Cascade Reactions

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$GaCl_3$-Mediated Reactions of Donor–Acceptor Cyclopropanes with Aromatic Aldehydes

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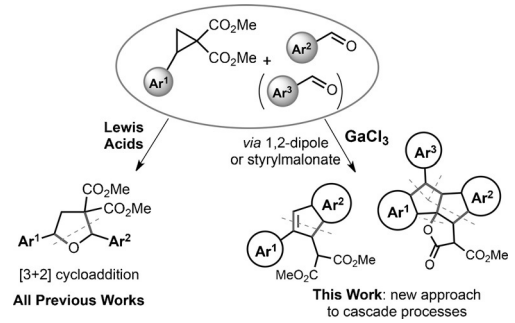
Abstract: *A new strategy for cascade assembly of substituted indenes and polycyclic lactones based on reactions of donor–acceptor cyclopropanes and styrylmalonates with aromatic aldehydes in the presence of $GaCl_3$ has been developed. The use of $GaCl_3$ makes it possible to principally change the direction of the reaction known in this series of substrates and to perform the process in a multicomponent version. Generation of formal 1,2-zwitterionic intermediates owing to complexation of dicarboxylate groups with $GaCl_3$ is the driving force of the reactions discovered. This method makes it possible to assemble indenylmalonates or indano[1′,2′:2,3]indano[2,1-b]furan-2-ones in one synthetic stage from readily available starting compounds with high regio- and diastereoselectivity. A mechanism of the reactions has been suggested using the ^{18}O label in benzaldehyde.*

Donor–acceptor cyclopropanes (DACs) that contain a strained three-membered ring combined with functional groups and act as sources of 1,3-zwitterions[1,2] are widely used in organic synthesis to assemble various carbo- and heterocyclic compounds, including natural compounds and their analogues.[1] To date, many types of DAC reactivity have been identified. However, the majority of them come down to the use of DACs as 1,3-zwitterions. Other possible directions of DAC transformations are of limited use thus far. For example, we have recently found a new type of processes that occur via generation of formal 1,2-zwitterions mediated by gallium compounds.[3] Thus, development of new ways for DAC reactions is an important problem and many current studies concentrate in this field.[2]

Only one pathway was known for reactions of DACs with aldehydes, namely, [3+2]-cycloaddition to give substituted tetrahydrofurans.[1,4] In this study, we have implemented a new strategy for controlling the DAC reactivity using the same substrates as an example. This approach is based on the strategy of the use of gallium arylalkylidenemalonate complexes.[3] It involves controlled sequential generation of these intermediates from arylcyclopropanedicarboxylates (ACDC) or their isomers, styrylmalonates,[5] in the presence of gallium compounds and their reactions with various substrates. The use of the approach we suggested allows a new type of cascade processes to be created, resulting in the assembly of complex carbo- and heterocyclic structures from simple starting compounds, and to cardinally change the known reaction pathways of DACs. This approach is demonstrated in Scheme 1.



Scheme 1. New type of DAC reactivity with aldehydes.

Fused carbo- and heterocycles belong to important classes of organic compounds. Thus, five-membered lactones and indenes are contained in various natural compounds (Figure 1) demonstrating a broad spectrum of biological activity,[6] such as antileishmanial, antiplasmodial, neurotrophic, neuroregulatoric, and cytotoxic activity. Indenes are used as ligands for the catalysis of stereoselective polymerization of alkenes, hydroamination and other processes,[7a,b] and also as precursors for synthesizing functional materials[7c,d] and compounds with luminescent properties.[7e,f,8]

Two different approaches were chosen for implementation of this strategy. The first one involved generation of

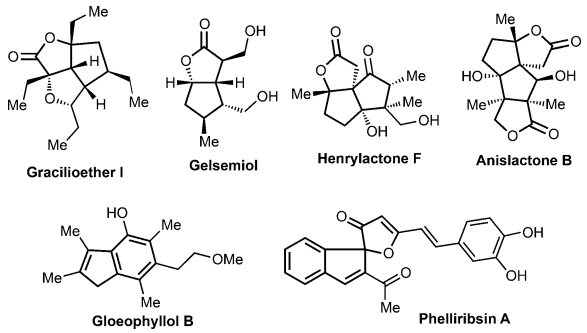


Figure 1. Examples of natural compounds incorporating the indene and condensed five-member lactone skeletons.

