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"Cyclopropanation of Cyclopropanes": $GaCl_3$-Mediated Ionic Cyclopropanation of Donor–Acceptor Cyclopropanes with Diazo Esters as a Route to Tetrasubstituted Activated Cyclopropanes

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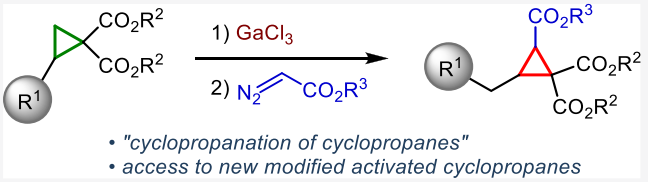
ABSTRACT: A new ionic cyclopropanation process involving the addition of diazo esters to donor–acceptor cyclopropanes (DAC) activated by $GaCl_3$ has been developed. The reactions occur via 1,2-zwitterionic gallium complexes with elimination of nitrogen in all cases to give 1,1,2,3-tetrasubstituted cyclopropanes as the main products. Also, a number of related processes with the formation of various polysubstituted cyclopropanes, alkenes, and cyclobutanes, including products of multiple diazo ester addition, have been developed. Obtained by the developed method tetrasubstituted cyclopropanes are activated cyclopropanes such as DAC and can be used for further synthesis in this capacity. Their new reaction with benzaldehyde promoted by $TiCl_4$ and involving one of the additional functional groups has been demonstrated, which leads to five-membered lactones. The mechanisms of the occurring processes, as well as the structures and stereochemistry of a rich range of products formed, are discussed in detail.



KEYWORDS: *Donor–acceptor cyclopropanes, Diazo esters, Gallium trichloride, Ionic cyclopropanation, 1,2-Zwitterionic intermediates, Tetrasubstituted cyclopropanes, Titanium tetrachloride, Lactones*

INTRODUCTION

The chemistry of cyclopropanes containing donor and acceptor substituents (DAC)[1,2] has lately been attracting an increasing attention of scientists due to their exceptional synthetic potential.[3,4] The push–pull effect of donor and acceptor substituents in DAC causes a strong polarization of the vicinal C–C bond, which enables its opening and implementation of processes involving this three-carbon synthon, in particular, cycloaddition, cyclization, aromatic annulation, and other reactions often accompanied by various rearrangements.[5−7]

A separate approach in the chemistry of DAC, in particular 2-arylcyclopropane-1,1-dicarboxylates (ACDC, **1**), involves the reactions that occur with 1,2-hydride shift in pregenerated 1,3-zwitterion **2** (Scheme 1).[8] It should be noted that this process is very typical if anhydrous gallium trichloride is used, and ACDC themselves act as sources of 1,2-zwitterionic synthons **3** in this case.[9] This strategy allowed the development of new types of chemical reactions of DAC with alkenes, alkynes, aromatic aldehydes, and other substrates.[10]

Despite the fast development of the chemistry of 1,2-zwitterionic intermediates, their reactions with 1,3-dipoles were studied only using benzyl azide as an example.[11] Simultaneously, numerous reactions of trapping of 1,3-zwitterionic intermediates by various 1,3-dipoles (nitrones, azides, nitrilimines, nitronates, and azomethines) that occur as formal (3 + 3)-cycloaddition were studied extensively.[12] On the other hand, diazo compounds were little studied as 1,3-dipoles in these reactions. To date, only a few works with participation of diazo compounds are known.[13] However, not the diazomethane moiety itself but a secondary 1,3-zwitterion that is either generated by diazotization of vinyl diazoacetate or formed in reactions of a diazo compound with ketones is involved in these processes (Scheme 1A).[13] One example of a reaction without nitrogen loss is known for vinylcyclopropanes under conditions of palladium(0) catalysis (Scheme 1B).[13c]

Attempts to conduct direct formal (3 + 3)-cycloaddition under typical conditions[14] (Scheme 1C) result in the loss of a nitrogen molecule and formation of products of C–C coupling of both substrates—substituted alkenes and cyclopropanes. Moreover, the main pathways are determined by the addition of a diazo ester to 1,3-zwitterionic intermediates being generated, followed by carbocationic rearrangements and fragmentation (Scheme 1D).[14]

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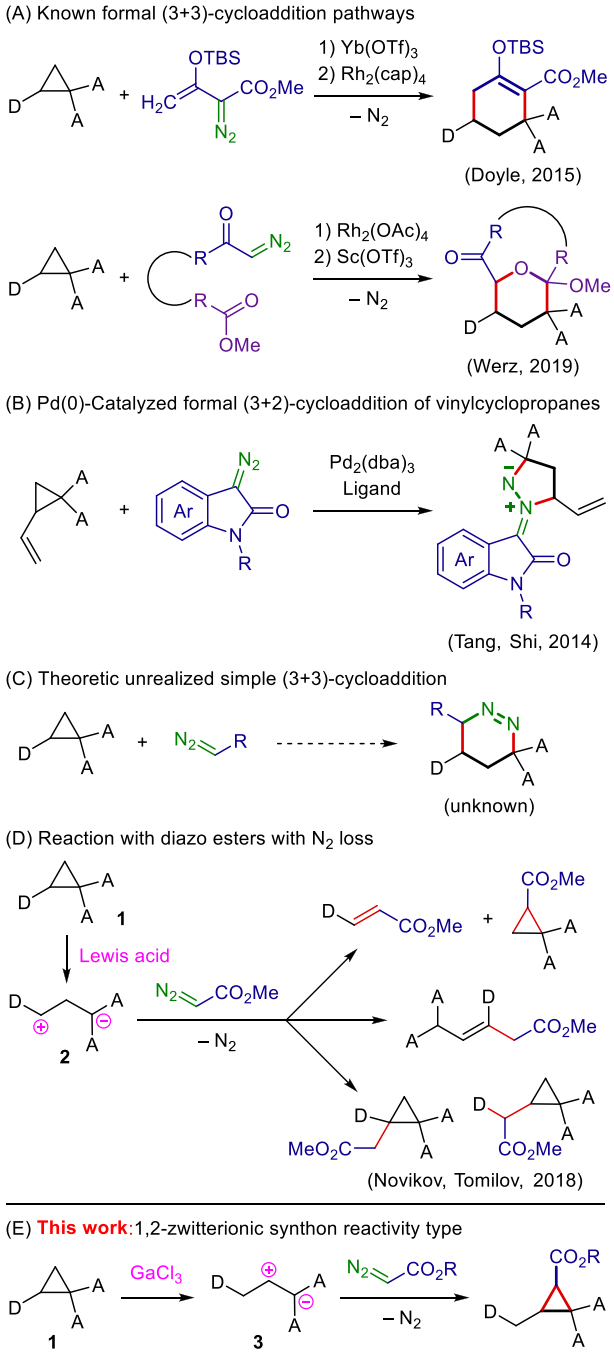
Scheme 1. Reactivity Pattern of D−A Cyclopropanes with Diazo Compounds

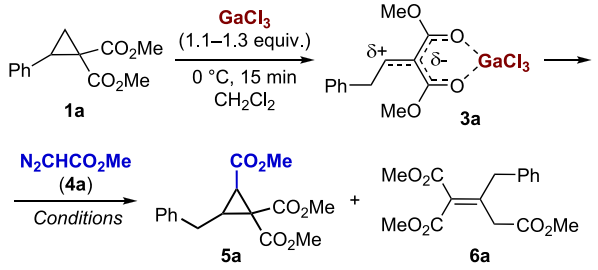


This study is a continuation of a series of studies on the chemical transformations of gallium 1,2-zwitterionic complexes generated from ACDC in the presence of $GaCl_3$ and is focused on a study of their reactivity with diazo compounds (Scheme 1E), primarily with diazo esters, since diazo alkanes are too unstable under conditions of catalysis with strong Lewis acids. A specific feature of this process is the implementation of the formal "cyclopropanation of cyclopropanes" (ring opening ring closing cyclopropanation (RORCC) of DAC) as a new approach to the synthesis of tetrasubstituted cyclopropanes based on trisubstituted DAC. Thus, this approach allows one to generate 1,2-zwitterionic synthons **3** and to create new DACs with advanced functionality based on existing DACs.

RESULTS AND DISCUSSION

To perform this process, ACDC **1** was chosen as the initial model substrates. They were initially treated with gallium trichloride to generate gallium 1,2-zwitterionic complexes **3**, which were then entered into reactions with diazo acetates **4**. The generation of intermediates **3** was carried out using the methods that we mastered previously.[10a,b] To optimize the second stage of the process, we used the reaction of intermediate **3a**, which was obtained from 2-phenylcyclopropane-1,1-diester **1a**, with methyl diazo acetate **4a** (Table 1).

Table 1. Optimization of the Reaction Conditions



entry	ratio **1a**/**4a**	T (°C)	t (min)	yields (%)[a] **5a**	*trans*/*cis*[b]	**6a**
1	1:2	25	30	45	1.4/1	12
2	1:2	40	15	48	1.5/1	15
3	1:2	−60	15	48	1.5/1	13
4	**1:2**	**15**	**15**	**60**[c]	**1.5/1**	**19**[c]
5	1:1	15	15	38	1.5/1	15
6[d]	1:10	15	15	9	2/1	<2
7[e]	1:2	84	30	31	1.6/1	14

[a]NMR yields; they were determined by ^{1}H NMR spectra using 1,4-dinitrobenzene as an internal standard. [b]Diastereomer ratio was determined by the ^{1}H NMR spectra. [c]Yields after column chromatography. [d]Adducts of double addition of the diazo esters are formed as major products. [e]1,2-DCE was used as a solvent (3 mL).

It was found that in a fairly broad temperature range, a new cyclopropane-containing product—the corresponding cyclopropane-1,1,2-tricarboxylate **5a** —is the main product of this reaction. Isomeric unsaturated triester **6a** is formed in parallel, though in a much smaller amount.

One can see from Table 1 that both reaction pathways giving isomeric compounds **5a** and **6a** practically do not change, which does not allow one to obtain each of them selectively. Likewise, we failed to make the formation of cyclopropane **5a** a stereoselective process (the ratio of *trans* and *cis*-isomers remains at ca. 1.5:1 level).

In order to change the regio- and stereoselectivity of the process, an attempt was made to use **4b,c** containing sterically hindered neopentyl and benzyl moieties in the reaction. In this case, the ratio of *trans*- and *cis*-isomers changed more significantly. The use of sterically hindered DAC with neopentyl substituents, alone or in combination with neopentyl diazo ester, does not allow one to achieve any significant increase in regio- and distereoselectivity, either. In general, it should be noted that the nature of substituents in the substrates does not allow one to identify clear regularities regarding their effect both on the degree of formation of cyclopropanes **5** and alkenes **6** and on the stereoselectivity of the formation of isomeric cyclopropanes **5**. We also showed

