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Stereoselective Double Lewis Acid/Organo-Catalyzed Dimerization of Donor–Acceptor Cyclopropanes into Substituted 2-Oxabicyclo[3.3.0]octanes

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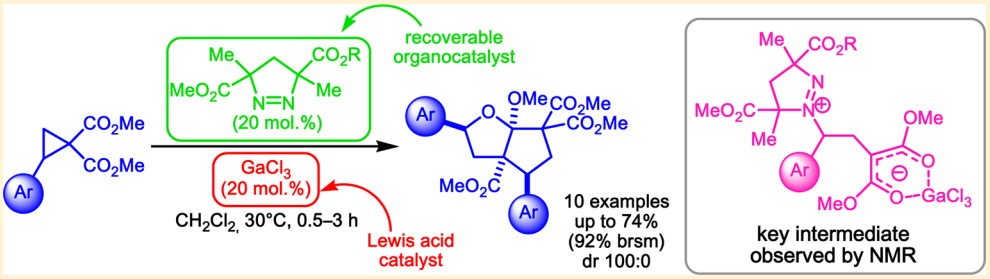
Supporting Information



ABSTRACT: A new approach for the dimerization of donor–acceptor cyclopropanes (2-arylcyclopropane-1,1-dicarboxylates) under double-catalysis conditions by treatment with 20 mol % of $GaCl_3$ and dimethyl 3,5-dimethyl-1-pyrazoline-3,5-dicarboxylate as a specific organocatalyst has been found. Under these conditions, the starting compounds are regio- and stereospecifically converted into polysubstituted 2-oxabicyclo[3.3.0]octanes. Two new rings, one C–O bond, and two C–C bonds are formed in this process, and four stereocenters are thus created. The reaction mechanism was thoroughly studied by NMR spectroscopy, and a number of intermediates were detected.

INTRODUCTION

The 2-oxabicyclo[3.3.0]octane fragment occurs in the structures of more than 80 natural compounds belonging to various groups and having a broad range of biological activity, such as antibacterial, antifungal, antifeedant, and immunosuppressant activity.[1] To date, compounds with this fragment were isolated from various natural sources (Figure 1). The existing synthetic methods for making of the 2-oxabicyclo[3.3.0]octane fragment generally involve various condensation reactions and are determined, to a considerable extent, by the structure of the target compounds. Setting the required stereochemistry of substituents is also a considerable problem of these methods.[2]

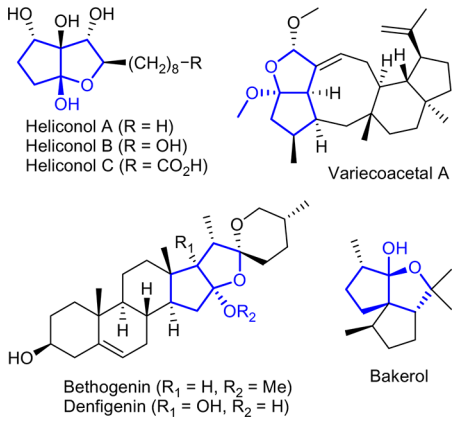


Figure 1. Examples of natural compounds with biological activity incorporating the 2-oxabicyclo[3.3.0]octane fragment.

In this study, we report a new synthetic strategy toward the 2-octabicyclo[3.3.0]octane core through an interaction of two molecules of donor–acceptor (DA) cyclopropanes that undergo cyclodimerization under double catalysis conditions. Donor–acceptor cyclopropanes (cyclopropanes with donor and acceptor substituents in vicinal position) have recently received considerable attention in contemporary organic synthesis as sources of 1,3-dipoles that are generated from them on treatment with Lewis acids.[3] The capability of donor–acceptor cyclopropanes to undergo [2 + 3]-, [3 + 3]-, and [3 + 4]-dipolar cycloaddition with various substrates[4] is currently used to build five-, six-, and seven-membered heterocycles. These reactions can be performed enantioselectively,[5] which makes them very attractive for application in organic synthesis. More than 20 full syntheses of natural compounds of various classes based on donor–acceptor cyclopropanes have been carried out to date.[6]

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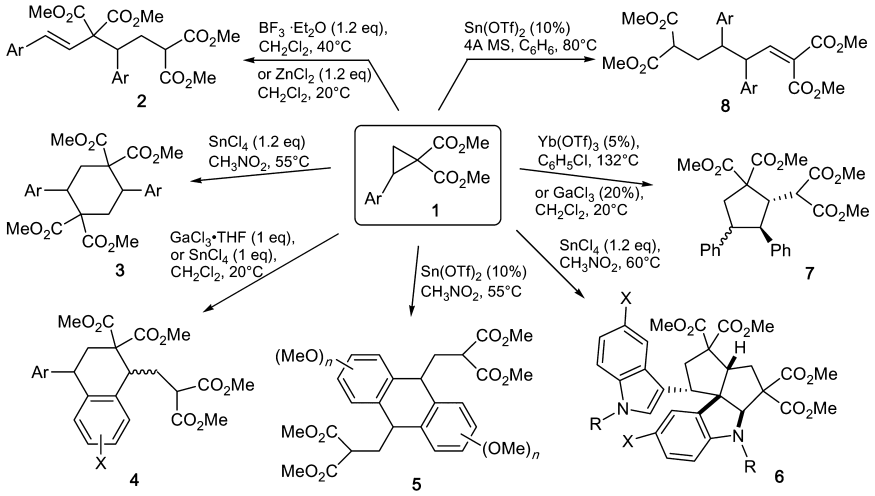
Scheme 1. Known Pathways of Dimerization of DA Cyclopropanes



It was shown recently[7,8] that, in the absence of unsaturated substrates or other compounds that trap the 1,3-dipoles being generated, donor–acceptor (DA) cyclopropanes themselves can undergo dimerization on treatment with Lewis acids; depending on the conditions and the nature of the aryl substituent, the reactions can give compounds of various classes. In fact, dimerization of 2-arylcyclopropanedicarboxylates **1** in the presence of 120 mol % of $ZnCl_2$ or $BF_3{\cdot}Et_2O$ in dichloromethane gave linear tetraesters **2** as the major products. Reactions of the same DA compounds in the presence of $SnCl_4$ in nitromethane gave cyclohexane-1,1,4,4-tetracarboxylates **3** in up to 80% yields.[8b] Treatment of 2-arylcyclopropanedicarboxylates **1**, which are not substituted at the *ortho*-position, with an equimolar amount of $SnCl_4$ in a low-polar solvent or in the presence of 10 mol % $Sn(OTf)_3$ in nitromethane gave dimers with electrophilic substitution in the aromatic ring, viz. compounds **4** or **5**, with yields up to 90%.[8b] Efficient formation of tetralin derivative **4a** also occurred on treatment of 2-phenylcyclopropanedicarboxylate **1a** with an equimolar amount of the $GaCl_3{\cdot}$THF complex (20 °C, 12 h).[7]

Heating of indole-containing cyclopropanedicarboxylates in nitromethane in the presence of $SnCl_4$ resulted in the coupling of the electrophilic and nucleophilic centers of two activated cyclopropane molecules followed by electrophilic *ipso*-attack to give pentaleno[1,6-*a*,*b*]indole derivatives **6** as the major isolable compounds.[9] Unlike some other dimers of DA cyclopropanes, this polycyclic structure was formed as a single diastereomer.

Yet another unusual direction of dimerization of DA cyclopropanes independently discovered by two groups of researchers[7,8a] involves their conversion to polysubstituted cyclopentanes *E,E*- and *E,Z*-**7** in yields higher than 70% on treatment with 20 mol % of anhydrous $GaCl_3$ in dichloromethane[7] or with 5 mol % of $Yb(OTf)_3$ in chlorobenzene under reflux conditions[8a] (Scheme 1). In the case of the reaction of methoxyphenyl-substituted cyclopropanes **1** in the presence of Lewis acids ($Sn(OTf)_3$, $Yb(OTf)_3$, or MgI_2) and molecular sieves, linear dimers **8** were also identified[8a] in which the C–C bond, like in diarylcyclopentanes **7**, was formed between carbon atoms of the same type bearing aryl substituents. Thus, unique pathways of diverse dimerization of DA cyclopropanes on treatment with Lewis acids have been revealed using esters of 2-aryl(hetaryl)cyclopropanedicarboxylic acids as an example. In this work, we have studied yet another option of dimerization of DA cyclopropanes, now involving the ester group.

RESULTS AND DISCUSSION

1. Dimerization of Donor–Acceptor Cyclopropanes into Substituted 2-Oxabicyclo[3.3.0]octanes. In all of the conversions of DA cyclopropanes on treatment with Lewis acids noted above, the formation of dimerization products occurred exclusively due to the formation of new C–C bonds. We have found that if a tetrasubstituted 1-pyrazoline derivative, namely 3,5-dicarboxylate **9**, is additionally used in this $GaCl_3$-promoted reaction, DA cyclopropanes undergo yet another unusual conversion. As a result of this reaction, the C=O fragment of one of the ester groups is incorporated into the cyclic system of the product to give polyfunctional 2-oxabicyclo[3.3.0]octane **10**. It was found that this process only occurred under double-catalysis conditions, i.e., in the presence of $GaCl_3$ as the Lewis acid and 3,5-dicarboxylate **9** as the organocatalyst, while no analogues of this process have been found in the literature.

To optimize the conditions of this dimerization, we chose the most popular DA cyclopropane **1a** as well as anhydrous $GaCl_3$ and pyrazoline **9a** as catalysts (Table 1); the latter compound was quantitatively obtained by 1,3-dipolar cycloaddition of alkyl 2-diazopropionates to methyl methacrylate (Scheme 2).[11] To some degree, this catalytic system was selected arbitrarily. The fact is that, while studying the reactivity DA cyclopropanes toward various pyrazolines in the presence of Lewis acids[10a] and using **9a** as a possible acceptor of 1,3-dipolar intermediates, we observed the formation of a new compound **10a** whose structure represented a dimer of the original cyclopropane, whereas no reaction products of **1a** with pyrazoline **9a** were revealed.

Double catalysts, $GaCl_3$ and 1-pyrazoline **9**, should be present in equal molar amounts; if the molar ratio changes in any direction, the yield of 2-oxabicyclo[3.3.0]octane **10a** decreases considerably. The use of 20, 30, or 50 mol % of $GaCl_3$ and the same amounts of organocatalyst **9a** almost do not affect the yield of the target product if the yield is calculated with respect to converted cyclopropane (brsm, based upon recovered starting material); if the molar amount of the catalyst is increased, conversion of **1a** decreases and the absolute yield of the products decreases as well (Table 1, entries 6, 8, and 10).

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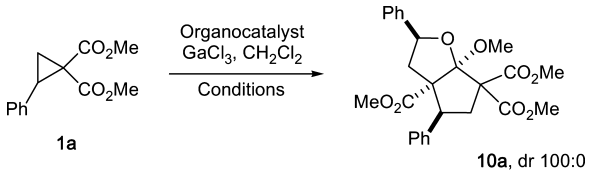
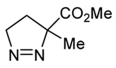
Table 1. Optimization of Reaction Conditions for the Cyclodimerization Reaction of 1a into 2-Oxabicyclo[3.3.0]octane 10a

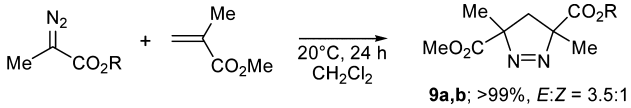


1a — 10a, dr 100:0

Entry	Organo-catalyst	Cat, mol.%	$GaCl_3$, mol.%	T, °C[a]	t, h[a]	Yield **10a**, % (brsm, %)[b]
1	—	—	20	20	0.2	—[c]
2	THF	100	100	20	12	—[d]
3	Ph–N=N–Ph	50	50	20	3	—[e]
4	*E*-**9a**	10	10	30	4	35[f,g]
5	*E*-**9a**	20	20	20	2.5	65[f,h]
6	*E*-**9a**	20	20	30	1.5	72 (90)[h]
7	*E*-**9a**	30	20	30	2	55[f,h]
8	*E*-**9a**	30	30	30	1.5	67 (96)[h]
9	*E*-**9a**	30	45	30	1	30[f,g]
10	*E*-**9a**	50	50	30	0.75	48 (95)[h]
11	*E*-**9a**	100	100	30	6	—[d]
12	*E*-**9a**	200	100	30	12	—[d]
13	*Z*-**9a**	20	20	30	1.5	60[f,h]
14	*E*-**9b**	20	20	30	1.5	75[f,h]
15	*E,Z*-**9b** (3.5:1)	20	20	30	1.5	70 (88)[h]
16	 **11**	50	50	20	0.2	—[i]

[a]Optimal time and temperature were defined by NMR monitoring of the reaction in an NMR tube. [b]Isolated yields (in parentheses, yields based on recovered starting materials). [c]Only dimer **7** was formed as a single product; for more details, see ref 7. [d]Only dimer **4** (Ar = Ph) was formed as a single product; for more details, see ref 7. [e]Only products of addition of **1a** to azobenzene were formed; for more details, see ref 12. [f]Yields determined by ^{1}H NMR. [g]Dimers **4** and **7** were formed as major products. [h]Dimers **2**, **4**, and **7** were also formed as minor products (yields 0–5% depending on conditions). [i]Only the product of addition of **1a** to pyrazoline **11** was formed; for more details, see ref 10.

