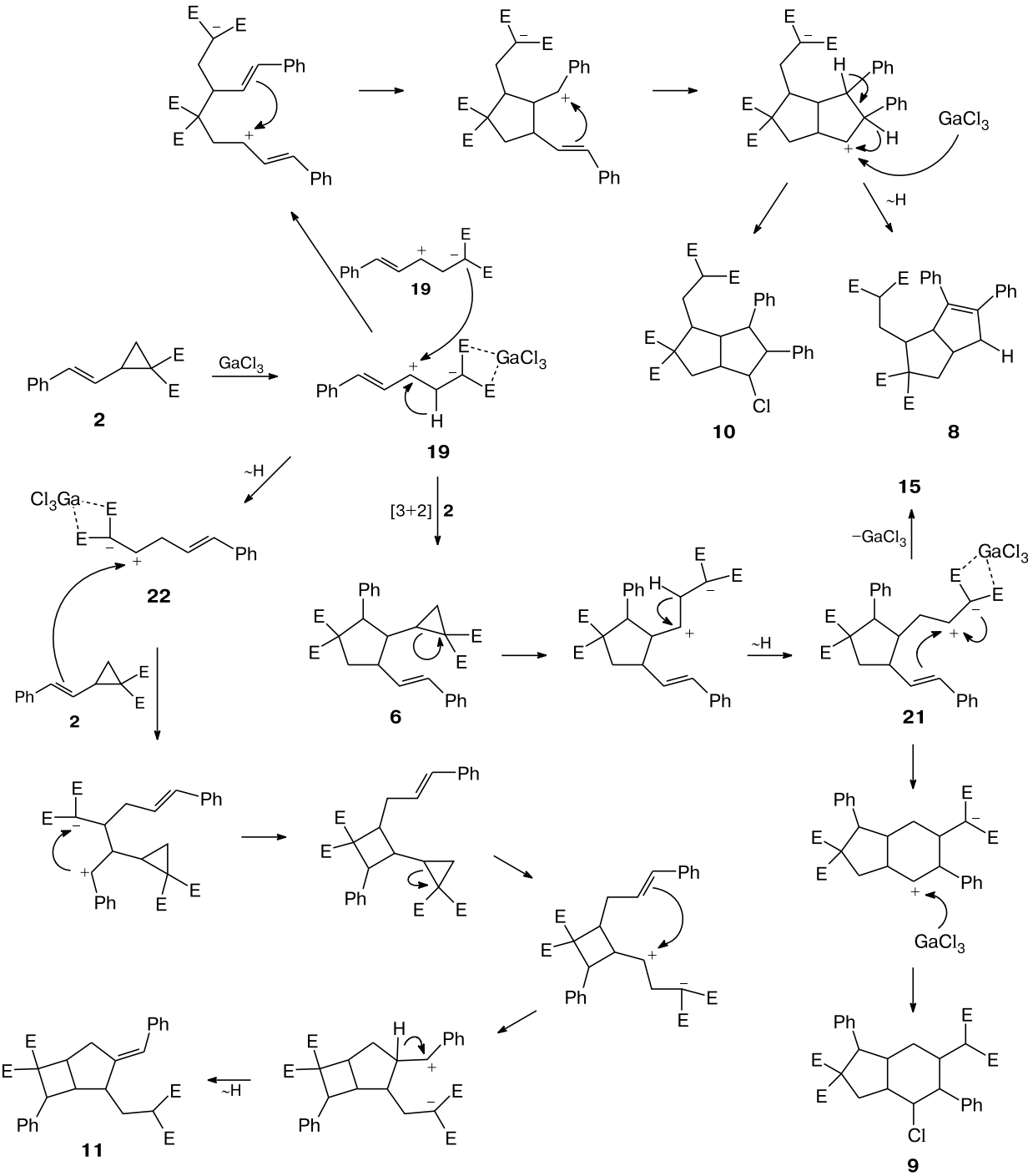



E = $CO_2Me$
*Note.* 1.3-ZwI is a classic 1,3-zwitterion, 1,5-ZwI is a 1,5-zwitterion.

the main directions are shown in blue). Minor directions are also versions of formal [3+2] cycloaddition, but already with the isomeric diene **4**. In this case, the cyclization of 1,5-zwitterion **20** is accompanied by the hydride shift with the formation of substituted octa-1,3,7-triene **16**.

