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Formal [3 + 2]-Cycloaddition of Donor–Acceptor Cyclopropanes to 1,3-Dienes: Cyclopentane Assembly

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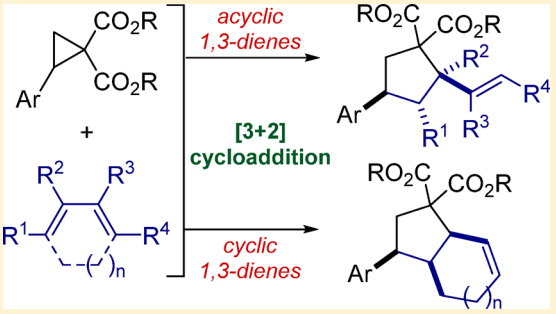
Supporting Information

ABSTRACT: We report a new simple method to access highly substituted cyclopentanes via Lewis acid-initiated formal [3 + 2]-cycloaddition of donor–acceptor cyclopropanes to 1,3-dienes. This process displays exceptional chemo- and regioselectivity as well as high diastereoselectivity, allowing for the synthesis of functionalized cyclopentanes and bicyclic cyclopentane-based structures in moderate to high yields. Moreover, one-pot synthesis of biologically relevant cyclopentafuranones, based on reaction of donor–acceptor cyclopropanes with dienes, has been developed.

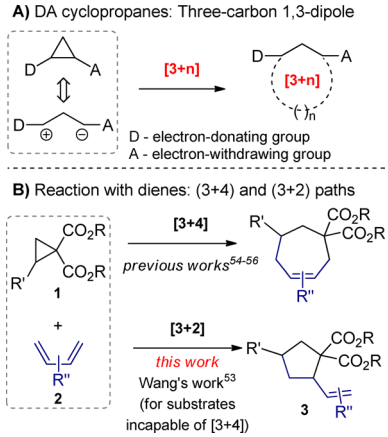


INTRODUCTION

Widespread occurrence of the cyclopentane framework in numerous synthetic and natural biologically active molecules (prostaglandins, steroids, terpenoids, etc.) stimulates extensive development of various strategies employed for the assembling of all-carbon five-membered rings.[1] In this context, [3 + 2]-cycloaddition of 1,3-carbodipoles to C–C double or triple bonds is among the most straightforward approaches to this scaffold,[2−6] although the generation of such dipoles is a challenging problem in general. Meanwhile, activated cyclopropanes[7−16] and, particularly, donor–acceptor (DA) cyclopropanes[17] are seen as well-proven synthetic equivalents of three-carbon 1,3-dipolar synthons (Scheme 1, A). This reactivity, provided by chemo- and regioselective ring opening of DA cyclopropanes under mild reaction conditions, defined their essential role as valuable building blocks for the construction of various ring systems.

To date, several convenient approaches to five-membered carbocyclic skeletons via Lewis acid-initiated formal [3 + 2]-cycloaddition of DA cyclopropanes to two-carbon dipolarophiles (namely, enol ethers,[18−28] alkynes,[29−32] allenes,[33−35] indoles,[36−41] furans,[42] etc.[43−52]) have been reported. Recently, intramolecular version of cross [3 + 2]-cycloaddition has been developed[53] for substrates which simultaneously contain DA cyclopropane and 1,3-diene moieties and are not able to form [3 + 4]-cycloadducts according to Bredt's rule. Meanwhile, as of now, there is no general method to assemble cyclopentanes via [3 + 2]-cycloaddition wherein common 1,3-conjugated dienes are used as dipolarophiles, although those compounds seem to be promising in the context of this goal.

Scheme 1. Donor–Acceptor Cyclopropanes in [3 + *n*]-Cycloadditions



Due to the dichotomy of such dienes reacting as 2π- and 4π-components, their reactions with DA cyclopropanes can proceed via both [3 + 2]- and [3 + 4]-cycloaddition pathways, leading to five- and seven-membered rings, respectively (Scheme 1, B). Recently, we reported several pioneering examples of DA cyclopropane [3 + 4]-cycloaddition that can be interpreted as a homoversion of the Diels–Alder reaction.[54−56] We revealed that such 1,3-dienes, as 1,3-diphenylisobensofuran and anthracenes, act efficiently as 4π-partners for DA cyclopropanes in these processes. An asymmetric version of

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[3 + 4]-cycloaddition for DA cyclopropanes to 2-siloxy-1,3-dienes was developed by Tang and co-workers just recently.[57] Moreover, an ability to form seven-membered carbocycles was revealed for cyclopentadiene in reactions with DA cyclopropanes.[58]

In line with our ongoing research related to DA cyclopropane reactivity toward 1,3-conjugated dienes,[54−56,58] herein we report a new approach to cyclopentane-based skeletons via formal [3 + 2]-cycloaddition of 2-aryl-substituted cyclopropane-1,1-diesters **1** to simple, commercially available acyclic and cyclic dienes **2**. It is noteworthy that this reaction exhibits exceptional chemoselectivity: among two possible directions, [3 + 2]-cycloaddition proceeds exclusively, while [3 + 4]-cycloaddition does not occur at all. The developed method allows for the synthesis of alkenylcyclopentanes **3** and related cyclopentane-embedded bicycles with several contiguous stereocenters in a highly regio- and stereoselective manner. Synthetic utility of the obtained polysubstituted cyclopentanes **3** is provided by the presence of several functionalities (C−C double bond, donor, and acceptor groups) in their molecules. This furnishes plural possibilities for the postmodification of the synthesized compounds into bioactive cyclopentane-derived products and challenging polycyclic architectures. In this work, we developed one-pot lactonization of **3**, opening a simple route to new representatives of the cyclopentafuranone family to which such bioactive compounds as sesquiterpenes merrilactone A, anislactones A and B, teucmosin, ginkgolides, and sinensilactam A belong.

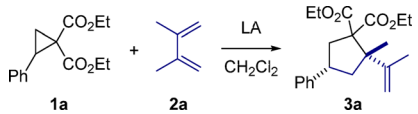
RESULTS AND DISCUSSION

Reactions of 2-Arylcyclopropane-1,1-diesters 1 with Acyclic 1,3-Dienes 2. At the beginning of our research, phenylcyclopropane-1,1-diester **1a** was examined as a model substrate in a reaction with 2,3-dimethylbutadiene (**2a**), prominent as one of the most active dienes in terms of the Diels−Alder reaction. The initial survey of a series of common Lewis acids ($Yb(OTf)_3$, $TiCl_4$, $SnCl_4$, TMSOTf, etc.) as initiators revealed that moderately activating $Yb(OTf)_3$, while being the most efficient catalyst for the formal [3 + 4]-cycloaddition of DA cyclopropanes to 1,3-diphenylisobenzofuran, does not catalyze the reaction between **1a** and **2a** even under prolonged heating (entries 1 and 2, Table 1). Meanwhile, in the case of strongly activating Lewis acids ($TiCl_4$ and $SnCl_4$), the reaction proceeds efficiently under mild conditions, leading to [3 + 2]-cycloadduct **3a** (entries 5 and 6, Table 1). The highest yield of **3a** has been obtained when $TiCl_4$ (1.2 equiv) was used as an initiator (entry 5, Table 1).

Next, we studied the scope of [3 + 2]-cycloaddition and examined the reactivity of aryl-substituted cyclopropane 1,1-diesters **1a−d** toward a range of diversely substituted butadienes **2a−d** (Table 2). DA cyclopropanes with electroneutral aryl substituents as donors were selected for this investigation because earlier we found that DA cyclopropanes bearing a highly nucleophilic aromatic group are prone to demonstrate the different chemoselectivity affording products with the participation of the arene moiety as a nucleophile.[55,58−62]

We found that all reactions proceeded with exceptional chemoselectivity, resulting in [3 + 2]-cycloadducts **3a−h** exclusively. Variations of substituents and their positions at the C−C double bond have no significant influence on the process efficiency: the reaction proceeds for unsubstituted butadiene (**2b**) as well as for dienes containing substituted terminal (**2a,c**) or internal (**2d**) double bonds. Moderate yields of **3a,b,d−f** are, apparently, caused by the processes of oligo- and polymerization that are typical for both dienes and DA cyclopropanes.[63−65] Products **3a−h** are formed as individual regioisomers in accordance with Markovnikov's rule. In the case of isoprene (**2c**), [3 + 2]-cycloaddition of cyclopropanes **1a,c,d**

Table 1. Optimization of Reaction Conditions for the Model [3 + 2]-Cycloaddition of Cyclopropane 1a to 2,3-Dimethylbutadiene (2a)[a,b]

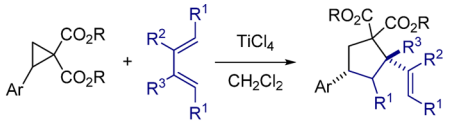


1a 2a 3a

entry	LA [mol %]	time [h]	T [°C]	Yield [%][c] (dr)[d]
1	$Yb(OTf)_3$ (5)	5	20	-[e]
2	$Yb(OTf)_3$ (5)	5	reflux	-[e]
3	$EtAlCl_2$ (110)	20	20	-[f]
4	$TiCl_4$ (50)	3	0 → 20	-[g]
5	**$TiCl_4$ (120)**	**3**	**−40 → 20**	**53 (85:15)**
6	$SnCl_4$ (120)	3	−40 → 20	42 (82:18)

[a]Reaction conditions: 0.09 M solution of **1a** (1 equiv) in CH_2Cl_2, **2a** (3 equiv). [b]Structure of the major isomer is depicted. [c]Isolated yield. [d]Diastereomeric ratios were determined by ^1H NMR data for crude reaction mixtures. [e]No conversion was observed. [f]Oligomeric and polymeric products were yielded primarily. [g]The product of nucleophilic ring opening of **1a** with the chloride ion, diethyl (2-chloro-2-phenylethyl)malonate,[55] was formed.

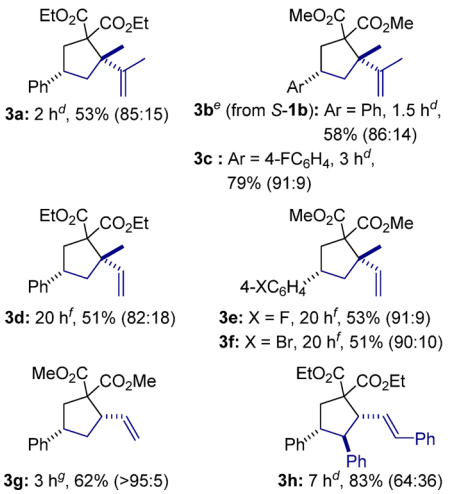
Table 2. [3 + 2]-Cycloaddition of 2-Arylcyclopropane-1,1-diesters 1a−d to Butadienes 2a−d[a,b,c]



1a-d 2a-d 3a-h

1a: R = Et, Ar = Ph
1b (*S*-**1b**): R = Me, Ar = Ph
1c: R = Me, Ar = 4-FC_6H_4
1d: R = Me, Ar = 4-BrC_6H_4

2a: R^1 = H, R^2 = R^3 = Me
2b: R^1 = R^2 = R^3 = H
2c: R^1 = R^2 = H, R^3 = Me
2d: R^1 = Ph, R^2 = R^3 = H



3a: 2 h[d], 53% (85:15)

3b[e] (from *S*-**1b**): Ar = Ph, 1.5 h[d], 58% (86:14)

3c : Ar = 4-FC_6H_4, 3 h[d], 79% (91:9)

3d: 20 h[f], 51% (82:18)

3e: X = F, 20 h[f], 53% (91:9)

3f: X = Br, 20 h[f], 51% (90:10)

3g: 3 h[g], 62% (>95:5)

3h: 7 h[d], 83% (64:36)

[a]Reaction conditions: 0.07−0.09 M solution of **1** (1 equiv), **2** (1.5−3 equiv), and $TiCl_4$ (1.2 equiv); all components were mixed at −40 to 0 °C. [b]Structures of the major isomers are depicted. [c]Isolated yield. [d]At reflux. [e]Product was obtained in racemic form. [f]At room temperature. [g]At −35 °C.

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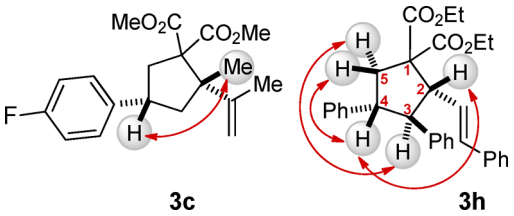
selectively proceeds toward the more substituted C−C double bond of diene **2c**, yielding cyclopentanes **3d−f**. The reaction mostly exhibits significant diastereoselectivity: cyclopentanes **3** are formed predominantly as diastereomers with a *cis*-arrangement of the aromatic substituent and the alkenyl fragment. Although three stereocenters are present in **3h**, this cyclopentane is formed as a mixture of two diastereomers as well. Exceptional diastereoselectivity was observed in the reaction of **1b** with butadiene (**2b**) wherein the *cis*-isomer of **3g** was formed individually. Under the studied conditions, the reaction of optically active cyclopropane (*S*)-**1b** with diene **2a** leads to racemic cyclopentane **3b**. Unfortunately, Danishefsky's diene was found to be extremely unstable under the reaction conditions—therefore, we failed to obtain any cycloadducts even at −60 °C. It is necessary to note that the remaining C−C double bond in **3** failed to give the product of double [3 + 2]-cycloaddition with excess of cyclopropane **1** even under significantly harsher conditions.