Scheme 2. Synthesis of Tetrasubstituted 1-Pyrazolines 9 as New Organocatalysts



9a,b; >99%, *E*:*Z* = 3.5:1

R = Me (**a**); Et (**b**)

However, decreasing the amount of the catalyst to 10 mol % also results in a decrease in the yield of 2-oxabicyclo[3.3.0]-octane **10a** because of an increase in reaction time and formation of a number of side products (entry 4). We believe that the use of $GaCl_3$ and pyrazoline **9** in the amount of 20 mol % of each at a temperature near 30 °C provides the most optimal conditions.

It turned out that only α,α'-tetrasubstituted 1-pyrazolines act as organocatalysts. In this case, the isomeric composition of pyrazolines **9** only slightly affects the yield of 2-oxabicyclooctanes **10**, though the yield of cyclodimer **10a** is somewhat higher if *E*-**9a** is used compared to the *Z*-isomer (Table 1, entries 6 and 13). It is also possible to use a mixture of *E*- and *Z*-isomers (entry 15) formed in the reaction, which makes it unnecessary to isolate the *E*-isomer. Along with dimethyl ester **9a**, mixed ester **9b** can be used just as successfully (entries 6 and 14).

Attempts to use tertiary amines, azobenzene, or other 1-pyrazolines containing hydrogen atoms at the α-position to the N=N bond only resulted in changes in reaction pathway and gave known compounds. In fact, the addition of $GaCl_3$ to cyclopropanedicarboxylate **1a** and 1-pyrazoline **11** (Table 1, entry 16) resulted in a very fast reaction and complete involvement of the catalyst used[10] without observable formation of 2-oxabicyclooctane **10a**.

Other Lewis acids, such as $SnCl_4$, $TiCl_4$, $BF_3{\cdot}Et_2O$, $EtAlCl_2$, $Sc(OTf)_3$, $Yb(OTf)_3$, $In(OTf)_3$, $Ni(ClO_4)_2$, $Cu(OTf)_2$, and $Sn(OTf)_2$, even in combination with the same organocatalyst **9a**, failed to give even traces of 2-oxabicyclo[3.3.0]octane **10a**. In some cases, the reaction progress was rather insignificant, while in other cases, they followed known pathways without involving the ester group of the starting cyclopropane **1a**. Thus, the formation of 2-oxabicyclooctane **10a** was only observed if the double catalyst, $GaCl_3$ and 1-pyrazoline **9**, was used (Table 1, entries 4–10 and 13–15).

The yield of 2-oxabicyclooctane **10a** is also noticeably restricted by its low stability in acidic media. The reaction mixture kept at room temperature for 24 h no longer contained any noticeable amount of the target compound; hence, the reaction time should be as short as possible. Furthermore, in order to isolate 2-oxabicyclooctanes successfully, we developed a special procedure that involved cooling of the reaction mixture below 0 °C, $GaCl_3$ deactivation with excess tetrahydrofuran due to complexation of $GaCl_3$ with the oxygen of THF molecule, solvent removal in vacuo, and immediate isolation of the product by means of column chromatography on silica gel. 2-Oxabicyclooctane **10a** obtained in this manner was found to be a stable compound that did not decompose on storage in the air or on heating up to 150 °C. Furthermore, chromatographic separation of the reaction mixture allows a nearly complete recovery of organocatalyst **9**, which can be reused without degradation of catalytic properties; in some cases, nonreacted cyclopropane **1** can be recovered as well.

Unlike the known dimers of DA cyclopropanes, e.g., compounds **4** and **7**, substituted 2-oxabicyclo[3.3.0]octane **10a** is formed stereospecifically as a single diastereomer. Its structure and stereochemistry were determined by mass spectrometry as well as ^{1}H and ^{13}C NMR 1D and 2D COSY, TOCSY, NOESY, HSQC, and HMBC spectroscopy. The NMR spectra contained two different isolated CH–CH_2 spin systems, signals of two nonsubstituted phenyl groups and of four methoxy groups. According to ^{13}C and HMBC NMR spectra (Figure 2, a), the molecule retained only three CO_2CH_3 groups, whereas the fourth group went into the formation of the cyclic system to give OCH_3 and a ketal carbon atom with a chemical shift of δ_C 118. Overall analysis of all interactions in the HMBC spectrum allows it to be inferred unambiguously that the structure of the product is a 2-oxabicyclo[3.3.0]octane derivative.

The relative stereochemistry of compound **10a** was unambiguously determined using the 2D ^{1}H NOESY NMR spectroscopy (Figure 2, b). The observed cross-peaks between the methoxy group at C(1) and the H(3) proton suggest the transoid arrangement of the OCH_3 and Ph groups at C(3).

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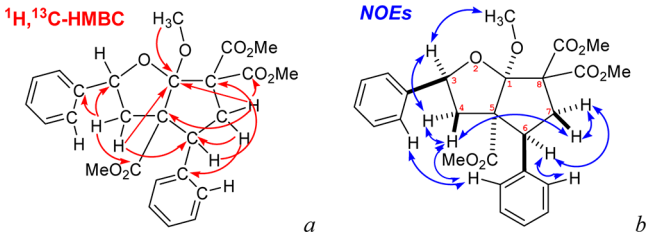
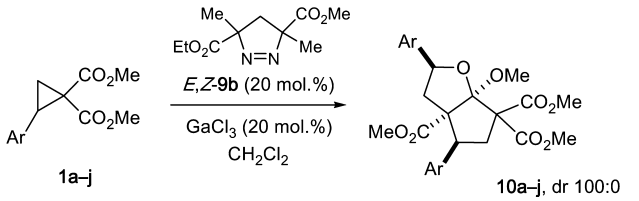


Figure 2. (a) Selected interactions in ^{1}H,^{13}C-HMBC spectra of compounds **10a** used for confirmation of the ring system. (b) Key cross-peaks in 2D ^{1}H NOESY spectra of compounds **10a** used for determination of the configuration.

Interaction of both CH_2 groups with each other and with the H(3) and H(5) protons, as well as the cross-peaks between the protons of the phenyl substituents, allowed us to assign all the other stereocenters in the molecule.

After the optimal conditions for synthesizing 2-oxabicyclooctane **10a** were found, we synthesized 2-arylcyclopropane-1,1-dicarboxylates **1b–j** with various substituents in the aromatic ring[13] and studied whether they could be dimerized into oxabicyclooctanes by treatment with $GaCl_3$ and pyrazolines *E,Z*-**9b** (Table 2). It was found that, in general, a methyl group

Table 2. Lewis Acid/Organocatalyzed Cyclodimerization of Various Cyclopropanedicarboxylates into Substituted 2-Oxabicyclo[3.3.0]octanes



entry	reagent	Ar	temp,[a] °C	time,[a] h	product	yield, % (brsm, %)[b,c]
1	**1a**	Ph	30	1.5	**10a**	72 (90)
2	**1b**	3-ClC_6H_4	30	3	**10b**	35 (72)
3	**1c**	3-BrC_6H_4	30	3	**10c**	38 (75)
4	**1d**	4-FC_6H_4	30	1	**10d**	74 (92)
5	**1e**	4-ClC_6H_4	30	1	**10e**	69 (86)
6	**1f**	4-BrC_6H_4	30	1	**10f**	70 (88)
7	**1g**	4-MeC_6H_4	30	1	**10g**	66 (82)
8	**1h**	4-$NO_2C_6H_4$	80	1.5	**10h**	<2[d]
9	**1i**	4-MeOC_6H_4	−20	1	**10i**	20 (22)[e]
10	**1j**	2-naphthyl	30	0.5	**10j**	65 (76)

[a]The optimum time and temperature were defined by means of NMR monitoring of the reaction in an NMR tube. [b]Isolated yields (the numbers in parentheses indicate the yields based on recovered original materials). [c]Dimers **2**, **4**, and **7** were also formed as minor products (yields 0–5% depending on conditions); for more details, see refs 7 and 8. [d]NMR yields in C_6D_5Cl: product **10h** is unstable under the reaction conditions and decomposes faster than it is formed; therefore, we failed to isolate compound **10h**. [e]Compound **12** was formed as the major product in a ∼50% yield; for more details, see ref 8b.

or halogen atoms (including the fluorine atom) at the *meta* and *para* positions of the phenyl ring, as well as a 2-naphthyl substituent, do not hinder the reaction to give 2-oxabicyclooctanes **10b–g,j** in quite acceptable yields (Table 2, entries 2–7 and 10). *meta*-Halosubstituted phenylcyclopropanedicarboxylates **1b,c** were found to be less reactive than **1a** or *para*-substituted phenylcyclopropanedicarboxylates **1d–g**.

Other dimers similar to compounds **2**, **4**, and **7** (Scheme 1) were also formed as side products;[7,8] they were easily separated during isolation of 2-oxabicyclooctanes by column chromatography on silica gel. The amount of side products depended on the reaction conditions and sometimes varied noticeably even when the reaction was reproduced under apparently identical conditions probably because of traces of water and other microimpurities in the starting reagents.

Introduction of a nitro group in the phenyl ring (compound **1h**) decreased its reactivity significantly (Table 2, entry 8), so the reaction temperature had to be increased. However, under these conditions, oxabicyclooctane **10h** decomposed considerably as soon as it was formed, and we were unable to isolate it in pure form. Nevertheless, we succeeded in detecting compound **10h** in the reaction mixture when the reaction was carried out in an NMR tube, based on characteristic signals of two different CH–Ar fragments (the chemical shifts differ only slightly from those of other compounds of this series, while the coupling constants are exactly the same).

On the contrary, 2-(4-methoxyphenyl)cyclopropanedicarboxylate **1i** was found to be more reactive than cyclopropane **1a**. In just a few minutes, the reaction carried out at room temperature gave a mixture of compounds that contained almost no original cyclopropane **1i**, nor the desired 2-oxabicyclooctane **10i**. However, by decreasing the temperature to −20 °C, we succeeded in observing the formation of 2-oxabicyclooctane **10i** in ∼20% yield (Table 2, entry 9). Tetramethyl 3a,4,6,7-tetrahydro-1*H*-cyclopenta[*c*]indene-3,3,5,5-(2*H*,5a*H*)-tetracarboxylate **12** formed in ∼50% yield (Scheme 3) and identical to the compound obtained previously[8b] was the major reaction product.

The structure and stereochemistry of 2-oxabicyclooctane **10b–g,i** were determined by ^{1}H and ^{13}C NMR 1D and 2D COSY, TOCSY, NOESY, HSQC, and HMBC spectroscopy, as for compound **10a**. The signals of H(3), H_2C(4), H(6), and H_2C(7) protons had the same coupling constants and similar chemical shifts for the entire series of compounds; all substituted 2-oxabicyclooctanes were individual stereoisomers, just like compound **10a**.

Dimethyl 2-(2-naphthyl)cyclopropanedicarboxylate (**1j**) was also rather reactive; in this case, the yield of 2-oxabicyclooctane **10j** (Table 2, entry 10) was comparable to that in the dimerization of the phenyl analogue **1a** or the *para*-substituted phenylcyclopropanedicarboxylates **1d–g**.

2. Mechanism of the Cyclodimerization of Donor–Acceptor Cyclopropanes into Substituted 2-Oxabicyclo[3.3.0]octanes. The cyclodimerization of donor–acceptor cyclopropanes into 2-oxabicyclooctanes **10** is a new and quite unusual process. Its distinctive features in comparison with other reactions of DA cyclopropanes include double catalysis involving a Lewis acid and an organocatalyst, participation of the C=O bond of the ester group, and the stereospecificity of the transformations that occur. The latter phenomenon is not so typical of Lewis acid-catalyzed reactions of DA cyclopropanes:[3] in fact, each of the cyclic dimers **3**, **4**, and **7** is formed as a mixture of two diastereomers. In order to identify the mechanism of formation of 2-oxabicyclooctanes **10**, we studied the intermediates formed in this reaction using NMR spectroscopy on various nuclei.