The cascade processes at the temperatures around −80 °C also proceed through the initial generation of the gallium complex **19** (Scheme 6), however, further processes are more complicated and have at least three independent cascade chains, in one of which the branching

**Scheme 6**



occurs only in the last step, with all of them being new and original. Moreover, all the processes proceed with clearly preset stereochemistry leading to the formation of the only diastereomer despite of the formation of several stereocenters.

Thus, the formation of the bicyclo[3.3.0]octane fragment of compounds **8** and **10** occurs *via* the reaction of two zwitterions **19** and two subsequent carbocationic cyclizations with the formation of two fused five-membered rings. Only the last step is different: dimer **8** is formed through the elimination of a proton and the double bond migration, while dimer **10** through the chloride anion addition.

The bicyclo[4.3.0]nonane structure **9** is formed from dimer **6**, which is actually yet another donor-acceptor cyclopropane. First, its treatment with $GaCl_3$ leads to the cyclopropane ring opening and a key 1,2-zwitterionic gallium complex **21** is generated after the proton migration, which then cyclizes with the formation of the six-membered ring (Scheme 6). The formation of intermediate **21** is confirmed by the isolation of its "decomplexed" form **15** as one of the minor products.

The fact of the formation of bicyclic dimer **11** containing a cyclobutane ring is very interesting. Generally speaking, it is not typical of the reactions involving DAC to give cyclobutanes, and the formation of compound **11** is a rare example. This pathway suggests the formation of a key 1,2-zwitterionic gallium complex **22**, which then reacts with the second molecule of the starting cyclopropane **2** with the intramolecular cyclization at the styryl double bond. After opening of the second cyclopropane ring, the second annulated five-membered ring is formed. The reaction conditions should not be too drastic in order not to open the cyclobutane ring formed. The last step, that is the proton migration to the malonyl fragment, forms the *exo*-cyclic double bond with the *E*-configuration of substituents; the low temperature of the reaction helps to avoid its isomerization to more favorable *endo*-cyclic double bond.

Special attention should be paid to compounds **9** and **11**, the formation of which requires involvement of 1,2-zwitterionic gallium complexes **21** and **22**, which are new examples of 1,2-zwitterionic reactivity of DAC.[17,29—32] A possibility of this type of transformations is provided by a specific feature of $GaCl_3$ to act as a Lewis acid, which was successfully used for styrylcyclopropane **2**, as well (see Scheme 6).

In conclusion, we for the first time accomplished and studied in detail the dimerization of 2-styrylcyclopropane-1,1-dicarboxylate upon treatment with gallium trichloride. Using a fine variation in the reaction conditions, we successfully developed and effected a wide range of cascade dimerization processes including generation and transformation of different carbo-centers, leading to the formation of original cyclic structures. In these reactions, the reaction centers of the styryl substituent were efficiently involved, which has not been done earlier for such a cyclopropane. Many compounds, despite the formation of several stereocenters, were obtained as the only diastereomer. A chlorine atom was introduced into some structures, that increased their functionality. The formation of a cyclobutane ring in one of the dimers is also interesting, since such cycles are formed extremely rare in similar reactions and are a unique type of the DAC reactivity. The only disadvantage of this range of reactions are the low yields of the dimeric products, caused by the ready proceeding of intramolecular rearrangement to cyclopentenedicarboxylate **3** and oligomerization processes. However, the low yields are partially compensated by the one-pot assembling the final structures and very high diastereoselectivity. This variety of the processes efficiently demonstrates importance of our new approaches to the diversification of the DAC reactivity types and leads to the development of new chemistry of this interesting class of compounds.