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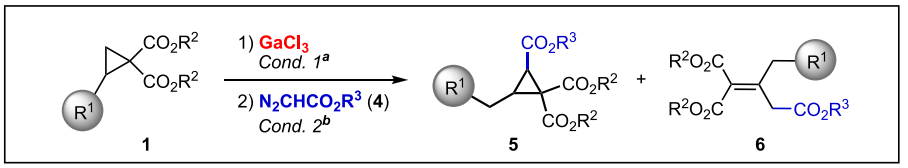
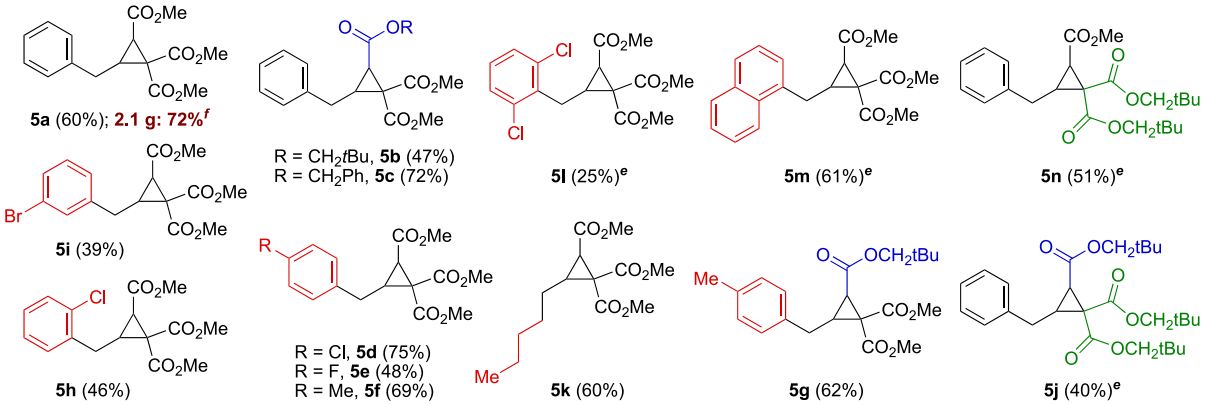
Table 2. Scope for the $GaCl_3$-Mediated Addition of Diazo Esters to D−A Cyclopropanes[a,b]





entry	starting ACDC			diazo ester		cyclopropanes obtained			alkene	
	1	Y	R	4	R^1	5	yield (%)	*trans/cis*[c]	6	yield (%)
1	**1a**	Ph	Me	**4a**	Me	**5a**	60	1.5:1	**6a**	19
2[f]	**1a**	Ph	Me	**4a**	Me	**5a**	72[f]	1.5:1	**6a**	19
3	**1a**	Ph	Me	**4b**	*t*-$BuCH_2$	**5b**	47	1.1:1	**6b**	21
4	**1a**	Ph	Me	**4c**	$PhCH_2$	**5c**	72	1.1:1	**6c**	18
5	**1b**	4-ClC_6H_4	Me	**4a**	Me	**5d**	75	1.4:1	**6d**	19
6	**1c**	4-FC_6H_4	Me	**4a**	Me	**5e**	48	1.4:1	**6e**	9
7	**1d**	4-MeC_6H_4	Me	**4a**	Me	**5f**	69	1.5:1	**6f**	21
8	**1d**	4-MeC_6H_4	Me	**4b**	*t*-$BuCH_2$	**5g**	62	1.2:1	**6g**	19
9	**1e**	2-ClC_6H_4	Me	**4a**	Me	**5h**	46	1.7:1	**6h**	27
10	**1f**	3-BrC_6H_4	Me	**4a**	Me	**5i**	39	1.3:1	**6i**	16
11	**1i**	2,6-$Cl_2C_6H_4$	Me	**4a**	Me	**5l**	25[d,e]	1.5:1	**6l**	17[d,e]
12	**1j**	1-Naphthyl	Me	**4a**	Me	**5m**	61[d,e]	1:1.4	**6m**	27[d,e]
13	**1g**	Ph	*t*-$BuCH_2$	**4a**	Me	**5n**	51[d,e]	2:1	**6n**	16[d,e]
14	**1g**	Ph	*t*-$BuCH_2$	**4b**	*t*-$BuCH_2$	**5j**	40[d]	1:1.2	**6j**	10[d]
15	**1h**	*n*-C_5H_{11}	Me	**4a**	Me	**5k**	60	1.3:1	**6k**	13

[a]Conditions 1: formation of complex **3** from ACDC (1 equiv.) and $GaCl_3$ (1.1−1.2 equiv) at 0−40 °C during 10−75 min (See Refs.[10a,b] and Experimental Section). [b]Conditions 2: diazo ester (2 equiv.) in CH_2Cl_2 was added to complex **3** at 15 °C and mixture was stirred 15 min. [c]Ratio of isomers was determined by ^1H NMR spectra. [d]NMR yield, yield was determined by ^1H NMR spectra using 1,4-dinitrobenzene as an internal standard. [e]Products were not isolated in pure form. [f]Gram-scale of the reaction: 2.1 g (9.0 mmol) of DAC **1a** was used.

that the action of $GaCl_3$ on cyclopropane **5a** under the reaction conditions (15 °C, 15 min) practically does not cause its isomerization to alkene **6a**.

In total, the scope for DAC is rather wide, and various DAC can be used to obtain cyclopropane triesters **5** in decent yields (Table 2). ACDC with substituents at various positions of the benzene ring, as well as *n*-butylcyclopropane **1h**, can be successfully used in the reaction and the substituents in the ester groups can be varied.

The mechanism of the occurring processes can be described as follows (Scheme 2, Figure 1). At the first stage, a relatively stable gallium complex **3** is generated. Its carbocationic center attacks the diazo compound with elimination of a nitrogen molecule and formation of a new 1,3-zwitterion **7** that should be very unstable (*path a*). The latter undergoes cyclization to give a complex of cyclopropanetricarboxylate **5** with $GaCl_3$ and partial isomerization into 1,2-zwitterionic gallium complex **8** that is the most stable species under the reaction conditions. After acid treatment of the reaction mixture, both complexes are converted into cyclopropane **5** or unsaturated triester **6** (Scheme 2). The other path of the formation of cyclopropane product **5** may occur directly from the diazonium intermediate that precedes zwitterion **3** by an intramolecular nucleophilic substitution by-passing the unstable species **3** (*path b*). In essence, the process under consideration resembles the formation of cyclopropane derivatives by the Corey-Chaykovsky reaction.[15] In this case, the Michael acceptor is strongly activated due to complexation with gallium trichloride, which allows it to react with such a weak nucleophile as diazo acetate.

To better understand the discovered process, its regularities, and mechanism, we have studied in details formed minor products during the reaction at various conditions (Table 3, Figure 2). Besides main compounds **5** and **6**, almost only products of double addition of the diazoacetate (MDA) are formed. Herewith, the summary yield may exceed 95%. However, the structures of these heavy products are highly different, and significantly depend on the reaction conditions and primarily on the excess of using diazoacetate (Table 3).

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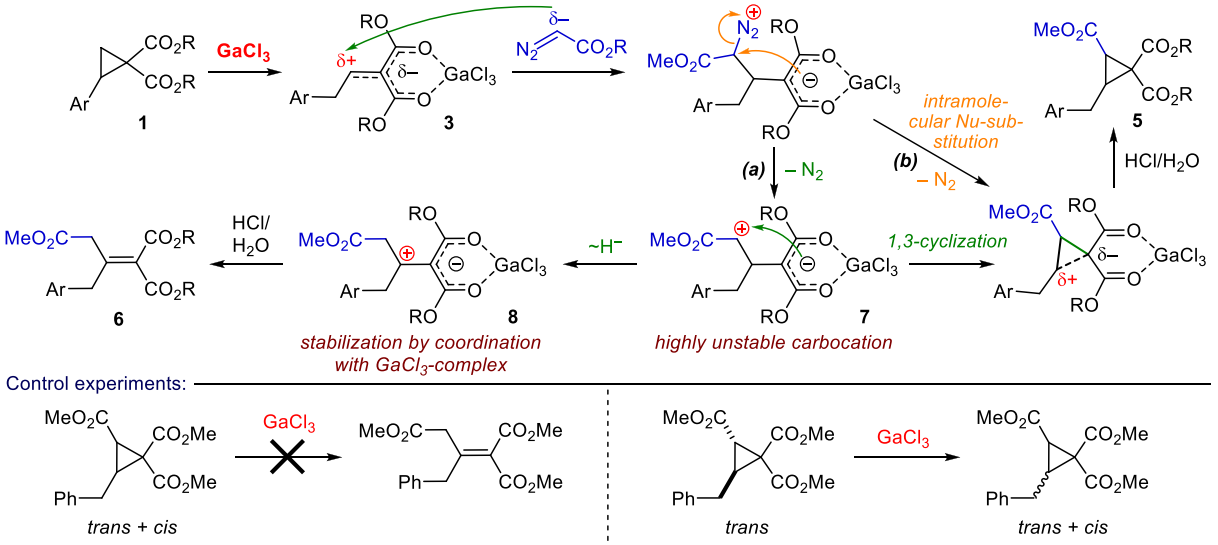
Scheme 2. Proposed Simplified Mechanism for the Formation of Cyclopropanes 5



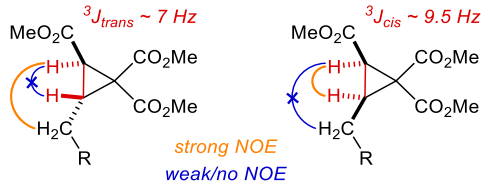
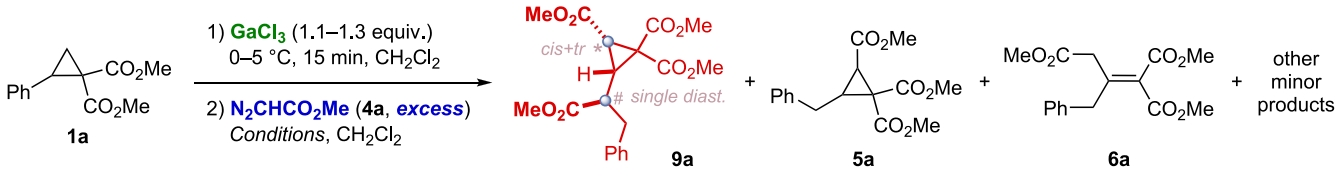
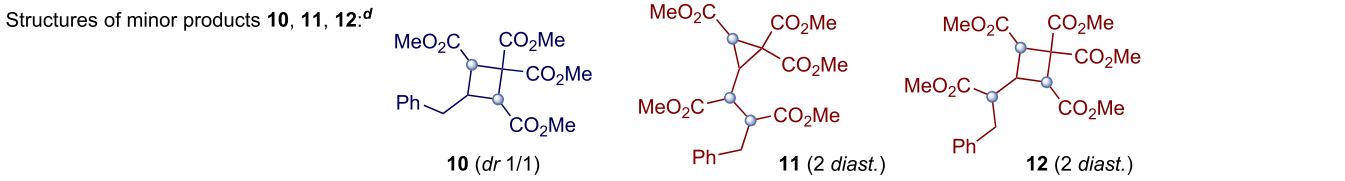


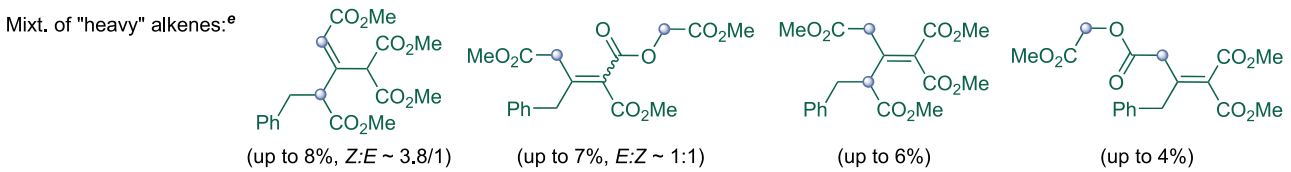
Figure 1. Analysis of stereochemistry for the *trans*- and *cis*-isomers of cyclopropane **5.**

Thus, minor cyclobutane structure **10** and cyclopropane **9a** are formed, when 2 equiv. of MDA was used (some preliminary data can be also found in our previous paper[14]). The last activated cyclopropane **9a** is quite interesting and contains four carboxylate groups and three new stereocenters. This cyclopropane **9a** can be prepared quite selectively using 10 equiv of MDA at 15 °C with yields of more than 55% (Table 3, Entry 2). It is formed primarily as one *cis*-diastereomer with single configuration of the acyclic stereocenter (Figure 2). Using a 10-fold excess of MDA, especially at a slightly elevated

Table 3. Double Addition of the Diazoacetate (MDA) to D−A Cyclopropane 1a and Formation of Heavy Products[a,b]







			products[a,b]; yield,[c] %; (*cis*/*trans* ratio)						
entry	**4a** (equiv.)	conditions	**9a**	**5a**	**6a**	**10**[d]	mixt. of alkenes[e]	**11**[d]	**12**[d]
1	**2**	15 °C, 15 min	7 (1:1)	60 (1:1.5)	19	3 (1:1)	<5	*n.d.*[f]	*n.d.*
2	**10**	15 °C, 15 min	**57 (2.4:1)**	9 (1:2)	<2	*n.d.*	15	*n.d.*	*n.d.*
3	**10**	30 °C, 15 min	35−40	10	<2	*n.d.*	**25−30**	*n.d.*	*n.d.*
4	**30**	15 °C, 15 min	<20	<5	*n.d.*	*n.d.*	20	**10**	**2−3**

[a]Determined main and minor products of multiple MDA addition at various reaction conditions. [b]Carbons from diazoacetate are indicated by light blue circles. [c]Averaged yields based on NMR data and data after column chromatography; accuracy ±2−3%; yields are indicated for typical experiments. [d]Structures of minor products **10, 11,** and **12**. [e]Mixt. of "heavy" alkenes. [f]*n.d.* = not detected.