It was originally assumed that on treatment with $GaCl_3$, cyclopropanedicarboxylate **1** is converted to intermediate **I**, which undergoes cyclization into methoxydihydrofuran **13** with involvement of pyrazoline **9**[3,7,14] and then into lactone **14**.

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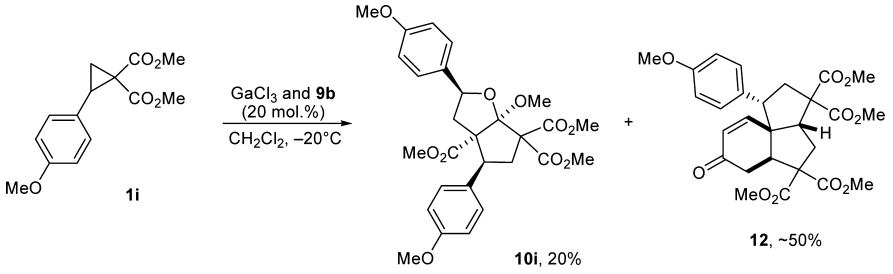
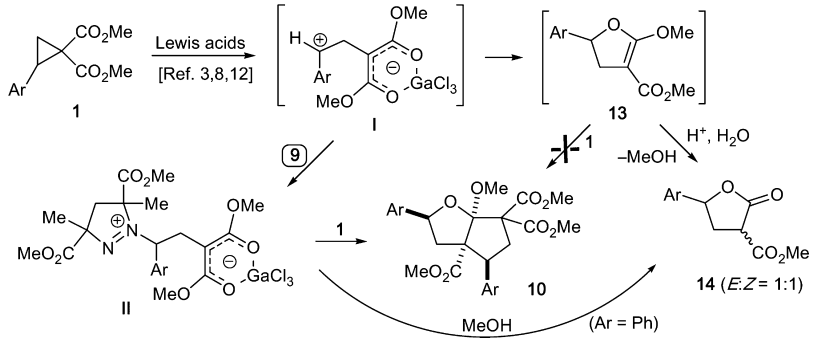
Scheme 3. Products of Cyclopropane 1i Dimerization



Scheme 4. Two Proposed Mechanisms of the Formation of 2-Oxabicyclooctanes 10



Theoretically, the resulting dihydrofuran **13** might add yet another cyclopropanedicarboxylate molecule by 1,3-dipolar cycloaddition (Scheme 4) to give compound **10**. However, this process is unlikely to occur, as additionally shown by special experiments on generation of methoxydihydrofuran **13** followed by introduction of the latter into the reaction. Furthermore, direct NMR observation of the formation of 2-oxabicyclooctanes **10** under double-catalysis conditions did not reveal even traces of compounds **13** or **14**. Moreover, the latter were not detected in the final reaction mixture, either, suggesting that the 2-oxabicyclooctanes were formed by a different mechanism.

As noted above, 1-pyrazoline **9** plays the key role in the formation of oxabicyclooctanes **10**. Monitoring of the reaction by NMR allowed us to observe the $GaCl_3$-catalyzed reaction of 1-pyrazoline **9** with a molecule of cyclopropanedicarboxylate **1a**, in which the formation of intermediate **II** was detected. The reaction took a few seconds after $GaCl_3$ was added; i.e., it occurred by several orders faster than the process as a whole. After that, intermediate **II** slowly added one more molecule of **1a** to give the end product **10a**, whereas $GaCl_3$ and the pyrazoline were involved in a new cycle.

Bipolar intermediate **II** was found to be rather stable and capable of persisting in a solution for several days even at room temperature due to the rather strong shielding of the pyrazoline fragment, which prevents reactions that occur in the case of other pyrazolines.[10] Nevertheless, we were unable to isolate complex **II** in individual form due to its sensitivity to moisture; nor we were able to obtain a solution of this intermediate in pure form. If equimolar amounts of cyclopropane **1a**, pyrazoline **9**, and gallium trichloride were used, a considerable amount of oligomeric products was formed and the content of complex **II** was rather low. Still, we succeeded in obtaining a sufficient amount of this complex to be able to characterize it by NMR spectroscopy on various nuclei in CD_2Cl_2 solution using an excess of the starting cyclopropane and 50 mol % of each $GaCl_3$ and pyrazoline **9b**.

The use of a mixture of *E*- and *Z*-isomers of pyrazoline **9b** was beneficial in comparison with individual isomer *E*-**9a**, since in this case several isomers of complex **II** were formed (Figure 3) and, though the signals in NMR spectra became much more

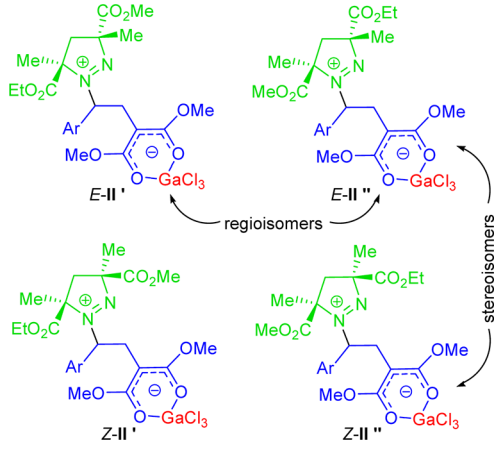


Figure 3. Isomers of intermediate **II** formed in the reaction mixture.

complex, they gave unambiguous information about the incorporation of pyrazoline into the complex. In particular, the ratio of each pair of *E*- and *Z*-isomers in the complex matched the stereoisomer ratio in the starting pyrazoline **9b** (~3.5:1).

The ^1H NMR spectrum of intermediate **II** (Figure 4, *a*) contains characteristic signals of CHPh protons that are observed as a set of triplets in low field at δ 6.1–6.5. Based on the 2D ^1H COSY spectrum (Figure 4, b), one can find the counterparts for these signals, which together correspond to the isolated CH–CH_2 fragment. In the ^{13}C NMR spectrum (Figure 4, c), the CHPh key fragment manifests itself as a broadened signal representing a number of isomers with similar structures, that has a chemical shift of about δ 100 matching its bonding

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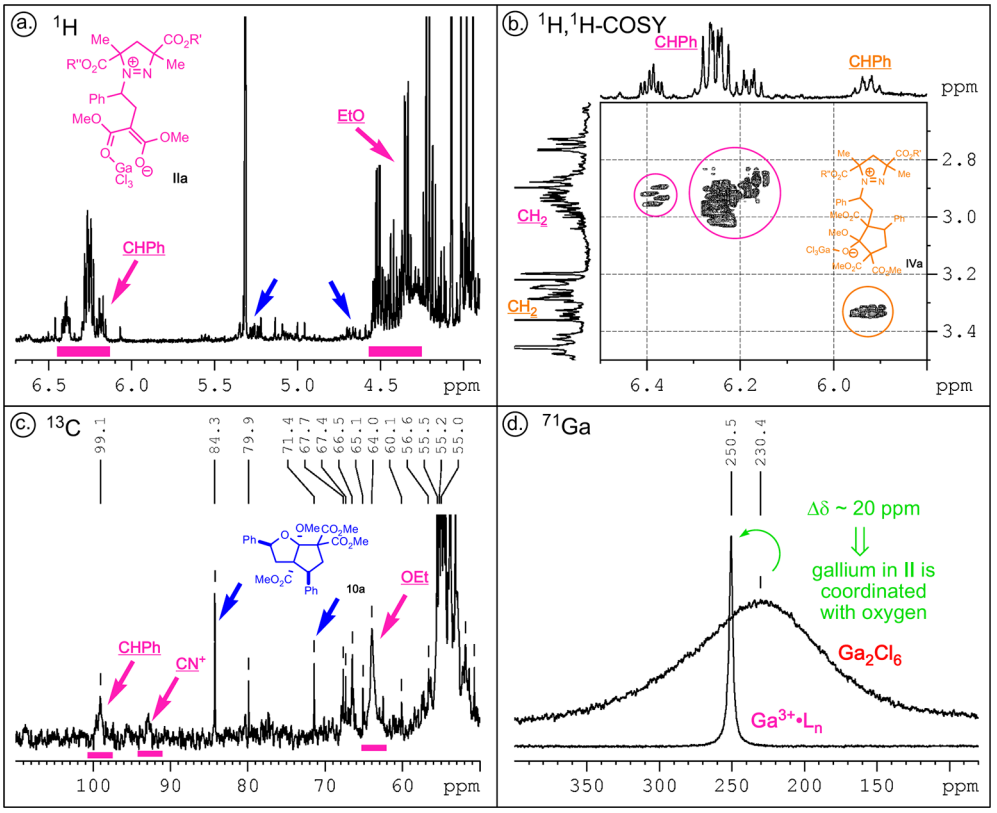

Figure 4. NMR spectra (400 MHz) of intermediate **II** in the reaction mixture. Conditions: **1a** (0.1 mmol), *E*,*Z*-**9b** (50 mol %), $GaCl_3$ (50 mol %), CD_2Cl_2 (0.5 mL), 20 °C: (a) ^{1}H NMR spectrum, *t* ~ 10 min; (b) ^{1}H,^{1}H−COSY, *t* 15−25 min; (c) ^{13}C{^{1}H} NMR spectrum, *t* 25−40 min; (d) ^{71}Ga-NMR spectra of intermediate **II** (bottom) compared with pure $GaCl_3$ in CD_2Cl_2 (top), *t* ~ 12 min. The colors of the compounds correspond to those in Scheme 5.

with a strong electron-withdrawing group, namely the N═N$^+$ fragment.

The ^{71}Ga NMR spectra also change considerably (Figure 4, d). Comparison of pure $GaCl_3$, which exists as a dimer in solution, to complex **II** shows a downfield shift of the signal to δ 20; this is quite a typical shift corresponding to gallium coordination with an oxygen atom.[15] Furthermore, the signal in the ^{71}Ga NMR spectrum of intermediate **II** was unexpectedly much narrower than that in the spectrum of $GaCl_3$; hence, it can be concluded that the surrounding of gallium is rather symmetrical and the complex should be monomeric and incorporate the majority of the gallium that is present in the solution, while dynamic and exchange processes are totally absent.

Experiments performed in an NMR tube under various conditions allowed us to detect a number of intermediates and the sequence of their transformations to the final product (Figure 5). In fact, addition of $GaCl_3$ to a solution of cyclopropane **1a** and pyrazoline **9b** at a molar ratio of 0.8:1:0.5 immediately gives intermediate **II** and a number of other $GaCl_3$ complexes with the original cyclopropane, which manifest themselves as a broad multiplet at δ_H 6 in the spectrum (Figure 5, I). We cannot say exactly what complexes are these due to lack of information. After 20−30 min, signals of another intermediate appear in the reaction mixture. They correspond to structures **III** or **IV** (Figure 5, II; Figure 4, b; Schemes 4 and 5) formed from intermediate **II** due to the addition of a second cyclopropane molecule.

After that, excess deuteromethanol was added to the reaction mixture in order to decompose gallium complexes (Figure 5, III, IV). Under these conditions, complexes **II** and **IV** become unstable and decompose with elimination of a 1-pyrazoline **9b** molecule; monomeric complex **II** was found to be much more stable than dimeric complex **IV** which disappeared almost instantly to give 2-oxabicyclooctane **10a** (Figure 5, III). This was unambiguously shown in a series of experiments: the amount of compound **10a** that was formed always matched the amount of decomposed complex **IV**, whereas oxabicyclooctane **10a** was not formed at all if **IV** was absent in the reaction mixture. It should be noted that complex **II** is decomposed only to a small extent over this period of time; the lifetime of this complex in the presence of methanol is approximately 24 h. Ultimately, it decomposes to give lactone **14** (Figure 5, IV; Scheme 4).

^{1}H NMR spectra were obtained as a result of monitoring of the reaction in NMR tube under optimal conditions to achieve the maximum yield of 2-oxabicyclooctane **10a** (pyrazoline **9b** and $GaCl_3$ were used in catalytic amounts; see Figure 6 for details).

It could be seen that the reaction starts actively at 30 °C and full conversion requires about 1−1.5 h. The concentration of intermediate **IIa** remains constant for the whole experiment and does not decrease after its termination. Therefore, the real conversion does not reach 100%. Formation of intermediate **IIa** is a key and necessary step for the dimerization process.