## Experimental

$^1H$ and $^{13}C$ NMR spectra were recorded on Bruker AMX-III 400 (400.1 and 100.6 MHz, respectively) and Bruker AVANCE II 300 spectrometer (300 and 75 MHz, respectively) for solutions in $CDCl_3$ containing 0.05% of $Me_4Si$ as an internal standard. Assignment of signals and determination of isomeric composition of compounds were carried out using homo- and heteronuclear 1D and 2D correlation spectra: 1D DEPT-135, 2D COSY, TOCSY, NOESY, HSQC, edited-HSQC and HMBC. IR spectra were recorded on a FT-IR spectrometer in solution of $CHCl_3$ (0.5—2%). High resolution mass spectra (HRMS) were recorded using electrospray ionization (ESI).[33] Thin-layer chromatography was carried out on Merck Silufol chromatographic plates. Merck silica gel 60 (0.040—0.063 mm) was used for preparative chromatography. Anhydrous $GaCl_3$ was purchased from Aldrich, all the manipulations with it were carried out under anhydrous argon. The solvents of the reagent grade quality (>99.5%) were used without additional purification. Dichloromethane for the work with $GaCl_3$ was first maintained over granulated KOH and then distilled over $P_2O_5$ under anhydrous argon.

**Synthesis of compounds 3—11 (general procedure).** Anhydrous gallium chloride was added to a solution of styrylmalonate **2** (200 mg, 0.678 mmol) in anhydrous dichloromethane (7.5 mL) under argon and the reaction mixture was stirred according to the conditions indicated in Schemes 2 or 4. All the conditions should be strictly followed. Then, a 5% solution of hydrochloric acid (5 mL) was added to the reaction mixture, which was extracted with dichloromethane (3×10 mL). The combined organic phases were dried with anhydrous $MgSO_4$ and the solvent was evaporated *in vacuo*. The obtained compounds were isolated and additionally purified using column and/or thin-layer chromatography, using mixtures of benzene and ethyl acetate in different ratios as an eluent. If necessary, a cascade of several sequential

chromatographic procedures was used for separation of diastereomers and isolation of pure compounds.

**Dimethyl 2-phenylcyclopent-3-ene-1,1-dicarboxylate (3).** The yield was 97%. A heavy colorless oil. $^1$H NMR (400 MHz, $CDCl_3$), δ: 7.28—7.14 (m, 5 H, Ph); 5.86 (ddd, 1 H, =CH, $J$ = 5.8 Hz, $J$ = 4.4 Hz, $J$ = 2.2 Hz); 5.69 (dq, 1 H, =CH, $J$ = 5.8 Hz, $J$ = 2.2 Hz); 4.89 (br.s, 1 H, CH); 3.75 (s, 3 H, OMe); 3.47 (ddd, 1 H, $H_a$, $CH_2$, $J$ = 17.5 Hz, $J$ = 4.7 Hz, $J$ = 2.4 Hz); 3.08 (s, 3 H, OMe); 2.82—2.74 (m, 1 H, $H_b$, $CH_2$).

**Dimethyl 2-((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl)malonate (4).** The yield was 20%. A heavy colorless oil. $^1$H NMR (400 MHz, $CDCl_3$), δ: 7.41—7.20 (m, 5 H, Ph); 6.78 (dd, 1 H, H(3), $J$ = 15.7 Hz, $J$ = 10.4 Hz); 6.57 (d, 1 H, H(4), $J$ = 15.7 Hz); 6.38 (dd, 1 H, H(2), $J$ = 15.3 Hz, $J$ = 10.4 Hz); 5.99 (dd, 1 H, H(1), $J$ = 15.3 Hz, $J$ = 9.0 Hz); 4.14 (d, 1 H, CH, $J$ = 9.0 Hz); 3.76 (s, 6 H, 2 OMe).