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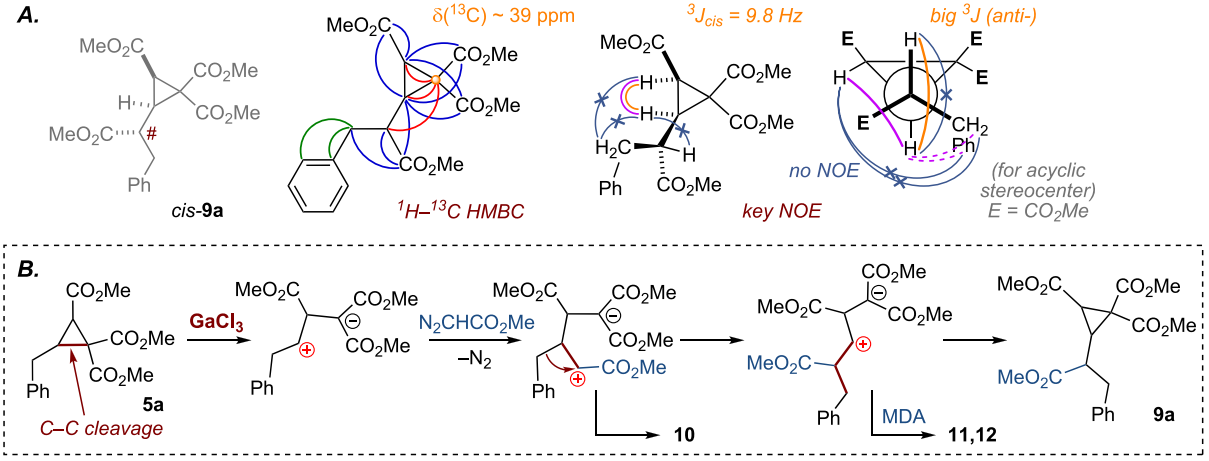

Figure 2. (A) Detailed analysis of skeleton and stereochemistry of the main isomer of cyclopropane **9a**. (B) Proposed mechanism for the formation of cyclopropane **9a**. Notes: coordination with $GaCl_3$ is omitted for clarity; configuration of the stereocenter indicated by (#) is proposed by NOE data, only one diastereomer is formed on this stereocenter.

temperature (30 °C), various confirmed alkene products of double MDA addition are also formed in quite significant quantities during the reaction (Table 3, Entries 2 and 3). Using a 30 equiv. of MDA, it can be obtained triple addition products—cyclopropane pentacarboxylate **11** and side isomeric cyclobutane pentacarboxylate **12** (Table 3, Entry 4). It should be noted that the formation of cyclobutanes in DAC reactions is extremely rare, even as a side reaction.[16] Cyclopropane products like **9a** were also detected and isolated for some other substituted D−A cyclopropanes **1** and also for a benzyl diazoacetate **4c**.

The main route to form the heavy products of double diazo ester addition is going through the initial formation of cyclopropane **5**, which is also activated by two carboxylate groups in strong Lewis acid conditions (Figure 2). This leads to further C−C cleavage of the cyclopropane ring and subsequent reaction with the second MDA molecule. Control mechanistic experiment also demonstrates an activation of a three-membered ring in cyclopropane **5a** in the presence of $GaCl_3$ (Scheme 2, bottom, right).

Separately, a confirmed formation of two products resulting from the decomposition of an excess of diazo ester under action of $GaCl_3$ without involving a DAC molecule should also be noted. These products can be obtained in significant quantities in some cases (Figure 3).

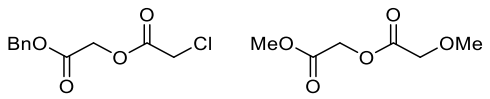

Figure 3. Detected products formed as a result of the side decomposition process of Bn and Me diazoacetates (left and right, respectively).

Further, in order to estimate the effect of additional substituents in the original DAC on the nature of conversion of the resulting zwitterionic intermediates, we studied the reaction of methyl diazo acetate with gallium complex **3i** obtained from 2,2-diphenylcyclopropane-1,1-dicarboxylate **1i**. It was found that in this case, the process occurs differently to give cyclobutanetricarboxylate **13** as the main product. Despite the presence of three stereo centers, this compound is formed as a sole *trans,trans* isomer (Scheme 3). The expected tetrasubstituted cyclopropane **5l** is formed in only 6−7% yield and, like in the case of ACDC **1**, as a mixture of *trans*- and *cis*-isomers. The amount of tetrasubstituted alkene **6l** formed remains at nearly the same level. The importance of this process should be noted separately, since the formation of cyclobutanes in DAC reactions is extremely rare, even as a side reaction.[16]

A distinctive feature of diphenyl-substituted cyclopropane diester **1i** is apparently that it, already during its formation, is partially isomerized into 1,3-zwitterion **15** due to phenyl migration. Further, both of these intermediates react with diazo acetate **4a** with elimination of nitrogen to generate 1,3-zwitterion **3i** in one case, and 1,4-zwitterion **16** in the other case. As expected, the first zwitterion either undergoes cyclization to substituted cyclopropane **5l** or is converted to alkene **6l**, while the second one mostly undergoes cyclization to cyclobutanetricarboxylate **13**. The latter gradually undergoes opening under the reaction conditions in the presence of $GaCl_3$ with addition of a chloride anion to give chloro derivative **14** (Scheme 4). It is interesting to note that, like cyclobutane **13**, trisubstituted lactone **14** is formed as a single stereoisomer only.

The resulting cyclopropanetricarboxylates **5** also belong to activated cyclopropanes that can be used as DAC in further reactions (Scheme 5). Moreover, they contain an additional functional group. We used **5a** as an example to study the possibility of their conversion under the effect of Lewis acids, with benzaldehyde as the classic model interceptor of a 1,3-zwitterion.[17] As expected, cyclopropane **5a** was found to be much less reactive than ACDC **1** due to the presence of a Bn group instead of Ph at position 2. The reaction occurred slowly even if strong Lewis acids, such as $GaCl_3$ or $SnCl_4$, were used and the process was performed under reflux conditions in CH_2Cl_2. The process occurred much better in the presence of $TiCl_4$, therefore we subsequently used this particular Lewis acid for optimizing the reaction conditions (Table 4).

It was found that more drastic conditions (reflux in 1,2-dichloroethane with a 1.5-fold excess of $TiCl_4$) resulted in the efficient reaction of **5a** with benzaldehyde to give dihydrofuran-2-ones **17** and **18**, as well as a chlorine-containing ester **19**. In addition, in the reaction mixture, we found the presence of isomeric trimethyl 5-benzyl-2-phenyltetrahydrofurane-3,3,4-tricarboxylates formed according to the usual scheme (3 +

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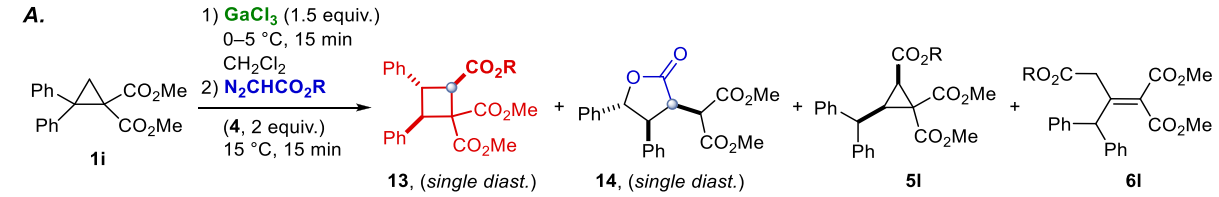
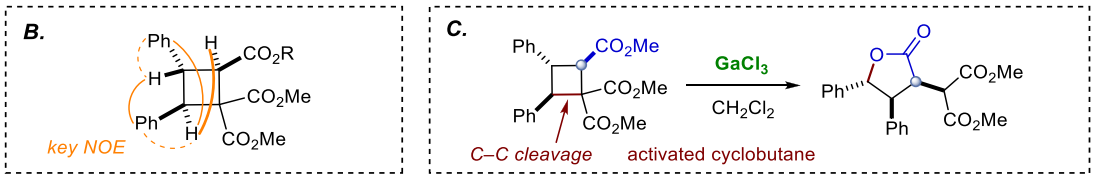
Scheme 3. Reaction of the 2,2-Ph,Ph-Disubstituted DAC 1i with Diazo Acetates in the Presence of $GaCl_3$: (A) General Reaction Pathways and Product Yields; (B) Analysis of the Stereochemistry of Main Cyclobutane Product 13; (C) Formation Route of the Lactone 14[a,b]

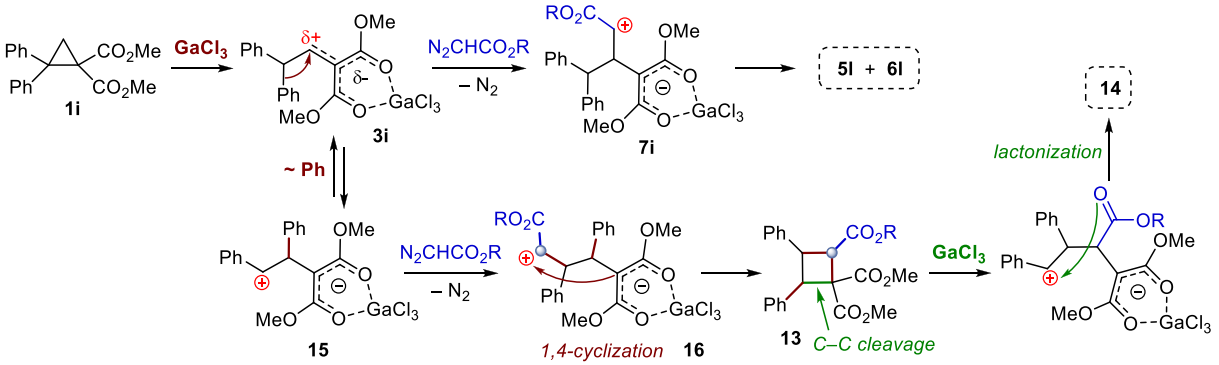


R = **Me**	**13a** (45%), (40%)[a]	**14a** (10%)	**5la** (12%, (6%)[a], *cis:tr* = 1.3/1)	**6la** (18%)
R = **Bn**	**13b** (43%)	**14b** (<3%)	**5lb** (16%, *cis:tr* = 2.4/1)	**6lb** (18%)

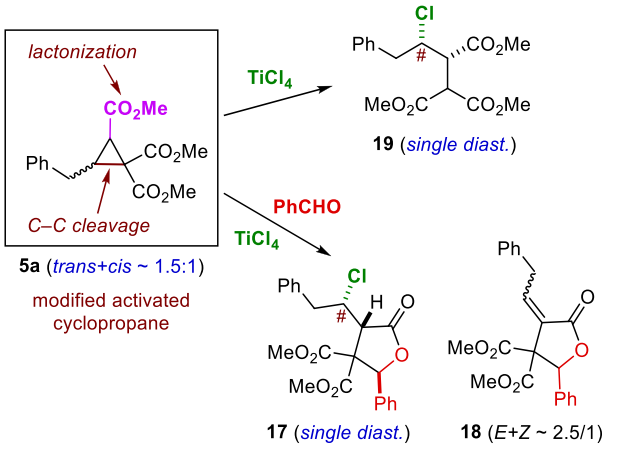


[a]NMR yields, yields after column chromatography are given in the second parentheses. [b]Carbons from diazoacetate are indicated by light blue circles.

Scheme 4. Proposed Mechanism for the Formation of Cyclobutanes 13



Scheme 5. Further Synthetic Utility of the Obtained Cyclopropanetricarboxylates 5 as D–A Cyclopropanes[a]



[a]Proposed configuration of this stereocenter (marked with #) by NOE data.

2)-cycloaddition of 1,3-zwitterion generated from the **5a** to benzaldehyde. However, due to the formation of a mixture of isomers and their small content, we did not conduct a detailed study of tetrahydrofuranetricarboxylates.

