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Lewis Acid-Triggered Vinylcyclopropane-Cyclopentene Rearrangement

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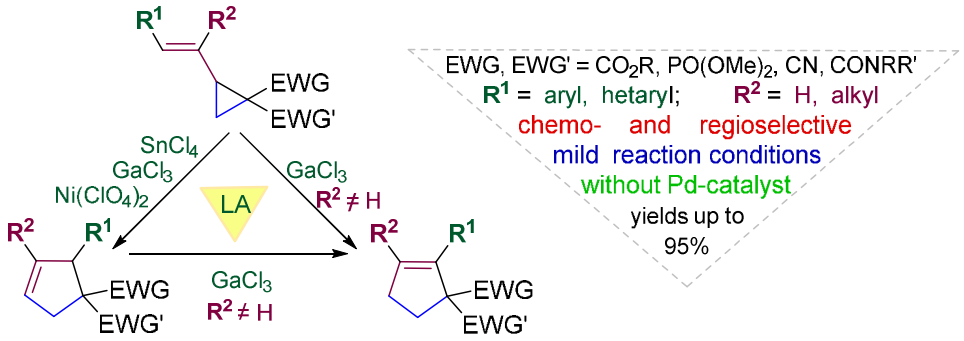


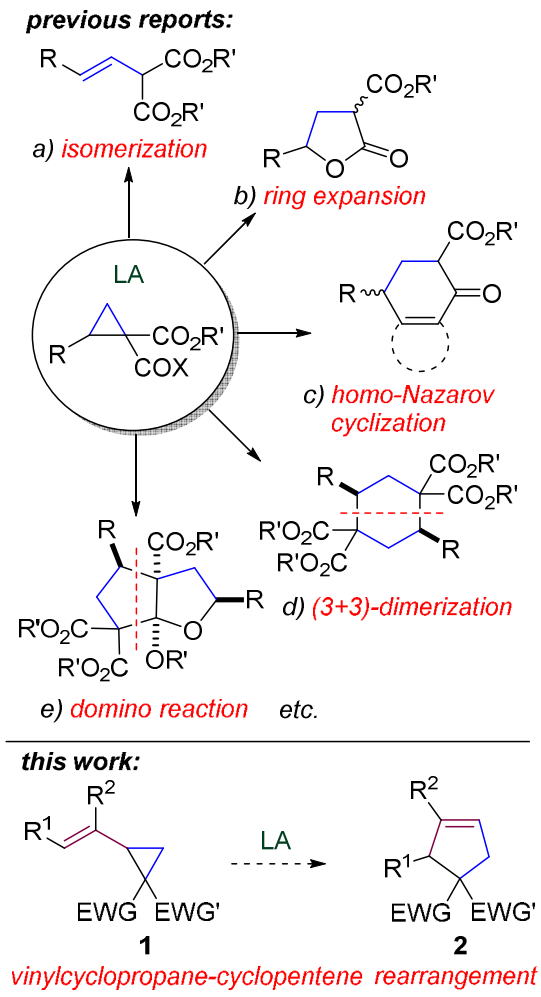
Abstract: We report a mild Lewis acid-induced isomerization of donor-acceptor cyclopropanes, containing an alkenyl moiety and diverse electron-withdrawing group(s) at the adjacent positions, into substituted cyclopentenes. We have found that 1,1,2-trisubstituted cyclopent-3-enes were exclusively obtained in yield of 51 to 99% when cyclopropanes with 2-substituted alkenyl group as a donor underwent isomerization. For cyclopropanes bearing trisubstituted alkenyl group either the corresponding cyclopent-3-enes or isomeric cyclopent-2-enes having two acceptor groups at the C(1) atom were formed, with the reaction selectivity being

determined by the applied Lewis acid. We have shown that the reactivity of the donor-acceptor cyclopropane increases with the increase of the electron-donating character of (hetero)aromatic group attached to the alkenyl moiety. The synthetic utility of the developed methodology was also demonstrated through the synthesis of polysubstituted cyclopentane and piperidine derivatives.