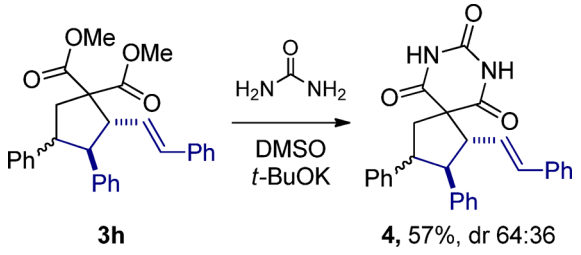
The assignment of the relative configuration of the major isomers of **3c,h** was made based on the NOESY experiments (Scheme 2). The minor isomer of **3h** was assigned to the C-4

Scheme 2. Representative NOE Responses for the Major Isomers of 3c,h



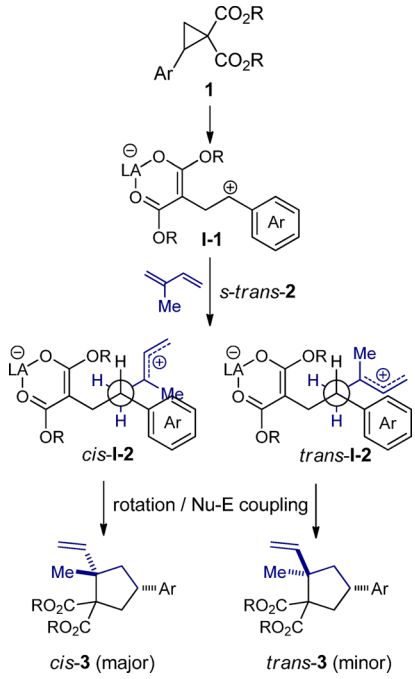
epimer of the major one. This assignment is based on the following criteria: (1) a downfield shift of the signals for H-3 and H-4 vs those for the major isomer[66] and (2) a high $^3J_{2-3}$ value of 11.7 Hz which is consistent with the $^3J_{2-3}$ estimated by the Karplus equation.[67,68] In order to provide unambiguous assignments of the relative configuration for the diastereomers of **3h** by means of single-crystal X-ray analysis, barbiturate **4** was obtained (Scheme 3). However, we failed to grow appropriate crystals from the diastereomeric mixture of **4**.

Scheme 3. Transformation of 3h to Barbiturate 4



Reaction Mechanism and Diastereoselectivity. According to the obtained results, the following mechanism can be proposed for the formal [3 + 2]-cycloaddition of cyclopropanes **1** to dienes **2** (Scheme 4). Coordination of a strongly activating Lewis acid at acceptor group(s) of cyclopropane **1** induces its ring opening into 1,3-zwitterionic species **I-1**. Transformation of optically active cyclopropane (*S*)-**1b** to *rac*-**3b** can be regarded as the evidence of **I-1** formation. In the next step, the electrophilic addition of the benzyl cation in **I-1** to one of the

Scheme 4. Proposed Mechanism and the Origin of Diastereoselectivity (Exemplified by the Reaction Involving Isoprene 2c)



C−C double bonds in diene **2** takes place, leading to new zwitterionic species **I-2**. For the asymmetrically substituted diene **2c**, this addition proceeds with the exceptional chemoselectivity providing the most stable species **I-2** with a tertiary cationic center. The formation of a cyclopentane ring is accomplished by the coupling of nucleophilic and electrophilic centers in the intermediate **I-2**.

In order to provide a better understanding of the origin of high *cis*-diastereoselectivity, we started with density functional theory (DFT) calculations[67] for the product **3**. For the model compounds **3d′** (the dimethyl ester analogue of **3d**) and **3g**, *cis*-isomers were calculated to be slightly less stable than the *trans*-isomers. Apparently, this excludes thermodynamic control of diastereoselectivity. Nevertheless, the relative energy barriers for two similar reactions correlate typically with the differences in the reaction energies. This is exemplified, for example, by linear free energy relationship ($\Delta G^{\ddagger} = \alpha + \beta \times \Delta_r G$, where α and β are coefficients) or some nonlinear dependencies of $\Delta G^{\ddagger}$ on $\Delta_r G$ (for example, the Marcus equation, $\Delta G^{\ddagger} = (\lambda + \Delta_r G)^2/4\lambda$, where λ is the total reorganization energy). However, these relationships are appropriate to the one-step processes only. Oppositely, the studied **1**-to-**3** cycloaddition is a stepwise reaction; the reaction thermodynamics is determined by the last step (low-barrier rotation around the single C−C bond and cation−anion coupling), but the kinetically controlled and diastereoselectivity determined step is definitely electrophilic attack of **I-1** on diene **2** yielding **I-2**. Assuming that the intrinsic activation energies for **I-1** into **I-2** transformation (α and λ in the equations above) are similar for two isomers, the difference in $\Delta G^{\ddagger}$ for their formation should be primarily determined by the relative stabilities of *cis*-**I-2** and *trans*-**I-2**.

Our DFT calculations, performed for the related model systems,[67] allowed us to determine the most stable conformers of *cis*-**I-2** and *trans*-**I-2** (Scheme 4), wherein only one *gauche*-repulsion exists between the alkenylium fragment and the aryl

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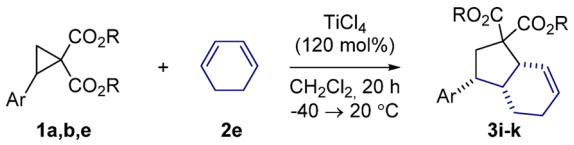
group. Intermediate *cis*-**I-2**, in turn, was found to be more stable vs *trans*-**I-2** due to lower *gauche*-hindrance provided by the methyl group rather than the allylic cation. Therefore, *cis*-**I-2** should prevail over *trans*-**I-2**, although subsequent *cis*-**I-2** transformation results in less stable *cis*-**3**. It is noteworthy that this model provides also a good explanation of the trend in diastereoselectivity variation for all studied 1,3-dienes.

Exceptional chemoselectivity manifesting itself in the occurrence of [3 + 2]-cycloaddition rather than [3 + 4]-cycloaddition can be also explained by kinetic control of the process. Similar to electrophilic addition to 1,3-dienes, wherein 1,2-addition has a lower barrier vs 1,4-addition,[69] [3 + 2]-cycloaddition should have a lower energy barrier since change of the bond order occurs for only one reacting C−C double bond of a diene existing predominantly in the more stable *s-trans*-form. The larger energy barrier for [3 + 4]-cycloaddition is related to the requirement of *s-trans*-into-*s-cis*-isomerization within acyclic diene and reorganization of all three bonds of a conjugated system of both acyclic and cyclic dienes in the transition state. The latter process provides more significant contribution to the energy barrier and apparently causes high chemoselectivity also for cyclic dienes for which *s-trans*-into-*s-cis*-isomerization is not required (see next section).

Reaction of 2-Arylcyclopropane-1,1-diesters 1 with Cyclic 1,3-Dienes 2. [3 + 2]-Cycloaddition of DA cyclopropanes **1** to common five- and six-membered cyclic 1,3-dienes opens an efficient route to [3.3.0] and [4.3.0]-carbobicycles. 1,3-Cyclohexadiene (**2e**) is rather stable in the presence of strong Lewis acids and readily gives hexahydroindenes **3i−k** during the [3 + 2]-cycloaddition of cyclopropanes **1a,b,e** under studied conditions (Scheme 5). Products **3i−k** were formed as mixtures of two diastereomers, among which isomers with the *cis*-arrangement of the aryl substituent and the cyclohexene fragment predominate.

Scheme 5. [3 + 2]-Cycloaddition of Cyclopropanes 1 to 1,3-Cyclohexadiene (2e)



1a,b,e **2e** **3i-k**

1a: R = Et, Ar = Ph **3i:** R = Et, Ar = Ph, 57% (64:36)
1b: R = Me, Ar = Ph **3j:** R = Me, Ar = Ph, 59% (62:38)
1e: R = Et, Ar = 4-FC_6H_4 **3k:** R = Et, Ar = 4-F-C_6H_4, 58% (68:32)

Cyclopentadiene (**2f**) was recently found to react efficiently with DA cyclopropanes that contain an electron-abundant aromatic substituent as a donor group.[58] In this case, however, the cyclopropane molecule displays different reactivity when an electrophilic center is still located at the benzyl C atom, whereas a nucleophilic center is at the *ortho*-position of the aromatic ring. Instead of any type of formal [3 + *n*]-cycloaddition, this reactivity provides the [3 + 4]-annulation product,[70] leading to bicyclo[3.2.1]octenes. In order to avoid the annulation route and to study the possibility of competition between [3 + 2]- and [3 + 4]-cycloaddition, we examined reactions of cyclopentadiene (**2f**) with cyclopropanes **1f,g**. These substrates were selected as model ones since the electron-rich 2,4,6-trimethoxyphenyl and styryl substituents enhance cyclopropane reactivity toward dienes while failing to provide [3 + *n*]-annulation. We found that the application of strongly activating Lewis acids (TMSOTf, $TiCl_4$, $SnCl_4$) caused significant polymerization of the initial compounds. Therefore, a series of moderately activating Lewis acids were studied as initiators of the reaction between cyclopropane **1f** and cyclopentadiene (**2f**) (Table 3).

When $Yb(OTf)_3$ was used as a catalyst in both nonpolar and polar solvents, the reaction afforded a complex mixture of products, among which [3 + 2]-cycloadduct **3l** is formed in low yield (entries 1−3, Table 3). In the presence of the less activating $Nd(OTf)_3$, the products of oligo- and polymerization are mainly formed (entries 4). The use of the more activating $Sn(OTf)_2$ allowed us to obtain product **3l** in low to good yields (entries 5 and 6). The best result was obtained when the reaction had been carried out under very mild conditions in a nonpolar solvent at −50 °C, followed by warming of the reaction mixture up to 5 °C (entry 6, Table 3). In this case, tetrahydropentalene **3l** was obtained in a 65% yield as a mixture of two diastereomers (78:22) with the predominance of the isomer with a *cis*-arrangement of the aryl group and the cyclopentene fragment. Surprisingly, bicyclo[2.2.1]heptene **5**[71] is formed as a side product under the conditions studied. Currently, the mechanism of its formation cannot be determined conclusively.

Analogously, the reaction of styryl-derived cyclopropane **1g** with cyclopentadiene (**2f**) leads to tetrahydropentalene **3m** with 58% yield and identical diastereoselectivity (Scheme 6).

Relative all-*cis*-configurations of the major isomers of **3l,m** were determined via careful analysis of NMR data including NOE experiments (Scheme 7). Moreover, the characteristic experimental $^3J_{2-3}$ values for the major isomer of **3l** (12.0 and 7.6 Hz) are consistent with those calculated for the *cis,cis*-**3l′** (the dimethyl analogue of **3l**, 12.3 and 3.9 Hz) and differ from the corresponding values for the *trans,cis*-**3l′** (6.9 and 1.0 Hz).[67]

In contrast to cyclohexadiene (**2e**) and cyclopentadiene (**2f**), cyclic dienes with electron-withdrawing groups, such as tetraphenylcyclopentadienone and pyran-2-one, failed to yield any adducts in the reaction with cyclopropanes **1** in the presence of various Lewis acids ($Yb(OTf)_3$, $Sc(OTf)_3$, $TiCl_4$, and $SnCl_4$).

Reaction of Cyclopropane 1b with Norbornadiene (6). Norbornadiene (**6**) is an unsaturated compound that has piqued interest of researchers studying various ring-forming processes. Despite the absence of conjugation between the two double C−C bonds in **6**, this diene can undergo cycloaddition with not only one but two double bonds participating, which leads to [*n* + 2]- or [*n* + 2 + 2]-cycloadducts, respectively.[72,73] In this work, we studied the reactivity of diene **6** toward cyclopropane **1b** (Table 4). We observed no reaction in the absence of a Lewis acid as well as in the presence of moderately activating Lewis acids, such as $Yb(OTf)_3$, $Sn(OTf)_2$, and $Sc(OTf)_3$ (entries 1 and 2). Strongly activating Lewis acids were found to initiate [3 + 2]-cycloaddition of cyclopropane **1b** to diene **6**, yielding **7** (entries 3−5). The best result was obtained when $SnCl_4$, acting as an initiator, was added to the reaction mixture at −60 °C, followed by its warming to room temperature (entry 5). Under these conditions **7** was formed as an exclusive low-molecular weight product in 58% yield.