**Methyl 2-hydroxy-1,1´-biphenyl-3-carboxylate (5).** The yield was 45%. A heavy colorless oil. IR ($CHCl_3$), ν/cm$^{-1}$: 3036, 3033, 3021, 3013, 2955, 2874, 1729, 1674, 1614, 1495, 1454, 1441, 1329, 1285, 1284, 1234. $^1$H NMR (400.1 MHz, $CDCl_3$), δ: 11.27 (s, 1 H, OH); 7.86 (dd, 1 H, H(4) or H(6), $J$ = 7.9 Hz, $J$ = 1.6 Hz); 7.61—7.55 (m, 2 H, *o*-Ph); 7.52 (dd, 1 H, H(6) or H(4), $J$ = 7.5 Hz, $J$ = 1.6 Hz); 7.47—7.39 (m, 2 H, *m*-Ph); 7.39—7.31 (m, 1 H, *p*-Ph); 6.98—6.91 (dd, 1 H, H(5), $J$ = 7.9 Hz, $J$ = 7.5 Hz); 3.98 (s, 3 H, OMe). $^{13}$C NMR (100.6 MHz, $CDCl_3$), δ: 170.1 (COO), 158.9 (C(2)), 137.1 (*ipso*-Ph), 136.6 and 128.9 (C(4) and C(6)), 130.4 and 112.5 (C(1) and C(3)), 128.8 (*o*-Ph), 128.0 (*m*-Ph), 127.8 (*p*-Ph), 119.0 (C(5)), 52.2 (OMe). HRMS (ESI), found: $m/z$ 251.0674; $C_{14}H_{12}NaO_3$; calculated: 251.0679 $[M + Na]^+$.

**Dimethyl (2*SR*,3*RS*,4*SR*)-3-[(*RS*)- and dimethyl (2*SR*,3*RS*,4*SR*)-3-[(*SR*)-2,2-bis(methoxycarbonyl)cyclopropyl]-2-phenyl-4-(*E*)-styrylcyclopentane-1,1-dicarboxylate (6).** The yield was 27%. The ratio of diastereomers 3 : 1.

Major diastereomer. A heavy colorless oil. IR ($CHCl_3$), ν/cm$^{-1}$: 3021, 2954, 2849, 1730, 1496, 1437, 1262, 1225 cm$^{-1}$. $^1$H NMR (400.1 MHz, $CDCl_3$), δ: 7.42—7.08 (m, 10 H, 2 Ph); 6.52 (d, 1 H, =CH, $J$ = 15.8 Hz); 6.21 (dd, 1 H, =CH, $J$ = 15.8 Hz, $J$ = 7.8 Hz); 4.13 (d, 1 H, H(2), $J$ = 6.6 Hz); 3.78, 3.67, 3.09, 2.86 (all s, 12 H, 4 OMe); 2.74—2.61 (m, 1 H, H(4)); 2.42—2.34 (m, 2 H, $H_2C(5)$); 2.36—2.25 (m, 1 H, CH); 2.01 (td, 1 H, H(3), $J$ = 9.7 Hz, $J$ = 6.6 Hz); 1.49 (dd, 1 H, $H_a$, $CH_2$, $J$ = 8.1 Hz, $J$ = 4.9 Hz); 1.34 (dd, 1 H, $H_b$, $CH_2$, $J$ = 9.3 Hz, $J$ = 4.9 Hz). $^{13}$C NMR (100.6 MHz, $CDCl_3$), δ: 172.7, 170.4, 169.5 and 168.6 (4 COO), 141.1 and 137.2 (2 *ipso*-Ph), 131.6 and 130.9 (HC=CH), 129.3, 128.7, 128.0, 127.5, 127.0 and 126.3 (2 Ph), 66.2 (C(1)), 56.4 (C(2)), 53.2, 52.6, 52.0 and 51.9 (4 OMe), 50.9 (C(3)), 48.5 (C(4)), 40.6 (C(5)), 34.0 (CH), 32.1 (C), 20.7 ($CH_2$). HRMS (ESI), found: $m/z$ 543.1975; $C_{30}H_{32}NaO_8$; calculated: 543.1989 $[M + Na]^+$.