It is important to note that an additional ester group introduced into a DAC from a diazo ester is involved in the formation of both products **17** and **18**. Furthermore, despite the fact that a mixture of *trans*- and *cis*-isomers **5a** was used in the reaction, dihydrofuran-2-one **17** was formed only as a single diastereomer, including the formation of a CH–Cl stereo center in the aliphatic chain (Scheme 5, Figure 4).

Thus, the low diastereoselectivity of the first process (the reaction of ACDC with diazo esters) does not at all interfere with the further use of compounds **5** as a mixture of isomers and the selectivity is "corrected" in the subsequent reactions (Scheme 5). The presence of side products, alkenes **6**, in the reaction mixture does not interfere with the process either.

The mechanism of the formation of dihydrofuran-2-ones **17** and **18** can be represented as a cascade of transformations demonstrated in Scheme 6. Under sufficiently drastic conditions in the presence of $TiCl_4$, the donor–acceptor bond in cyclopropane **5a** is broken and a benzaldehyde molecule is added to the resulting 1,3-zwitterion. Subsequently, a series of intramolecular transformations occurs, resulting in the selective formation of five-membered lactones **17** and **18**.

Aliphatic triester **19** arises as a result of a competing process of transfer of chlorine anion from $TiCl_4$ in the generated 1,3-zwitterionic intermediate **20**; moreover, this process is most likely realized in the intermolecular version. It is logical that

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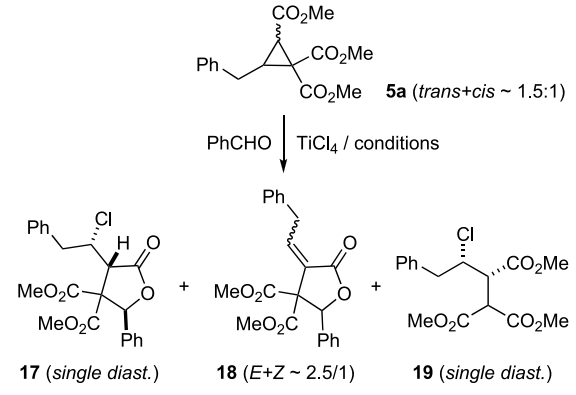
Table 4. Optimization of the Reaction Conditions for a Reaction of Cyclopropane 5a with Benzaldehyde



entry[a]	lewis acid (LA)	ratio 5a/LA/PhCHO	T (°C)	t (h)	yield (%)[b] 17	18[c]	19
1	$GaCl_3$	2:1:6	40	2	–[d]	–[d]	–[d]
2	$SnCl_4$	3:1:6	40	3	–[d]	–[d]	–[d]
3	$TiCl_4$	3:1:6	40	3	3	2	70[e]
4	$TiCl_4$	1:1:3.5	84	3	12	7	10
5	$TiCl_4$	1:2:2.5	84	3	22[e]	13[e]	16
6	**$TiCl_4$**	**1:1.5:2.5**	**84**	**3**	**37[e]**	**35[e]**	**20[e]**
7	$TiCl_4$	1:1.5:2.5	84	6	35	23	12
8	$TiCl_4$	1:1.5:2.5	84	1	26	10	22
9	$TiCl_4$	1:1.5:1	84	3	20	13	20
10	$TiCl_4$	1:1.5:5	84	3	21	26	13

[a]1,2-DCE (DCM) was used as a solvent (3 mL). [b]NMR yield; they were determined by ^{1}H NMR spectra using 1,4-dinitrobenzene as an internal standard. [c]A mixture of (*E* + *Z*)-isomers in ratio ~ 2.5:1. [d]No reaction. [e]Yield after column chromatography.

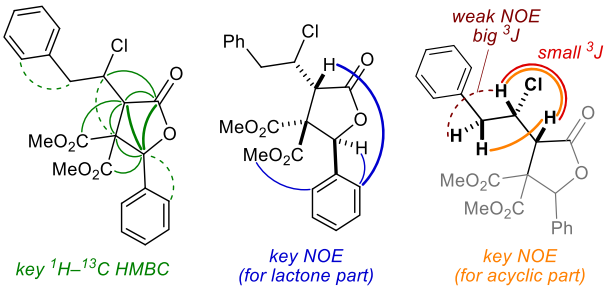


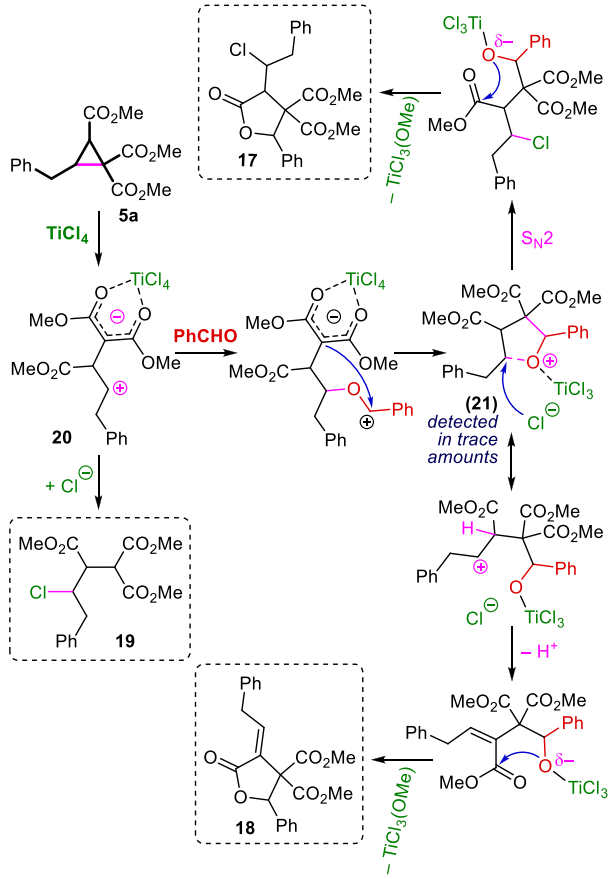
Figure 4. Analysis of structure and stereochemistry for the lactone **17**.

the formation of this compound becomes dominant at 40 °C (instead of 84 °C), when the interaction of the zwitterion 15 with the aldehyde has not yet occurred (Table 4, Entry 3).

CONCLUSIONS

In conclusion, a new process involving the addition of diazo esters to donor–acceptor cyclopropanes (DACs) activated by $GaCl_3$ (via 1,2-zwitterionic gallium synthons) has been developed. In all the cases, the reactions occur with elimination of nitrogen to give 1,1,2,3-tetrasubstituted cyclopropanes as the main products, along with isomeric alkenes. In the case of 2,2-diphenylcyclopropane-1,1-dicarboxylate, along with the formation of the corresponding cyclopropane and alkene, 1,2-migration of a phenyl group in the initial 1,2-zwitterionic synthon easily takes place to give 3,4-diphenylcyclobutane-

Scheme 6. Proposed Simplified Mechanism for the Formation of Lactones 17 and 18[a]



[a]Coordination with $TiCl_4$ is given in a simplified version only for demonstration a general mechanistic pathway and does not reflect a real picture.

1,1,2-tricarboxylate. The mechanism of the occurring processes is discussed.

EXPERIMENTAL SECTION

General Experimental Details. All reagents and solvents were used as commercial grade chemicals without additional purification. All operations with $GaCl_3$, $SnCl_4$, and $TiCl_4$ were carried out under a dry argon atmosphere. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on 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. Determinations of structures and stereochemistry of obtained compounds and assignments of ^{1}H and ^{13}C signals were made with the aid of 1D and 2D gradient/nongradient DEPT-135, COSY, NOESY, HSQC, and HMBC spectra. Diffusion NMR spectra (2D DOSY using LED pulse sequence with bipolar gradient pulses) were used for estimation of molecular weights in solution.[18] IR spectra were obtained on a FT-IR spectrometer in KBr plates (thin layer). Mass spectra were recorded using electron impact ionization (EI, 70 eV, direct inlet probe). High-resolution mass spectra were obtained using simultaneous electrospray (ESI-TOF).[19]

Synthesis of Starting Cyclopropanes 1a–g. Starting cyclopropanes **1a–g** (ACDC) were synthesized from the corresponding aromatic aldehydes through a standard synthetic sequence of Knoevenagel/Corey–Chaykovsky reactions.[2,10b,17b]

Typical Experimental Procedure for Reactions of DACs 1a–g with Diazocompounds 4a–c. All operations were performed under a dry argon atmosphere. A solid $GaCl_3$ (0.45–0.85 mmol) was

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added to a solution of DACs **1a**−**g** (0.4−0.7 mmol) in dry dichloromethane (2−3 mL) and reaction mixture was stirred at 0−40 °C during 10−75 min (see Refs.[10a,b]). Then diazo compound **4** was added to a solution of 1,2-zwitterionic intermediate and a mixture was stirred at 15 °C during 15 min. After that, an aqueous solution of HCl (5%) was added at room temperature until a pH of 3 was achieved, and the reaction mixture was extracted with CH_2Cl_2 (3 × 7 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was purified by flash chromatography on silica gel (eluent: benzene−EtOAc (100:1) to benzene−EtOAc (10:1)) to afford the expected products. The yields of compounds obtained are given taking into account their content in the intermediate fractions. The resulting compounds could be additionally purified on a Silufol chromatographic plate (20 × 20 cm) using hexane−acetone (10:1) as an eluent. A mixture of *trans*- and *cis*-isomers is usually formed. Diastereomers are practically inseparable in most cases using standard column chromatography on SiO_2 or PTLC because their R_f are usually very close, but in several cases, isomers were easily separated. In other cases, it is possible to describe the ^1H and ^{13}C NMR spectra of each isomer without any problems even for inseparable mixtures using of a set of 2D correlation NMR experiments.

Trimethyl 3-benzylcyclopropane-1,1,2-tricarboxylate (5a) and trimethyl 2-benzylprop-1-ene-1,1,3-tricarboxylate (6a). The title compounds were prepared according to the general procedure from ACDC **1a** (164 mg, 0.7 mmol), $GaCl_3$ (141 mg, 0.8 mmol), and methyl diazoacetate (139 mg, 1.38 mmol). After column chromatography on SiO_2 compounds *cis*- and *trans*-**5a**, and **6a** were isolated in yields 51.4 mg (24%), 77.2 mg (36%), and 40.8 mg (19%), respectively. Compound *cis*-**5a**: colorless oil. IR (KBr): $\overline{\nu}$ 3051, 1736, and 1729 br (C═O), 1439, 1278, 1237, 1182, 1127 cm^{-1}. HRMS (ESI-TOF) *m/z*: calcd for $[M + Na]^+$ $C_{16}H_{18}O_6Na$ 329.0995; found, 329.0996. ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.35−7.19 (m, 5H, Ph), 3.72, 3.78, and 3.83 (all s, 3 × 3H, 3 OMe), 3.34 (dd, 1H, CH_bPh, ^2J = 15.4 Hz, ^3J = 5.3 Hz), 3.15 (dd, 1H, CH_aPh, ^2J = 15.4 Hz, ^3J = 9.5 Hz), 2.70 (d, 1H, H(2), ^3J = 9.5 Hz), 2.24 (ddd, 1H, H(3), ^3J = 5.3 Hz, $^3J_{cis}$ = 9.5 Hz, ^3J = 5.3 Hz) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.4, 168.8, and 165.5 (3 COO), 140.0 (*i*-Ph), 128.6 and 128.4 (*o*- and *m*-Ph), 126.4 (*p*-Ph), 53.4, 52.7, and 52.2 (3 OMe), 39.4 (C(1)), 33.7 (C(3)), 30.3 (C(2)), 29.2 (CH_2). Compound *trans*-**5a**: colorless oil. IR (KBr): $\overline{\nu}$ 3051, 1739, and 1730 br (C═O), 1437, 1276, 1237, 1182, 1127 cm^{-1}. HRMS (ESI-TOF) *m/z*: calcd for $[M + Na]^+$ $C_{16}H_{18}O_6Na$ 329.0995; found, 329.0998. ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.23−7.35 (m, 5H, Ph), 3.77, 3.72, and 3.71 (all s, 3 × 3H, 3 OMe), 2.96 and 2.85 (both dd, 2 × 1H, CH_2Ph, ^2J = 15.3 Hz, ^3J = 7.2 Hz), 2.82−2.66 (m, 2H, H(2) and H(3)) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.7, 167.0, and 166.6 (3 COO), 138.7 (*i*-Ph), 128.6, and 128.1 (*o*- and *m*-Ph), 126.5 (*p*-Ph), 53.0, 52.9, and 52.4 (3 OMe), 42.0 (C(1)), 32.8 (C(3)), 32.7 (C(2)), 31.8 (CH_2). Compound **6a**: Colorless oil. IR (KBr): $\overline{\nu}$ 3037, 2954, 1734 br (C═O), 1436, 1257, 1191, 1178, 1062 cm^{-1}. HRMS (ESI-TOF) *m/z*: calcd for $[M + H]^+$ $C_{16}H_{18}O_6H$ 307.1176; found, 307.1178. ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.34−7.23 (m, 5H, Ph), 3.74 (s, 2H, CH_2), 3.86, 3.79 and 3.66 (all s, 3 × 3H, 3 OMe), 3.45 (s, 2H, $C\underline{H}_2Ph$) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.7, 166.4 and 164.5 (3 COO), 151.4 (C(2)), 136.1 (*i*-Ph), 129.5 (C(1)), 128.7 and 127.8 (*o*- and *m*-Ph), 127.1 (*p*-Ph), 52.5, 52.3, and 52.1 (3 OMe), 41.5 (CH_2), 37.1 (CH_2Ph).