The reaction exhibits exceptional diastereoselectivity: cycloadduct **7** is formed as an *exo-trans*-isomer exclusively. Its structure and the relative arrangement of substituents in the molecule were revealed in the 1D and 2D NMR experiments, including NOE ones. The NMR analysis of **7** confirmed the presence of the cyclopentane fragment *exo*-fused to norbor-

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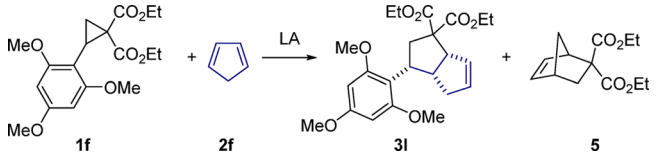
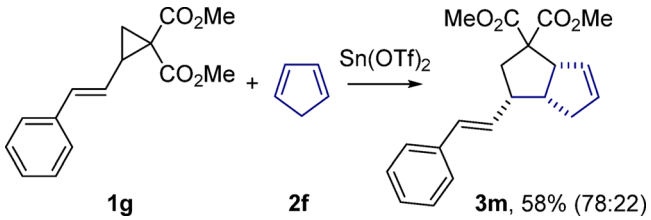
Table 3. Optimization of Reaction Conditions for the [3 + 2]-Cycloaddition of Cyclopropane 1f to Cyclopentadiene (2f)[a]



entry	LA [mol %]	solv.	time [h]	T [°C]	yield [%][b] (dr) 3l	5
1	$Yb(OTf)_3$ (5)	CH_2Cl_2	20	20	8[c]	<5[c]
2	$Yb(OTf)_3$ (5)	CH_2Cl_2	1	0	12[c]	<5[c]
3	$Yb(OTf)_3$ (5)	CH_3NO_2	20	20	18[c]	<5[c]
4	$Nd(OTf)_3$ (10)	CH_2Cl_2	3	20[d]	-[e]	-[e]
5	$Sn(OTf)_2$ (5)	CH_3NO_2	1	−10	25	<5
6	**$Sn(OTf)_2$ (5)**	**CH_2Cl_2**	**2**	**−50 → 5**	**65 (78:22)[f]**	**15[f]**

[a]Reaction conditions: 0.09 M solution of **1f** (1 equiv) and **2f** (4 equiv). [b]NMR yield. [c]Complex mixture of products is formed. [d]Identical result was obtained when the reaction was carried out at 0 °C. [e]Oligomeric and polymeric products are mainly formed. [f]Isolated yield. Diastereomeric ratio was determined by ^{1}H NMR data for the crude reaction mixture.

Scheme 6. [3 + 2]-Cycloaddition of Cyclopropane 1g to Cyclopentadiene (2f)



Scheme 7. Representative NOE Responses for the Major Isomers of 3l,m

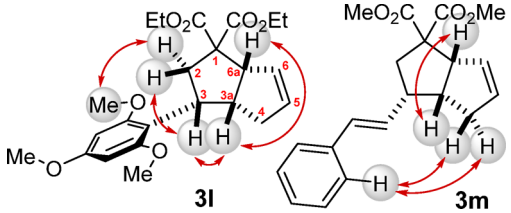
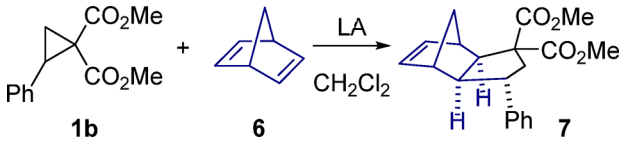


Table 4. [3 + 2]-Cycloaddition of Cyclopropane 1b to Norbornadiene (6)[a]

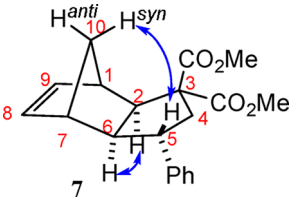


entry	LA [mol %]	time [h]	T [°C]	yield [%]
1	-	25	40	-[b]
2	$Yb(OTf)_3$ (5)	10	40	-[b]
3	$TiCl_4$ (120)	20	20	<10[c]
4	$SnCl_4$ (120)	4	−60 → 40	37[d]
5	$SnCl_4$ (120)	20	−60 → 20	58[d]

[a]Reaction conditions: 0.1 M solution of **1b** (1 equiv) in CH_2Cl_2, **6** (3.25 equiv). [b]No conversion was observed. [c]NMR yield; $MeNO_2$ was used as an internal standard. Oligomeric and polymeric products as well as dimethyl (2-chloro-2-phenylethyl)malonate were yielded primarily. [d]Isolated yield.

nene: besides the strong NOE response between H-5 and *syn*-H-10 and the absence of it between *syn*-H-10 and H-2 or *syn*-H-10 and H-6, values of the spin−spin coupling constants for the protons of the bridge system are consistent with the *exo*-configuration (Scheme 8). For H-2 and H-6, spin−spin coupling constants with the bridgehead protons H-1 and H-7 were not evident in the spectrum ($^3J_{1,2}$ and $^3J_{6,7}$ ∼ 0 Hz), whereas W-constants with the bridged *anti*-H-10 atom were observed ($^4J_{2,10anti}$, $^4J_{6,10anti}$ = 1.5 Hz). The value of $^3J_{2,6}$ = 9.3 Hz is typical for *cis*-oriented protons in the related tricyclic systems. The phenyl group in **7** is *cis*-oriented with the H-2 and H-6 atoms. This fact is confirmed by NOE experiments together with the values of $^3J_{4,5}$ = 12.3 and 6.2 Hz. The aforementioned values are in agreement with the values (14.4 and 5.2 Hz) calculated by the Karplus equation for structure **7** optimized by DFT calculations.[67] The analogous values calculated for the C-5 epimer of **7** are 9.8 and 0.0 Hz, respectively. Moreover, **7** is 28.1 kJ mol^{-1} more stable than its C-5 epimer but 4.8 kJ mol^{-1} less stable than the *endo-trans*-isomer of **7**. This evidence definitely supports the kinetic control of *exo*-attack of the activated cyclopropane on the C−C double bond of norbornadiene.

Scheme 8. Representative NOE Responses for 7



The stereochemistry of the reaction between cyclopropane **1b** and diene **6** yielding the *exo*-fused product **7** is in accordance with the reported formation of *exo*-cycloadducts in reactions of **6** with other 1,3-dipolar reagents, which is described as predominant or even exclusive.[74−76] This is the first example of [3 + 2]-cycloaddition wherein a diene without a system of conjugated double bonds efficiently reacts with DA cyclopropanes.

One-Pot Transformation of 2-Arylcyclopropane-1,1-diesters 1 into Cyclopentafuranones. The presence of several functionalities in products **3** allows for their subsequent transformations into valuable compounds of various classes. In this work, we developed a simple approach to γ-butyrolactone-

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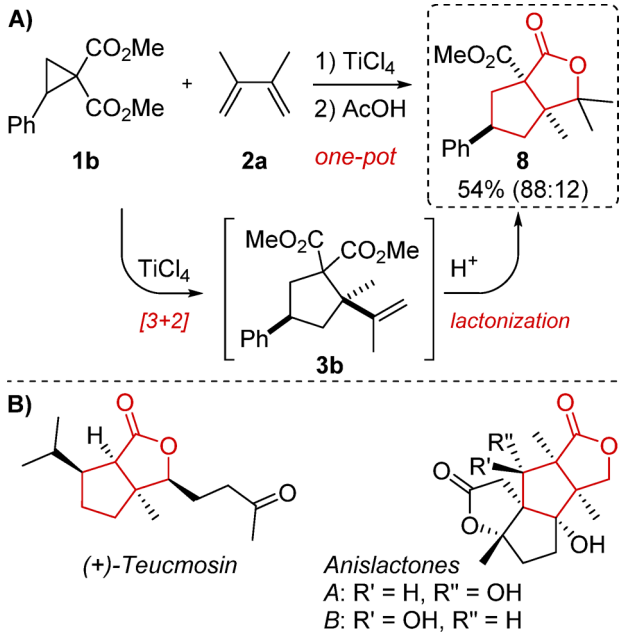
fused cyclopentanoids **8** via a one-pot procedure involving the [3 + 2]-cycloaddition of cyclopropane **1** to diene **2** followed by the lactonization of the resulting vinylcyclopentane **3** under acidic conditions into **8** (**A**, Scheme 9). Compounds of this

Scheme 9. One-Pot Transformation of Cyclopropane 1b into Cyclopentafuranone 8 (A) and Selected Examples of Natural Cyclopentafuranones (B)



type garner interest due to the wide occurrence of the cyclopentafuranone structural fragment in biologically active natural and synthetic compounds (**B**, Scheme 9).

CONCLUSION

We have developed a new convenient approach to cyclopentane-derived compounds via formal [3 + 2]-cycloaddition of DA cyclopropanes to 1,3-conjugated dienes. All studied reactions proceed chemoselectively as [3 + 2]-cycloaddition, thereby disabling competitive [3 + 4]-cycloaddition. The method affords opportunities to employ cheap commonly used 1,3-dienes and easily available DA cyclopropanes of trivial structure for reliable syntheses of functionalized alkenylcyclopentanes and more complex polycyclic cyclopentane-containing structures in an exceptionally regioselective and highly stereoselective manner. Moreover, norbornadiene, which does not contain a system of conjugated double bonds, was found to also undergo [3 + 2]-cycloaddition while reacting with DA cyclopropanes. According to the results obtained, a stepwise mechanism has been proposed for the formation of two new C−C bonds during the assembly of five-membered rings in this [3 + 2]-cycloaddition. The synthesized compounds can be applied as useful building blocks in various transformations due to the presence of a double bond, an aromatic fragment, and ester groups, which are all easily modifiable. More challenging postmodifications are evidently related to the synthesis of bioactive natural compounds and their synthetic analogues. In this regard, we have developed a new rapid access to pharmacologically relevant cyclopentafuranones based on the one-pot procedure: [3 + 2]-cycloaddition of DA cyclopropanes to dienes followed by lactonization.

EXPERIMENTAL SECTION

General Information. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, or 600 and 150 MHz, respectively, at room temperature and referenced to residual solvent signals (δ_H = 7.24 and δ_C = 77.1 ppm for $CDCl_3$). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, double doublet. Coupling constants (J) are in Hertz. The structures of synthesized compounds were elucidated with the aid of 1D NMR (^{1}H, ^{13}C, DEPT-90 and 135) and 2D NMR (COSY ^{1}H−^{1}H, XHCORR ^{13}C−^{1}H, HSQC ^{13}C−^{1}H, HMBC ^{13}C−^{1}H, NOESY ^{1}H−^{1}H) spectroscopy. Melting points (mp) were determined by means of a capillary melting point apparatus, and the values are uncorrected. Mass spectra (GC-MS) were obtained using electrospray ionization (ESI). The elemental compositions were determined on a CHN analysis instrument. Column chromatography was performed on silica gel 60 (230−400 mesh, Merck). All studied Lewis acids and dienes are available commercially. 2-Arylcyclopropane-1,1-diesters **1** were prepared by published procedures.[77] Preparation of dimethyl (2*S*)-2-phenylcyclopropane-1,1-dicarboxylate (**1b**) was described earlier.[78] All experiments were carried out under an argon atmosphere using freshly distilled and dry solvents.

General Procedure for the $TiCl_4$-Induced Reaction of Dialkyl 2-Arylcyclopropane-1,1-dicarboxylates 1 with 1,3-Dienes 2. The solution of $TiCl_4$ (0.7−1.2 mmol) in CH_2Cl_2 (1 mL) was added to the solution of cyclopropane **1** (1.0 mmol) in CH_2Cl_2 at reduced temperature (see below). To the resulted mixture the solution of diene (2.0−4.0 mmol) in CH_2Cl_2 was added. The reaction mixture was stirred at indicated temperature for the time specified and then poured into 10 mL of saturated aqueous solution of $NaHCO_3$. After extraction with CH_2Cl_2 (3 × 10 mL), combined organic fractions were washed with aqueous EDTA disodium salt solution (3 × 10 mL) then with water (2 × 10 mL) and dried with anhydrous Na_2SO_4. The solvent was evaporated under vacuum, and the final residue was purified by column chromatography (SiO_2) to yield cyclopentanes **3**.