Minor diastereomer. A heavy colorless oil. IR ($CHCl_3$), ν/cm$^{-1}$: 3021, 2953, 2852, 1731, 1496, 1437 cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$), δ: 7.37—7.11 (m, 10 H, 2 Ph); 6.51 (d, 1 H, =CH, $J$ = 15.7 Hz); 6.05 (dd, 1 H, =CH, $J$ = 15.7 Hz, $J$ = 8.4 Hz); 4.12 (d, 1 H, H(2), $J$ = 10.9 Hz); 3.74, 3.66, 3.00, 2.99 (all s, 12 H, 4 OMe); 2.87 (dd, 1 H, $H_a$(5), $J$ = 13.6 Hz, $J$ = 12.0 Hz); 2.63—2.53 (m, 1 H, H(3)); 2.27—2.16 (m, 2 H, $H_a$(5) and H(4)); 1.83 (td, 1 H, CH, $J$ = 9.7 Hz, $J$ = 8.4 Hz); 1.02 (dd, 1 H, $H_a$, $CH_2$), $J$ = 9.7 Hz, $J$ = 4.9 Hz); 0.94—0.87 (m, 1 H, $H_b$, $CH_2$). $^{13}$C NMR (100.6 MHz, $CDCl_3$), δ: 172.7, 170.8, 170.5 and 168.6 (4 COO), 140.9 and 137.4 (2 *ipso*-Ph), 131.4 and 130.1 (HC=CH), 128.8, 128.7, 128.0, 127.9, 126.4 and 126.2 (2 Ph), 64.8 (C), 57.0 (C(2)), 53.0, 52.7, 52.2 and 51.9 (4 OMe), 48.8 (C(4)), 47.7 (C(3)), 40.5 (C(5)), 32.5 (CH), 29.0 (C), 19.3 ($CH_2$). HRMS (ESI), found: $m/z$ 543.1981; $C_{30}H_{32}NaO_8$; calculated: 543.1989 $[M + Na]^+$.

**Tetramethyl (3*RS*),3a*SR*,4*SR*,6a*SR*- and tetramethyl (3*SR*),3a*SR*,4*SR*,6a*SR*-4-phenyl-3-(*E*)-styrylhexahydropentalene-1,1,5,5-tetracarboxylate (7).** The yield was 27%. A mixture of diastereomers (the ratio of 1.5 : 1). A heavy colorless oil. IR ($CHCl_3$), ν/cm$^{-1}$: 3021, 2954, 2928, 2847, 2401, 1729, 1602, 1496, 1455, 1436, 1272, 1224 cm$^{-1}$. HRMS (ESI), found: $m/z$ 543.1981; $C_{30}H_{32}NaO_8$; calculated: 543.1989 $[M + Na]^+$.

Major diastereomer. $^1$H NMR (400 MHz, $CDCl_3$), δ: 7.34—6.95 (m, 10 H, 2 Ph); 6.04 (d, 1 H, =CH, $J$ = 15.7 Hz); 5.84 (dd, 1 H, =CH, $J$ = 15.7 Hz, $J$ = 7.8 Hz); 3.88 (d, 1 H, H(4), $J$ = 11.8 Hz); 3.84, 3.75, 3.74 and 2.99 (all s, 12 H, 4 OMe); 3.00—2.91 (m, 1 H, $H_a$(2)); 2.83—2.74 (m, 1 H, H(6a)); 2.72—2.62 (m, 1 H, H(3a)); 2.66—2.58 (m, 1 H, $H_b$(2)); 2.56—2.47 (m, 2 H, H(3) and $H_a$(6)); 2.33—2.25 (m, 1 H, $H_b$(6)). $^{13}$C NMR (100.6 MHz, $CDCl_3$), δ: 172.7, 172.5, 170.2 and 169.3 (4 COO), 138.0 and 137.6 (2 *ipso*-Ph), 131.7 and 130.0 (HC=CH), 128.8, 128.5, 128.1 and 126.3 (4 *o*-Ph and 4 *m*-Ph), 127.3 and 127.1 (2 *p*-Ph), 71.0 (C(5)), 57.7 (C(1)), 56.2 (C(3a)), 54.6 (C(6a)), 52.9, 52.8, 52.5 and 52.1 (4 OMe), 51.8 (C(4)), 45.5 (C(2)), 33.5 (C(6)), 33.3 (C(3)).