Introduction

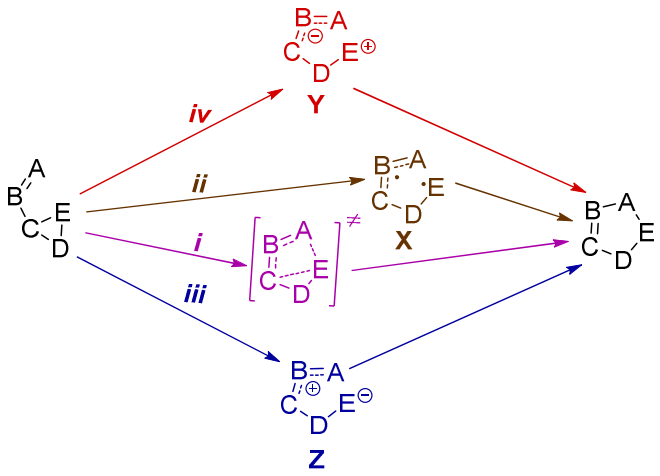
Donor-acceptor (D–A) cyclopropanes are recognized as an archetype of activated small-ring systems that undergo numerous transformations offering access to important synthetic targets with excellent efficiency and selectivity.[1-3] D-A cyclopropanes not only demonstrate high reactivity against a broad scope of reaction partners but also can be involved into various Lewis acid-promoted processes *that do not require any other reagents*. Examples of these atom-economic reactions include isomerizations to acyclic products (Scheme 1, ***a***),[4] various ring expansions (Scheme 1, ***b***),[5] homo-Nazarov cyclization (Scheme 1, ***c***)[6,7] and other cycloisomerizations,[4a,8] multiple types of cyclodimerizations, wherein cyclopropanes act as two-, three-, and more than three-atom components, pairwise combination of which provides various cyclic systems (Scheme 1, ***d***),[9,10] intramolecular cycloadditions[11,12] as well as other processes.[13] In addition, a few examples of the Lewis acid-induced vinylcyclopropane-cyclopentene rearrangement (VCR) have been reported.[10a,14]

Scheme 1. **Examples of Lewis Acid-Induced Transformations of Donor-Acceptor Cyclopropanes in the Absence of an Additional Reaction Partner**



From the theoretical point of view, VCR and its heteroatom variants represent the most interesting and challenging ring enlargement reactions[15,16] as they can proceed by either concerted (Scheme 2, path ***i***) or stepwise mechanism. In the last case either biradical **X** (Scheme 2, path ***ii***) or zwitter-ionic species **Y** or **Z** (Scheme 2, paths ***iii*** and ***iv***) can be formed as an intermediate.

Scheme 2. **Mechanisms for the Vinylcyclopropane-to-Cyclopentene Rearrangement and Its Heteroatom Variants**



While significant advances in mechanistic study of VCR were achieved, a synthetic application of this reaction is still restricted as under the typical reaction conditions (heating at 300–600 °C[16,17] or photolysis[18]) it proceeds *via* the formation of biradical intermediate **X** (Scheme 2, path ***ii***) thereby the desired process is often accompanied by diverse side reactions.[18b,19] To solve this problem, transition metal-catalyzed VCR's were developed.[20] However, transition metal complexes are also able to induce the isomerization of vinylcyclopropanes into 1,3-dienes and other processes.[21] As a result, the efficiency of transition metal-catalyzed VCR differs significantly between various substrates. Therefore, alternative synthetic protocols for chemoselective ring expansion of vinylcyclopropanes as practical and versatile methods for the construction of cyclopentene-based skeletons are still highly required.