Diethyl 2-Methyl-2-(prop-1-en-2-yl)-4-phenylcyclopentane-1,1-dicarboxylate (3a). The solution of $TiCl_4$ (0.15 mL, 1.37 mmol) in CH_2Cl_2 (1 mL) was added to the solution of cyclopropane **1a** (0.30 g, 1.15 mmol) in CH_2Cl_2 (7 mL) at −20 °C. To the resulted mixture the solution of 2,3-dimethylbutadiene (**2a**) (0.30 g, 3.75 mmol) in CH_2Cl_2 (5 mL) was added dropwise for 10−15 min. The reaction mixture was allowed to warm to room temperature and then refluxed for 2 h. The workup was performed according to the general procedure, leading to **3a**: yield 210 mg (53%); dr 85:15. (**2*RS*,4*RS***)-**3a** (major isomer) was isolated as light-yellow oil; R_f = 0.62 ($CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.26 (t, ^3J = 7.1 Hz, 3 H, CH_3), 1.29 (t, ^3J = 7.1 Hz, 3 H, CH_3), 1.48 (s, 3 H, CH_3), 1.95 (dd, ^2J = 12.3 Hz, ^3J = 6.6 Hz, 1 H, H^a-5), 1.98 (s, 3 H, CH_3), 2.60 (dd, ^2J = 14.6 Hz, ^3J = 8.6 Hz, 1 H, H^a-3), 2.68 (br. d, ^2J = 12.3 Hz, 1 H, H^b-5), 2.93 (dd, ^2J = 14.6 Hz, ^3J = 10.5 Hz, 1 H, H^b-3), 3.38−3.48 (m, 1 H, C-4), 4.14 (q, ^3J = 7.1 Hz, 2 H, CH_2O), 4.23 (q, ^3J = 7.1 Hz, 2 H, CH_2O), 4.85 (br. s, 1 H, CH_2═), 4.95 (br. s, 1 H, CH_2═), 7.20−7.25 (m, 1 H, Ph), 7.31−7.36 (m, 2 H, Ph), 7.49 (br. d, ^3J = 7.5 Hz, 2 H, Ph); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.9 (CH_3), 14.0 (CH_3), 21.9 (CH_3), 23.9 (CH_3), 40.8 (C-4), 42.8 (C-3), 47.8 (C-5), 54.5 (C-2), 60.8 (CH_2O), 61.1 (CH_2O), 66.5 (C-1), 111.7 (CH_2═), 126.2 (CH, Ph), 127.6 (2 × CH, Ph), 128.4 (2 × CH, Ph), 144.8 (C), 149.4 (C), 170.9 (CO_2Et), 172.6 (CO_2Et); IR (film) 2960, 1748, 1730, 1453, 1371, 1251, 1188, 1097, 1037 cm^{-1}. Anal. Calcd for $C_{21}H_{28}O_4$: C, 73.23; H, 8.19. Found: C, 72.85; H, 8.01.

Dimethyl 2-Methyl-2-(prop-1-en-2-yl)-4-phenylcyclopentane-1,1-dicarboxylate (3b). The solution of $TiCl_4$ (0.17 mL, 1.54 mmol) in CH_2Cl_2 (1.5 mL) was added to the solution of cyclopropane **1b** (0.30 g, 1.28 mmol) in CH_2Cl_2 (3 mL) at −5 °C. To the resulted mixture the solution of 2,3-dimethylbutadiene (**2a**) (0.30 g, 3.75 mmol) in CH_2Cl_2 (2 mL) was added dropwise for 2−3 min. The reaction mixture was allowed to warm to room temperature and then refluxed for 1.5 h. The workup was performed according to the general procedure, leading to **3b**; yield 234 mg (58%); dr 86:14. (**2*RS*,4*RS***)-**3b** (major isomer) was isolated as colorless oil; R_f = 0.59

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(petroleum ether−diethyl ether, 2:1). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.43 (s, 3 H, CH_3), 1.89 (dd, ^2J = 12.3 Hz, ^3J = 6.6 Hz, 1 H, H^a-5), 1.92 (s, 3 H, CH_3), 2.57 (dd, ^2J = 14.6 Hz, ^3J = 8.7 Hz, 1 H, H^a-3), 2.62 (dd, ^2J = 12.3 Hz, ^3J = 12.5 Hz, 1 H, H^b-5), 2.91 (dd, ^2J = 14.6 Hz, ^3J = 10.3 Hz, 1 H, H^b-3), 3.38−3.45 (m, 1 H, H-4), 3.67 (s, 3 H, CH_3O), 3.74 (s, 3 H, CH_3O), 4.84 (br. s, 1 H, CH_2=), 4.91 (br.s, 1 H, CH_2=), 7.21−7.24 (m, 1 H, Ph), 7.30−7.36 (m, 2 H, Ph), 7.45 (br. d, ^3J = 7.7 Hz, 2 H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 21.6 (CH_3), 24.0 (CH_3), 40.8 (C-4), 42.7 (C-3), 47.6 (C-5), 52.0 (CH_3O), 52.1 (CH_3O), 54.6 (C-2), 66.8 (C-1), 111.6 (CH_2=), 126.3 (CH, Ph), 127.5 (2 × CH, Ph), 128.4 (2 × CH, Ph), 144.6 (C), 149.4 (C), 171.4 (CO_2Me), 173.0 (CO_2Me); IR (film) 2970, 2880, 1740, 1640, 1610, 1500, 1460, 1440, 1390, 1270, 1210, 1170, 1100, 1050, 920, 750, 720 cm^{-1}; GC-MS: m/z (%) = 316 (22) [M]$^+$, 284 (33), 257 (29), 256 (84), 253 (28), 199 (49), 197 (54), 171 (32), 170 (46), 169 (22), 167 (23), 157 (56), 145 (100), 129 (27), 121 (27), 115 (52), 113 (79), 91 (42). Anal. Calcd for $C_{19}H_{24}O_4$: C, 72.13; H, 7.65. Found: C, 72.45; H, 7.91. (**2*RS*,4*SR*)-3b** (minor isomer) was isolated as a fraction containing traces of the major isomer; R_f = 0.54 (petroleum ether−diethyl ether, 2:1). ^{1}H NMR ($CDCl_3$, 600 MHz)[79] δ 1.37 (s, 3 H, CH_3), 1.85 (s, 3 H, CH_3), 2.51 (dd, ^2J = 9.6 Hz, ^3J = 13.0 Hz, 1 H, CH_2), 2.87 (dd, ^2J = 9.6 Hz, ^3J = 14.4 Hz, 1 H, CH_2), 3.61 (s, 3 H, CH_3O), 3.76 (s, 3 H, CH_3O), 4.81 (br. s, 1 H, CH_2=), 4.90 (br. s, 1 H, CH_2=); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 21.9 (CH_3), 24.6 (CH_3), 40.2 (CH), 42.6 (CH_2), 46.1 (CH_2), 52.3 (CH_3O), 52.5 (CH_3O), 54.6 (C), 68.0 (C), 111.0 (CH_2=), 126.0 (CH, Ph), 127.3 (2 × CH, Ph), 128.4 (2 × CH, Ph), 145.2 (C), 149.1 (C), 169.8 (CO_2Me), 172.3 (CO_2Me).

Dimethyl 4-(4-Fluorophenyl)-2-methyl-2-(prop-1-en-2-yl)-cyclopentane-1,1-dicarboxylate (3c). The solution of $TiCl_4$ (0.12 mL, 1.13 mmol) in CH_2Cl_2 (1 mL) was added to the solution of cyclopropane **1c** (0.30 g, 0.94 mmol) in CH_2Cl_2 (5 mL) at −20 °C. To the resulted mixture the solution of 2,3-dimethylbutadiene (**2a**) (0.30 g, 3.75 mmol) in CH_2Cl_2 (2 mL) was added dropwise for 10−15 min. The reaction mixture was allowed to warm to room temperature and then refluxed for 3 h. The workup was performed according to the general procedure, leading to **3c**; yield 280 mg (79%); dr 91:9. (**2*RS*,4*RS*)-3c** (major isomer) was isolated as light-yellow oil; R_f = 0.54 (petroleum ether−diethyl ether, 3:1). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.44 (s, 3 H, CH_3), 1.88 (ddd, ^2J = 12.3 Hz, ^3J = 6.7 Hz, ^4J = 1.0 Hz, 1 H, H^a-5), 1.93 (d, ^4J = 1.2 Hz, 3 H, CH_3), 2.53 (dd, ^2J = 14.7 Hz, ^3J = 8.6 Hz, 1 H, H^a-3), 2.57 (dd, ^2J = 12.3 Hz, ^3J = 12.0 Hz, 1 H, H^b-5), 2.86 (dd, ^2J = 14.7 Hz, ^3J = 10.5 Hz, ^4J = 1.0 Hz, 1 H, H^b-3), 3.40 (dddd, ^3J = 12.0 Hz, ^3J = 10.5 Hz, ^3J = 8.6 Hz, ^3J = 6.7 Hz, 1 H, C-4), 3.67 (s, 3 H, CH_3O), 3.74 (s, 3 H, CH_3O), 4.82−4.84 (m, 1 H, CH_2=), 4.91 (br. s, 1 H, CH_2=), 6.99−7.02 (m, 2 H, Ar), 7.41−7.44 (m, 2 H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5 (CH_3), 23.8 (CH_3), 40.0 (CH), 42.7 (CH_2), 47.7 (CH_2), 52.0 (CH_3O), 52.1 (CH_3O), 54.6 (C), 66.8 (C), 111.7 (CH_2=), 115.1 (d, $^2J_{CF}$ = 21 Hz, 2 × CH, Ar), 130.0 (d, $^3J_{CF}$ = 8 Hz, 2 × CH, Ar), 140.3 (C), 149.2 (C), 161.5 (d, $^1J_{CF}$ = 246 Hz, CF), 171.3 (CO_2Me), 173.0 (CO_2Me); IR (film) 2970, 2880, 1740, 1620, 1600, 1520, 1450, 1460, 1385, 1320, 1245, 1170, 1095, 1045, 905, 840, 788 cm^{-1}; GC-MS: m/z (%) = 334 (12) [M]$^+$, 302 (16), 274 (46), 215 (35), 199 (36), 188 (27), 175 (26), 146 (21), 145 (76), 133 (38), 122 (23), 113 (100), 109 (47), 59 (38). Anal. Calcd for $C_{19}H_{23}FO_4$: C, 68.25; H, 6.93. Found: C, 68.61; H, 7.25. (**2*RS*,4*SR*)-3c** (minor isomer) was isolated as a fraction containing traces of the major isomer; R_f = 0.46 (petroleum ether−diethyl ether 3:1). ^{1}H NMR ($CDCl_3$, 600 MHz)[79] δ 1.36 (s, 3 H, CH_3), 1.91 (d, ^4J = 1.2 Hz, 3 H, CH_3), 4.77 (br. s, 1 H, CH_2=), 4.88−4.90 (m, 1 H, CH_2=), 6.95−6.98 (m, 2 H, Ar), 7.30−7.35 (m, 2 H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz)[77] δ 21.6 (CH_3), 23.8 (CH_3), 39.2 (CH), 41.8 (CH_2), 45.9 (CH_2), 52.0 (CH_3O), 52.1 (CH_3O), 54.3 (C), 67.5 (C), 110.6 (CH_2=), 114.7 (d, $^2J_{CF}$ = 20 Hz, 2 × CH, Ar), 128.5 (d, $^3J_{CF}$ = 8 Hz, 2 × CH, Ar), 139.9 (C), 148.4 (C).

Diethyl 2-Methyl-4-phenyl-2-vinylcyclopentane-1,1-dicarboxylate (3d). The solution of $TiCl_4$ (0.22 mL, 2.00 mmol) in CH_2Cl_2 (1 mL) was added to the solution of cyclopropane **1a** (0.40 g, 1.52 mmol) in CH_2Cl_2 (5 mL) at −30 °C. To the resulted mixture the solution of 2-methylbutadiene (**2c**) (0.40 g, 5.88 mmol) in CH_2Cl_2 (5 mL) was added dropwise for 10−15 min. The reaction mixture was stirred at −20 °C for 2 h, allowed to warm to room temperature, and stirred at this temperature for an additional 20 h. The workup was performed according to the general procedure, leading to **3d**; yield 260 mg (51%); light-yellow oil; mixture of diastereomers (82:18); R_f = 0.54 ($CHCl_3$). (**2*RS*,4*RS*)-3d** (major isomer): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.25 (t, ^3J = 7.2 Hz, 3 H, CH_3), 1.28 (s, 3 H, CH_3), 1.31 (t, ^3J = 7.2 Hz, 3 H, CH_3), 2.06 (dd, ^2J = 12.6 Hz, ^3J = 7.8 Hz, 1 H, CH_2), 2.37 (dd, ^2J = 14.9 Hz, ^3J = 8.3 Hz, 1 H, CH_2), 2.60 (dd, ^2J = 12.6 Hz, ^3J = 11.8 Hz, 1 H, CH_2), 3.06 (dd, ^2J = 14.9 Hz, ^3J = 9.6 Hz, 1 H, CH_2), 3.46−3.57 (m, 1 H, CH), 4.17 (q, ^3J = 7.2 Hz, 2 H, OCH_2), 4.25 (q, ^3J = 7.2 Hz, 2 H, OCH_2), 5.03−5.10 (m, 2 H, CH_2=), 6.34 (dd, $^3J_{cis}$ = 10.6 Hz, $^3J_{trans}$ = 17.8 Hz, 1 H, CH=), 7.20−7.39 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1 (2 × CH_3), 23.7 (CH_3), 40.9 (CH), 41.0 (CH_2), 46.1 (CH_2), 51.4 (C), 61.1 (2 × CH_2O), 67.2 (C), 112.93 (CH_2=), 126.2 (CH, Ph), 127.5 (2 × CH, Ph), 128.5 (2 × CH, Ph), 143.08 (CH=), 145.2 (C), 170.6 (CO_2Et), 171.8 (CO_2Et); GC-MS: m/z (%) = 330 (53) [M]$^+$, 256 (62), 239 (33), 183 (74), 173 (63), 127 (65), 91 (59), 29 (41). (**2*RS*,4*SR*)-3d** (minor isomer): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.27 (t, ^3J = 7.2 Hz, 3 H, CH_3), 1.29 (t, ^3J = 7.2 Hz, 3 H, CH_3), 1.36 (s, 3 H, CH_3), 2.21−2.26 (m, 1 H, CH_2), 2.44−2.52 (m, 1 H, CH_2), 2.62−2.67 (m, 1 H, CH_2), 2.90 (dd, ^2J = 14.6 Hz, ^3J = 9.8 Hz, 1 H, CH_2), 3.46−3.57 (m, 1 H, CH), 4.17−4.25 (m, 4 H, 2 × OCH_2), 5.11−5.18 (m, 2 H, CH_2=), 6.25 (dd, $^3J_{cis}$ = 10.6 Hz, $^3J_{trans}$ = 17.4 Hz, 1 H, CH=), 7.20−7.39 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1 (2 × CH_3), 22.9 (CH_3), 40.6 (C-4), 41.2 (C-3), 46.8 (C-5), 49.8 (C-2), 61.1 (2 × CH_2O), 67.0 (C), 112.85 (CH_2=), 126.1 (CH, Ph), 127.2 (2 × CH, Ph), 128.8 (2 × CH, Ph), 143.09 (CH=), 145.4 (C), 170.6 (CO_2Et), 171.8 (CO_2Et); GC-MS: m/z (%) = 330 (48) [M$^+$], 269 (21), 256 (64), 239 (39), 183 (100), 167 (38), 157 (33), 141 (25), 127 (62), 115 (49), 104 (23), 91 (52), 77 (21), 29 (54). IR (film) 2980, 2938, 1779, 1729, 1449, 1368, 1247, 1197, 1098, 1032 cm^{-1}. Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.79; H, 8.15.