Gram-scale synthetic procedure for trimethyl 3-benzylcyclopropane-1,1,2-tricarboxylate (5a) and trimethyl 2-benzylprop-1-ene-1,1,3-tricarboxylate (6a). The title compounds were prepared according to the general procedure from ACDC **1a** (2.1 g, 9.0 mmol), $GaCl_3$ (1.8 g, 10.1 mmol) and methyl diazoacetate (1.8 g, 18.0 mmol). After column chromatography on SiO_2 compounds *cis*- and *trans*-**5a** and **6a** were isolated in yields 1.9 g (72%) and 0.5 g (19%), respectively.

1,1-Dimethyl 2-neopentyl 3-benzylcyclopropane-1,1,2-tricarboxylate (5b) and 1,1-dimethyl 3-neopentyl 2-benzylprop-1−ene-1,1,3-tricarboxylate (6b). The title compounds were prepared according to the general procedure from ACDC **1a** (93.7 mg, 0.4 mmol), $GaCl_3$ (79.3 mg, 0.45 mmol) and neopentyl diazoacetate **4b** (125 mg, 0.8 mmol). After column chromatography on SiO_2 cyclopropanes **5b** as a mixture of *cis*- and *trans*-isomers in ratio 1:1.1 and alkene **6b** were isolated in yields 68.1 mg (47%) and 30.4 mg (21%), respectively. Compound **5b**: colorless oil. IR (KBr): $\overline{\nu}$ 3037, 2957, 1730 br (C═O), 1438, 1273, 1196, 1171, 1119 cm^{-1}. HRMS (ESI-TOF) *m/z*: calcd for $[M + H]^+$ $C_{20}H_{26}O_6H$ 363.1802; found, 363.1806. Isomer *cis*-**5b**: ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.39−7.21 (m, 5H, Ph), 3.82 and 3.76 (both s, 2 × 3H, 2 OMe), 3.74 (s, 2H, OCH_2), 3.38 (dd, 1H, CH_bPh, ^2J = 15.4 Hz, ^3J = 5.2 Hz), 3.19 (dd, 1H, CH_aPh, ^2J = 15.4 Hz, ^3J = 9.6 Hz), 2.75 (d, 1H, H(2), ^3J = 9.6 Hz), 2.23 (ddd, 1H, H(3), ^3J = 9.6 Hz, $^3J_{cis}$ = 9.6 Hz, ^3J = 5.2 Hz), 0.94 (s, 9H, *t*-Bu) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.4, 168.5 and 166.6 (3 COO), 140.0 (*i*-Ph), 128.6 and 128.5 (*o*- and *m*-Ph), 126.5 (*p*-Ph), 74.6 (OCH_2), 53.0 and 52.6 (2 OMe), 39.5 (C(1)), 33.8 (C(3)), 31.2(C), 30.5 (C(2)), 29.2 (CH_2), 26.3 (*t*-Bu). Isomer *trans*-**5b**: ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.39−7.21 (m, 5H, Ph), 3.84 (s, 2H, OCH_2), 3.78 and 3.72 (both s, 2 × 3H, 2 OMe), 2.68−3.00 (m, 4H, H(2), H(3), CH_2Ph), 0.94 (s, 9H, *t*-Bu) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.6, 167.2 and 165.5 (3 COO), 140.0 (*i*-Ph), 128.6 and 128.5 (*o*- and *m*-Ph), 126.5 (*p*-Ph), 74.6 (OCH_2), 53.3 and 52.9 (2 OMe), 42.0 (C(1)), 33.8 (C(3)), 31.7 (CH_2), 31.4 (C), (C(2)), 26.4 (*t*-Bu). Compound **6b**: colorless oil. IR (KBr): $\overline{\nu}$ 3024, 1729, 1260, 1175 cm^{-1}. HRMS (ESI-TOF) *m/z*: calcd for $[M + H]^+$ $C_{20}H_{26}O_6H$ 363.1800; found, 363.1802. ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.32−7.20 (m, 5H, Ph), 3.84 and 3.77 (both s, 2 × 3H, 2 OMe), 3.73 and 3.72 (both s, 2 × 2H, $H_2C(3)$ and OCH_2), 3.46 (s, 2H, CH_2Ph), 0.91 (s, 9H, *t*-Bu) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.2, 166.5 and 164.5 (3 COO), 151.3 (C(2)), 136.1 (*i*-Ph), 129.5 and 128.8 (*o*- and *m*-Ph), 127.3 (C(1)), 127.1 (*p*-Ph), 74.3 (OCH_2), 52.5 and 52.2 (2 OMe), 41.5 (CH_2), 37.4 (CH_2Ph), 31.3(C), 26.4 (*t*-Bu).

2-Benzyl 1,1-dimethyl 3-benzylcyclopropane-1,1,2-tricarboxylate (5c) and 3-benzyl 1,1-dimethyl 2-benzylprop-1−ene-1,1,3-tricarboxylate (6c). The title compounds were prepared according to the general procedure from ACDC **1a** (89.1 mg, 0.38 mmol), $GaCl_3$ (75.7 mg, 0.43 mmol) and neopentyl diazoacetate **4c** (132 mg, 0.75 mmol). After column chromatography on SiO_2 cyclopropanes **5c** as a mixture of *cis*- and *trans*-isomers in ratio 1:1.1 and alkene **6c** were isolated in yields 104.4 mg (72%) and 26.1 mg (18%), respectively. HRMS (ESI-TOF) *m/z*: calcd for $[M + H]^+$ $C_{22}H_{22}O_6H$ 383.1489; found, 383.1490. Isomer *cis*-**5c**: ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.39−7.16 (m, 5H, Ph), 5.15 (s, 2H, OCH_2), 3.64, and 3.77 (both s, 2 × 3H, 2 OMe), 3.32 (dd, 1H, CH_bPh, ^2J = 15.5 Hz, ^3J = 5.7 Hz), 3.16 (dd, 1H, CH_aPh, ^2J = 15.5 Hz, ^3J = 9.4 Hz), 2.75 (d, 1H, H(2), ^3J = 9.4 Hz), 2.22 (ddd, 1H, H(3), ^3J = 9.4 Hz, $^3J_{cis}$ = 9.4 Hz, ^3J = 5.7 Hz) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.1, 168.2 and 167.0 (3 COO), 128.56, 128.50, 128.42 and 128.36 (*o*- and *m*-Ph in 2 Ph), 128.3 and 126.3 (2 *p*-Ph), 67.1 (OCH_2), 53.3 and 52.8 (2 OMe), 39.5(C), 33.9 (C(3)), 30.3 (C(2)), 29.2 (CH_2). Isomer *trans*-**5c**: ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.39−7.16 (m, 5H, Ph), 5.16 (s, 2H, OCH_2), 3.70 and 3.78 (both s, 2 × 3H, 2 OMe), 2.95 (dd, 1H, CH_bPh, ^2J = 15.4 Hz, ^3J = 5.7 Hz), 2.84 (dd, 1H, CH_aPh, ^2J = 15.4 Hz, ^3J = 9.4 Hz), 2.86−2.69 (m, 2H, H(2) and H(3)) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.4, 166.5 and 165.4 (3 COO), 128.58 and 128.51, 128.39, 128.12 (*o*- and *m*-Ph in 2 Ph), 128.2 and 126.5 (2 *p*-Ph), 67.0 (OCH_2), 53.0 and 52.6 (2 OMe), 42.1(C), 32.9 and 32.2 (C(3) and (C(2)), 31.7 (CH_2). Compound **6c**: colorless oil. HRMS (ESI-TOF) *m/z*: calcd for $[M + H]^+$ $C_{22}H_{22}O_6H$ 383.1479; found, 383.1489. ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.40−7.16 (m, 2 × 5H, 2 Ph), 5.12 (OCH_2), 3.88 and 3.75 (both s, 2 × 3H, 2 OMe), 3.76 (CH_2), 3.53 (s, 2H, CH_2Ph). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.1, 166.4 and 165.5 (3 COO), 151.2 (C(2)), 136.0 and 135.7 (*i*-Ph), 129.5, 128.8, 128.5, and 128.2 (*o*- and *m*-Ph in 2 Ph), 128.0 (C(1)), 128.4 and 127.1 (2 *p*-Ph), 66.7 (OCH_2), 52.5 and 52.3 (OMe), 41.6 (CH_2), 37.4 (CH_2Ph).

Trimethyl 3-(4-chlorobenzyl)cyclopropane-1,1,2-tricarboxylate (5d) and trimethyl 2-(4-chlorobenzyl)prop-1−ene-1,1,3-tricarboxylate (6d). The title compounds were prepared according to the general procedure from ACDC **1b** (145 mg, 0.54

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mmol), $GaCl_3$ (105 mg, 0.6 mmol) and methyl diazoacetate **4a** (109 mg, 1.08 mmol). After column chromatography on SiO_2 cyclopropanes **5d** as a mixture of *cis*- and *trans*-isomers in ratio 1:1.4 and alkene **6d** were isolated in yields 137.3 mg (75%) and 35.0 mg (19%), respectively. Compound **5d**: light yellow oil. IR (KBr): $\overline{\nu}$ 3052, 1737 and 1729 br (C═O), 1493, 1437, 1275, 1237, 1171, 1123 cm^{-1}. HRMS (ESI-TOF) *m/z*: calcd for $[M + H]^+$ $C_{16}H_{17}O_6ClH$ (for ^{35}Cl) 341.0786; found, 341.0779. Isomer *cis*-**5d**: ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.20−7.15 and 7.31−7.26 (both d, 2 × 2H, C_6H_4), 3.82, 3.78 and 3.71 (all s, 3 × 3H, 3 OMe), 3.29 (dd, 1H, CH_bPh, ^2J = 15.5 Hz, ^3J = 5.7 Hz), 3.11 (dd, 1H, CH_aPh, ^2J = 15.5 Hz, ^3J = 9.4 Hz), 2.69 (d, 1H, H(2), ^3J = 9.4 Hz), 2.18 (ddd, 1H, H(3), ^3J = 9.4 Hz, $^3J_{cis}$ = 9.4 Hz, ^3J = 5.7 Hz) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 170.5, 169.3 and 165.4 (3 COO), 138.4 (*i*-Ar), 128.9 and 129.8 (*o*- and *m*-Ar), 128.7 (*p*-Ar), 53.4, 52.7 and 52.2 (3 OMe), 39.5 (C(1)), 33.3 (CH_2), 30.1 and 28.6 (C(3) and C(2)). Isomer *trans*-**5d**: ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.31−7.26 and 7.20−7.15 (both m, 2 × 2H, C_6H_4), 3.76, 3.71 and 3.70 (all s, 3 × 3H, 3 OMe), 2.92 (dd, 1H, CH_bPh, ^2J = 15.4 Hz, ^3J = 6.7 Hz), 2.81 (dd, 1H, CH_aPh, ^2J = 15.4 Hz, ^3J = 7.2 Hz), 2.78−2.60 (m, 2H, H(2) and H(3)) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.5, 168.7 and 166.9 (3 COO), 137.2 (*i*-Ar), 132.9 (*p*-Ar), 129.4 and 128.6 (*o*- and *m*-Ar), 53.0, 52.9 and 52.6 (3 OMe), 42.0 (C(1)), 32.7 and 32.4 (C(2) and C(3)), 31.0 (CH_2). Compound **6d**: light yellow oil. IR (KBr): $\overline{\nu}$ 3048, 1733 br (C═O), 1493, 1436, 1277, 1185, 1094 cm^{-1}. HRMS (ESI-TOF) *m/z*: calcd for $[M + H]^+$ $C_{16}H_{17}O_6ClH$ (for ^{35}Cl) 341.0786; found, 341.0786. ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.32−7.16 (m, 4H, C_6H_4), 3.71 (s, 2H, CH_2), 3.86, 3.80 and 3.66 (all s, 3 × 3H, 3 OMe), 3.42 (s, 2H, CH_2Ph) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.6, 166.2 and 164.5 (3 COO), 150.6 (C(2)), 134.8 (*i*-Ar), 130.4 (*p*-Ar), 130.8 and 128.8 (*o*- and *m*-Ar), 128.5 (C(1)), 52.5, 52.3 and 52.1 (3 OMe), 40.7 (CH_2), 37.2 (CH_2Ph).