For *o*-C_6H_4Cl and *o*-$C_6H_4OCH_3$ 2-substituted cyclopropanes **1**, which do not produce the corresponding intermediate **II** does, making the corresponding 2-oxabicyclooctanes **10** even in trace amounts were not successful. It can be seen from the NMR spectra that 1-pyrazoline **9b** binds to the complex **IIa** not

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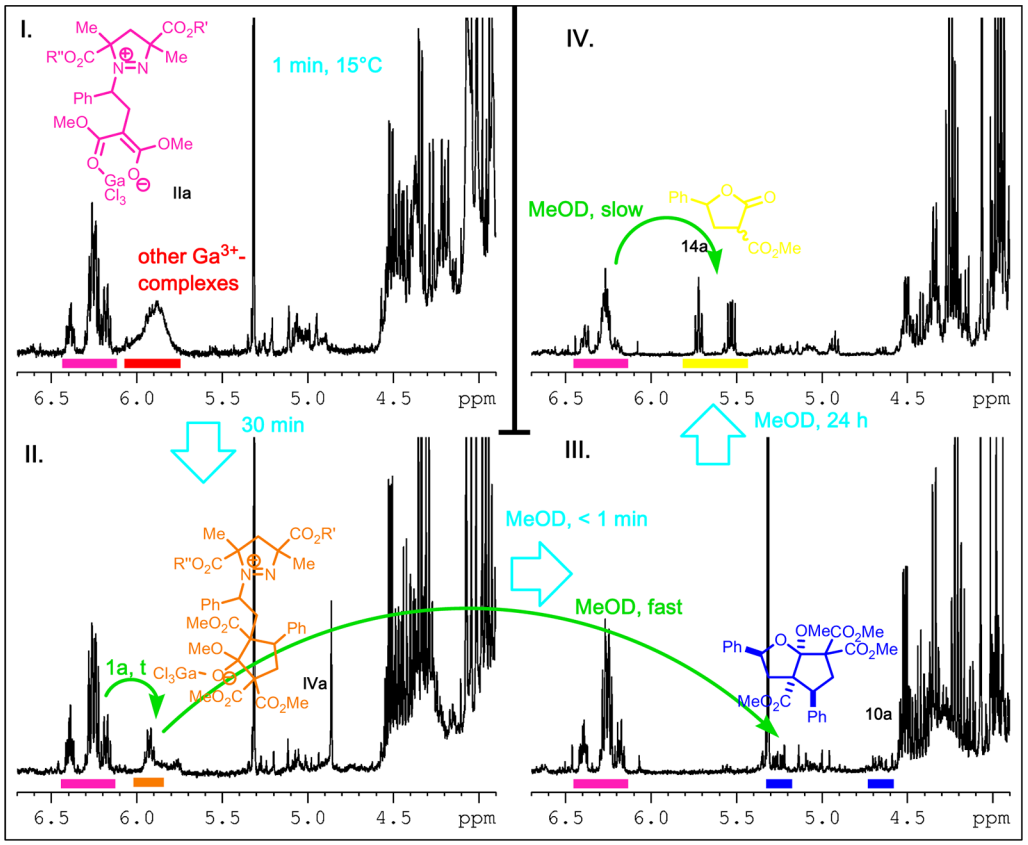
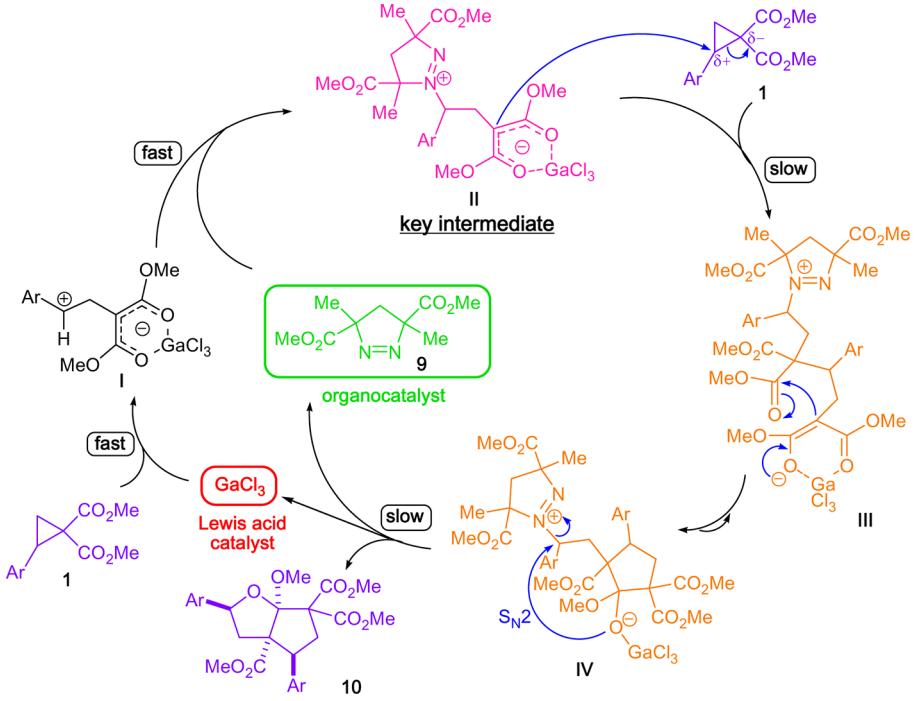


Figure 5. Performing the reaction in an NMR tube for detection of the intermediates and the sequence of their formation (400 MHz). Conditions: **1a** (0.13 mmol), *E,Z*-**9b** (50 mol %), $GaCl_3$ (80 mol %), CD_2Cl_2 (0.5 mL), 15 °C. (I) t = 1 min; (II) t = 30 min; (III) t = 30 min, then addition of CD_3OD; (IV) CD_3OD, 24 h (the solvent was replaced by $CDCl_3$). Thin green arrows indicate the formation of intermediates and products. The colors of the compounds correspond to those in Scheme 4.

Scheme 5. Possible Catalytic Cycle for Dimerization of Donor–Acceptor Cyclopropanes To Form 2-Oxabicyclooctanes[a]



[a]The colors correspond to the signals in the NMR spectra in Figures 4 and 5.

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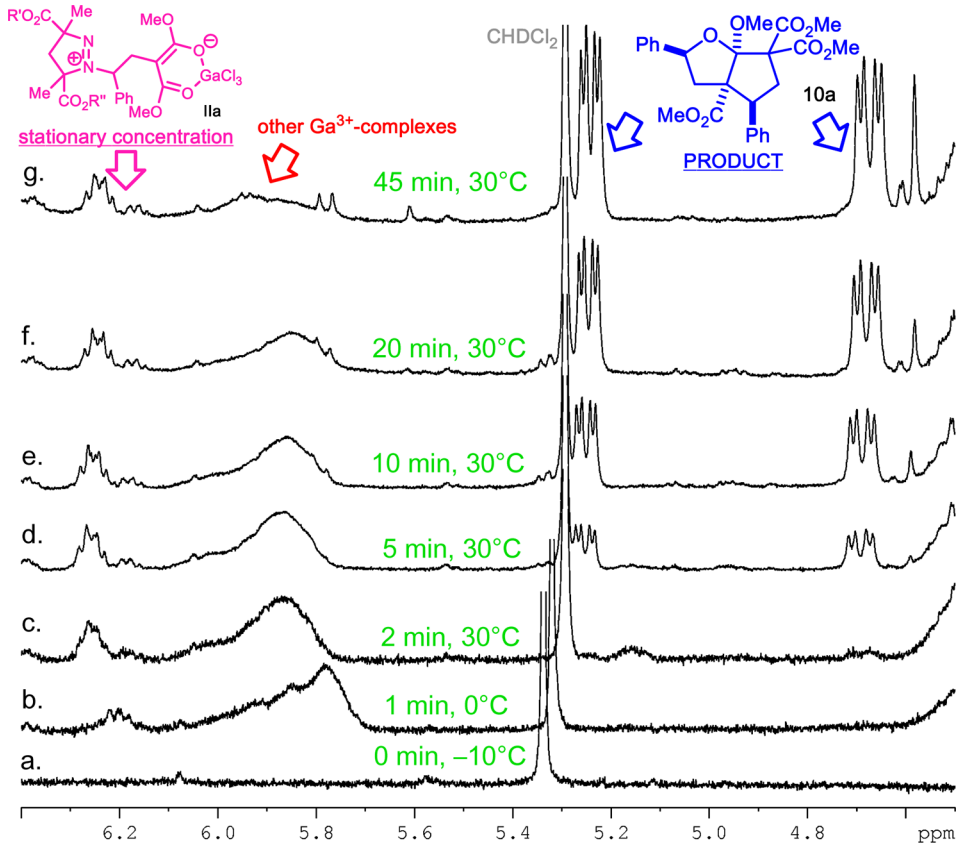

Figure 6. Monitoring of the dimerization reaction of cyclopropane **1a** with formation of 2-oxabicyclooctane **10a** in NMR tube (400 MHz). Arrows indicate the signals of the corresponding compounds. Conditions: **1a** (0.25 mmol), *E*,*Z*-**9b** (25 mol %), $GaCl_3$ (25 mol %), CD_2Cl_2 (0.6 mL), 30 °C. (a) −10 °C (before $GaCl_3$ was added); (b) 1 min, 0 °C; (c) 2 min, 30 °C; (d) 5 min, 30 °C; (e) 10 min, 30 °C; (f) 20 min, 30 °C; (g) 45 min, 30 °C. The colors of the compounds correspond to those in Scheme 5.

completely, a part of it is involved in another complexes and another part of it is present in free form in the solution. Toward the end of the reaction complex **IVa** (two triplets at 6.0 ppm) is accumulated in the trace amounts, its concentration can be notably increased if the reaction is carried out at lower temperature (Figure 5, II).

All of the same patterns are observed for cyclopropanedicarboxylates with other aryl substituents (**1b**−**j**) as for the phenyl-substituted derivative (**1a**), the mechanism of the reaction and intermediates are analogous, and NMR spectra for reaction mixtures are similar.

Thus, the NMR data on various nuclei were used to study the detailed mechanism of the new reaction, i.e., dimerization of cyclopropanedicarboxylates to give 2-oxabicyclo[3.3.0]octanes **10** under conditions of double catalysis with gallium trichloride and 1-pyrazolines. The general mechanism of the transformations observed is presented in Scheme 5.

The mechanism of this process involves two catalytic cycles including the addition of a Lewis acid ($GaCl_3$) and an organocatalyst (1-pyrazoline). The main role of the Lewis acid is to activate the cyclopropane ring by coordination to two carboxylate groups (intermediate **I**), whereas the role of the organocatalyst is to stabilize it by formation of a zwitterion intermediate **II**. It was found that these functions could only be performed by anhydrous $GaCl_3$, on the one hand, and pyrazolines of type **9**, on the other hand.

According to spectral data, 1-pyrazoline **9** is not directly attached to the Lewis acid but plays the role of temporary protection of the carbocationic center in the catalytic cycle. The requirements for such "protection" are very high: it should not be bound too strongly (otherwise it would not be eliminated when needed) or too weakly (otherwise it will be removed prematurely). A compound used as the "protection" should not give stable complexes with the donor−acceptor cyclopropane and should have sufficiently bulky substituents to ensure high stereoselectivity of the reaction.

First, cyclopropane **1** is opened into intermediate **I** under the action of $GaCl_3$, and a molecule of 1-pyrazoline **9** is added to **I** to give the key intermediate **II** whose concentration is nearly constant throughout the reaction. Both processes occur very quickly. After that, intermediate **II** slowly adds the second molecule of cyclopropanedicarboxylate **1** to give intermediates **III** and **IV**, the latter of which is probably detected by NMR spectroscopy (the key stage in the formation of the first ring). At the last stage, intermediate **IV** undergoes S_N2 intramolecular 1,5-cyclization with elimination of a 1-pyrazoline **9** molecule to give the final compound **10**. At this stage $GaCl_3$ and the organocatalyst are regenerated and re-enter the reaction. The two last stages occur rather slowly and affect the overall process rate. Since each of 2-oxabicyclooctanes **10** is formed as a single isomer, it may be assumed that a particular configuration of substituents is due to the possibility of "folding" of intermediates **II** and **III**, which results in proximity of the pyrazoline and malonic fragments due to electrostatic interaction and stereospecific formation of two new C−C bonds and a C−O bond.