We hypothesized that the development of new VCR versions proceeding under mild reaction conditions could be possible due to the change of the reaction mechanism. If biradical intermediate **X** is responsible for occurring undesired side reactions, a proper selection of substituents in starting vinylcyclopropane as well as reagents or catalyst applied can provide the generation of zwitter-ionic intermediate of **Z** type. It is conceivable that the heterolytic cleavage of three-membered ring with the formation of **Z** can be facilitated by the decoration of the C=C bond in the parent vinylcyclopropane with a cation-stabilizing group, on the one hand, and the introduction of anion-stabilizing substituent(s) at the vicinal position of cyclopropane, on the other.[22] Such substrates can be regarded as a subclass of D-A cyclopropanes. Similar to other D-

A cyclopropanes, they can be additionally activated by a Lewis acid *via* its coordination to acceptor group(s) increasing the stabilization of the anionic moiety and favouring zwitter-ion **Z** formation.

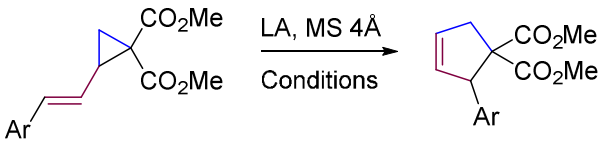
In this work we report the results of our investigation of the Lewis acid-induced rearrangement of D-A cyclopropanes **1**, containing diverse electron-withdrawing groups and a broad variety of substituents at the alkenyl moiety, into the corresponding cyclopentenes **2**.

Results and Discussion

We started our research by the optimization of the reaction conditions for the isomerization of **1** with previously described alkenylcyclopropanes **1a**,**b** as model substrates (Table 1). We found that Lewis acids influence the efficiency of rearrangement of substrates **1a** and **1b** into the corresponding cyclopentenes **2a**,**b** in different manner. Weakly activating Lewis acids, such as MgI_2, $ZnCl_2$, $Sn(OTf)_2$, $Ni(ClO_4)_2{\cdot}6H_2O$ were not efficient in inducing VCR of **1a** (Table 1, entries 1-5). Use of strongly activating Lewis acids ($AlCl_3$, $BF_3{\cdot}OEt_2$) also failed to produce the target cyclopentene **2a** since complex mixtures of unidentified products were formed as a result of multiple side processes (Table 1, entries 9, 10). However, Lewis acids with moderate activity ($TiCl_4$, $SnCl_4$) were found to initiate **1a**-to-**2a** rearrangement in moderate yields (Table 1, entries 6-8). The best result was obtained when VCR of **1a** was induced by $GaCl_3$; cyclopentene **2a** was obtained in 81% yield (Table 1, entry 11). On the other hand, cyclopentene **2b** was obtained in 15% yield only when $GaCl_3$ was used as an initiator, predominantly due to oligomerization of the more active substrate **1b** (Table 1, entry 13). Similar result was also found when VCR of **1b** was induced by MgI_2 (Table 1, entry 14). Weakly activating $Yb(OTf)_3$ failed to catalyze **1b**-to-**2b** rearrangement at room temperature (Table 1, entry 16). However, slightly more active $Sc(OTf)_3$ and $Ni(ClO_4)_2{\cdot}6H_2O$ produced the target cyclopentene **2b** in excellent yields (Table 1, entries 18, 19). To summarize, we found that VCR of the less reactive 2-styrylcyclopropane-1,1-diester **1a** can be efficiently initiated with $GaCl_3$ or other moderately active Lewis acids. Oppositely, cyclopropane **1b**, wherein *para*-methoxy group

in the styryl moiety provides additional stabilization of the zwitter-ionic intermediate of **Z** type, rearranged into the corresponding cyclopentene **2b** under the treatment of such weakly activating Lewis acids, as $Sc(OTf)_3$ and $Ni(ClO_4)_2 \cdot 6H_2O$. Interestingly that $SnCl_4$ was found to be rather efficient catalyst for the rearrangement of both substrates (Table 1, entries 8, 15).