Dimethyl 4-(4-Fluorophenyl)-2-methyl-2-vinylcyclopentane-1,1-dicarboxylate (3e). The solution of $TiCl_4$ (0.055 mL, 0.50 mmol) in CH_2Cl_2 (1 mL) was added to the solution of cyclopropane **1c** (0.11 g, 0.44 mmol) in CH_2Cl_2 (3 mL) at −40 °C. To the resulted mixture the solution of 2-methylbutadiene (**2c**) (0.095 g, 1.40 mmol) in CH_2Cl_2 (2 mL) was added dropwise for 10−15 min. The reaction mixture was allowed to warm to room temperature and stirred for an additional 20 h. The workup was performed according to the general procedure, leading to **3e**; yield 74 mg (53%); colorless oil; mixture of diastereomers (91:9); R_f = 0.4 (petroleum ether−ethyl acetate, 4:1). (**2*RS*,4*RS*)-3e** (major isomer): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.27 (s, 3 H, CH_3), 2.02 (dd, ^2J = 12.5 Hz, ^3J = 7.9 Hz, 1 H, CH_2), 2.34 (dd, ^2J = 14.8 Hz, ^3J = 8.3 Hz, 1 H, CH_2), 2.54 (dd, ^2J = 12.5 Hz, ^3J = 11.8 Hz, 1 H, CH_2), 3.02 (dd, ^2J = 14.8 Hz, ^3J = 10.6 Hz, 1 H, CH_2), 3.45−3.51 (m, 1 H, CH), 3.70 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 5.05 (d, $^3J_{trans}$ = 17.4 Hz, 1 H, CH_2=), 5.07 (d, $^3J_{cis}$ = 10.9 Hz, 1 H, CH_2=), 6.28 (dd, $^3J_{cis}$ = 10.9 Hz, $^3J_{trans}$ = 17.4 Hz, 1 H, CH=), 6.97−7.01 (m, 2 H, Ar), 7.31−7.35 (m, 2 H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 23.7 (CH_3), 40.2 (CH), 41.1 (CH_2), 45.9 (CH_2), 51.6 (C), 52.2 (CH_3O), 52.3 (CH_3O), 67.2 (C), 113.2 (CH_2=), 115.16 (d, $^2J_{CF}$ = 21 Hz, 2 × CH, Ar), 128.9 (d, $^3J_{CF}$ = 8 Hz, 2 × CH, Ar), 140.7 (C), 142.7 (CH=), 161.9 (d, $^1J_{CF}$ = 245 Hz, C, Ar), 171.0 (CO_2Me), 172.33 (CO_2Me). (**2*RS*,4*SR*)-3e** (minor isomer): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.33 (s, 3 H, CH_3), 2.18 (dd, ^2J = 12.9 Hz, ^3J = 9.2 Hz, 1 H, CH_2), 2.41 (dd, ^2J = 9.0 Hz, ^3J = 5.0 Hz, 1 H, CH_2), 2.43 (dd, ^2J = 9.0 Hz, ^3J = 6.6 Hz, 1 H, CH_2), 2.81 (dd, ^2J = 12.9 Hz, ^3J = 11.6 Hz, 1 H, CH_2), 3.59−3.67 (m, 1 H, CH), 3.72 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 5.10 (d, $^3J_{cis}$ = 10.9 Hz, 1 H, CH_2=), 5.13 (d, $^3J_{trans}$ = 17.4 Hz, 1 H, CH_2=), 6.18 (dd, $^3J_{cis}$ = 10.9 Hz, $^3J_{trans}$ = 17.4 Hz, 1 H, CH=), 6.97−7.01 (m, 2 H, Ar), 7.31−7.35 (m, 2 H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 22.8 (CH_3), 39.9 (CH), 41.4 (CH_2), 46.8 (CH_2), 51.3 (C), 52.2 (CH_3O), 52.3 (CH_3O), 67.2 (C), 113.2 (CH_2=), 115.19 (d, $^2J_{CF}$ = 21 Hz, 2 × CH, Ar), 128.7 (d, $^3J_{CF}$ = 8 Hz, 2 × CH, Ar), 140.7 (C), 142.8 (CH=), 164.9 (d, $^1J_{CF}$ = 245 Hz, C, Ar), 171.1 (CO_2Me), 172.34 (CO_2Me); IR (film) 2970, 1725, 1640, 1605, 1520, 1440, 1255, 1210, 1105, 1030,

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935, 870, 775 cm^{-1}; GC-MS: *m/z* (%) = 320 (10) $[M]^+$, 261 (18), 260 (84), 201 (98), 153 (25), 145 (100), 133 (50), 113 (85), 109 (50), 59 (34). Anal. Calcd for $C_{18}H_{21}FO_4$: C, 67.49; H, 6.61. Found: C, 67.35; H, 6.81.

Dimethyl 4-(4-Bromophenyl)-2-methyl-2-vinylcyclopentane-1,1-dicarboxylate (3f). The solution of $TiCl_4$ (0.06 mL, 0.55 mmol) in CH_2Cl_2 (1 mL) was added to the solution of cyclopropane **1d** (0.16 g, 0.51 mmol) in CH_2Cl_2 (4 mL) at −40 °C. To the resulted mixture the solution of 2-methylbutadiene (**2c**) (0.10 g, 1.47 mmol) in CH_2Cl_2 (2.5 mL) was added dropwise for 10−15 min. The reaction mixture was allowed to warm to room temperature and stirred for an additional 20 h. The workup was performed according to the general procedure, leading to **3f**; yield 100 mg (51%); colorless oil; mixture of diastereomers (90:10); R_f = 0.60 (petroleum ether−ethyl acetate, 4:1). (**2*RS*,4*RS*)-3f** (major isomer): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.25 (s, 3 H, CH_3), 2.06 (dd, ^2J = 12.5 Hz, ^3J = 7.9 Hz, 1 H, CH_2), 2.32 (dd, ^2J = 14.9 Hz, ^3J = 8.1 Hz, 1 H, CH_2), 2.53 (dd, ^2J = 12.5 Hz, ^3J = 11.8 Hz, 1 H, CH_2), 3.03 (dd, ^2J = 14.9 Hz, ^3J = 10.7 Hz, 1 H, CH_2), 3.40−3.50 (m, 1 H, CH), 3.69 (s, 3 H, OCH_3), 3.77 (s, 3 H, OCH_3), 5.04 (dd, ^2J = 0.9 Hz, $^3J_{trans}$ = 17.4 Hz, 1 H, CH_2═), 5.07 (dd, ^2J = 0.9 Hz, $^3J_{cis}$ = 10.8 Hz, 1 H, CH_2═), 6.26 (dd, $^3J_{cis}$ = 10.8 Hz, $^3J_{trans}$ = 17.4 Hz, 1 H, CH═), 7.26 (d, ^3J = 8.3 Hz, 2 H, Ar), 7.42 (d, ^3J = 8.3 Hz, 2 H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 23.6 (CH_3), 40.3 (CH), 40.8 (CH_2), 45.6 (CH_2), 51.6 (C), 52.2 (CH_3O), 52.3 (CH_3O), 67.16 (C), 113.2 (CH_2═), 118.1 (C), 129.2 (2 × CH, Ar), 131.5 (2 × CH, Ar), 142.6 (CH═), 144.0 (C), 170.9 (CO_2Me), 172.2 (CO_2Me). (**2*RS*,4*SR*)-3f** (minor isomer): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.32 (s, 3 H, CH_3), 2.17 (dd, ^2J = 14.6 Hz, ^3J = 3.4 Hz, 1 H, CH_2), 2.39 (dd, ^2J = 9.2 Hz, ^3J = 4.6 Hz, 1 H, CH_2), 2.42 (dd, ^2J = 9.2 Hz, ^3J = 6.0 Hz, 1 H, CH_2), 2.89 (dd, ^2J = 14.6 Hz, ^3J = 10.0 Hz, 1 H, CH_2), 3.40−3.50 (m, 1 H, CH), 3.60 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 5.09 (br. d, $^3J_{cis}$ = 10.8 Hz, 1 H, CH_2═), 5.11 (br. d, $^3J_{trans}$ = 17.4 Hz, 1 H, CH_2═), 6.19 (dd, $^3J_{cis}$ = 10.8 Hz, $^3J_{trans}$ = 17.4 Hz, 1 H, CH═), 7.06 (d, ^3J = 8.4 Hz, 2 H, Ar), 7.36 (d, ^3J = 8.4 Hz, 2 H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 22.6 (CH_3), 34.4 (CH_2), 34.6 (CH_2), 42.2 (CH), 51.5 (C), 52.2 (CH_3O), 52.3 (CH_3O), 67.20 (C), 119.9 (CH_2═), 121.1 (C, Ar), 130.1 (2 × CH, Ar), 131.3 (2 × CH, Ar), 141.2 (C), 142.7 (CH═), 170.4 (CO_2Me), 171.2 (CO_2Me); IR (Nujol) 3097, 2965, 1735, 1640, 1595, 1498, 1440, 1380, 1270, 1205, 1085, 1020, 920, 833 cm^{-1}; GC-MS: *m/z* (%) = 382 (14), 380 (20) $[M]^+$, 322 (49), 320 (44), 263 (28), 261 (31), 185 (31), 183 (37), 169 (26), 167 (20), 153 (29), 145 (100), 113 (91), 59 (53). Anal. Calcd for $C_{18}H_{21}BrO_4$: C, 56.70; H, 5.55. Found: C, 56.35; H, 5.75.

Dimethyl (2*RS*,4*RS*)-4-Phenyl-2-vinylcyclopentane-1,1-dicarboxylate (3g). The solution of $TiCl_4$ (0.12 mL, 1.1 mmol) in CH_2Cl_2 (2 mL) was added to the solution of cyclopropane **1b** (0.23 g, 1.0 mmol) in CH_2Cl_2 (8 mL) at −40 °C. To the resulted mixture butadiene (**2b**) (4.0 mmol, 4 mL of 1 M solution in CH_2Cl_2) was added dropwise for 10−15 min. The reaction mixture was stirred at −40 to −35 °C for 3 h and then allowed to warm to room temperature. The workup was performed according to the general procedure, leading to **3g**; yield 180 mg (62%); colorless oil; R_f = 0.7 ($CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.87−1.96 (m, 1 H, H^a-3), 2.26−2.32 (m, 1 H, H^b-3), 2.62 (ddd, ^2J = 13.9 Hz, ^3J = 8.5 Hz, ^4J = 1.3 Hz, 1 H, H^a-5), 2.68 (dd, ^2J = 13.9 Hz, ^3J = 11.4 Hz, 1 H, H^b-5), 3.08−3.17 (m, 1 H, H-4), 3.48−3.54 (m, 1 H, H-2), 3.72 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 5.09 (ddd, ^2J = 1.5 Hz, $^3J_{cis}$ = 10.2 Hz, ^4J = 0.9 Hz, 1 H, CH_2═), 5.17 (ddd, ^2J = 1.5 Hz, $^3J_{trans}$ = 17.2 Hz, ^4J = 1.3 Hz, 1 H, CH_2═), 5.86 (ddd, ^3J = 7.6 Hz, $^3J_{cis}$ = 10.2 Hz, $^3J_{trans}$ = 17.2 Hz, 1 H, CH═), 7.20−7.26 (m, 2 H, Ph), 7.30−7.36 (m, 3 H, Ph); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.4 (CH_2), 41.9 (CH_2), 43.5 (CH), 49.5 (C), 52.3 (CH_3O), 52.7 (CH_3O), 63.8 (C), 116.3 (CH_2═), 126.5 (CH, Ph), 127.2 (2 × CH, Ph), 128.5 (2 × CH, Ph), 137.1 (CH═), 143.4 (C), 171.5 (CO_2Me), 172.7 (CO_2Me); IR (film) 2963, 1750, 1730, 1460, 1372, 1250, 1192, 1093, 1035 cm^{-1}. Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.99; H, 7.23.