As noted above, intermediate **II** proves to be unstable to action of electrophiles, in whose presence it degrades in two

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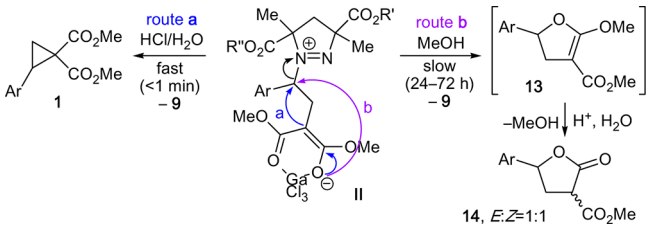
pathways (Scheme 6). Diluted hydrochloric acid fully decomposes intermediate **II** within several minutes eliminating a molecule of starting 1-pyrazoline **9** as a result of S_N2 substitution by the attack of malonyl carbon atom at CHN fragment (Scheme 6, route a). Apparently, 1-pyrazoline **9** is a good leaving group. The role of electrophile is likely to destruct a stable gallium complex. In the process a molecule of original cyclopropanedicarboxylate **1** is formed. Namely, intermediate **II** decomposes into two initial components from which it formed, and gallium moves into aqueous phase. This decomposition route allows us to recover a part of cyclopropane **1** and all organocatalyst **9** during dimerization reaction.

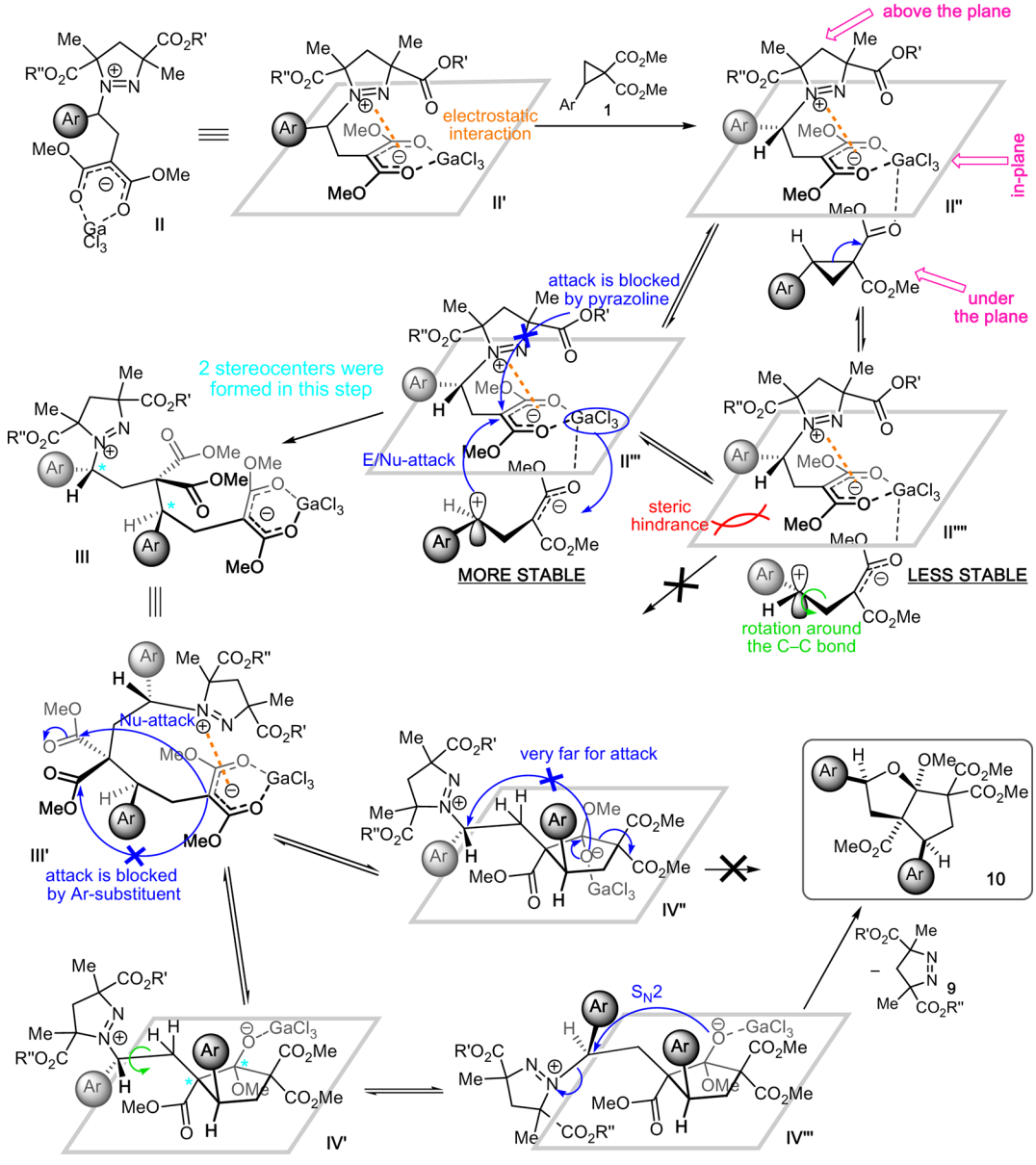
Scheme 6. Two Pathways of the Decomposition of Intermediate II



Another decomposition route of compound **II** occurs in the presence of methanol (Scheme 6, route b). The decomposition rate in this case is much lower and the other product is obtained. Intramolecular O-alkylation of gallium enolate release dihydrofuran **13** which upon hydrolysis lead to lactone **14**. It should be noted that under the conditions of 2-oxabicyclooctanes **10** synthesis during cyclopropane dimerization these pathways of intermediate **II** decomposition are not affected; in particular even traces of compounds **13** and **14** are not observed.

3. Possible Elucidations of Stereochemistry of the Dimerization Reaction of Donor–Acceptor Cyclopro-

Scheme 7. Elucidation of the Stereochemistry of the Dimerization Process According to the Mechanism in Scheme 5



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panes into 2-Oxabicyclo[3.3.0]octanes Using a Proposed Mechanism. Using suggested mechanism of the dimerization process we were able to predict and explain the stereochemistry of formed 2-oxabicyclooctanes **10** (Scheme 7).

Intermediate **II** is a zwitterion in a noncoordinating solvent such as CH_2Cl_2, where charges are greatly separated from each other. Because of the absence of counterions (external equalizers of the charge), it is favorable for intermediate **II** to fold so that positive and negative charges approximated and compensated each other (structure **II′**). As a result of this fragment, 1-pyrazoline is found over the plain of the malonyl anion, which completely blocks the approach of the second molecule of donor−acceptor cyclopropane from one side (structure **II″** and **II‴**). It can be considered that the second molecule of cyclopropane adds in two stages: initially it is coordinated as a ligand by the ester group on Ga-atom in the complex **II′**(intermediate **II″**) due to which σ-bond of cyclopropane ring is activated to form an electrophilic center (intermediates **II‴** and **II⁗**). Aryl substituent in the intermediate **II″** has less sterically hindered position due to rotation around C−C bond: the reaction proceeds via more favorable intermediate **II‴**, while less favorable **II⁗** has no time to react (this stage is slow). As a result of addition of second molecule of cyclopropane intermediate **III** is initially formed, in which two from four stereocenters were already created stereospecifically.

Intermediate **III** (as **II**) is also a zwitterion with well-separated charges, and likewise, it folds with strong closing of charged pyrazoline and malonyl fragments for charge compensation. The resulting complex **III′** undergoes intramolecular nucleophilic attack by malonyl fragment on carbonyl group. In this intermediate one of the two ester groups comes within short distance of the aryl substituent located in between, which results in full blockade of the attack at this ester group. As a result the nucleophilic attack of malonyl anion proceeds only on one ester group. Thus the third stereocenter is formed.

Now we consider the formation of the fourth stereocenter. Theoretically, formation of two isomeric cyclopentanes **IV′** and **IV″** on carbon atom which was a part of the carbonyl group is possible. But in contrast to **IV′** cyclopentane **IV″** cannot further undergo intramolecular cyclization because nucleophilic oxygen is directed to the opposite side of pyrazoline fragment. Because only one isomer of oxabicyclooctane **10** is formed in rather high yield, it could be presumed that intermediates **IV′** and **IV″** are in equilibrium and ultimately they transform into **10**. After S_N2 process inversion of the configuration of one stereocenters takes place, the final product **10** is obtained as a single stereoisomer.

CONCLUSION

A new dimerization pathway of donor−acceptor cyclopropanes (2-arylcyclopropanedicarboxylates) into 2-oxabicyclo[3.3.0]-octanes has been revealed. It occurs under conditions of double catalysis with a Lewis acid ($GaCl_3$) and an organocatalyst (α,α'-tetrasubstituted 1-pyrazolines). In this process, donor−acceptor cyclopropanes demonstrate a new type of reactivity; unlike the other known dimerizations of DA cyclopropanes, it involves the C═O bond of the ester group. The reaction is accompanied by the formation of two new rings and four stereocenters with exceptional stereoselectivity. The dimerization products, i.e., 2-oxabicyclooctanes, may be of interest as biologically active compounds or as synthetic blocks.

EXPERIMENTAL SECTION

General Experimental Details. All reagents and solvents used were commercial grade chemicals without additional purification. All operations with $GaCl_3$ were carried out under dry argon atmosphere. TLC analysis was performed on Silufol chromatographic plates. For preparative chromatography, silica gel 60 (0.040−0.063 mm) was used. ^1H and ^{13}C NMR spectra were recorded on a 400 MHz (400.1 and 100.6 MHz, respectively) and 300 MHz (300.1 and 75.5 MHz, respectively) spectrometers in $CDCl_3$ containing 0.05% Me_4Si as the internal standard. Assignments of ^1H and ^{13}C signals were made with the aid of 2D COSY, NOESY, HSQC, and HMBC spectra where necessary. ^{35}Cl, ^{69}Ga, and ^{71}Ga NMR spectra were recorded on a 400 MHz spectrometer (39.2, 96.0, and 122.0 MHz, respectively); standards, NaCl and $Ga(NO_3)_3$ solutions in water, respectively. ^{19}F NMR spectra were recorded on a 300 MHz spectrometer (282.4 MHz); standard, $CFCl_3$. Monitoring of the reactions in NMR tube were made in CD_2Cl_2 solution containing 0.05% Me_4Si as the internal standart. IR spectra were obtained on a FT-IR spectrometer in $CHCl_3$ solution (1%). Mass spectra were recorded using electron impact ionization (EI, 70 eV, direct inlet probe). High-resolution mass spectra were obtained using simultaneous electospray (ESI). The elemental compositions were determined on a CHN alalyzer instrument.

General Procedure for the Synthesis of Cyclopropanes 1a−j. The solution of aromatic aldehyde (0.1 mol), dimethyl malonate (13.2 g, 0.1 mol), piperidine (0.85 g, 0.01 mol), and acetic acid (1.2 g, 0.02 mol) in 40 mL of C_6H_6 was refluxed with a Dean−Stark attachment for 3 h until no water was extracted. The reaction mixture was washed with HCl (5% in water, 3 × 20 mL) and $NaHCO_3$ (5% in water, 3 × 20 mL). The organic layer was dried over Na_2SO_4, and the solvent was removed in vacuo. The pure arylidenemalonate was prepared as a thick slightly colored oil in quantity yields, which crystallized on standing. The melting point and spectroscopic data correspond to described in the literature.[13] The obtained arylidenemalonates were used in the next step without additional purification.

To a stirred suspension of NaH (0.39 g, 16.1 mmol) in dry DMSO (15 mL) under argon atmosphere was added trimethylsulfoxonium iodide (3.60 g, 15.4 mmol) under the same conditions. Then a solution of arylidenemalonate (14 mmol) in dry DMSO (6 mL) was added in a single portion. The resulted mixture was stirred at room temperature, poured into H_2O−ice (50 g), and extracted with diethyl ether (3 × 30 mL). The combined organic layers were washed with water (3 × 40 mL), dried over $MgSO_4$, and concentrated in vacuo to give the pure cyclopropanes **1** in good yields.