Table 1. Optimization of Reaction Conditions[a,b]



1a,b a: Ar = Ph b: Ar = 4-$MeOC_6H_4$ **2a,b**

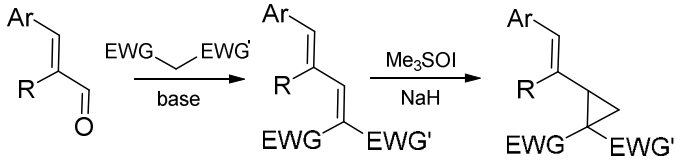
Entry	1,2	LA [mol %]	Solvent	Time [h]	T [°C]	Yield [%][c]
1	**a**	MgI_2 (20)	CH_2Cl_2	4	20	-
2	**a**	$Sn(OTf)_2$ (5)	CH_2Cl_2	24	20	-
3	**a**	$ZnCl_2$ (300)	CH_2Cl_2	5	40	40
4	**a**	$ZnCl_2$ (300)	CH_2Cl_2	9	40	46
5	**a**	$Ni(ClO_4)_2$ $6H_2O$ (20)	$C_2H_4Cl_2$	3	83	23[c,d]
6	**a**	$TiCl_4$ (110)	CH_2Cl_2	0.5; 3	–40–20; 20	41
7	**a**	$TiCl_4$ (110)	CH_2Cl_2	0.5; 3	–40–20; 40	59
8	**a**	**$SnCl_4$ (110)**	**CH_2Cl_2**	**2**	**40**	**63**
9	**a**	BF_3 Et_2O (105)	CH_2Cl_2		–60–20; 20	-[d]
10	**a**	$AlCl_3$ (150)	$C_2H_4Cl_2$	0.5	83	-[d]
11	**a**	**$GaCl_3$ (110)**	**CH_2Cl_2**	**1**	**20**	**81**
12	**a**	$GaCl_3$ (110)[e]	CH_2Cl_2	1	20	60
13	**b**	$GaCl_3$ (100)	CH_2Cl_2	1	20	15[d]
14	**b**	MgI_2 (20)	CH_2Cl_2	6	20	15[d]
15	**b**	$SnCl_4$ (110)	CH_2Cl_2	1.5	40	87[c]
16	**b**	$Yb(OTf)_3$ (5)	CH_2Cl_2	5	20	-[f]

17	**b**	**$Ni(ClO_4)_2$ $6H_2O$ (20)**	**CH_2Cl_2**	**4**	**20**	**95**
18	**b**	**$Sc(OTf)_3$ (10)**	**CH_2Cl_2**	**3**	**20**	**91**

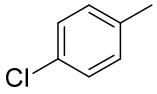
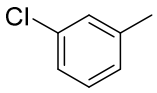
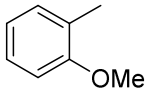
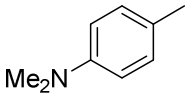
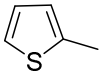
[a] Isolated yields. [b] Concentration of **1a** in the corresponding solvent is *ca.* 0.07 M. [c] NMR yield. [d] Complex mixture of products. [e] 0.5 M solution in pentane. [f] No conversion.

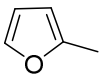
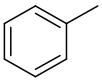
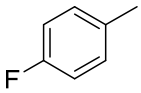
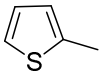
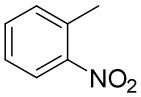
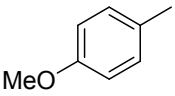
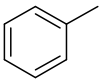
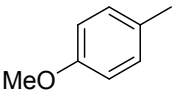
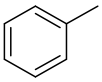
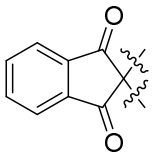
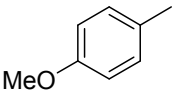
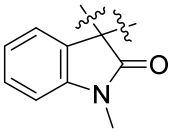
To study the Lewis acid-induced VCR in detail, we synthesized a broad series of D-A cyclopropanes **1** bearing diverse substituents at the alkenyl moiety and various acceptor groups. The general synthetic scheme includes Knoevenagel condensation of commercially available or easily prepared cinnamic aldehydes **3** and their heterocyclic analogs with various CH-acids, followed by cyclopropanation of the adducts **4** with Corey-Chaykovsky ylide (Table 2).

Table 2. **Synthesis of Cyclopropanes 1**.