Trimethyl 3-(4-fluorobenzyl)cyclopropane-1,1,2-tricarboxylate (5e) and trimethyl 2-(4-fluorobenzyl)prop-1−ene-1,1,3-tricarboxylate (6e). The title compounds were prepared according to the general procedure from ACDC **1c** (176 mg, 0.7 mmol), $GaCl_3$ (132 mg, 0.75 mmol) and methyl diazoacetate **4a** (141 mg, 1.4 mmol). After column chromatography on SiO_2 cyclopropanes **5e** as a mixture of *cis*- and *trans*-isomers in ratio 1:1.4 and alkene **6e** were isolated in yields 109.2 mg (48%) and 20.5 mg (9%), respectively. Compound **5e**: light yellow oil. IR (KBr): $\overline{\nu}$ 3051, 1739 and 1729 br (C═O), 1511, 1438, 1270, 1172, 1123 cm^{-1}. HRMS (ESI-TOF) *m/z*: calcd for $[M + H]^+$ $C_{16}H_{17}O_6FH$ 325.1082; found, 325.1083. Isomer *cis*-**5e**: ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.22−7.16 (m, 2H, *m*-Ar), 7.02−6.95 (m, 2H, *o*-Ar), 3.81, 3.77 and 3.71 (all s, 3 × 3H, 3 OMe), 3.29 (dd, 1H, CH_bPh, ^2J = 15.4 Hz, ^3J = 5.9 Hz), 3.11 (dd, 1H, CH_aPh, ^2J = 15.4 Hz, ^3J = 9.1 Hz), 2.68 (d, 2H, H(2)), 2.18 (ddd, 1H, H(3), ^3J = 9.3 Hz, $^3J_{cis}$ = 9.3 Hz, ^3J = 5.9 Hz) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.3, 168.7 and 165.4 (3 COO), 161.5 (d, *p*-Ar, $^1J_{CF}$ = 233 Hz), 135.6 (d, *i*-Ar, $^4J_{CF}$ = 2.2 Hz), 129.8 (d, *m*-Ar, $^3J_{CF}$ = 6.2 Hz), 115.2 (d, *o*-Ar, $^2J_{CF}$ = 21.6 Hz), 53.3, 52.6 and 52.2 (3 OMe), 39.4 (C(1)), 32.7 (CH_2), 30.1 and 28.4 (C(3) and C(2)). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −116.9 ppm. Isomer *trans*-**5e**: ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.22−7.16 (m, 2H, *m*-Ar), 7.02−6.95 (m, 2H, *o*-Ar), 3.76, 3.70 and 3.69 (all s, 3 × 3H, 3 OMe), 2.65−2.75 (m, 2H, H(2) and H(3)), 2.88 (dd, 1H, CH_bPh, ^2J = 15.3 Hz, ^3J = 6.8 Hz), 2.76 (dd, 1H, CH_aPh, ^2J = 15.3 Hz, ^3J = 7.2 Hz) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.5, 166.9 and 165.5 (3 COO), 161.4 (d, *p*-Ar, $^1J_{CF}$ = 233 Hz), 134.4 (d, *i*-Ar, $^4J_{CF}$ = 2.1 Hz), 129.7 (d, *m*-Ar, $^3J_{CF}$ = 6.2 Hz), 115.3 (d, *o*-Ar, $^2J_{CF}$ = 21.6 Hz), 53.1, 52.7 and 52.4 (3 OMe), 42.0 (C(1)), 33.6 (CH_2), 32.7 and 30.9 (C(3) and C(2)). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −116.7 ppm. Compound **6e**: light yellow oil. IR (KBr): $\overline{\nu}$ 3017, 2401, 1738 and 1728 br (C═O), 1510, 1436, 1263, 1172 cm^{-1}. HRMS (ESI-TOF) *m/z*: calcd for $[M + H]^+$ $C_{16}H_{17}O_6FH$ 325.1085; found, 325.1082. ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.29−7.19 (m, 2H, *m*-Ar), 7.05−6.96 (m, 2H, *o*-Ar), 3.70 (s, 2H, CH_2), 3.86, 3.80 and 3.66 (all s, 3 × 3H, 3 OMe), 3.43 (s, 2H, CH_2Ph) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 166.9 (2 COO), 166.3 (COO), 162.4 (d, *p*-Ar, $^1J_{CF}$ = 235 Hz), 151.0 (C(2)), 131.7 (d, *i*-Ar, $^4J_{CF}$ = 2.2 Hz), 131.1 (d, *m*-Ar, $^3J_{CF}$ = 6.1 Hz), 127.9 (C(1)), 115.5 (d, *o*-Ar, $^2J_{CF}$ = 21.4 Hz), 52.5, 52.3 and 52.1 (3 OMe), 40.6 (CH_2), 37.1 (CH_2Ph). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −115.5 ppm.

Trimethyl 3-(4-methylbenzyl)cyclopropane-1,1,2-tricarboxylate (5f) and trimethyl 2-(4-methylbenzyl)prop-1-ene-1,1,3-tricarboxylate (6f). The title compounds were prepared according to the general procedure from ACDC **1d** (136 mg, 0.55 mmol), $GaCl_3$ (109 mg, 0.62 mmol) and methyl diazoacetate **4a** (113 mg, 1.1 mmol). After column chromatography on SiO_2 cyclopropanes **5f** as a mixture of *cis*- and *trans*-isomers in ratio 1:1.5 and alkene **6f** were isolated in yields 121 mg (69%) and 37.3 mg (21%), respectively. Compound **5f**: colorless oil. IR (KBr): $\overline{\nu}$ 3052, 1741 and 1724 br (C═O), 1516, 1438, 1266, 1171, 1120 cm^{-1}. HRMS (ESI-TOF) *m/z*: calcd for $[M + H]^+$ $C_{17}H_{20}O_6H$ 321.1324; found, 321.1333. Isomer *cis*-**5f**: ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.12 (br. s, 4H, C_6H_4), 3.83, 3.76 and 3.72 (all s, 3 × 3H, 3 OMe), 3.29 (dd, 1H, CH_bPh, ^2J = 15.3 Hz, ^3J = 5.4 Hz), 3.10 (dd, 1H, CH_aPh, ^2J = 15.3 Hz, ^3J = 9.4 Hz), 2.68 (d, 1H, H(2), ^3J = 9.5 Hz), 2.34 (s, 3H, Me), 2.21 (ddd, 1H, H(3), ^3J = 9.5 Hz, $^3J_{cis}$ = 9.5 Hz, ^3J = 5.4 Hz) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.4, 168.8 and 165.5 (3 COO), 136.9 and 135.8 (*i*- and *p*-Ar), 129.2 and 128.3 (*o*- and *m*-Ar), 53.0, 52.4 and 52.1 (3 OMe), 39.4 (C(1)), 32.7 (CH_2), 31.4 and 28.8 (C(3) and C(2)), 21.0 (Me). Isomer *trans*-**5f**: ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.13 (br. s, 4H, C_6H_4), 3.77, 3.73 and 3.70 (all s, 3 × 3H, 3 OMe), 2.89 (dd, 1H, CH_bPh, ^2J = 15.5 Hz, ^3J = 6.9 Hz), 2.81 (dd, 1H, CH_aPh, ^2J = 15.5 Hz, ^3J = 7.2 Hz), 2.80−2.65 (m, 2H, H(2) and H(3) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.7, 167.0 and 166.6 (3 COO), 136.0 and 135.6 (*i*- and *p*-Ar), 129.3 and 128.0 (*o*- and *m*-Ar), 53.3, 53.0 and 52.6 (3 OMe), 42.1 (C(1)), 33.8 (CH_2), 31.4 and 30.2 (C(3) and C(2)), 21.0 (Me). Compound **6f**: colorless oil. IR (KBr): $\overline{\nu}$ 3046, 2401, 1737 and 1728 br (C═O), 1436, 1299, 1281, 1169, 1119 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{20}O_6H$ 321.1333; found, 321.1327. ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.11−7.06 (m, 4H, C_6H_4), 3.84, 3.77 and 3.64 (all s, 3 × 3H, 3 OMe), 3.42 (s, 2H, CH_2Ph), 2.31 (s, 3H, Me) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.7, 166.4 and 164.5 (3 COO), 151.4 (C(2)), 143.0 (*i*-Ar), 129.3 and 129.4 (*o*- and *m*-Ar), 129.0 (C(1)), 52.5, 52.3 and 52.1 (3 OMe), 41.2 (CH_2), 37.1 (CH_2Ph), 21.0 (Me).

1,1-Dimethyl 2-neopentyl 3-(4-methylbenzyl)-cyclopropane-1,1,2-tricarboxylate (5g) and 1,1-dimethyl 3-neopentyl 2-(4-methylbenzyl)prop-1−ene-1,1,3-tricarboxylate (6g). The title compounds were prepared according to the general procedure from ACDC **1d** (188.8 mg, 0.76 mmol), $GaCl_3$ (140.6 mg, 0.79 mmol) and neopenthyl diazoacetate (237.6 mg, 1.52 mmol). After column chromatography on SiO_2 compounds **5g** (*cis*/*trans* ∼ 1:1.2) and **6g** were isolated in yields 177.4 mg (62%) and 54.4 mg (19%), respectively. Compound **5g**: colorless oil. HRMS (ESI-TOF) *m/z*: calcd for $[M + H]^+$ $C_{21}H_{28}O_6H$ 377.1959; found, 377.1960. Isomer *cis*-**5g**: ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.17−7.07 (m, 4H, Ar), 3.74 (s, 2H, OCH_2), 3.77 and 3.73 (both s, 2 × 3H, 2 OMe), 3.30 (dd, 1H, CH_bPh, ^3J = 15.3 Hz, ^2J = 5.2 Hz), 3.12 (dd, 1H, CH_aPh, ^3J = 15.3 Hz, ^3J = 9.6 Hz), 2.74 (d, 1H, H(2), $^3J_{cis}$ = 9.6 Hz), 2.33 (s, 3H, Me), 2.22 (ddd, 1H, H(3), ^3J = 9.6 Hz, $^3J_{cis}$ = 9.6 Hz, ^3J = 5.2 Hz), 0.94 (s, 9H, *t*-Bu) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.4, 167.2 and 165.5 (3 COO), 135.7 (*i*-Ph), 128.9 (*p*-Ph), 128.2 and 127.9 (*o*- and *m*-Ph), 74.5 (OCH_2), 53.0 and 52.6 (2 OMe), 39.3 (C(1)), 34.0 (C(3)), 31.2(C), 30.5 (C(2)), 28.8 (CH_2), 26.3 (*t*-Bu), 21.0 (Me). Isomer *trans*-**5g**: ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.17−7.07 (m, 4H, Ar), 3.76 (s, 2H, OCH_2), 3.81 and 3.75 (both s, 2 × 3H, 2 OMe), 2.94−2.82 (m, 2H, CH_2Ph), 2.82−2.66 (m, 2H, H(2) and H(3)), 2.33 (s, 3H, Me), 0.95 (s, 9H, *t*-Bu) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.6, 168.5 and 166.6 (3 COO), 136.9 (*i*-Ph), 129.2 and 129.1 (*o*- and *m*-Ph), 129.0 (*p*-Ph), 74.6 (OCH_2), 53.3 and 52.9 (2 OMe), 41.9 (C(1)), 32.9 (C(3)), 31.4 (C(2)), 31.3(C), 31.2 (CH_2), 26.4 (*t*-Bu), 20.9 (Me). Compound **6g**: Colorless oil. HRMS (ESI-TOF) *m/z*: calcd for $[M + H]^+$ $C_{21}H_{28}O_6H$ 377.1959; found, 377.1951. ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.17−7.08 (m, 4H, Ar), 3.85 (s, 2H, CH_2), 3.77 and 3.75 (both s, 2 × 3H, 2 OMe), 3.47 (s, 2H, CH_2), 2.32 (s, 3H, Me), 0.92 (s, 9H, *t*-Bu). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.2, 166.5 and

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164.5 (3 COO), 151.6 (C(2)), 136.7 (*i*-Ph), 132.9 (*p*-Ar), 129.4 and 129.3 (*o*- and *m*-Ar), 129.0 (C(1)), 74.3 (OCH_2), 52.4 and 52.2 (2 OMe), 41.1 (CH_2), 37.3 (CH_2Ar), 31.3(C), 26.3 (*t*-Bu), 21.0 (Me).