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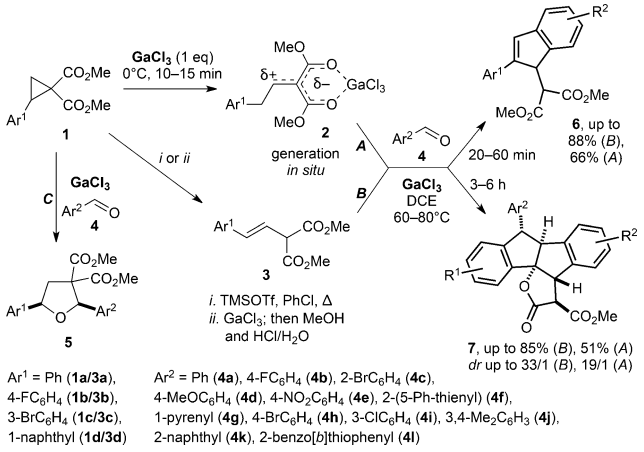
gallium arylalkylidenemalonate complex from ACDC **1**.[3a,b,d] The former complex **2** was immediately used in the reaction with an aldehyde in the presence of an additional amount of $GaCl_3$. The second approach that was found to be more efficient involved preliminary isomerization of ACDC to styrylmalonate **3**,[5] which was then used in the reaction with aldehyde **4** in the presence of $GaCl_3$. Irrespective of the reaction conditions, addition of $GaCl_3$ to a mixture of cyclopropane **1** and aldehyde **4** resulted in usual [3+2]-cycloaddition to give ordinary tetrahydrofurans **5**.[1,4] Under the conditions that we developed, it became possible to perform the process in such a way that it gave substituted indenes **6** or pentacyclic lactones **7** as the main reaction products, whereas tetrahydrofurans **5** were not formed at all (Scheme 2). Highly diastereoselective cascade assembly of compounds **7** with formation of five stereocenters is particularly interesting.



Scheme 2. General synthetic method for the reaction of DACs and aldehydes.

To optimize the conditions that result in indenes **6** or lactones **7**, we performed a broad series of experiments using cyclopropane **1a** or isomeric styrylmalonate **3a** and benzaldehyde **4a** (Scheme 2, $Ar^1 = Ar^2 = Ph$). A few key points required for successful implementation of the strategy chosen should be noted. First, the reaction should be performed by preliminary synthesis of compounds **2** or **3** with a mandatory excess of anhydrous $GaCl_3$ that neutralizes the formation of water and methanol in the reaction (see below). Second, the process should be carried out with some excess of the aldehyde required for suppressing dimerization and oligomerization reactions. It is principally important to use $GaCl_3$, since the reaction does not occur at all with other Lewis acids.

The degree of formation of indenes **6a** or lactones **7a** is determined by the reaction time to a considerable extent, which allows one to obtain each of them selectively. This regularity allows us to assume that lactone **7a** is formed from indene **6a**, which is formed already in 20 min at 60 °C, while its complete conversion into lactone **7a** requires a few hours.

The two approaches used (*A* and *B*) are similar and only differ in the number of dimers formed from the starting ACDC. It should be noted that in the absence of an aldehyde, all the three compounds **1a**, **2a** and **3a** react identically in the presence of $GaCl_3$ to give the same dimers.[3a,5b] However, if an aldehyde is present, dimerization of styrylmalonate **3a** occurs much more slowly than that of Ga complex **2**, which explains the higher efficiency of the styrylmalonate approach. At the same time, these two approaches result in nearly the same composition of the products of the reaction with aldehydes and manifest almost the same process regularities.

A number of substituted indenes **6b–j** and lactones **7b–j** was obtained by the method that we developed. Each was obtained selectively and in good yield (Scheme 2, Table 1, Figures 2 and 3). Both ACDC (**1b–d**) and aldehydes (**4b–j**) can contain substituents. Moreover, heteroaromatic aldehydes can also be used. The reaction direction is mainly controlled by time, as well as by using a smaller excess of an aldehyde and $GaCl_3$ in the case of the synthesis of indenes **6** (Table 1). The optimum time is 0.3–1 h for indenes and 3–6 h for lactones. In the case of less-reactive and more sterically

Table 1: Scope of the reactions.[a,b]