3 **4** **1**

Entry	**1,3,4**	Ar	R	EWG	EWG'	Yield (%)[a] [dr][b] **4**	**1**[c]
1	**c**		H	CO_2Me	CO_2Me	96[d]	67
2	**d**		H	CO_2Me	CO_2Me	88[d]	69
3	**e**		H	CO_2Me	CO_2Me	87[d]	76
4	**f**		H	CO_2Me	CO_2Me	79[d]	61
5	**g**		H	CO_2Me	CO_2Me	61[d]	76

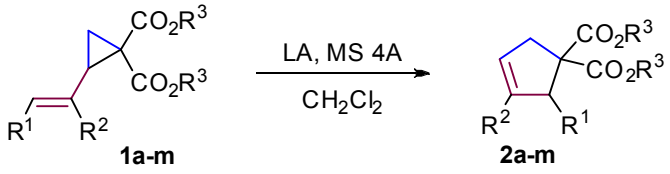
6	**h**		H	CO_2Me	CO_2Me	71[d]	85
7	**i**		Me	CO_2Me	CO_2Me	82[d]	74
8	**j**		Me	CO_2Me	CO_2Me	78[d]	65
9	**k**		CH_2Ph	CO_2Me	CO_2Me	71[d] (59:41)	70 (65:35)
10	**l**		H	CO_2Me	CO_2Me	74[d]	58
11	**n**		H	$PO(OMe)_2$	CO_2Me	87[d] (61:39)	67 (56:44)
12	**o**		H	CN	CO_2Me	77[e]	65 (65:35)
13	**p**		H	CN	CO_2Me	93[e]	71 (94:6)
14	**q**		H			68[d]	88
15	**r**		H			37[f] (72:28)	49 (54:46)

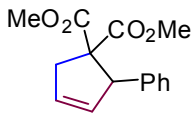
[a] Isolated yields. [b] Diastereomeric ratios [dr] were determined by NMR data for reaction mixtures. [c] **4** (1.0 equiv.), Me_3SOI (1.2 equiv.), NaH (1.2 equiv.) in DMF or DMSO (0.15 M). [d] Dimethyl malonate (1 equiv.), ArCHO (1 equiv.), AcOH (0.2 equiv.) and piperidine (0.02 equiv.) in toluene or benzene (0.33 M). [e] Methyl cyanoacetate (1 equiv.), ArCHO (1 equiv.), and piperidine (0.10 equiv.) in methanol (1.1 M). [f] N-methyloxindole (1.0 equiv.), ArCHO (1.5 equiv.), NaOH (2 equiv.) in EtOH−H_2O (1:1, 0.25 M).

Then we investigated the scope of acid-induced VCR using vinylcyclopropanes with diverse acceptor groups and a variety of substituents (alkyl, aryl, hetaryl) at the vinylic carbon atoms (Table 3). The reactions were performed under the optimal conditions, earlier found for

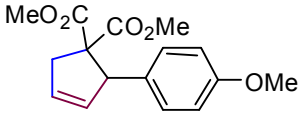
the model reactions, taking into account relative electron donating ability of various (hetero)aromatic groups of the substrate. Thereby, 4-chlorostyryl- and 3-chlorostyryl-substituted cyclopropanes **1c**,**d** wherein electron-donating ability of aromatic group is similar to that of unsubstituted styryl group in **1a** were found to behave analogously to cyclopropane **1a**. Namely, they produced cyclopentenes **2c**,**d** in high yields under the treatment with $GaCl_3$ and in moderate yields under the treatment with $SnCl_4$. Oppositely, reactivity of cyclopropanes **1e**,**f** containing electron-enriched styryl substituents is similar to that of substrate **1b**; and cyclopentenes **2e**,**f** were obtained in excellent yield when rearrangement was induced by $SnCl_4$, $Sc(OTf)_3$ or $Ni(ClO_4)_2 \cdot 6H_2O$. Futhermore, we found that *p*-(dimethylamino)styryl-substituted cyclopropane **1f** rearranged into cyclopentene **2f** during the purification on silica. In other words, silica gel acidity is sufficient to induce its isomerization. Evidently, highly electron-enriched aromatic groups increase noticeably the polarization of the breaking C–C bond in three-membered ring that facilitates the formation of zwitter-ionic intermediate **Z**.