Dimethyl 2-(3-chlorophenyl)cyclopropane-1,1-dicarboxylate (1b): yield 3.0 g, 80%; colorless oil; IR ($CHCl_3$) ν 3020, 2955, 2903, 2849, 1727 br (O═CO), 1642, 1599, 1572, 1516, 1479, 1439, 1368, 1336, 1286, 1224 cm^{-1}; ^1H NMR ($CDCl_3$, 400.1 MHz) δ 1.74 (dd, 1H, CH_2, ^3J = 9.2 Hz, ^2J = 5.3 Hz), 2.15 (dd, 1H, CH_2, ^3J = 8.0 Hz, ^2J = 5.3 Hz), 3.18 (dd, 1H, CH, ^3J = 9.2 and 8.0 Hz), 3.42 and 3.79 (both s, 2 × 3H, $2OCH_3$), 7.07 (m, 1H, C_6H_4), 7.20 (m, 3H, C_6H_4); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 19.1 (CH_2(3)), 31.8 (CH(2)), 37.2 (C(1)), 52.3 and 52.9 ($2OCH_3$), 126.7 (CH(4′)), 127.7 (CH(6′)), 128.8 (CH(2′)), 129.4 (CH(5′)), 134.1 (C(3′)), 136.9 C(1′)), 166.7 and 169.9 (2COO); MS (m/z) 270 (2) and 268 (9) (M^+), 238 (3) and 336 (9) ($M^+ - CH_3OH$), 210 (6) and 208 (18) ($M^+ - HCO_2CH_3$), 165 (8), 155 (66), 149 (49), 129 (36), 115 (57), 103 (12), 89 (19), 75 (16), 59 (100), 39 (20); HRMS (ESI) calcd for $C_{13}H_{13}{}^{35}ClO_4$ M + H 269.0575, M + Na 291.0395, M + K 307.0134, found m/z 269.0579, 291.0391, 307.0138.

General Procedure for the Synthesis of Pyrazolines 9a,b. The solution of methyl or ethyl diazopropionate (10 mmol)[11] and methyl methacrylate (25 mmol) in 10 mL of CH_2Cl_2 was stirred at room temperature for 24 h to complete decoloration. The solvent was removed in vacuo to give the pure pyrazoline **9** as a colorless oil (mixture of diastereomers, E/Z ~ 3.5:1) in ~99% yield. The mixture of diastereomers could be separated by column chromatography on silica gel (benzene−EtOAc, 20:1) to give the pure products.

***(E,Z)*-3-Ethyl-5-methyl 4,5-dihydro-3,5-dimethyl-3*H*-pyrazole-3,5-dicarboxylate (9b).** The pyrazoline **9b** (mixture of diastereomers, E/Z ~ 3.5:1) was prepared from ethyl diazopropionate

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(1.28 g, 10 mmol) and methyl methacrylate (2.50 g, 25 mmol) as a colorless oil: yield 2.25 g, 99%. Anal. Calcd for $C_{10}H_{16}N_2O_4$: C, 52.62; H 7.06; N, 12.27. Found: C, 52.82; H, 7.20; N, 12.08. *E*-Isomer: colorless oil. ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 1.30 (t, 3H, CH_2CH_3, ^3J = 7.1 Hz), 1.66 (s, 6H, $2CH_3$), 2.01 (s, 2H, CH_2(4)), 3.80 (s, 3H, OCH_3), 4.24 (q, 2H, CH_2CH_3, ^3J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 13.9 (CH_2CH_3), 22.6 ($2CH_3$), 38.4 (CH_2(4)), 52.9 (OCH_3), 61.9 (CH_2CH_3), 97.87 and 97.95 (C(3) and C(5)), 170.3 and 170.9 (2COO). *Z*-Isomer: colorless oil; ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 1.27 (t, 3H, CH_2CH_3, ^3J = 7.1 Hz), 1.715 and 1.723 (both s, 2 × 3H, $2CH_3$), 1.32−2.77 (both d, 2 × 1H, CH_2(4), ^2J = 13.5), 3.76 (s, 3H, OCH_3), 4.20 (q, 2H, CH_2CH_3, ^3J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 15.2 (CH_2CH_3), 23.5 and 23.8 ($2CH_3$), 38.8 (CH_2(4)), 52.6 (OCH_3), 61.8 (CH_2CH_3), 97.1 (C(3) and C(5)), 170.0 and 170.7 (2COO).

General Procedure for $GaCl_3$/Pyrazoline-Catalyzed Dimerization Reaction of Donor−Acceptor Cyclopropanes into 2-Oxabicyclo[3.3.0]octanes. All operations were performed under dry argon atmosphere. A solution of cyclopropane **1** (1 mmol) and pyrazoline **9** (0.2 mmol, 20 mol %) in 5 mL of dry dichloromethane was cooled to −10 °C. Then the solid $GaCl_3$ (0.2 mmol, 20 mol %) was added in one portion at −10 °C under vigorous stirring, and reaction mixture was heated to 30 °C and stirred for the time indicated in Table 2. The reaction mixture was cooled to −10 °C, the cold tetrahydrofuran (THF, 1 mL) was added for the destruction of gallium complexes, and the solvent was evaporated under vacuum at −10 °C. The residue was separated immediately by column chromatography on silica gel (benzene−EtOAc, 20:1) to afford starting cyclopropane **1** (15−50% was recovered), oxabicyclooctane **10** (yields, see Table 2) and starting pyrazoline **9** (∼96−99% was recovered). If necessary, the resulting oxabicyclooctane **10** may be additionally purified by flash chromatography on silica gel (hexane−acetone, 5:1) to give a pure product.

(1*R,3*S**,5*S**,6*S**)-Trimethyl 1-methoxy-3,6-diphenyl-2-oxabicyclo[3.3.0]octane-5,8,8-tricarboxylate (10a).** The title compound was prepared according to the general procedure as a single diastereomer in 169 mg yield (72%, 90% brsm). Compound **10a**: colorless thick oil; IR ($CHCl_3$) ν 3055, 2987, 2955, 1735 br (C═O), 1603, 1550, 1495, 1436, 1423 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 1.39 (dd, 1H, *syn*-H(4), ^2J = 13.1, ^3J = 11.2 Hz), 2.37 (dd, 1H, *anti*-H(4), ^2J = 13.1, ^3J = 4.5 Hz), 2.56 (dd, 1H, *anti*-H(7), ^2J = 13.6, ^3J = 5.6 Hz), 2.99 (dd, 1H, *syn*-H(7), ^2J = 13.6, ^3J = 14.3 Hz), 3.50 (s, 3H, OCH_3), 3.80, 3.82, and 3.89 (all s, 3 × 3H, $3CO_2CH_3$), 4.74 (dd, 1H, H(6), ^3J = 14.3 and 5.6 Hz), 5.26 (dd, 1H, H(3), ^3J = 11.2 and 4.5 Hz), 7.14 (m, 2H, 2 *o*-CH, Ph at C(6)), 7.16 (m, 1H, *p*-CH, Ph at C(6)), 7.22 (m, 2H, 2 *m*-CH, Ph at C(6)), 7.27 (m, 2H, 2 *o*-CH, Ph at C(3)), 7.28 (m, 1H, *p*-CH, Ph at C(3)), 7.32 (m, 2H, 2 *m*-CH, Ph at C(3)); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 35.6 (CH_2(7)), 43.2 (CH(6)), 43.4 (CH_2(4)), 52.0 (OCH_3), 52.6 and 52.7 ($3CO_2CH_3$, 1C and 2C respectively), 65.9 (C(8)), 70.1 (C(5)), 82.9 (CH(4)), 118.0 (C(1)), 125.7 (2 *o*-CH, Ph at C(3)), 126.8 (*p*-CH, Ph at C(6)), 127.5 (2 *o*-CH, Ph at C(6)), 127.9 (*p*-CH, Ph at C(3)), 128.5 (2 *m*-CH, Ph at C(6)), 128.6 (2 *m*-CH, Ph at C(3)), 139.0 (*i*-C, Ph at C(6)), 140.1 (*i*-C, Ph at C(3)), 168.5, 168.7, and 172.6 (3COO); HRMS (ESI) calcd for $C_{26}H_{28}O_8$ M + Na, 491.1676, 2M + Na 959.3461, found *m*/*z* 491.1672, 959.3444.

(1*R,3*S**,5*S**,6*S**)-Trimethyl 1-Methoxy-3,6-bis(3-chlorophenyl)-2-oxabicyclo[3.3.0]octane-5,8,8-tricarboxylate (10b).** The title compound was prepared according to the general procedure as a single diastereomer in 95 mg yield (35%, 72% brsm). Compound **10b**: colorless thick oil; IR ($CHCl_3$) ν 3020, 2954, 2928, 2854, 1734 br (O═CO), 1598, 1573, 1518, 1478, 1458, 1435, 1367, 1332, 1251, 1223 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 1.30 (dd, 1H, *syn*-H(4), ^2J = 13.0, ^3J = 11.1 Hz), 2.39 (dd, 1H, *anti*-H(4), ^2J = 13.0, ^3J = 4.5 Hz), 2.54 (dd, 1H, *anti*-H(7), ^2J = 13.6, ^3J = 5.6 Hz), 2.89 (dd, 1H, *syn*-H(7), ^2J = 13.6, ^3J = 14.2 Hz), 3.49 (s, 3H, OCH_3), 3.80, 3.85, and 3.88 (all s, 3 × 3H, $3CO_2CH_3$), 4.71 (dd, 1H, H(6), ^3J = 14.2 and 5.6 Hz), 5.24 (dd, 1H, H(3), ^3J = 11.1 and 4.5 Hz), 7.01 (m, 1H, C_6H_4), 7.12 (m, 2H, C_6H_4), 7.16 (m, 2H, C_6H_4), 7.24 (m, 3H, C_6H_4); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 35.5 (CH_2(7)), 42.9 (CH(6)), 43.1 (CH_2(4)), 52.2 (OCH_3), 52.82, 52.85, and 52.87 ($3CO_2CH_3$), 65.7 (C(8)), 69.9 (C(5)), 82.0 (CH(4)), 118.0 (C(1)), 123.7, 125.7, 125.8, 127.2, 127.7, 128.1, 129.8, and 130.0 (8CH, $2C_6H_4$), 134.6 (2CCl, $2C_6H_4$), 141.0 and 142.0 (2 *i*-C, $2C_6H_4$), 168.3, 168.4, and 172.1 (3COO); MS (*m*/*z*) 536 (2, M^+ − H), 504 (3, M^+ − CH_3OH − H), 445 (59, M^+ − OCH_3 − CO_2CH_3), 366 (31), 334 (41), 314 (25), 267 (25), 207 (19), 191 (19), 138 (97), 113 (59), 71 (53), 59 (100), 43 (79), 29 (73); HRMS (ESI) calcd for $C_{26}H_{26}{}^{35}Cl_2O_8$ M + Na 559.0897, found *m*/*z* 559.0891.

(1*R,3*S**,5*S**,6*S**)-Trimethyl 1-Methoxy-3,6-bis(3-bromophenyl)-2-oxabicyclo[3.3.0]octane-5,8,8-tricarboxylate (10c).** The title compound was prepared according to the general procedure as a single diastereomer in 118 mg yield (38%, 75% brsm). Compound **10c**: colorless thick oil; IR ($CHCl_3$) ν 3020, 2977, 2954, 2846, 1735 br (O═CO), 1596, 1569, 1517, 1478, 1435, 1360, 1332, 1252, 1223 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 1.30 (dd, 1H, *syn*-H(4), ^2J = 13.0, ^3J = 11.0 Hz), 2.41 (dd, 1H, *anti*-H(4), ^2J = 13.0, ^3J = 4.5 Hz), 2.54 (dd, 1H, *anti*-H(7), ^2J = 13.6, ^3J = 5.6 Hz), 2.89 (dd, 1H, *syn*-H(7), ^2J = 13.6, ^3J = 14.3 Hz), 3.50 (s, 3H, OCH_3), 3.81, 3.86, and 3.89 (all s, 3 × 3H, $3CO_2CH_3$), 4.71 (dd, 1H, H(6), ^3J = 14.3 and 5.6 Hz), 5.25 (dd, 1H, H(3), ^3J = 11.0 and 4.5 Hz), 7.06 (m, 1H, H(6′)), 7.11 (m, 1H, H(5′)), 7.18 (m, 1H, H(6″)), 7.19 (m, 1H, H(5″)), 7.29 (m, 1H, H(2′)), 7.32 (m, 1H, H(4′)), 7.40 (m, 1H, H(4″)), 7.41 (m, 1H, H(2″)); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 35.5 (CH_2(7)), 42.9 (CH(6)), 43.1 (CH_2(4)), 52.2 (OCH_3), 52.82, 52.84, and 52.89 ($3CO_2CH_3$), 65.7 (C(8)), 69.9 (C(5)), 81.9 (CH(4)), 118.0 (C(1)), 122.7 and 122.8 (2CBr, $2C_6H_4$), 124.1 (CH(6″)), 126.2 (CH(6′)), 128.7 (CH(2″)), 130.1 (CH(5′)), 130.2 (CH(5″)), 130.3 (CH(4′)), 130.6 (CH(2′)), 131.0 (CH(4″)), 141.3 and 142.2 (2 *i*-C, $2C_6H_4$), 168.3, 168.4, and 172.1 (3COO); MS (*m*/*z*) 534 (3, M^+ − OCH_3 − CO_2CH_3), 410 (3), 378 (3), 313 (8), 282 (8), 251 (7), 202 (11), 182 (100), 159 (13), 145 (42), 113 (38), 103 (14), 77 (9), 59 (90), 32 (29); HRMS (ESI) calcd for $C_{26}H_{26}{}^{79}Br_2O_8$ M + Na 646.9887, found *m*/*z* 646.9884.