Trimethyl 3-(2-chlorobenzyl)cyclopropane-1,1,2-tricarboxylate (5h) and trimethyl 2-(2-chlorobenzyl)prop-1−ene-1,1,3-tricarboxylate (6h). The title compounds were prepared according to the general procedure from ACDC **1e** (134 mg, 0.5 mmol), $GaCl_3$ (99 mg, 0.57 mmol) and methyl diazoacetate **4a** (100 mg, 1.0 mmol). After column chromatography on SiO_2 cyclopropanes *cis*- and *trans*-**5h** (ratio 1:1.7) and alkene **6h** were isolated in yields 28.9 mg (17%), 49.2 mg (29%) and 45.9 mg (27%), respectively. Compound *cis*-**5h**: light yellow oil. HRMS (ESI-TOF) *m/z*: calcd for $[M + H]^+$ $C_{16}H_{17}O_6ClH$ 341.0786; found, 341.0787. ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.42−7.36, 7.30−7.25 and 7.23−7.17 (all m, 2H + 1H + 1H, C_6H_4), 3.83, 3.79 and 3.73 (all s, 3 × 3H, 3 OMe), 3.50 (dd, 1H, CH_bPh, ^2J = 15.5 Hz, ^3J = 5.4 Hz), 3.23 (dd, 1H, CH_aPh, ^2J = 15.5 Hz, ^3J = 9.0 Hz), 2.69 (d, 1H, H(2), ^3J = 9.3 Hz), 2.33 (ddd, 1H, H(3), ^3J = 9.3 Hz, $^3J_{cis}$ = 9.3 Hz, ^3J = 5.4 Hz) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.3, 168.8 and 165.4 (3 COO), 137.6 (*i*-Ar), 134.2 (C−Cl), 130.3, 129.5, 127.9 and 126.9 (4 CH in Ar), 53.3, 52.7 and 52.2 (3 OMe), 39.3 (C(1)), 31.9 (C(3)), 30.2 (C(2)), 27.1 (CH_2Ph). Compound *trans*-**5h**: colorless oil. ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.29−7.16 and 7.40−7.35 (both m, 2 × 2H, C_6H_4), 3.78, 3.72 and 3.71 (all s, 3 × 3H, 3 OMe), 3.08 (dd, 1H, CH_bPh, ^2J = 15.9 Hz, ^3J = 6.8 Hz), 2.97 (dd, 1H, CH_aPh, ^2J = 15.9 Hz, ^3J = 7.3 Hz), 2.82−2.73 (m, 2H, H(2) and H(3)) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.6, 166.9 and 166.6 (3 COO), 136.6 (*i*-Ar), 133.9 (C−Cl), 129.6, 129.5, 127.9and 127.0 (4 CH in Ar), 53.1, 53.0 and 52.4 (3 OMe), 41.9 (C(1)), 32.7 (C(3)), 31.3 (C(2)), 29.6 (CH_2Ph). Compound **6h**: colorless oil. IR (KBr): $\overline{\nu}$ 3051, 2398, 1733 br (C═O), 1436, 1282, 1187 cm^{-1}. HRMS (ESI-TOF) *m/z*: calcd for $[M + H]^+$ $C_{16}H_{17}O_6ClH$ (for ^{35}Cl) 341.0786; found, 341.0779. ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.43−7.20 (m, 4H, C_6H_4), 3.95 (s, 2H, CH_2), 3.84, 3.80 and 3.65 (all s, 3 × 3H, 3 OMe), 3.44 (s, 2H, CH_2Ph) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.6, 166.1 and 164.6 (3 COO), 135.0 and 134.1 (2 C in Ar), 131.1, 129.6, 128.5 and 127.1 (4 CH in Ar), 52.5, 52.3 and 52.1 (3 OMe), 38.2 (CH_2), 37.4 (CH_2).

Trimethyl 3-(3-bromobenzyl)cyclopropane-1,1,2-tricarboxylate (5i). The title compound was prepared according to the general procedure from ACDC **1f** (109 mg, 0.35 mmol), $GaCl_3$ (72.2 mg, 0.41 mmol) and methyl diazoacetate **4a** (70.2 mg, 0.7 mmol). According to NMR spectra, the yields of the expected compounds *cis*- and *trans*-**5i** and **6i** are 17, 22 and 16%. After column chromatography on SiO_2 only *cis*-**5i** was collected in pure state in yield 20.9 mg (∼16%) (*trans*-**5i** and **6i** were mixed with other compounds). Colorless oil. IR (KBr): $\overline{\nu}$ 3056, 1730 br (C═O), 1438, 1268, 1187, 1128 cm^{-1}. HRMS (ESI-TOF) *m/z*: calcd for $[M + H]^+$ $C_{16}H_{17}O_6BrH$ 385.0281; found, 385.0282. ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.42−7.36 and 7.23−7.16 (both m, 2 × 2H, C_6H_4), 3.82, 3.79 and 3.73 (all s, 3 × 3H, 3 OMe), 3.31 (dd, 1H, CH_bPh, ^2J = 15.4 Hz, ^3J = 5.6 Hz), 3.12 (dd, 1H, CH_aPh, ^2J = 15.4 Hz, ^3J = 9.3 Hz), 2.69 (d, 1H, H(2), ^2J = 9.4 Hz), 2.19 (ddd, 1H, H(3), ^3J = 9.4 Hz, $^3J_{cis}$ = 9.4 Hz,^3J = 5.6 Hz) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.2, 168.7 and 165.3 (3 COO), 142.3 (*i*-Ar), 131.6, 130.1, 129.5, 127.1 (4 CH in Ar), 122.6 (C−Br), 53.4, 52.7 and 52.3 (3 OMe), 39.3 (C(1)), 33.2 (C(3)), 30.0 (C(2)), 28.9 (CH_2).

Trineopentyl 3-benzylcyclopropane-1,1,2-tricarboxylate (5j) and trineopentyl 2-benzylprop-1-ene-1,1,3-tricarboxylate (6j). The title compounds were prepared according to the general procedure from ACDC **1g** (189.3 mg, 0.55 mmol), $GaCl_3$ (101 mg, 0.57 mmol) and neopenthyl diazoacetate (170.7 mg, 1.09 mmol). After column chromatography on SiO_2 compounds **5j** (*cis*/*trans* ∼ 1.2:1) and **6j** were isolated in yields 103.7 mg (40%) and 25.9 mg (10%), respectively. Compound **5j**: colorless oil. HRMS (ESI-TOF) *m/z*: calcd for $[M + H]^+$ $C_{28}H_{42}O_6H$ 475.3048; found, 475.3052. Isomer *cis*-**5j**: ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.35−7.19 (m, 5H, Ph), 3.86, 3.76 and 3.73 (all s, 3 × 2H, 3 OCH_2), 3.38 (dd, 1H, CH_bPh, ^2J = 15.3 Hz, ^2J = 5.3 Hz), 3.22 (dd, 1H, CH_aPh, ^2J = 15.3 Hz, ^3J = 9.6 Hz), 2.77 (d, 1H, H(2), $^3J_{cis}$ = 9.6 Hz), 2.22 (ddd, 1H, H(3), ^3J = $^3J_{cis}$ = 9.6 Hz, ^3J = 5.3 Hz), 0.96, 0.94 and 0.89 (all s, 3 × 9H, 3 *t*-Bu) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 166.8, 166.1 and 165.2 (3 COO), 138.9 (*i*-Ph), 128.5 and 128.1 (*o*- and *m*-Ph), 126.2 (*p*-Ph), 74.8, 74.7 and 74.5 (3 × OCH_2), 41.7 (C(1)), 33.8 (C(3)), 31.5(C), 31.4 and 29.2 (C(2) and CH_2), 26.4, 26.3, 26.2 (3 *t*-Bu). Isomer *trans*-**5j**: ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.35−7.19 (m, 5H, Ph), 3.90, 3.89 and 3.79 (all s, 3 × 2H, 3 OCH_2), 3.05 (dd, 1H, H(3), ^3J = 15.4 Hz, ^3J = 6.3 Hz), 2.85 (dd, 1H, CH_aPh, ^2J = 15.4 Hz, ^3J = 9.5 Hz), 2.80−2.68 (m, 2H, H(2) and H(3)), 0.97 (s, 18H, 2 *t*-Bu), 0.95 (s, 9H, *t*-Bu) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.6, 169.4 and 168.6 (3 COO), 140.2 (*i*-Ph), 128.4 and 128.3 (*o*- and *m*-Ph), 126.4 (*p*-Ph), 75.5, 75.4 and 75.3 (3 × OCH_2), 39.8 (C(1)), 32.5 (C(3)), 31.5 (C), 31.4 and 30.1 (CH_2 and C(2)), 26.6, 26.5 and 26.4 (3 *t*-Bu). Compound **6j**: Colorless oil. HRMS (ESI-TOF) *m/z*: calcd for $[M + H]^+$ $C_{16}H_{18}O_6H$ 307.1176; found, 307.1178. ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.32−7.25 (m, 5H, Ph), 3.96, 3.89 and 3.74 (all s, 3 × 2H, 3 OCH_2), 3.73 (s, 2H, CH_2), 3.54 (s, 2H, CH_2Ph), 0.99, 0.96 and 0.94 (all s, 3 × 9H, 3 *t*-Bu) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.2, 166.5 and 164.0 (3 COO), 150.2 (C(2)), 136.2 (*i*-Ph), 129.5 and 128.7 (*o*- and *m*-Ph), 128.0 (C(1)), 127.1 (*p*-Ph), 75.1, 74.4 and 74.3 (3 OCH_2), 41.5 (CH_2), 37.2 (CH_2Ph), 26.4 (3 *t*-Bu).