Table 3. **Scope of Alkenylcyclopropanes 1**[a,b]

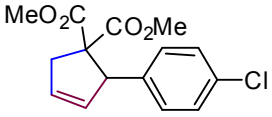




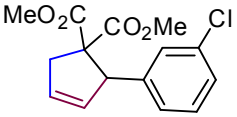
2a, $GaCl_3$, rt, 1 h, 81%[c]
$SnCl_4$, Δ, 2 h, 63%



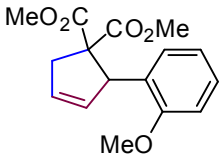
2b, $Sc(OTf)_3$, rt, 3 h, 91%
$Ni(ClO_4)_2$, rt, 4 h, 95%[d]
$SnCl_4$, Δ, 1.5 h, 87%



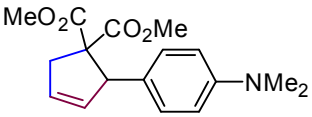
2c, $GaCl_3$, rt, 1 h, 93%[c]
$SnCl_4$, Δ, 2 h, 65%



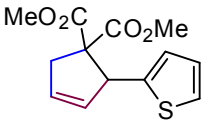
2d, $GaCl_3$, rt, 1 h, 86%[c]
$SnCl_4$, Δ, 2 h, 41%



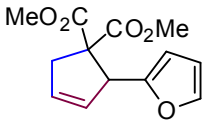
2e, $SnCl_4$, Δ, 1.5 h, 90%
$Sc(OTf)_3$, rt, 3 h, 98%
$Ni(ClO_4)_2$, rt, 4 h, 95%



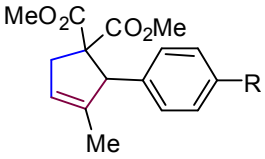
2f, $SnCl_4$, -10°C, 2 h, 79%
SiO_2, 98%
$Sc(OTf)_3$, rt, 3 h, 94%



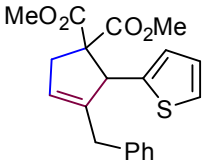
2g, $SnCl_4$, -40→-10°C, 2 h, 32%
$Ni(ClO_4)_2$, 60°C, 3 h, 71%[e]



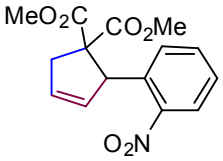
2h, $SnCl_4$, 0°C→Δ, 0.5 h, 21%
$Ni(ClO_4)_2$, Δ, 1.1 h, 51%



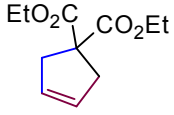
2i, R=H, $TiCl_4$, Δ, 1.5 h, 71%
$SnCl_4$, Δ, 3 h, 67%
2j, R=F, $SnCl_4$, Δ, 2 h, 80%



2k, $SnCl_4$, Δ, 1.5 h, 70%



2l, $SnCl_4$, Δ, 2 h, 0%[f]
$GaCl_3$, Δ, 1 h, 0%[c,g]



2m, $GaCl_3$, Δ, 1 h, 0%[c,g]
$SnCl_4$, -10°C, 2 h, 0%[f,h]

[a] Isolated yields. [b] 0.07 M Solution of cyclopropane **1** was treated with Lewis acid (1.0 equiv. of $GaCl_3$, 1.1–1.5 equiv. of $SnCl_4$, 0.1 equiv. of $Sc(OTf)_3$, 0.2 or 1.0 equiv. of $Ni(ClO_4)_2 \cdot 6H_2O$) under the specified conditions. [c] Reaction was performed in DCE. [d] In all experiments $Ni(ClO_4)_2$ was used as hexahydrate. [e] Reaction was performed in α,α,α-trifluorotoluene. [f] Chlorides **5a**,**b** were obtained as single products. [g] Hex-2,4-dienoates **6a**,**b** were obtained. [h] Reaction was performed in nitromethane.