(1*R,3*S**,5*S**,6*S**)-Trimethyl 1-Methoxy-3,6-bis(4-fluorophenyl)-2-oxabicyclo[3.3.0]octane-5,8,8-tricarboxylate (10d).** The title compound was prepared according to the general procedure as a single diastereomer in 186 mg yield (74%, 92% brsm). Compound **10d**: colorless thick oil; IR ($CHCl_3$) ν 3020, 2954, 1734 br (O═CO), 1608, 1513, 1458, 1436, 1332, 1284, 1252 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 1.31 (dd, 1H, *syn*-H(4), ^2J = 13.0 Hz, ^3J = 11.1 Hz), 2.32 (dd, 1H, *anti*-H(4), ^2J = 13.0 Hz, ^3J = 4.4 Hz), 2.52 (dd, 1H, *anti*-H(7), ^2J = 13.6 Hz, ^3J = 5.6 Hz), 2.93 (dd, 1H, *syn*-H(7), ^2J = 13.6 Hz, ^3J = 14.3 Hz), 3.49 (s, 3H, OCH_3), 3.804, 3.807, and 3.88 (all s, 3 × 3H, $3CO_2CH_3$), 4.70 (dd, 1H, H(6), ^3J = 14.3 and 5.6 Hz), 5.24 (dd, 1H, H(3), ^3J = 11.1 and 4.4 Hz), 6.92 (m, 2H, 2 *m*-CH, Ar at C(6), $^3J_{HF}$ = 8.7 Hz), 7.00 (m, 2H, 2 *m*-CH, Ar at C(3), $^3J_{HF}$ = 8.7 Hz), 7.12 (m, 2H, 2 *o*-CH, Ar at C(6), $^4J_{HF}$ = 5.4 Hz), 7.24 (m, 2H, 2 *o*-CH, Ar at C(3), $^4J_{HF}$ = 5.4 Hz); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 35.9 (CH_2(7)), 42.5 (CH(6)), 43.3 (CH_2(4)), 52.1 (OCH_3), 52.73 and 52.78 ($3CO_2CH_3$, 1C and 2C respectively), 65.7 (C(8)), 70.0 (C(5)), 82.3 (CH(4)), 115.3 (d, 2 *m*-CH, Ar at C(6), $^2J_{CF}$ = 21.1 Hz), 115.5 (d, 2 *m*-CH, Ar at C(3), $^2J_{CF}$ = 21.5 Hz), 117.9 (C(1)), 127.4 (d, 2 *o*-CH, Ar at C(3), $^3J_{CF}$ = 8.1 Hz), 129.0 (d, 2 *o*-CH, Ar at C(6), $^3J_{CF}$ = 7.8 Hz), 134.5 (d, *i*-C, Ar at C(6), $^4J_{CF}$ = 3.1 Hz), 135.8 (d, *i*-C, Ar at C(3), $^4J_{CF}$ = 3.0 Hz), 161.9 (d, *p*-C, Ar at C(6), $^1J_{CF}$ = 245.6 Hz), 162.5 (d, *p*-C, Ar at C(3), $^1J_{CF}$ = 246.2 Hz), 168.4, 168.6, and 172.3 (3COO); ^{19}F NMR ($CDCl_3$, 282.4 MHz) δ −116.6 (tt, 1F, $^2J_{FH}$ = 8.7 Hz, $^3J_{FH}$ = 5.4 Hz), −115.1 (tt, 1F, $^2J_{FH}$ = 8.7 Hz, $^3J_{FH}$ = 5.4 Hz); MS (*m*/*z*) 413 (1), 318 (3), 282 (2), 269 (2), 259 (6), 251 (9), 241 (4), 220 (3), 191 (3), 159 (3), 145 (8), 139 (10), 133 (23), 122 (100), 113 (15), 109 (24), 96 (6), 83 (5), 69 (3), 59 (60), 45 (5), 32 (6); HRMS (ESI) calcd for $C_{26}H_{26}F_2O_8$ M + Na, 527.1488 found *m*/*z* 527.1487.

(1*R,3*S**,5*S**,6*S**)-Trimethyl 1-Methoxy-3,6-bis(4-chlorophenyl)-2-oxabicyclo[3.3.0]octane-5,8,8-tricarboxylate (10e).** The title compound was prepared according to the general procedure as a single diastereomer in 185 mg yield (69%, 86% brsm). Compound **10e**: colorless thick oil; IR ($CHCl_3$) ν 3020, 2977, 2955, 2926, 2899, 1734 br (O═CO), 1522, 1495, 1436, 1419, 1249 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 1.28 (dd, 1H, *syn*-H(4), ^2J = 13.0 Hz, ^3J = 11.1

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Hz), 2.33 (dd, 1H, *anti*-H(4), ^2J = 13.0 Hz, ^3J = 4.5 Hz), 2.51 (dd, 1H, *anti*-H(7), ^2J = 13.6 Hz, ^3J = 5.6 Hz), 2.90 (dd, 1H, *syn*-H(7), ^2J = 13.6 Hz, ^3J = 14.3 Hz), 3.49 (s, 3H, OCH_3), 3.804, 3.810, and 3.87 (all s, 3 × 3H, $3CO_2CH_3$), 4.70 (dd, 1H, H(6), ^3J = 14.3 and 5.6 Hz), 5.23 (dd, 1H, H(3), ^3J = 11.1 and 4.5 Hz), 7.08 (m, 2H, C_6H_4), 7.19 (m, 2H, C_6H_4), 7.20 (m, 2H, C_6H_4), 7.29 (m, 2H, C_6H_4); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 35.6 (CH_2(7)), 42.6 (CH(6)), 43.2 (CH_2(4)), 52.1 (OCH_3), 52.76, 52.79, and 52.82 ($3CO_2CH_3$), 65.7 (C(8)), 69.9 (C(5)), 82.2 (CH(4)), 117.9 (C(1)), 127.0, 128.7, 128.8, and 128.9 (8CH, $2C_6H_4$), 132.9 and 133.8 (2 *p*-C, $2C_6H_4$), 137.3 and 138.4 (2 *i*-C, $2C_6H_4$), 168.4, 168.5, and 172.2 (3COO); MS (*m*/*z*) 275 (1), 207 (3), 205 (3), 203 (3), 159 (3), 155 (6), 149 (10), 145 (8), 140 (36), 139 (19), 138 (100), 125 (12), 113 (21), 103 (11), 77 (8), 59 (92), 41 (11); HRMS (ESI) calcd for $C_{26}H_{26}{}^{35}Cl_2O_8$ M + Na, 559.0897, found *m*/*z* 559.0894.

(1*R,3*S**,5*S**,6*S**)-Trimethyl 1-Methoxy-3,6-bis(4-bromophenyl)-2-oxabicyclo[3.3.0]octane-5,8,8-tricarboxylate (10f).** The title compound was prepared according to the general procedure as a single diastereomer in 220 mg yield (70%, 88% brsm). Compound **10f**: colorless thick oil; IR ($CHCl_3$) ν 3020, 2954, 2846, 1734 br (O═CO), 1594, 1517, 1491, 1458, 1436, 1411, 1367, 1332, 1251, 1223 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 1.28 (dd, 1H, *syn*-H(4), ^2J = 13.0 Hz, ^3J = 11.1 Hz), 2.33 (dd, 1H, *anti*-H(4), ^2J = 13.0 Hz, ^3J = 4.5 Hz), 2.51 (dd, 1H, *anti*-H(7), ^2J = 13.5 Hz, ^3J = 5.6 Hz), 2.89 (dd, 1H, *syn*-H(7), ^2J = 13.5 Hz, ^3J = 14.3 Hz), 3.48 (s, 3H, OCH_3), 3.804, 3.810, and 3.87 (all s, 3 × 3H, $3CO_2CH_3$), 4.69 (dd, 1H, H(6), ^3J = 14.3 and 5.6 Hz), 5.22 (dd, 1H, H(3), ^3J = 11.1 and 4.5 Hz), 7.02 (m, 2H, 2 *o*-CH, Ar at C(6)), 7.13 (m, 2H, 2 *o*-CH, Ar at C(3)), 7.35 (m, 2H, 2 *m*-CH, Ar at C(6)), 7.45 (m, 2H, 2 *m*-CH, Ar at C(3)); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 35.5 (CH_2(7)), 42.7 (CH(6)), 43.2 (CH_2(4)), 52.1 (OCH_3), 52.76, 52.79, and 52.82 ($3CO_2CH_3$), 65.7 (C(8)), 69.9 (C(5)), 82.2 (CH(4)), 118.0 (C(1)), 121.0 (CBr, Ar at C(6)), 121.9 (CBr, Ar at C(3)), 127.3 (2 *o*-CH, Ar at C(3)), 129.3 (2 *o*-CH, Ar at C(6)), 131.6 (2 *m*-CH, Ar at C(6)), 131.8 (2 *m*-CH, Ar at C(3)), 137.8 (*i*-C, Ar at C(6)), 139.0 (*i*-C, Ar at C(3)), 168.3, 168.5, and 172.2 (3COO); MS (*m*/*z*) 592 (1, $M^+ - CH_3OH - H_2$), 534 (10, $M^+ - OCH_3 - CO_2CH_3$), 412 (9), 378 (11), 313 (20), 282 (14), 251 (16), 201 (20), 184 (100), 145 (80), 113 (72), 77 (20), 59 (100), 32 (70); HRMS (ESI) calcd for $C_{26}H_{26}{}^{79}Br_2O_8$ M + Na 646.9887, found *m*/*z* 646.9877.

(1*R,3*S**,5*S**,6*S**)-Trimethyl 1-Methoxy-3,6-bis(4-methylphenyl)-2-oxabicyclo[3.3.0]octane-5,8,8-tricarboxylate (10g).** The title compound was prepared according to the general procedure as a single diastereomer in 164 mg yield (66%, 82% brsm). Compound **10g**: colorless thick oil; IR ($CHCl_3$) ν 3020, 2977, 2954, 2926, 1733 br (O═C−O), 1517, 1476, 1435, 1331, 1249, 1224 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 1.38 (dd, 1H, *syn*-H(4), ^2J = 13.1 Hz, ^3J = 11.2 Hz), 2.25 (s, 3H, CH_3, Ar at C(6)), 2.31 (s, 3H, CH_3, Ar at C(3)), 2.33 (dd, 1H, *anti*-H(4), ^2J = 13.1 Hz, ^3J = 4.5 Hz), 2.52 (dd, 1H, *anti*-H(7), ^2J = 13.6 Hz, ^3J = 5.6 Hz), 2.96 (dd, 1H, *syn*-H(7), ^2J = 13.6 Hz, ^3J = 14.3 Hz), 3.48 (s, 3H, OCH_3), 3.794, 3.799, and 3.87 (all s, 3 × 3H, $3CO_2CH_3$), 4.68 (dd, 1H, H(6), ^3J = 14.3 and 5.6 Hz), 5.22 (dd, 1H, H(3), ^3J = 11.2 and 4.5 Hz), 7.02 (s, 4H, 2 *o*-CH and 2 *m*-CH, Ar at C(6)), 7.12 (m, 2H, 2 *m*-CH, Ar at C(3)), 7.17 (m, 2H, 2 *o*-CH, Ar at C(3)); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.0 (CH_3, Ar at C(6)), 21.2 (CH_3, Ar at C(3)), 35.7 (CH_2(7)), 42.9 (CH(6)), 43.5 (CH_2(4)), 52.0 (OCH_3), 52.6 and 52.7 ($3CO_2CH_3$, 1C and 2C respectively), 65.9 (C(8)), 70.1 (C(5)), 82.9 (CH(4)), 117.9 (C(1)), 125.7 (2 *o*-CH, Ar at C(3)), 127.4 (2 *o*-CH, Ar at C(6)), 129.1 (2 *m*-CH, Ar at C(3)), 129.2 (2 *m*-CH, Ar at C(6)), 135.9 (*i*-C, Ar at C(6)), 136.4 (*p*-C, Ar at C(6)), 137.2 (*i*-C, Ar at C(3)), 137.6 (*p*-C, Ar at C(3)), 168.6, 168.8, and 172.6 (3COO). MS (*m*/*z*) 405 (1), 347 (1), 255 (1), 187 (3), 185 (2), 159 (3), 145 (3), 136 (7), 129 (16), 118 (100), 105 (15), 91 (10), 59 (11); HRMS (ESI) calcd for $C_{28}H_{32}O_8$ M + Na, 519.1989, found *m*/*z* 519.1979.