Trimethyl 3-penthylcyclopropane-1,1,2-tricarboxylate (5k) and trimethyl 2-penthylprop-1-ene-1,1,3-tricarboxylate (6k). The title compounds were prepared according to the general procedure from ACDC **1h** (86.1 mg, 0.4 mmol), $GaCl_3$ (79.4 mg, 0.45 mmol) and methyl diazoacetate **4a** (80.2 mg, 0.8 mmol). After column chromatography on SiO_2 cyclopropanes *cis*- and *trans*-**5k** (ratio ∼ 1:1.3) and alkene **6k** were isolated in yields 29.8 mg (26%), 38.8 mg (34%) and 15.0 mg (13%), respectively. Compound *cis*-**5k**: colorless oil. HRMS (ESI-TOF) *m/z*: calcd for $[M + H]^+$ $C_{14}H_{22}O_6H$ 287.1489; found, 287.1491. ^1H NMR (300.1 MHz, $CDCl_3$): δ 3.76, 3.74 and 3.70 (all s, 3 × 3H, 3 OMe), 2.59 (d, 1H, (H(2), ^3J = 9.5 Hz), 1.95−1.87 (m, 2H, H(3) and $H_bC(4)$), 1.74−1.68 (m, 1H, $H_aC(4)$), 1.35−1.26 (m, 6H, 3 CH_2), 0.88 (t, 3H, Me, ^3J = 6.9 Hz) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.8, 168.7 and 165.6 (3 COO), 53.2, 52.5 and 52.0 (3 OMe), 39.1 (C(1)), 33.4 (C(3)), 30.3 (C(2)), 31.4 and 29.0 (C(5) and C(6)), 23.5 (C(4)), 22.5 (C(7)), 13.9 (Me). Compound *trans*-**5k**: colorless oil. ^1H NMR (300.1 MHz, $CDCl_3$): δ 3.78, 3.76 and 3.71 (all s, 3 × 3H, 3 OMe), 2.58 (d, 1H, H(2), ^3J = 7.1 Hz), 2.34 (q, 1H, H(3), ^3J = 7.1 Hz), 1.55−1.25 (m, 8H, 4CH_2), 0.90 (t, 3H, Me, ^3J = 6.9 Hz) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 170.0, 167.1 and 166.9 (3 COO), 52.9, 52.8 and 52.3 (3 OMe), 42.0 (C(1)), 32.9 (C(3)), 32.6 (C(2)), 31.1, 28.2, 25.9 and 22.4 (4 CH_2), 13.9 (Me). Compound **6k**: colorless oil. IR (KBr): $\overline{\nu}$ 3033, 3022, 2401, 1730 br (C═O), 1434, 1268, 1177 cm^{-1}. HRMS (ESI-TOF) *m/z*: calcd for $[M + H]^+$ $C_{14}H_{22}O_6H$ 287.1489; found, 287.1488. ^1H NMR (300.1 MHz, $CDCl_3$): δ 3.80, 3.74 and 3.70 (all s, 3 × 3H, 3 OMe), 3.57 (s, 2H, $H_2C(3)$), 2.34−2.28 (m, 2H, $H_2C(4)$), 1.51−1.43 (m, 2H, $H_2C(5)$), 1.38−1.25 (m, 4H, $H_2C(6)$ and $H_2C(7)$), 0.89 (t, 3H, Me, ^3J = 6.9 Hz) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 169.9, 166.4 and 164.7 (3 COO), 154.1 (C(2)), 119.1 (C(1)), 52.1 (3 OMe), 38.3 (C(3)), 36.5 (C(4)), 31.7 (C(6)), 27.1 (C(5)), 22.3 (C(7)), 13.9 (Me).

Reaction of DAC 1i with Methyl Diazoacetate. This reaction was carried out according to the typical experimental procedure using ACDC **1i** (125 mg, 0.4 mmol), $GaCl_3$ (85.1 mg, 0.48 mmol) and methyl diazoacetate **4a** (80.1 mg, 0.8 mmol). The residue after removal of solvents was purified by passing through a small column of silica gel and a wide fraction of the reaction products was collected (about 150 mg, light yellow oil). According to NMR spectra, the resulting product contained cyclopropane **5l**, alkene **6l**, cyclobutane **13**, and lactone **14** in the molar ratio ∼ 1:3:6.3:1.5.

*Trimethyl 3-benzhydrylcyclopropane-1,1,2-tricarboxylate (**5l**)*, NMR yield 6−7%, ratio *cis*/*trans* ∼ 1.3:1. HRMS (ESI-TOF) *m/z*: calcd for $[M + Na]^+$ $C_{22}H_{22}O_6Na$ 405.1309; found, 405.1305. *cis*-Isomer: ^1H NMR (300.1 MHz, $CDCl_3$): δ 4.72 (d, 1H, CH, ^3J = 9.9 Hz), 2.78 (d, 1H, H(3), $^3J_{cis}$ = 9.8 Hz), 2.74 (dd, 1H, H(2), ^3J = 9.9 Hz, $^3J_{cis}$ = 9.8 Hz). *trans*-Isomer: ^1H NMR (300.1 MHz, $CDCl_3$): δ 3.98 (d, 1H,

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CH, ^3J = 10.8 Hz), 3.11 (dd, 1H, H(3), ^3J = 10.8 Hz, $^3J_{trans}$ = 7.1 Hz), 2.96 (d, 1H, H(2), $^3J_{trans}$ = 7.1 Hz) ppm. Signals of methoxy and phenyl groups both isomers overlap strongly.

*Trimethyl 2-benzhydrylprop-1-ene-1,1,3-carboxylate (**6l**)*, NMR yield 18%. HRMS (ESI-TOF) *m/z*: calcd for $[M + Na]^+$ $C_{22}H_{22}O_6Na$ 405.1309; found, 405.1302. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.45−7.24 (m, 2 Ph), 5.50 (s, 1H, CH), 3.63 (s, 2H, CH_2), 3.78, 3.65 and 3.47 (all s, 3 × 3H, 3 OMe) ppm.^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 169.4, 166.5 and 164.5 (3 COO), 152.3 (C(2)), 139.0, 129.7, 129.1, 56.0 (CH), 52.4, 52.1 and 51.7 (3 OMe), 37.3 (CH_2).

*Trimethyl (2RS,3SR,4RS)-3,4-diphenylcyclobutane-1,1,2-tricarboxylate (**13**)*, NMR yield 40%. HRMS (ESI-TOF) *m/z*: calcd for $[M + Na]^+$ $C_{22}H_{22}O_6Na$ 405.1309; found, 405.1303. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.45−7.24 (m, 2 Ph), 4.58 (dd, 1H, H(3), ^3J = 9.8 and 11.0 Hz), 4.36 (d, 1H, H(2), ^3J = 11.0 Hz), 3.92, 3.79 and 3.34 (all s, 3 × 3H, 3 OMe), 3.52 (d, 1H, H(4), ^3J = 9.8 Hz) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 171.5, 170.9 and 168.0 (3 COO), 141.4, 137.0, 127.7 and 126.8 (2 C_{Ar}, 10 CH_{Ar}), 60.7 (C(1)), 53.1, 52.3 and 52.2 (3 OMe), 48.5 (C(2)), 48.1 (C(4)), 40.9 (C(3)).

*Dimethyl 2-((3RS,4SR,5RS)-2-oxo-4,5-diphenyltetrahydrofuran-3-yl)-malonate (**14**)*, NMR yield 10%. HRMS (ESI-TOF) *m/z*: calcd for $[M + Na]^+$ $C_{21}H_{20}O_6Na$ 391.1152; found, 391.1147. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 5.32 (d, 1H, H(5), ^3J = 9.8 Hz), 4.02 (d, 1H, CH, ^3J = 5.2 Hz), 3.96 (dd, 1H, H(4), ^3J = 9.8 and 12.9 Hz), 3.76 (dd, 1H, H(3), ^3J = 5.2 and 12.9 Hz)) ppm. Signals of methoxy and phenyl groups overlap strongly.

Reaction of DAC 5a with Benzaldehyde in the Presence of $TiCl_4$. A mixture of cyclopropane-1,1,2-tricarboxylate **5a** (61.3 mg, 0.2 mmol), benzaldehyde (53.0 mg, 0.5 mmol), and $TiCl_4$ (0.033 mL, 0.3 mmol) in 1,2-dichloroethane (3 mL) under a dry argon atmosphere was refluxed about 3 h. Then reaction mixture was cooled and an aqueous solution of HCl (5%) was added until a pH of 3 was achieved. The reaction mixture was extracted with CH_2Cl_2 (3 × 7 mL), the organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was purified by flash chromatography on silica gel (eluent: benzene−EtOAc (100:1) to benzene−EtOAc (10:1)) to afford three main compounds: chlorinated lactone **17**, unsaturated lactone **18** and butanetricarboxylate **19**.

*Dimethyl (2RS,4RS)-4-((SR)-1-chloro-2-phenylethyl)-5-oxo-2-phenyldihydrofuran-3,3-(2H)-dicarboxylate (**17**)*. This compound was isolated in yield 30.8 mg (37%) as a single isomer. Colorless oil. IR (KBr): $\bar{\nu}$ 3038, 1783 and 1737 br (C═O), 1436, 1278, 1181 cm^{-1}. HRMS (ESI-TOF) *m/z*: calcd for $[M + H]^+$ $C_{22}H_{21}O_6ClH$ (for ^{35}Cl) 417.1098; found, 417.1099. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.43−7.31 (m, 10H, 2 Ph), 6.38 (s, 1H, H(5)), 4.50 (dt, 1H, CHCl, ^3J = 7.5 and 1.9 Hz), 3.88 (s, 3H, OMe), 3.84 (d, 1H, H(3), ^3J = 1.9 Hz), 3.60 and 3.44 (both dd, 2 × 1H, CH_2, ^2J = 14.1 Hz, ^3J = 7.5 Hz), 3.14 (s, 3H, OMe) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 171.2 (CO), 167.6 and 166.8 (2 COO), 136.8 and 134.5 (*i*-Ph), 129.5, 128.8, 128.2 and 126.5 (*o*- and *m*-Ph), 129.1 and 127.3 (*p*-Ph), 81.7 (C(5)), 65.7 (C(4)), 58.7 (C(6)), 53.4 and 52.9 (2 OMe), 50.7 (C(3)), 42.2 (CH_2).

*Dimethyl (E,Z)-5-oxo-2-phenyl-4-(2-phenylethylidene)-dihydrofuran-3,3-(2H)-dicarboxylate (**18**)*. This compound was isolated in yield 24.2 mg (∼35%) as the mixture of *Z*- and *E*-isomers in ratio 2.2:1. Colorless oil. HRMS (ESI-TOF) *m/z*: calcd for $[M + H]^+$ $C_{22}H_{20}O_6H$ 381.1325; found, 381.1333. *Major isomer*: ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.39−7.26 (m, 10H, 2 Ph), 7.00 (t, 1H, ═CH, ^3J = 7.7 Hz), 6.28 (s, 1H, H(5)), 4.40 and 4.25 (both dd, 2 × 1H, CH_2, ^2J = 16.3 Hz, ^3J = 7.7 Hz), 3.84 and 3.21 (both s, 2 × 2H, 2 OMe) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 168.0, 167.9 and 167.5 (2 COO and C(2)), 149.8 (═CH), 135.6 and 135.5 (2 *i*-Ph), 128.8 and 128.7 (2 *p*-Ph), 128.6, 128.3, 126.7 and 126.6 (*o*- and *m*-Ph, (2 Ph)), 122.5 (C(3)), 80.6 (C(5)), 53.7 and 52.6 (2 OMe), 34.0 (CH_2), 29.7 (C(4)). *Minor isomer*: ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.39−7.26 (m, 10H, 2 Ph), 7.21 (t, 1H, ═CH,^3J = 7.7 Hz), 6.39 (s, 1H, H(5)), 3.89−3.81 and 3.78−3.70 (both m, CH_2), 3.87 and 3.19 (both s, 2 × 2H, 2 OMe) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 168.3, 168.2 and 167.7 (2 COO and C(2)), 149.0 (═CH), 135.5 and 135.3 (2 *i*-Ph), 128.4 and 126.9 (2 *p*-Ph), 129.2, 128.7, 128.5 and 126.7 (*o*- and *m*-Ph, (2 Ph)), 122.3 (C(3)), 81.3 (C(5)), 53.9 and 52.5 (2 OMe), 38.2 (C(4)), 36.4 (CH_2).

*Trimethyl (2SR,3RS)-3-chloro-4-phenylbutane-1,1,2-tricarboxylate (**19**)*. This compound, together with the isomer ***E*-18** as an impurity, was isolated in yield 15.9 mg (∼20%) as a single isomer. Colorless oil. HRMS (ESI-TOF) *m/z*: calcd for $[M + H]^+$ $C_{16}H_{19}O_6ClH$ 343.0943; found, 343.0947. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.38−7.24 (m, 5H, Ph), 4.25 (ddd, 1H, H(3), ^3J = 10.8, 6.0 and 2.4 Hz), 4.17 (d, 1H, H(1), ^3J = 10.8 Hz), 3.83, 3.75 and 3.72 (all s, 3 × 3H, 3 OMe), 3.62 (dd, 1H, H(2), ^3J = 10.8 Hz, ^3J = 2.4 Hz), 3.35 (dd, 1H, H_b(4), ^2J = 14.2 Hz, ^3J = 6.4 Hz), 3.13 (dd, 1H, H_a(4), ^2J = 14.2 Hz, ^3J = 8.5 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 171.7 (COO), 169.6 (2 COO), 137.2 (*i*-Ph), 129.3 and 128.9 (*o*- and *m*-Ph), 126.8 (*p*-Ph), 60.4 (C(3)), 53.0 (2 OMe), 52.4 (OMe), 51.8 (C(1)), 49.3 (C(2)), 42.8 (C(4)).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02983.

Copies of ^{1}H, ^{13}C, and 2D NMR spectra for isolated products (PDF)

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Notes

The authors declare no competing financial interest.

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