Minor diastereomer. $^1$H NMR (400 MHz, $CDCl_3$), δ: 7.34—6.95 (m, 10 H, 2 Ph); 6.08—6.05 (m, 2 H, HC=CH); 3.84, 3.76, 3.72, 3.01 (all s, 12 H, 4 OMe); 3.83 (d, 1 H, H(4), $J$ = 12.5 Hz); 3.35 (dd, 1 H, $H_a$(2), $J$ = 14.8 Hz, $J$ = 8.0 Hz); 2.97—2.89 (m, 1 H, H(3a)); 2.82—2.76 (m, 1 H, H(3)); 2.56—2.45 (m, 2 H, H(6a) and $H_a$(6)); 2.35—2.25 (m, 2 H, $H_b$(2) and $H_b$(6)). $^{13}$C NMR (100.6 MHz, $CDCl_3$), δ: 173.1, 171.0, 170.7, 170.6 (4 COO), 138.1 and 137.7 (2 *ipso*-Ph), 131.8 and 129.0 (HC=CH), 128.5, 128.1, 128.0 and 126.4 (4 *o*-Ph and 4 *m*-Ph), 127.2 and 127.1 (2 *p*-Ph), 70.2 (C(5)), 57.1 (C(1)), 54.5 (C(3a)), 53.0, 52.8, 52.7 and 52.0 (4 OMe), 43.1 (C(6a)), 48.7 (C(4)), 45.3 (C(2)), 36.9 (C(3)), 33.3 (C(6)).

**Dimethyl (1*SR*,3a*RS*,6a*RS*)-1-[3-methoxy-2-(methoxycarbonyl)-3-oxopropyl]-5,6-diphenyl-3,3a,4,6a-tetrahydropentalene-2,2(1*H*)-dicarboxylate (8).** The yield was 19%. A heavy colorless oil. IR ($CHCl_3$), ν/cm$^{-1}$: 3021, 2955, 2848, 2401, 1731, 1495, 1436, 1267, 1225 cm$^{-1}$. $^1$H NMR (400.1 MHz, $CDCl_3$), δ: 7.28—7.00 (m, 10 H, 2 Ph); 3.73, 3.68, 3.57, 3.55 (all s, 12 H, 4 OMe); 3.54—3.48 (m, 1 H, H(6a)); 3.20—3.10 (m, 1 H, H(3a)); 3.14 (t, 1 H, CH), $J$ = 7.2 Hz); 3.00 (ddq, 1 H, $H_a$(4), $J$ = 16.6 Hz, $J$ = 9.3 Hz, $J$ = 1.4 Hz); 2.73 (m, 1 H, $H_b$(4)); 2.72 (dd, 1 H, $H_a$(3), $J$ = 13.5 Hz, $J$ = 8.3 Hz); 2.63 (dd, 1 H, H(1), $J$ = 12.8 Hz, $J$ = 7.1 Hz); 2.14 (dd, 1 H, $H_b$(3), $J$ = 13.5 Hz, $J$ = 7.1 Hz); 1.92—1.77 (m, 2 H, $CH_2$). $^{13}$C NMR (100.6 MHz, $CDCl_3$), δ: 171.9, 171.1, 169.7 and 169.5 (4 COO), 139.8 (C(8)), 137.8, 137.5 (2 *ipso*-Ph), 136.6 (C(5)), 129.1, 128.2 (4 *o*-Ph), 128.5, 127.9 (4 *m*-Ph), 126.9 and 126.8 (2 *p*-Ph), 65.1 (C(2)), 63.1 (C(6a)), 52.8, 52.5, 52.4 and 52.4 (4 OMe), 49.8 (CH), 47.9 (C(1)), 44.5 (C(3a)), 42.3 (C(3)), 37.6 (C(3a)), 31.8 ($CH_2$). HRMS (ESI), found: $m/z$ 543.1979; $C_{30}H_{32}NaO_8$; calculated: 543.1989 $[M + Na]^+$.