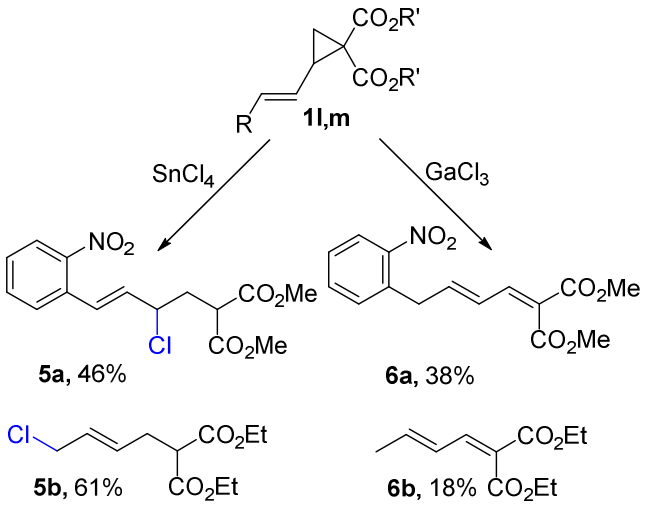
Nevertheless, $SnCl_4$-induced rearrangement of 2-(2-thienylethenyl)- and 2-(2-furylethenyl)cyclopropane-1,1-diesters **1g**,**h** into the corresponding cyclopentenes **2g**,**h** proceeded with low yields despite the electron-rich nature of these heteroaromatic substituents. Presumably, this can be explained by the propensity of thiophene-substituted D-A cyclopropanes to the Lewis acid-induced cationic oligomerization[4d,23] and well-known susceptibility of the furan ring to the acidic conditions.[24,25] Fortunately, the use of $Ni(ClO_4)_2$ $6H_2O$ as catalyst

allowed to overcome these complications and obtain the target cyclopentenes **2g**,**h** in reasonable yields.

Substrates **1i-k** bearing an alkyl group at the α-position of C=C bond were found to undergo successfully the studied isomerization under treatment with $SnCl_4$ affording polysubstituted cyclopentenes **2i-k** in good yields. It is noteworthy that $SnCl_4$-induced isomerization of cyclopropane **1g** proceeded under cooling while the same Lewis acid induced rearrangement of 2-(2-thienyl-1-phenylpropen-2-yl)cyclopropane-1,1-dicarboxylate **1k** under reflux only. At the same time, cyclopentene **2k** was formed in the better yield. Presumably, the presence of alkyl group decelerates the goal rearrangement but even more efficiently influences undesired side reactions such as oligomerization suppressing them.

As opposed to the above-mentioned examples, the treatment of cyclopropane **1l**, containing 2-nitrostyryl substituent, and cyclopropane **1m**, bearing no substituents at the vinyl moiety, with $SnCl_4$ did not produce the target cyclopentenes at all. Instead, acyclic compounds **5a**,**b** were obtained in moderate yields *via* three-membered ring opening with chloride ion (Scheme 3). The attempts to induce VCR of **1l**,**m** with $GaCl_3$ were also unsuccessful. In this case chlorine-free products **6a**,**b**, containing 1,3-diene moiety conjugated to the ester groups, were obtained as single low-molecular-weight products.