Entry	Reagents		$GaCl_3$ [eq.]	**4** [eq.]	*T* [°C]	*t* [h]	Product	Yield [%]	d.r.
1	**3a**	**4a**	2	4	60	0.25	**6a**	71	–
2	**3a**	**4b**	2	4	60	0.25	**6b**	78	–
3	**3a**	**4c**	1	2	60	2	**6c**	75	–
4	**3a**	**4d**	2	4	60	1.5	**6d**	77	–
5[c]	**3a**	**4e**	1	3	100	3	**6e**	74	–
6	**3a**	**4f**	1	1.5	60	1	**6f**	73	–
7[c]	**3a**	**4g**	1	1.5	85	1	**6g**	74	–
8	**3b**	**4c**	1	2	60	1	**6h**	72	–
9	**3c**	**4a**	2	4	60	1	**6i**	88	–
10	**3d**	**4a**	1.2	6	50	2	**6j**	26	–
11	**3a**	**4a**	2	4	60	2.5	**7a**	77	91/9
12	**3a**	**4b**	2	4	60	4	**7b**	85	94/6
13	**3a**	**4h**	2	4	60	4	**7c**	78	97/3
14	**3a**	**4i**	3	4	60	5	**7d**	73	97/3
15	**3a**	**4j**	1	4	60	3	**7e**+**7f**	74[d]	90/10
16	**3a**	**4c**	2	4	60	6	**7g**	39	95/5
17	**3b**	**4a**	2.5	5	60	4	**7h**	66	88/12
18	**3c**	**4a**	2	4	60	6	**7i**	75	87/13
19	**3d**	**4a**	1.5	6	60	3	**7j**	15	95/5

[a] See Scheme 2, Figure 2, and Figure 3); for selected examples and full tables, see the Supporting Information. [b] General reaction conditions: 0.5 mmol **1** or **3** in 4–6 mL of 1,2-dichloroethane. [c] PhCl as solvent. [d] **7e**/**7f** ca. 1:1; d.r. for each isomer.

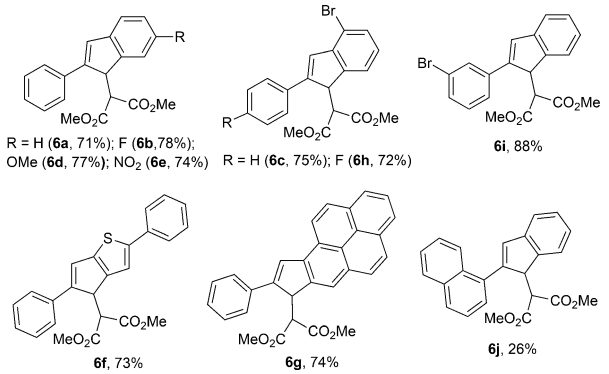


Figure 2. Scope of the reaction for indenes **6**.

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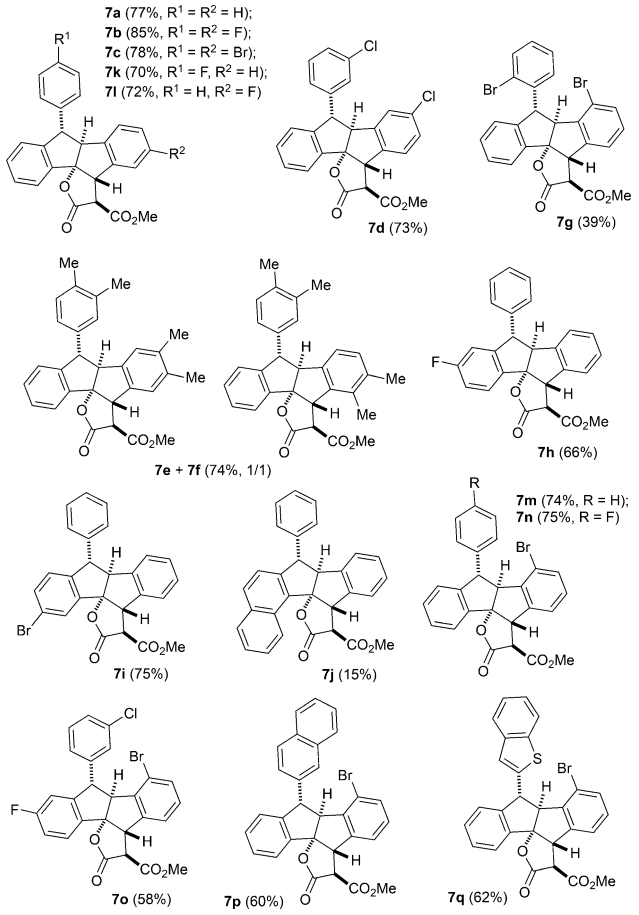


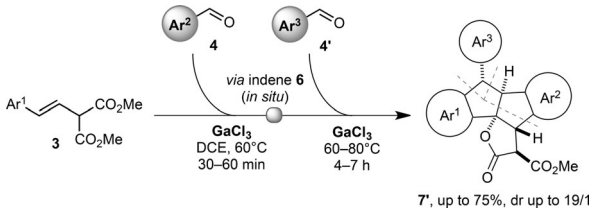
Figure 3. Scope of the two and three component reactions for pentacyclic lactones **7a–q**.

loaded aldehydes, the reaction time increases and higher temperatures are sometimes required.