Diethyl 3,4-Diphenyl-2-[(*E*)-2-phenylvinyl]cyclopentane-1,1-dicarboxylate (3h). The solution of $TiCl_4$ (0.08 mL, 0.73 mmol) in CH_2Cl_2 (1 mL) was added to the solution of cyclopropane **1a** (0.27 g, 1.03 mmol) in CH_2Cl_2 (10 mL) at 0 °C. To the resulted mixture the solution of (*E*,*E*)-1,4-diphenyl-1,3-butadiene (**2d**) (0.23 g, 1.53 mmol) in CH_2Cl_2 (5 mL) was added dropwise. The reaction mixture was refluxed for 7 h. The workup was performed according to the general procedure, leading to **3h**; yield 400 mg (83%); colorless oil; mixture of diastereomers (64:36); R_f = 0.86 ($CHCl_3$). (**2*RS*,3*SR*,4*RS*)-3h** (major isomer): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.08 (t, ^3J = 7.2 Hz, 3 H, CH_3), 1.26 (t, ^3J = 7.2 Hz, 3 H, CH_3), 2.68 (dd, ^2J = 14.0 Hz, ^3J = 7.7 Hz, 1 H, H^a-5), 2.90 (dd, ^2J = 14.0 Hz, ^3J = 11.7 Hz, 1 H, H^b-5), 3.21 (ddd, ^3J = 7.7 Hz, ^3J = 11.3 Hz, ^3J = 11.7 Hz, 1 H, H-4), 3.28 (dd, ^3J = 10.8 Hz, ^3J = 11.3 Hz, 1 H, H-3), 3.85 (dd, ^3J = 8.7 Hz, ^3J = 10.8 Hz, 1 H, H-2), 4.11 (q, ^3J = 7.2 Hz, 2 H, CH_2O), 4.29 (q, ^3J = 7.2 Hz, 2 H, CH_2O), 6.10 (dd, ^3J = 8.7 Hz, ^3J = 15.9 Hz, 1 H, CH═), 6.28 (d, ^3J = 15.9 Hz, 1 H, CH═), 6.87−6.93 (m, 1 H, Ph), 7.20−7.35 (m, 14 H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 14.2 (2 × CH_3), 41.6 (CH_2), 52.0 (CH), 55.3 (CH), 58.9 (CH), 61.6 (2 × CH_2O), 63.1 (C), 126.23 (3 × CH), 126.6 (2 × CH), 127.6 (3 × CH), 128.0 (2 × CH), 128.36 (4 × CH), 128.42 (2 × CH), 133.00 (CH), 137.2 (C), 140.3 (C), 141.4 (C), 171.3 (CO_2Et), 172.5 (CO_2Et); GC-MS *m/z* (%) = 468 (23) $[M]^+$, 394 (100), 377 (49), 321 (27), 243 (37), 229 (62), 179 (39), 141 (47), 115 (69), 91 (80), 30 (44), 29 (49). (**2*RS*,3*SR*,4*SR*)-3h** (minor isomer): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.12 (t, ^3J = 7.2 Hz, 3 H, CH_3), 1.28 (t, ^3J = 7.2 Hz, 3 H, CH_3), 2.56 (dd, ^2J = 14.6 Hz, ^3J = 4.8 Hz, 1 H, H^a-5), 3.15 (dd, ^2J = 14.6 Hz, ^3J = 8.3 Hz, 1 H, H^b-5), 3.77−3.80 (ddd, ^3J = 4.8, ^3J = 8.3, ^3J = 8.9 Hz, 1 H, H-4), 3.79−3.85 (dd, ^3J = 8.9, ^3J = 11.7 Hz, 1 H, H-3), 3.95 (dd, ^3J = 8.0 Hz, ^3J = 11.7 Hz, 1 H, H-2), 4.06 (q, ^3J = 7.2 Hz, 2 H, CH_2O), 4.23 (q, ^3J = 7.2 Hz, 2 H, CH_2O), 6.13 (dd, ^3J = 8.0 Hz, ^3J = 16.0 Hz, 1 H, CH═), 6.37 (d, ^3J = 16.0 Hz, 1 H, CH═), 6.87−6.93 (m, 1 H, Ph), 7.20−7.35 (m, 14 H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 14.3 (2 × CH_3), 39.7 (CH_2), 48.9 (CH), 51.0 (CH), 53.5 (CH), 61.7 (2 × CH_2O), 63.9 (C), 126.0 (2 × CH), 126.18 (2 × CH), 127.2 (CH), 127.29 (2 × CH), 127.33 (CH), 127.5 (2 × CH), 127.7 (2 × CH), 128.6 (2 × CH), 128.8 (2 × CH), 132.98 (CH), 137.3 (C), 139.0 (C), 142.0 (C), 171.9 (CO_2Et), 172.2 (CO_2Et); GC-MS: *m/z* (%) = 468 (14) $[M]^+$, 394 (64), 331 (30), 321 (32), 229 (55), 207 (93), 173 (100), 115 (83), 91 (90), 30 (67), 29 (46); IR (film) 3028, 2981, 1728, 1602, 1495, 1452, 1367, 1255, 1096, 1031, 969, 748, 698 cm^{-1}. Anal. Calcd for $C_{31}H_{32}O_4$: C, 79.46; H, 6.88. Found: C, 79.68; H, 6.91.

2,3-Diphenyl-1-[(*E*)-styryl]-7,9-diazaspiro[4.5]decane-6,8,10-trione (4). To a solution of **3h** (200 mg, 0.454 mmol) in DMSO (0.9 mL) urea (163 mg, 2.72 mmol) and KO*t*Bu (112 mg, 1.0 mmol) were added sequentially at room temperature. The reaction mixture was stirred for 1 h, diluted with EtOAc (20 mL), and washed with 0.1 N HCl (aq.) solution (20 mL). The aqueous phase was extracted with EtOAc (3 × 25 mL), and combined organic fractions were washed with water (2 × 25 mL) and brine (25 mL) and dried over Na_2SO_4. The solvent was evaporated under vacuum, and the final residue was purified by column chromatography (SiO_2, eluent:petroleum ether−ethyl acetate, 1:1); yield 210 mg (57%); white solid; mixture of diastereomers ((1*RS*,2*SR*,3*RS*)-**A**/(1*RS*,2*SR*,3*SR*)-**B** = 64:36); R_f = 0.61 (petroleum ether−ethyl acetate, 1:1). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 2.55 (dd, ^2J = 13.6 Hz, ^3J = 10.2 Hz, 1 H, CH_2, **A**), 2.70 (dd, ^2J = 13.6 Hz, ^3J = 8.2 Hz, 1 H, CH_2, **A**), 2.74 (dd, ^2J = 14.5 Hz, ^3J = 9.3 Hz, 1 H, CH_2, **B**), 2.88 (dd, ^2J = 14.5 Hz, ^3J = 5.4 Hz, 1 H, CH_2, **B**), 3.28−3.33 (m, 1 H, CH, **A**), 3.43−3.51 (m, 2 H, CH, **A**), 3.72 (dd, ^3J = 9.6 Hz, ^3J = 12.3 Hz, 1 H, CH, **B**), 3.83 (ddd, ^3J = 5.4 Hz, ^3J = 9.3 Hz, ^3J = 9.6 Hz, 1 H, CH, **B**), 4.03 (dd, ^3J = 9.4 Hz, ^3J = 12.3 Hz, 1 H, CH, **B**), 5.71 (dd, ^3J = 9.4 Hz, ^3J = 15.8 Hz, 1 H, CH═, **B**), 5.83 (dd, ^3J = 9.6 Hz, ^3J = 15.8 Hz, 1 H, CH═, **A**), 6.14 (d, ^3J = 15.8 Hz, 1 H, CH═, **A**), 6.32 (d, ^3J = 15.8 Hz, 1 H, CH═, **B**), 6.57 (br. d, ^3J = 7.3 Hz, 1 H, Ph, **A**), 6.71−7.13 (m, 14 H + 15 H, Ph, **A**, **B**); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 39.1 (CH_2, **B**), 41.2 (CH_2, **A**), 50.0 (CH, **B**), 52.8 (CH, **B**), 54.4 (CH, **B**), 58.3 (CH, **A**), 59.6 (C, **A**), 61.5 (C, **B**), 64.1 (CH, **A**), 124.5 (CH, **B**), 124.6 (CH, **A**), 125.67 (CH, **B**), 125.72 (2 × CH, **B**), 126.1 (CH, **A**), 126.2 (2 × CH, **A**), 126.4 (2 × CH, **B**), 126.5 (CH, **A**), 127.3 (2 × CH, **B**), 127.42 (CH, **A**), 127.44 (CH, **B**), 127.51 (2 × CH, **A**), 127.55 (2 × CH, **A**), 127.59 (2 × CH, **B**), 127.61 (CH, **A**), 128.0 (CH, **B**), 128.08 (2 × CH, **A**), 128.12 (2 × CH, **A**), 128.17 (2 × CH, **A**), 128.18 (2 × CH, **A**), 128.6 (2 × CH, **B**), 128.8 (CH, **A**), 129.5 (CH, **B**), 135.2 (C, **A**), 136.1 (C, **B**), 138.1 (C, **B**),

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138.6 (C, **A**), 141.4 (C, **A**), 142.5 (C, **B**), 150.1 (C+C, **A**, **B**), 172.9 (CO, **B**), 173.0 (CO, **A**), 173.8 (CO, **B**), 174.5 (CO, **A**). Anal. Calcd for $C_{28}H_{24}N_2O_3$: C, 77.04; H, 5.54; N, 6.42. Found: C, 76.78; H, 5.78; N, 6.31.

Diethyl 3-Phenyl-2,3,3a,4,5,7a-hexahydro-1*H*-indene-1,1-dicarboxylate (3i). The solution of $TiCl_4$ (0.15 mL, 1.36 mmol) in CH_2Cl_2 (1 mL) was added to the solution of cyclopropane **1a** (0.29 g, 1.1 mmol) in CH_2Cl_2 (20 mL) at −30 °C. To the resulted mixture the solution of cyclohexadiene **2e** (0.20 g, 2.5 mmol) in CH_2Cl_2 (5 mL) was added dropwise for 10−15 min. The reaction mixture was stirred at −20 °C for 1 h and then allowed to warm to room temperature and stirred for an additional 20 h. The workup was performed according to the general procedure, leading to **3i**; yield 210 mg (57%); colorless oil; mixture of diastereomers (*cis*-**A**/*trans*-**B** = 62:38); R_f = 0.65 ($CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.28 (t, ^3J = 7.2 Hz, 3 H+3 H, CH_3, **A**,**B**), 1.29 (t, ^3J = 7.2 Hz, 3 H+3 H, CH_3, **A**,**B**), 1.35−1.45 (m, 1 H+1 H, CH_2, **A**,**B**), 1.67−1.75 (m, 1 H+1 H, CH_2, **A**,**B**), 1.78−1.85 (m, 1 H, CH_2, **B**), 1.88−2.12 (m, 1 H+2 H, CH_2, **A**,**B**), 2.01 (dd, ^2J = 13.7 Hz, ^3J = 10.3 Hz, 1 H, CH_2, **A**), 2.27−2.48 (m, 2 H+1 H, CH, **A**,**B**, CH_2, **A**), 3.00 (dd, ^2J = 13.7 Hz, ^3J = 8.3 Hz, 1 H, CH_2, **A**), 3.22−3.36 (m, 1 H+2 H, CHPh, **A**,**B**, CH_2, **B**), 3.55−3.61 (m, 1 H, CH, **A**), 3.65−3.72 (m, 1 H, CH, **B**), 4.11−4.34 (m, 4 H+4 H, OCH_2, **A**,**B**), 5.59 (br. d, ^2J = 10.1 Hz, 1 H, CH═, **A**), 5.70−5.76 (m, 1 H, CH═, **B**), 5.81−5.86 (m, 1 H+1 H, CH═, **A**,**B**), 7.20−7.35 (m, 5 H+5 H, Ph, **A**,**B**); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1 (CH_3, **A**,**B**), 14.2 (CH_3, **A**,**B**), 19.2 (CH_2, **B**), 21.5 (CH_2, **A**), 22.9 (CH_2, **A**), 24.3 (CH_2, **B**), 36.1 (CH_2, **B**), 42.3 (CH_2, **A**), 43.6 (CH, **B**), 44.3 (CH, **B**), 46.0 (CH, **A**), 45.2 (CH, **A**), 46.8 (CH, **B**), 47.0 (CH, **A**), 61.1 (CH_2O, **A**), 61.2 (CH_2O, **B**), 61.4 (CH_2O, **A**), 61.6 (CH_2O, **B**), 63.1 (C, **B**), 63.4 (C, **A**), 125.1 (CH═, **B**), 125.8 (CH═, **A**), 126.3 (CH, Ph, **B**), 126.4 (CH, Ph, **A**), 127.5 (2 × CH, Ph, **A**), 128.1 (2 × CH, Ph, **B**), 128.2 (2 × CH, **B**), 128.5 (2 × CH, Ph, **A**), 128.9 (CH═, **A**), 129.6 (CH═, **B**), 139.9 (C, **B**), 144.0 (C, **A**), 170.9 (CO_2Et, **A**), 171.3 (CO_2Et, **B**), 172.4 (CO_2Et, **A**), 173.3 (CO_2Et, **B**); IR (film) 3447, 3030, 2948, 1730, 1496, 1440, 1257, 1162, 1100, 758, 700 cm^{-1}. Anal. Calcd for $C_{21}H_{26}O_4$: C, 73.66; H, 7.65. Found: C, 73.85; H, 7.85.