**Dimethyl (1*RS*,3a*SR*,4*RS*,5*SR*,6*RS*,7a*SR*)-4-chloro-6-(1,3-dimethoxy-1,3-dioxopropan-2-yl)-1,5-diphenyloctahydro-*2H*-indene-2,2-dicarboxylate (9).** The yield was 20%. A heavy colorless oil. IR ($CHCl_3$), ν/cm$^{-1}$: 3065, 3020, 2955, 2930, 2850, 2400, 1728, 1602, 1496, 1455, 1455, 1436, 1273, 1224 cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$), δ: 7.42—7.16 (m, 10 H, 2 Ph); 4.00 (dd, 1 H, H(4), *J* = 10.9 Hz, *J* = 10.3 Hz); 3.90 (d, 1 H, H(1), *J* = 12.3 Hz); 3.75, 3.65, 3.50, 3.04 (all s, 12 H, 4 OMe); 3.12 (d, 1 H, CH, *J* = 3.3 Hz); 2.91 (dd, 1 H, H(5), *J* = 11.8 Hz, *J* = 10.3 Hz); 2.66 (dd, 1 H, $H_a$(3), *J* = 13.8 Hz, *J* = 12.0 Hz); 2.54 (dd, 1 H, $H_b$(3), *J* = 13.8 Hz, *J* = 7.0 Hz); 2.49 (dddd, 1 H, H(6), *J* = 12.2 Hz, *J* = 11.8 Hz, *J* = 3.5 Hz, *J* = 3.3 Hz); 2.18 (dddd, 1 H, H(7a), *J* = 12.3 Hz, *J* = 12.2 Hz, *J* = 12.0 Hz, *J* = 3.0 Hz); 1.94 (dddd, 1 H, H(3a), *J* = 12.2 Hz, *J* = 12.0 Hz, *J* = 10.9 Hz, *J* = 7.0 Hz); 1.88 (ddd, 1 H, $H_a$(7), *J* = 13.0 Hz, *J* = 3.5 Hz, *J* = 3.0 Hz); 1.39 (ddd, 1 H, $H_b$(7), *J* = 13.0 Hz, *J* = 12.2 Hz, *J* = 12.0 Hz). $^{13}$C NMR (100.6 MHz, $CDCl_3$), δ: 172.9, 171.1, 169.1, 168.5 (4 COO), 140.1 and 137.6 (2 *ipso*-Ph), 128.8 and 128.3 (4 *o*-Ph and 4 *m*-Ph), 127.7 and 127.3 (2 *p*-Ph), 68.2 (C(4)), 64.4 (C(2)), 56.2 (C(1)), 55.8 (C(5)), 52.9, 52.4, 52.2 and 52.2 (4 OMe), 52.7 (C(3a)), 51.7 (CH), 46.7 (C(7a)), 44.1 (C(6)), 39.2 (C(3)), 30.5 (C(7)). HRMS (ESI), found: *m*/*z* 557.1950; $C_{30}H_{34}ClO_8$; calculated: 557.1937 $[M + H]^+$.