To expand the method, we managed to create an efficient approach for three-component selective coupling of two different aldehydes. This approach is based on preliminary generation of indenes **6** (or their complexes with $GaCl_3$) under strictly controlled conditions from a styrylmalonate and one of aldehydes **4**. After that, another aldehyde **4′** and an additional amount of $GaCl_3$ are added to the reaction mixture. Provided that the conditions are strictly observed at both stages, it becomes possible to perform the process with high regioselectivity to give nearly a single cross-lactone **7′** of the four possible compounds (Scheme 3, Table 2, Figure 3).

The synthetic potential and efficiency of this method were well demonstrated in selective incorporation of two quite similar aldehydes (**4a** and **4b**) successively into different positions of the pentacycle (**7k** and **7l**). The process regioselectivity proved to be remarkably high, as almost no coupling products from two same aldehydes were formed.

The method that we developed has a powerful synthetic potential that allows one to assemble complex heteropolycyclic structures with high regio- and diastereoselectivity from three simple starting compounds. Obviously, the suggested approach has general applicability and can be easily expanded to other substrates in the future.



Scheme 3. Synthetic method for the three-component reaction of **3** with two different aldehydes.

Table 2: Scope of the three-component reaction for cross-pentacyclic lactones **7′**.[a]

Entry	Reagents (**3**/**4**/**4′**)			$GaCl_3$ [eq.][b]	**4′**[b] [eq.]	T[b] [°C]	t[b] [h]	Product	Yield [%]	d.r.
1	**3a**	**4a**	**4b**	2.5	8	60	4	**7k**	70	89/11
2	**3a**	**4b**	**4a**	2.5	8	60	4	**7l**	72	90/10
3	**3a**	**4c**	**4a**	2.5	6	60	5	**7m**	74	94/6
4	**3a**	**4c**	**4b**	2.5	6	60	7	**7n**	75	90/10
5	**3b**	**4c**	**4i**	2	6	60	4	**7o**	58	92/8
6	**3a**	**4c**	**4k**	2	3	80	6	**7p**	60	95/5
7	**3a**	**4c**	**4l**	2.5	6	60	6	**7q**	62	91/9

[a] See Scheme 3, Figure 3. General reaction conditions on the first stage: **3** (0.5 mmol) in 1,2-dichloroethane (4–6 mL) at 60 °C for 30 min (entries 1 and 2) or 1 h (entries 3–7), molar ratio **3**/**4**/$GaCl_3$ = 1:1.5:1. [b] Conditions on the second stage.

In all cases, the high diastereoselectivity of formation of pentacyclic lactones **7** should be noted: the reaction involving the formation of five stereo centers gives only two diastereomers with considerable predomination of one of them (Figure 3). The minor diastereomer is related to the position of the ester group.

The constitution and configuration of the obtained compounds were uniquely determined by ^1H, ^{13}C, and ^{19}F NMR spectroscopy. A full set of modern 2D NMR experiments, such as COSY, NOESY, HSQC, HSQC-TOCSY, and HMBC, were used. For compounds **7a** and **7p** (Figure 4), X-ray analysis was carried out.

The following simplified mechanism can be assumed. The key point consists of generation of gallium intermediate **I** that exists in solution in equilibrium with gallium arylalkylidenemalonate complex **2**. The aldehyde itself apparently does not react with complex **2**, since it also activated under these

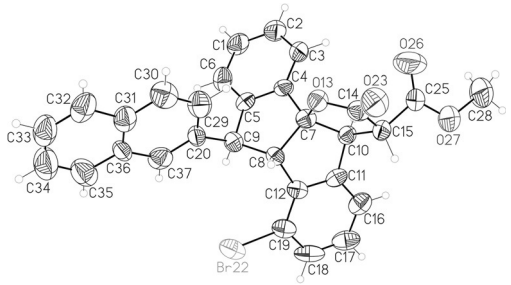


Figure 4. ORTEP diagram of **7p**, with ellipsoids set at 50% probability.[10]