Dimethyl 3-Phenyl-2,3,3a,4,5,7a-hexahydro-1*H*-indene-1,1-dicarboxylate (3j). The solution of $TiCl_4$ (0.20 mL, 1.82 mmol) in CH_2Cl_2 (1 mL) was added to the solution of cyclopropane **1b** (0.30 g, 1.28 mmol) in CH_2Cl_2 (5 mL) at −25 °C. To the resulted mixture the solution of cyclohexadiene **2e** (0.50 g, 6.25 mmol) in CH_2Cl_2 (5 mL) was added dropwise for 10 min. The reaction mixture was allowed to warm to 0 °C for 1 h and then to room temperature and stirred at this temperature for an additional 20 h. The workup was performed according to the general procedure, leading to **3j**; yield 238 mg (59%); colorless oil; mixture of diastereomers (*cis*-**A**/*trans*-**B** = 62:38); R_f = 0.67 ($CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) for isomer **A** δ 1.33−1.45 (m, ^2J = 13.3 Hz, 1 H, H^a-4), 1.65−1.73 (m, ^2J = 13.3 Hz, 1 H, H^b-4), 1.88−1.94 (m, $^3J_{6,5}$ = 4.0 Hz, 1 H$_{eq}$, H^a-5), 2.00 (dd, ^2J = 13.7 Hz, $^3J_{3,2}$ = 8.2 Hz, 1 H, H^a-2), 2.03−2.10 (m, $^3J_{6,5}$ = 3.4 Hz, 1 H$_{ax}$, H^b-5), 2.40−2.50 (m, 1 H$_{ax}$, H-3a), 2.98 (dd, ^2J = 13.7 Hz, $^3J_{3,2}$ = 10.4 Hz, 1 H, H^b-2), 3.20−3.30 (m, 1 H, H-3), 3.58 (m, $^4J_{7a,6}$ = 2.2 Hz, $^3J_{7a,7}$ = 2.3 Hz, $^3J_{3a,7a}$ = 7.8 Hz, 1 H, H-7a), 3.73 (s, 3 H, CH_3O), 3.75 (s, 3 H, CH_3O), 5.47−5.52 (m, $^3J_{7a,7}$ = 2.3 Hz, $^3J_{7,6}$ = 10.3 Hz, 1 H, H-7), 5.83 (m, $^3J_{6,5b}$ = 3.4 Hz, $^3J_{6,5a}$ = 4.0 Hz, 1 H, H-6), 7.20−7.32 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$, 100 MHz) for the mixture of two isomers δ 19.1 (C-4, **B**), 21.4 ($^1J_{CH}$ = 130 Hz, C-5, **A**), 22.8 ($^1J_{CH}$ = 129 Hz, C-4, **A**), 24.3 (C-5, **B**), 36.0 (C-2, **B**), 42.3 ($^1J_{CH}$ = 134 Hz, C-2, **A**), 43.4 (C-3a, **B**), 44.5 (C-7a, **B**), 45.12 ($^1J_{CH}$ = 132 Hz, C-7a, **A**), 45.14 ($^1J_{CH}$ = 132 Hz, C-3a, **A**), 46.9 (C-3, **B**), 47.0 ($^1J_{CH}$ = 131 Hz, C-3, **A**), 52.2 ($^1J_{CH}$ = 147 Hz, CH_3O, **A**), 52.3 (CH_3O, **B**), 52.7 ($^1J_{CH}$ = 147 Hz, CH_3O, **A**), 52.9 (CH_3O, **B**), 63.2 (C-1, **A**), 63.4 (C-1, **A**), 124.8 (C-7, **B**), 125.6 ($^1J_{CH}$ = 157 Hz, C-7, **A**), 126.3 (CH, Ph, **B**), 126.4 ($^1J_{CH}$ = 160 Hz, CH, Ph, **A**), 127.2 (2 × CH, Ph, **B**), 128.0 (2 × CH, Ph, **B**), 128.2 ($^1J_{CH}$ = 157 Hz, 2 × CH, Ph, **A**), 128.5 ($^1J_{CH}$ = 160 Hz, 2 × CH, Ph, **A**), 129.0 (C-6, **A**), 129.8 (C-6, **B**), 139.7 (C, Ph, **B**), 143.8 (C, Ph, **A**), 171.3 (CO_2Me, **A**), 171.7 (CO_2Me, **B**), 172.8 (CO_2Me, **A**), 173.6 (CO_2Me, **B**); GC-MS for isomer **A**: *m*/*z* (%) = 314 (38) [M]$^+$, 254 (100), 195 (44), 115 (26), 91 (23); GC-MS for isomer **B**: *m*/*z* (%) = 314 (33) [M]$^+$, 254 (100), 195 (47), 115 (31), 91 (28); IR (film) 3443, 3027, 2950, 1732, 1496, 1435, 1257, 1160, 1105, 756, 701 cm^{-1}. Anal. Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. Found: C, 72.32; H, 7.10.

Diethyl 3-(4-Fluorophenyl)-2,3,3a,4,5,7a-hexahydro-1*H*-indene-1,1-dicarboxylate (3k). The solution of $TiCl_4$ (0.17 mL, 1.55 mmol) in CH_2Cl_2 (1 mL) was added to the solution of cyclopropane **1e** (0.36 g, 1.28 mmol) in CH_2Cl_2 (20 mL) at −30 °C. To the resulted mixture the solution of cyclohexadiene **2e** (0.50 g, 6.25 mmol) in CH_2Cl_2 (5 mL) was added dropwise for 10−15 min. The reaction mixture was stirred at −20 °C for 1 h and then allowed to warm to room temperature and stirred for an additional 20 h. The workup was performed according to the general procedure, leading to **3k**; yield 200 mg (58%); colorless oil; mixture of isomers (*cis*-**A**/*trans*-**B** = 68:32); R_f = 0.55 ($CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.27 (t, ^3J = 7.2 Hz, 3 H+3 H, CH_3, **A**,**B**), 1.29 (t, ^3J = 7.2 Hz, 3 H+3 H, CH_3, **A**,**B**), 1.35−1.45 (m, 1 H, CH_2, **A**), 1.57−1.63 (m, 1 H, CH_2, **B**), 1.66−1.74 (m, 1 H+1 H, CH_2, **A**,**B**), 1.78−2.06 (m, 1 H+3 H, CH_2, **A**,**B**), 1.94 (dd, ^2J = 13.7 Hz, ^3J = 10.4 Hz, 1 H, CH_2, **A**), 2.28−2.43 (m, 2 H+1 H, CH, **A**,**B**, CH_2, **A**), 2.97 (dd, ^2J = 13.7 Hz, ^3J = 8.3 Hz, 1 H, CH_2, **A**), 3.17−3.35 (m, 1 H+2 H, CHPh, **A**,**B**, CH_2, **B**), 3.55−3.62 (m, 1 H, CH, **A**), 3.66−3.75 (m, 1 H, CH, **B**), 4.11−4.33 (m, 4 H+4 H, OCH_2, **A**, **B**), 5.55 (br. d, ^2J = 10.2 Hz, 1 H, CH═, **A**), 5.69−5.74 (m, 1 H, CH═, **B**), 5.79−5.85 (m, 1 H+1 H, CH═, **A**,**B**), 6.98−7.04 (m, 2 H+2 H, Ph, **A**,**B**), 7.17−7.24 (m, 2 H+2 H, Ph, **A**,**B**); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0 (CH_3, **A**,**B**), 14.1 (CH_3, **A**,**B**), 19.1 (CH_2, **B**), 21.3 (CH_2, **A**), 22.7 (CH_2, **A**), 24.2 (CH_2, **B**), 36.3 (CH_2, **B**), 42.4 (CH_2, **A**), 43.5 (CH, **B**), 44.2 (CH, **B**), 44.8 (CH, **A**), 45.2 (CH, **A**), 46.1 (CH, **B**), 46.3 (CH, **A**), 61.2 (CH_2O, **A**), 61.3 (CH_2O, **B**), 61.4 (CH_2O, **A**), 61.6 (CH_2O, **B**), 63.1 (C, **B**), 63.3 (C, **A**), 114.9 (d, $^2J_{CF}$ = 20 Hz, 2 × CH, *p*-F-C_6H_4, **B**), 115.3 (d, $^2J_{CF}$ = 21 Hz, 2 × CH, *p*-F-C_6H_4, **A**), 125.0 (CH═, **B**), 125.7 (CH═, **A**), 128.74 (d, $^3J_{CF}$ = 7 Hz, 2 × CH, Ph, **A**), 128.75 (CH═, **A**), 129.3 (d, $^3J_{CF}$ = 8 Hz, 2 × CH, Ph, **B**), 129.6 (CH═, **B**), 135.5 (C, **B**), 139.5 (C, **A**), 162.5 (d, $^1J_{CF}$ = 246 Hz, C, *p*-F-C_6H_4, **B**), 163.9 (d, $^1J_{CF}$ = 244 Hz, C, *p*-F-C_6H_4, **A**), 170.8 (CO_2Et, **A**), 171.2 (CO_2Et, **B**), 172.3 (CO_2Et, **A**), 173.0 (CO_2Et, **B**); IR (film) 3450, 3017, 2953, 1740, 1500, 1243, 1160, 1107, 770, 700 cm^{-1}. Anal. Calcd for $C_{21}H_{25}FO_4$: C, 69.98; H, 6.99. Found: C, 70.15; H, 6.89.

Diethyl 3-(2,4,6-Trimethoxyphenyl)-3,3a,4,6a-tetrahydropentalene-1,1(2*H*)-dicarboxylate (3l). To the solution of cyclopropane **1f** (0.2 g, 0.57 mmol) and cyclopentadiene (**2f**) (0.15 g, 2.27 mmol) in CH_2Cl_2 (1 mL) was added $Sn(OTf)_2$ (24 mg, 10 mol % to **1f**) at −50 °C in the presence of 4 Å molecular sieves. The reaction mixture was allowed to slowly warm to −20 °C, stirred for 15 min, and then warmed to 5 °C and stirred at this temperature for an additional 2 h. The workup was performed according to the general procedure, leading to **3l**; yield 155 mg (65%); white solid; mp 173−174 °C; mixture of isomers (78:22); R_f = 0.38 (petroleum ether−diethyl ether, 1:1). (**3*RS*,3a*RS*,6a*RS***)-**3l** (major isomer): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.24 (t, ^3J = 7.2 Hz, 3 H, CH_3), 1.28 (t, ^3J = 7.2 Hz, 3 H, CH_3), 2.10−2.12 (m, 1 H, H^a-4), 2.29 (dddd, ^2J = 16.8 Hz, ^3J = 5.1 Hz, ^3J = 7.9 Hz, ^4J = 2.6 Hz, 1 H, H^b-4), 2.45 (dd, ^2J = 12.9 Hz, ^3J = 12.0 Hz, 1 H, H^a-2), 2.51 (dd, ^2J = 12.9 Hz, ^3J = 7.6 Hz, 1 H, H^b-2), 3.24 (dddd, ^3J = 1.9 Hz, ^3J = 7.9 Hz, ^3J = 9.5 Hz, ^3J = 10.5 Hz, 1 H, H-3a), 3.71 (ddd, ^3J = 7.6 Hz, ^3J = 10.5 Hz, ^3J = 12.0 Hz, 1 H, H-3), 3.76 (s, 6 H, CH_3O), 3.80 (s, 3 H, CH_3O), 4.10−4.16 (m, 1 H, H-6a), 4.13−4.19 (m, 2 H, CH_2O), 4.23−4.29 (m, 2 H, CH_2O), 5.51−5.58 (m, 1 H, H-5), 5.65−5.68 (m, 1 H, H-6), 6.15 (s, 2 H, CH, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 14.1 (CH_3), 14.2 (CH_3), 37.7 (CH_2), 39.4 (CH_2), 40.6 (CH), 45.7 (CH), 55.2 (CH_3O), 55.7 (2 × CH_3O), 57.0 (CH), 60.7 (CH_2O), 61.0 (CH_2O), 63.5 (C), 91.1 (2 × CH, Ar), 110.7 (C, Ar), 130.1 (CH═), 131.4 (CH═), 159.5 (C, Ar), 159.8 (2 × C, Ar), 171.5 (CO_2Et), 172.9 (CO_2Et); GC-MS: *m*/*z* (%) = 419 (27) [M+1]$^+$, 418 (100) [M]$^+$, 351 (43), 344 (36), 307 (35), 306 (66), 271 (47), 263 (29), 207 (43), 195 (32), 194 (49), 181 (62), 179 (29), 178 (33), 168 (49); IR (film) 2960, 1735, 1580, 1455, 1235, 1140, 1050, 985, 915, 830, 810, 705 cm^{-1}. Anal. Calcd for $C_{23}H_{30}O_7$: C, 66.01; H, 7.32. Found: C, 65.91; H, 7.34.