(1*R,3*S**,5*S**,6*S**)-Trimethyl 1-methoxy-3,6-bis(4-nitrophenyl)-2-oxabicyclo[3.3.0]octane-5,8,8-tricarboxylate (10h).** The reaction was performed in an NMR tube. To a solution of cyclopropane **1** (0.2 mmol) and pyrazoline **9** in 0.5 mL of dry C_6D_5Cl was added the solid $GaCl_3$ in one portion at room temperature under vigorous shaking. After that, the reaction mixture was heated to 80 °C and was allowed to stand during 1.5 h without rotation. The NMR spectra were recorded from the reaction mixture at regular time intervals. The compound **10h** was observed in ^{1}H NMR spectra of the reaction mixture. Its yield did not exceed 2% and its concentration was permanent during 1 h (because the rates of formation and decomposition were similar), after that **10h** completely decomposed. Attempts to isolate the compound **10h** were unsuccessful due to its decomposition. **10h**: part of ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 4.67 (dd, 1H, H(6), ^3J ~ 13 and 5 Hz), 5.59 (dd, 1H, H(3), ^3J = 11 and 5 Hz). Other signals overlapped with signals of the major compounds.

(1*R,3*S**,5*S**,6*S**)-Trimethyl 1-Methoxy-3,6-bis(4-methoxyphenyl)-2-oxabicyclo[3.3.0]octane-5,8,8-tricarboxylate (10i).** A solution of cyclopropane **1i** (150 mg, 0.57 mmol) and pyrazoline **9b** (26 mg, 0.11 mmol, 20 mol %) in 3 mL of dry dichloromethane was cooled to −40 °C. Then the solid $GaCl_3$ (20 mg, 0.11 mmol, 20 mol %) was added in one portion at −40 °C under vigorous stirring, and the reaction mixture was heated to −20 °C and stirred for 1 h. After that the cold tetrahydrofuran (0.7 mL) was added for the destruction of gallium complexes and the solvent was evaporated under vacuum at −20 °C. The residue was separated immediately by column chromatography on silica gel (benzene−EtOAc, 20:1) to afford starting cyclopropane **1i** (15 mg, 10%), oxabicyclooctane **10i** (30 mg, 20% (22% brsm)), compound **12** (75 mg, 50% (56% brsm)), and starting pyrazoline **9b** (25 mg, 97%). The resulting oxabicyclooctane **10i** was additionally purified by flash chromatography on silica gel (hexane−acetone, 5:1) to give a pure product. Compound **10i**: colorless thick oil; IR ($CHCl_3$) ν 3020, 2976, 2956, 2936, 2900, 2841, 1731 br (O═C−O), 1613, 1515, 1461, 1437, 1392, 1249, 1224 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 1.39 (dd, 1H, *syn*-H(4), ^2J = 13.0 Hz, ^3J = 11.2 Hz), 2.30 (dd, 1H, *anti*-H(4), ^2J = 13.0 Hz, ^3J = 4.5 Hz), 2.50 (dd, 1H, *anti*-H(7), ^2J = 13.6 Hz, ^3J = 5.6 Hz), 2.95 (dd, 1H, *syn*-H(7), ^2J = 13.6 Hz, ^3J = 14.5 Hz), 3.48 (s, 3H, OCH_3), 3.73 and 3.78 (both s, 2 × 3H, $2OCH_3$ from Ar), 3.79 and 3.87 (both s, 6H and 3H, respectively, $3CO_2CH_3$), 4.66 (dd, 1H, H(6), ^3J = 14.5 and 5.6 Hz), 5.21 (dd, 1H, H(3), ^3J = 11.2 and 4.5 Hz), 6.76 (m, 2H, 2 *m*-CH, C_6H_4'), 6.85 (m, 2H, 2 *m*-CH, C_6H_4''), 7.07 (m, 2H, 2 *o*-CH, C_6H_4'), 7.21 (m, 2H, 2 *o*-CH, C_6H_4''); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 35.9 (CH_2(7)), 42.5 (CH(6)), 43.4 (CH_2(4)), 52.0 (OCH_3), 52.6 and 52.7 (1C and 2C respectively, $3CO_2CH_3$), 55.3 and 55.4 ($2OCH_3$ from Ar), 65.9 (C(8)), 70.1 (C(5)), 82.7 (CH(4)), 113.9 (2 *m*-CH, C_6H_4'), 114.0 (2 *m*-CH, C_6H_4''), 117.8 (C(1)), 127.0 (2 *o*-CH, C_6H_4''), 128.6 (2 *o*-CH, C_6H_4'), 131.0 and 132.3 (2 *i*-C, $2C_6H_4$), 158.5 and 159.5 (2 *p*-C, $2C_6H_4$), 168.6, 168.8, and 172.7 (3COO). MS (*m*/*z*, %): 331 (1), 303 (1), 291 (4), 279 (1), 265 (7), 250 (2), 234 (2), 225 (5), 203 (11), 190 (6), 173 (7), 164 (7), 151 (29), 145 (47), 135 (57), 134 (100), 121 (26), 91 (24), 77 (20), 59 (62); HRMS (ESI) calcd for $C_{28}H_{32}O_{10}$ M + Na, 551.1888, found *m*/*z* 551.1888.

(1*R,3*S**,5*S**,6*S**)-Trimethyl 1-Methoxy-3,6-bis(2-naphthyl)-2-oxabicyclo[3.3.0]octane-5,8,8-tricarboxylate (10j).** The title compound was prepared according to the general procedure as a single diastereomer in 185 mg yield (65%, 76% brsm). Compound **10j**: colorless thick oil; IR ($CHCl_3$) ν 3020, 2976, 2954, 2846, 1733 br (O═CO), 1633, 1602, 1510, 1436, 1392, 1337, 1328, 1252, 1223 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 1.53 (dd, 1H, *syn*-H(4), ^2J = 13.0 Hz, ^3J = 11.2 Hz), 2.43 (dd, 1H, *anti*-H(4), ^2J = 13.0 Hz, ^3J = 4.5 Hz), 2.70 (dd, 1H, *anti*-H(7), ^2J = 13.5 Hz, ^3J = 5.5 Hz), 3.16 (dd, 1H, *syn*-H(7), ^2J = 13.5 Hz, ^3J = 14.2 Hz), 3.56 (s, 3H, OCH_3), 3.84, 3.88, and 3.95 (all s, 3 × 3H, $3CO_2CH_3$), 4.94 (dd, 1H, H(6), ^3J = 14.2 and 5.5 Hz), 5.46 (dd, 1H, H(3), ^3J = 11.2 and 4.5 Hz), 7.26 (dd, 1H, CH(3″), ^3J = 8.6 Hz, ^4J = 1.7 Hz), 7.35−7.47 (m, 5H, CH(3′), CH(6′), CH(7′), CH(6″) and CH(7″)), 7.62 (br.s, 1H, CH(1″)), 7.67 (d, 1H, CH(4″), ^3J = 8.6 Hz), 7.69−7.81 (m, 6H, CH(1′), CH(4′), CH(5′), CH(8′), CH(5″) and CH(8″)); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 35.8 (CH_2(7)), 43.1 (CH_2(4)), 43.4 (CH(6)), 52.1 (OCH_3), 52.73 and 52.78 ($3CO_2CH_3$, 1C and 2C respectively), 66.0 (C(8)), 70.1 (C(5)), 83.0 (CH(4)), 118.2 (C(1)), 123.5 (CH(3′)), 124.5 (CH(1′)), 125.78, 125.85, 126.01, 126.10, 126.15, and 126.25 (CH(1″), CH(3″), CH(6′), CH(7′), CH(6″) and CH(7″)), 127.5, 127.7, 127.9, 128.0, 128.1, and

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128.4 (CH(4′), CH(4″), CH(5′), CH(8′), CH(5″) and CH(8″)), 132.4 (C(4a″)), 133.15, 133.22, and 133.31 (C(4a′), C(8a′) and C(8a″)), 136.6 (C(2″)), 137.4 (C(2′)), 168.6, 168.8, and 172.6 (3COO); MS (m/z): 535 (5, $M^+ - CH_3OH - H$), 477 (1), 428 (5), 382 (11), 368 (15), 350 (7), 336 (12), 322 (8), 308 (9), 291 (8), 277 (32), 249 (15), 223 (18), 165 (52), 154 (100), 141 (23), 128 (16), 113 (14), 59 (67), 32 (31); HRMS (ESI) calcd for $C_{34}H_{32}O_8$ M + Na 591.1989, found m/z 591.1990.

Monitoring of the Reaction in an NMR Tube. All operations were performed under dry argon atmosphere in an NMR tube. A solution of cyclopropane **1** (0.2 mmol) and pyrazoline **9** in 0.5 mL of dry CD_2Cl_2 was cooled to −30 °C. Then the solid $GaCl_3$ was added in one portion at temperature under vigorous shaking, the NMR tube was placed in NMR spectrometer, reaction mixture was gradually heated to a target temperature and was standing for a necessary time without rotation. The NMR spectra were recorded from the reaction mixture at regular time intervals. If it was necessary the 0.1−0.2 mL CD_3OD was added to a NMR tube for the destruction of gallium complexes. Spectroscopic data of intermediate **IIa**. Red solution in CD_2Cl_2 (mixture of eight regio- and stereoisomers, ratio ~1:1:1:1:3.5:3.5:3.5:3.5): ^{1}H NMR (CD_2Cl_2, 400.1 MHz) δ 1.20−1.45 (all t, 54H, 8 × CH_2CH_3, ^3J = 7.1−7.2 Hz), 1.60−1.80 (all s, 54H, 8 × CH_3 at C(3)), 1.95−2.05 (all s, 54H, 8 × CH_3 at C(5)), 2.10−2.25 (all s, 28H, *E*-isomer, 4 × CH_2(4)), 2.70−2.95 (all d, 8H, *Z*-isomer, 4 × CH_2(4)), 2.80−3.05 (m, 36H, 8 × CH_2(2′), ^3J = 7.4, 6.4, 6.3 Hz), 3.35−4.05 (all s, 162H, 24OCH_3), 4.30−4.55 (all q, 36H, 8 × CH_2CH_3, ^3J = 7.1−7.2 Hz), 6.18 (2 × t, 2H, *Z*-isomer, 2 × H(1′), ^3J = 6.3 Hz), 6.25 (4 × t, 14H, *E*-isomer, 4 × H(1′), ^3J = 6.4 Hz), 6.39 (2 × t, 2H, *Z*-isomer, 2 × H(1′), ^3J = 7.4 Hz), 7.15−7.60 (m, 90H, 8Ph); ^{13}C NMR (CD_2Cl_2, 100.6 MHz, all signals are broad) δ 15.3 (CH_2CH_3), 24.0 and 24.3 (CH_3 at C(3)), 25.1 (CH_3 at C(5)), 40.5 and 43.0 (CH_2(4) and CH_2(2′)), 52−56 (OCH_3), 64.0 (CH_2CH_3), C(3) − overlapped with other signals, 93.0 (C(5)), 99.0 (CH(1′)), 109.0 (C(3′)), 127−133 (CH, Ph), 139.5 (*i*-C, Ph), 154.9 (C(4′)), 169−173 (COO), 176.0 (COO); ^{35}Cl NMR (CD_2Cl_2, 39.2 MHz) δ 235 (br s, $W_{1/2}$ ~ 7800 Hz); ^{69}Ga NMR (CD_2Cl_2, 96.0 MHz) δ 251 (s, $W_{1/2}$ ~ 750 Hz); ^{71}Ga NMR (CD_2Cl_2, 122.0 MHz) δ 250.5 (s, $W_{1/2}$ ~ 350 Hz).

■ ASSOCIATED CONTENT

Supporting Information

Copies of NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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