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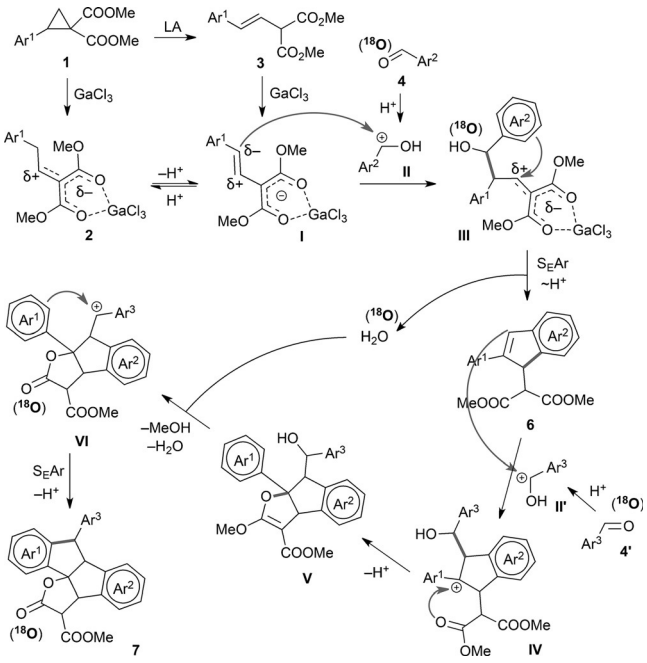
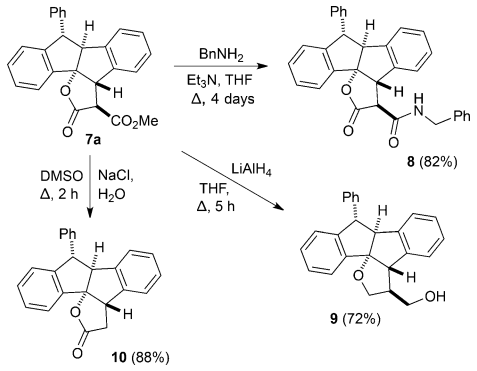
conditions and is an electrophile. At the same time, both intermediates (complexes **2** and **I**) can give dimerization products, this process being quite characteristic of gallium arylalkylidenemalonate complex **2**. Conversely, the dimerization rate of intermediate **I** in the presence of an aldehyde is noticeably smaller and the method for generation of intermediates strongly affects the equilibrium between them. If styrylmalonate **3** is used, generation of the target intermediate **I** occurs initially (in this process, the reactive proton is apparently transferred to the aldehyde). Subsequently, it reacts with activated aldehyde **II** to give intermediate **III** with polarized double bond. The latter undergoes intramolecular electrophilic substitution at the aromatic ring to give indenes **6** (possibly as a gallium complex). This is accompanied by elimination of water, which later participates at the lactonization stage. Indenes **6** can be either isolated at this stage or used in further reactions (Scheme 4; for simplification, complexation with $GaCl_3$ is omitted everywhere after intermediate **III**). For example, indene **6** can react at the double bond with the second activated aldehyde molecule, with cyclization through one of the carboxy groups (intermediates **IV**–**VI**) and electrophilic substitution at Ar^1.



Scheme 4. Proposed simplified mechanism.

It has been shown in the reaction of **3a** with ^{18}O-benzaldehyde (degree of enrichment ca. 50%) that the final product **7a** contains the isotopic label in the keto group of the lactone ring and the original isotopic enrichment remains unchanged (the same aldehyde was used for both steps; Scheme 4). The label leaves intermediates **III** and **V** in the form of water $H_2{}^{18}O$ (possibly bound with gallium), which is then used for hydrolysis of the lactone ring. Incorporation of the isotopic label into compound **7** was detected using mass spectrometry and NMR spectroscopy on ^{17}O nuclei with which labeled benzaldehyde was also enriched (13-fold enrichment in comparison with the natural content).

The compounds obtained contain various functional groups that can be easily modified. For example, the carboxy group was converted into an amide group and reduced to a hydroxy group to give compounds **8** and **9**, as well as hydrolyzed and decarboxylated to give compound **10** with retention of the lactone ring (Scheme 5).



Scheme 5. Some simple modifications for the furanoncarboxylate **7a**.

In conclusion, we have developed a new class of cascade processes based on arylcyclopropanedicarboxylates or isomeric styrylmalonates with aldehydes in the presence of gallium compounds as an alternative to the [3+2]-cycloaddition reaction known previously. This strategy based on generation of formal 1,2-zwitterionic complexes of geminal dicarboxylates with gallium halides makes it possible to perform new selective reactions giving substituted indenes or indanoindanes fused with a lactone ring. A three-component version of coupling of styrylmalonates with two different aldehydes has been developed. The suggested approach has general applicability and allows one to assemble complex heteropolycyclic structures from simple starting compounds with high regio- and diastereoselectivity.

Acknowledgements

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Keywords: carbo- and heterocycles · cascade reactions · cyclopropanes · donor–acceptor systems · gallium trichloride

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[10] CCDC 1475754 (**7p**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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