Diethyl Bicyclo[2.2.1]hept-5-ene-2,2-dicarboxylate (5).[71] Compound **5** was obtained as a byproduct during the synthesis of **3l**. Yield of **5**: 20 mg (15%); colorless oil; R_f 0.66 (petroleum ether−

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diethyl ether 1:1). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.24 (t, ^3J = 7.1 Hz, 3 H, CH_3), 1.26 (t, ^3J = 7.1 Hz, 3 H, CH_3), 1.50−1.54 (m, 1 H), 1.68 (d, ^2J = 8.8 Hz, 1 H, H-7), 2.02 (dd, ^2J = 12.4 Hz, ^3J = 2.9 Hz, 1 H, H-3), 2.11 (dd, ^2J = 12.4 Hz, ^3J = 3.6 Hz, 1 H, H-3), 2.92 (br. s, 1 H, H-4), 3.40 (br. s, 1 H, H-1), 4.15−4.26 (m, 4 H, 2 × CH_2O), 6.01 (dd, ^3J = 2.9 Hz, ^3J = 5.6 Hz, 1H), 6.27 (dd, ^3J = 3.0 Hz, ^3J = 5.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 13.0 (2 × CH_3), 35.8 (CH_2), 42.0 (CH), 48.7 (CH_2), 49.7 (CH), 60.4 (CH_2O), 60.7 (CH_2O), 61.3 (C), 133.6 (CH═), 139.6 (CH═), 170.9 (CO_2Et), 172.6 (CO_2Et).

Dimethyl 3-[(*E*)-Styryl]-2,3,3a,4-tetrahydropentalene-1,1-(6a*H*)-dicarboxylate (3m). To the stirred solution of cyclopropane **1g** (0.260 g, 1.0 mmol) and cyclopentadiene (**2f**) (0.20 g, 3.03 mmol) in CH_2Cl_2 (6 mL) was added $Sn(OTf)_2$ (45 mg, 11 mol % to **1g**) in the presence of 4 Å molecular sieves. The reaction mixture was stirred at room temperature for 1 h and then under reflux for an additional 3 h. The workup was performed according to the general procedure, leading to **3m**; yield 189 mg (58%); colorless oil; mixture of diastereomers (78:22); R_f = 0.64 (petroleum ether−ethyl acetate, 4:1). (**3*RS*,3a*SR*,6a*SR***)-**3m** (major isomer): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.78 (dd, ^2J = 12.3 Hz, ^3J = 10.0 Hz, 1 H, H-2), 2.22−2.25 (m, 1 H, H-4), 2.45−2.50 (m, 1 H, H-4), 2.55−2.61 (m, 2 H, H-3, H-3a), 2.64 (dd, ^2J = 12.3 Hz, ^3J = 5.8 Hz, 1 H, H-2), 3.73 (s, 3 H, CH_3O), 3.74 (s, 3 H, CH_3O), 4.16−4.19 (m, 1 H, H-6a), 5.48−5.50 (m, 1 H, H-5), 5.69−5.71 (m, 1 H, H-6), 6.09 (dd, ^3J = 15.8 Hz, ^3J = 7.5 Hz, 1 H, H-1′), 6.43 (d, ^3J = 15.8 Hz, 1 H, H-2′), 7.19−7.22 (m, 1 H, *p*-CH, Ph), 7.28−7.31 (m, 2 H, *m*-CH, Ph), 7.34−7.36 (m, 2 H, *o*-CH, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 37.1 (CH_2), 42.3 (CH_2), 47.9 (CH), 50.1 (CH), 52.0 (CH_3O), 52.7 (CH_3O), 56.8 (CH), 63.1 (C), 126.1 (2 × CH), 127.1 (CH), 128.5 (2 × CH), 129.8 (CH), 130.2 (CH), 131.4 (CH), 132.1 (CH), 137.4 (C), 171.2 (CO_2Me), 172.8 (CO_2Me). (**3*RS*,3a*RS*,6a*RS***)-**3m** (minor isomer): ^{13}C NMR ($CDCl_3$, 150 MHz) δ 34.7 (CH_2), 42.3 (CH_2), 48.7 (CH), 49.8 (CH), 52.3 (CH_3O), 52.8 (CH_3O), 56.0 (CH), 63.9 (C), 125.6 (2 × CH), 126.6 (CH), 128.4 (2 × CH), 130.7 (CH), 131.5 (CH), 133.6 (CH), 134.5 (CH), 139.8 (C), 170.5 (CO_2Me), 172.5 (CO_2Me); GC-MS: *m*/*z* (%) = 326 $[M]^+$ (68), 294 (26), 267 (39), 266 (100), 208 (30), 207 (100), 206 (39), 205 (20), 179 (25), 175 (32), 165 (37), 141 (44), 129 (42), 128 (35), 117 (21), 115 (52), 103 (20), 91 (57). Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.41; H, 6.91.

Dimethyl (1*RS*,5*SR*,7*SR*)-5-Phenyltricyclo[5.2.1.0^{2,6}]dec-8-ene-3,3-dicarboxylate (7). The solution of $SnCl_4$ (0.18 mL, 1.5 mmol) in CH_2Cl_2 (2 mL) was added to the stirred solution of cyclopropane **1b** (280 mg, 1.2 mmol) and norbornadiene (**6**) (360 mg, 3.9 mmol) in CH_2Cl_2 (12 mL) at −60 °C in the presence of 4 Å molecular sieves. The reaction mixture was allowed to warm to room temperature and stirred for an additional 20 h. The workup was performed according to the general procedure, leading to **7**; yield 233 mg (58%); colorless oil; R_f = 0.37 (petroleum ether−ethyl acetate, 5:1). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.52−1.58 (m, ^2J = 9.3 Hz, $^3J_{7,10}$ = 1.5 Hz, $^3J_{1,10}$ = 1.5 Hz, $^4J_{2,10}$ = 1.6 Hz, $^4J_{6,10}$ = 1.6 Hz, 1 H, *anti*-H-10), 1.66 (br. d, ^2J = 9.3 Hz, 1 H, *syn*-H-10), 2.29−2.32 (m, ^2J = 12.5 Hz, $^3J_{5,4''}$ = 12.3 Hz, 1 H, *exo*-H-4), 2.34 (br. t, $^3J_{2,6}$ = 9.3 Hz, $^3J_{7,6}$ = 9.0 Hz, 1 H, H-6), 2.54−2.59 (m, 1 H, H-7), 3.09−3.13 (m, 1 H, H-1), 3.18−3.22 (m, $^3J_{6,5}$ = 9.0 Hz, $^3J_{4',5}$ = 6.2 Hz, $^3J_{4'',5}$ = 12.3 Hz, 1 H, H-5), 3.21−3.25 (m, ^2J = 12.5 Hz, $^3J_{5,4'}$ = 6.2 Hz, 1 H, *endo*-H-4), 3.57 (d, $^3J_{1,2}$ = 3.0 Hz, 1 H, H-2), 3.61 (s, 3 H, CH_3O), 3.68 (s, 3 H, CH_3O), 6.00 (dd, $^3J_{7,8}$ = 3.0 Hz, $^3J_{9,8}$ = 5.7 Hz, 1 H, H-8), 6.14 (dd, $^3J_{1,9}$ = 3.0 Hz, $^3J_{8,9}$ = 5.7 Hz, 1 H, H-9), 7.14−7.27 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 42.9 (C-10), 43.6 ($^1J_{CH}$ = 150 Hz, C-1, C-7), 46.8 (C-4), 48.5 ($^1J_{CH}$ = 128 Hz, C-5), 51.9 ($^1J_{CH}$ = 143 Hz, C-2), 52.6 (CH_3O), 52.8 (CH_3O), 55.0 ($^1J_{CH}$ = 139 Hz, C-6), 60.9 (C-3), 126.4 (CH, Ph), 127.3 (2 × CH, Ph), 128.5 (2 × CH, Ph), 138.3 (CH═), 139.1 (CH═), 143.5 (C, Ph), 171.6 (CO_2Me), 172.6 (CO_2Me). Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.35; H, 6.54.

Methyl 1,1,6a-Trimethyl-3-oxo-5-phenylhexahydro-1*H*-cyclopenta[c]furan-3a-carboxylate (8). The solution of $TiCl_4$ (0.17 mL, 1.54 mmol) in CH_2Cl_2 (1.5 mL) was added to the solution of cyclopropane **1b** (0.30 g, 1.28 mmol) in CH_2Cl_2 (3 mL) at −5 °C. To the resulted mixture the solution of 2,3-dimethylbutadiene (**2a**) (0.30 g, 3.75 mmol) in CH_2Cl_2 (0.7 mL) was added dropwise for 2−3 min. The reaction mixture was allowed to warm to room temperature and refluxed for 1 h. Then, glacial acetic acid (0.73 mL, 12.8 mmol) was added, and the mixture was additionally refluxed for 5 min. The workup was performed according to the general procedure, leading to **8**; yield 209 mg (54%); light-yellow liquid; mixture of diastereomers; dr 88:12; R_f = 0.38 (petroleum ether−diethyl ether, 1:1). (**3a*RS*,5*RS*,6a*SR***)-**8** (major isomer): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.22 (s, 3 H, CH_3), 1.41 (s, 3 H, CH_3), 1.43 (s, 3 H, CH_3), 1.91 (ddd, ^2J = 12.3 Hz, ^3J = 5.5 Hz, ^4J = 2.0 Hz, 1 H, H^a-6), 2.06 (dd, ^2J = 12.3 Hz, ^3J = 12.5 Hz, 1 H, H^b-6), 2.40 (dd, ^2J = 14.1 Hz, ^3J = 10.9 Hz, 1 H, H^a-4), 2.98 (ddd, ^2J = 14.1 Hz, ^3J = 8.8 Hz, ^4J = 2.0 Hz, 1 H, H^b-4), 3.46−3.52 (m, 1 H, CHPh), 3.80 (s, 3 H, CH_3O), 7.22−7.33 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 17.9 (CH_3), 23.0 (CH_3), 25.5 (CH_3), 43.6 (CH_2), 44.0 (CH), 46.6 (CH_2), 52.7 (CH_3O), 58.1 (C), 65.0 (C), 86.9 (C-1), 126.8 (CH, Ph), 127.0 (2 × CH, Ph), 128.6 (2 × CH, Ph), 142.0 (C), 171.2 (CO_2Me), 176.2 (CO_2Me). (**3a*RS*,5*SR*,6a*SR***)-**8** (minor isomer): ^{1}H NMR ($CDCl_3$, 600 MHz)[79] δ 1.19 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 1.51 (s, 3 H, CH_3), 2.15−2.20 (m, 2 H, CH_2), 2.56 (dd, ^2J = 13.2 Hz, ^3J = 6.7 Hz, 1 H, CH_2), 2.85 (dd, ^2J = 13.2 Hz, ^3J = 9.3 Hz, 1 H, CH_2), 3.61 (s, 3 H, CH_3O); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 22.1 (CH_3), 25.1 (CH_3), 27.2 (CH_3), 42.6 (CH_2), 42.7 (CH), 46.8 (CH_2), 52.5 (CH_3O), 58.1 (C), 65.0 (C), 86.9 (C-1), 127.5 (CH, Ph), 127.8 (2 × CH, Ph), 128.5 (2 × CH, Ph), 142.0 (C), 169.8 (CO_2Me), 175.6 (CO_2Me); GC-MS *m*/*z* (%) = 302 $[M]^+$ (10), 197 (10), 187 (14), 186 (14), 185 (100), 183 (14), 169 (10), 157 (22), 153 (21), 141 (14), 129 (10), 115 (12), 91 (23), 77 (10), 43 (15); IR (film) 2730, 1770, 1740, 1460, 1732, 1440, 1380, 1280, 1250, 1160, 1130, 1110, 1090, 1040, 920, 750, 710 cm^{-1}. Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.42; H, 7.48.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02146.

^{1}H and ^{13}C NMR spectra and results of DFT calculations (PDF)

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Notes

The authors declare no competing financial interest.

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