**Dimethyl (1*SR*,3a*RS*,4*SR*,5*RS*,6*RS*,6a*RS*)-4-chloro-1-[3-methoxy-2-(methoxycarbonyl)-3-oxopropyl]-5,6-diphenylhexahydropentalene-2,2(*1H*)-dicarboxylate (10).** The yield was 14%. A heavy colorless oil. IR ($CHCl_3$), ν/cm$^{-1}$: 3064, 3032, 3025, 3015, 2955, 2847, 1730, 1602, 1495, 1437, 1272, 1235, 1235, 1229, 1222, 1211 cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$), δ: 7.42—7.04 (m, 10 H, 2 Ph); 3.76, 3.75, 3.73, 3.62 (all s, 12 H, 4 OMe); 3.96 (dd, 1 H, H(4), *J* = 10.8 Hz, *J* = 9.5 Hz); 3.45—3.37 (m, 1 H, CH); 3.41—3.31 (m, 1 H, H(5)); 3.29—3.15 (m, 1 H, H(3a)); 3.20—3.11 (m, 1 H, H(6)); 2.90 (dd, 1 H, $H_a$(3), *J* = 13.8 Hz, *J* = 8.4 Hz); 2.82—2.73 (m, 1 H, H(1)); 2.63—2.51 (m, 1 H, H(6a)); 2.07—1.97 (m, 1 H, $H_b$(3)); 1.94—1.81, 1.63—1.51 (both m, 2 H, $CH_2$). $^{13}$C NMR (100.6 MHz, $CDCl_3$), δ: 172.2, 171.0, 169.9 and 169.5 (4 COO), 142.4 and 137.9 (2 *ipso*-Ph), 128.7, 128.5 (4 *m*-Ph), 127.8 and 127.7 (4 *o*-Ph), 127.3, 126.8 (2 *p*-Ph), 128.8, 128.17, 128.16, 127.9, 127.1 and 126.7 (2 *p*-Ph), 70.2 (C(4)), 66.5 (C(5)), 66.1 (C(2)), 57.4 (C(6)), 56.1 (C(6a)), 52.9, 52.7, 52.5 and 52.4 (4 OMe), 51.6 (C(3a)), 49.9 (C(1)), 49.4 (CH), 39.5 (C(3)), 30.2 ($CH_2$). HRMS (ESI), found: *m*/*z* 579.1757; $C_{30}H_{33}ClNaO_8$; calculated: 579.1756 $[M + Na]^+$.

**Dimethyl (1*RS*,2*RS*,5*SR*,7*RS*)-3-((*E*)-benzylidene)-2-[3-methoxy-2-(methoxycarbonyl)-3-oxopropyl]-7-phenylbicyclo-[3.2.0]heptane-6,6-dicarboxylate (11).** The yield was 22%. A heavy colorless oil. IR ($CHCl_3$), ν/cm$^{-1}$: 3036, 3011, 2955, 2929, 2853, 1730, 1646, 1601, 1496, 1437, 1276, 1235 cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$), δ: 7.40—7.15 (m, 10 H, 2 Ph); 6.50 (s, 1 H, =CH); 3.93 (d, 1 H, H(7), *J* = 8.0 Hz); 3.73, 3.60, 3.33, 3.14 (s, 12 H, 4 OMe); 3.61—3.58 (m, 1 H, H(5)); 3.51 (t, 1 H, CH, *J* = 7.3 Hz); 3.03 (t, 1 H, H(1), *J* = 7.7 Hz); 2.84—2.75 (m, 1 H, $H_a$(4)); 2.55 (d, 1 H, $H_b$(4), *J* = 17.8 Hz); 2.48 (dd, 1 H, H(2), *J* = 10.1 Hz, *J* = 6.0 Hz); 2.07—1.99 (m, 2 H, $CH_2$). $^{13}$C NMR (100.6 MHz, $CDCl_3$), δ: 170.0, 169.9, 169.8 and 169.7 (4 COO), 145.8 (C(3)), 138.2 and 137.6 (2 *ipso*-Ph), 128.8, 128.17, 128.16, 127.9 (12 *o*-Ph and 4 *m*-Ph), 127.1 and 126.7 (2 *p*-Ph), 126.5 (=CH), 61.5 (C(6)), 52.7, 52.6, 52.2 and 52.0 (4 OMe), 52.2 (C(2)), 50.1 (CH), 47.3 (C(7)), 41.9 (C(1)), 40.4 (C(5)), 32.8 ($CH_2$), 30.0 (C(4)). HRMS (ESI), found: *m*/*z* 543.1981; $C_{30}H_{32}NaO_8$; calculated: 543.1989 $[M + Na]^+$.

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