Scheme 3. $SnCl_4$- and $GaCl_3$-Induced Transformations of 1l,m



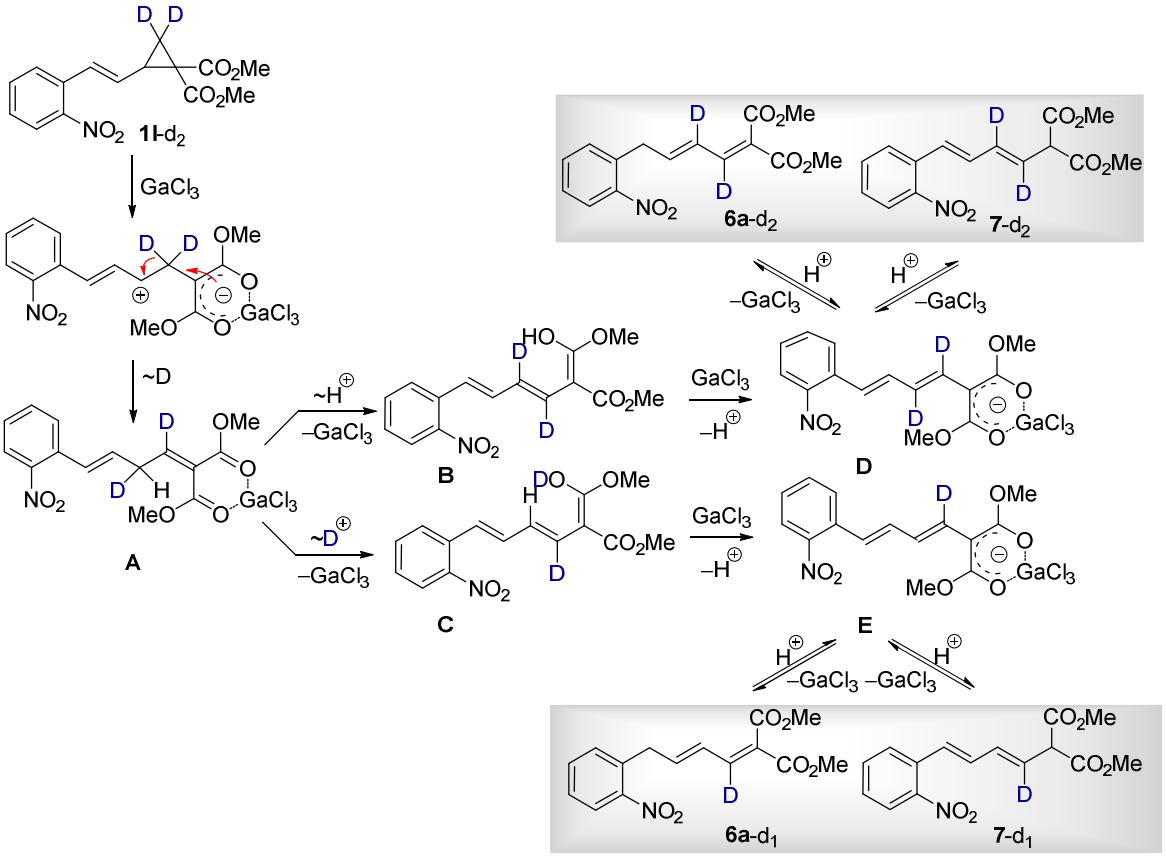
These results clearly indicate that zwitter-ionic intermediate **Z** should be stable enough to adopt the pentagon-like conformation required for the formation of five-membered ring. When cationic center is insufficiently stabilized, other processes compete efficiently with VCR. In the case of $SnCl_4$ as a catalyst products of three-membered ring opening with the chloride ion were obtained, with Lewis acid applied being a source of the nucleophile. With $GaCl_3$, that is not prone to provide the chloride ion for reactions with these or other subtrates, the isomerization of D-A cyclopropanes **1** into the corresponding dienes predominates.[26]

The different chemoselectivity in the reactions of cyclopropanes **1l** and **1m** is consistent with the results of investigations of the reactivity of diverse 2-alkenylcyclopropane-1,1-diesters against various nucleophiles. The principal factor influencing the direction of the nucleophilic attack is the presence of substituent(s) at the alkenyl moiety: when alkenyl group has substituent(s) at the β-carbon atom, products of S_N2-like reaction are usually formed,[27] while cyclopropanes with unsubstituted vinyl group, such as **1m**, react *via* both S_N2-like and S_N2'-like mechanisms depending on the reaction conditions and the nature of nucleophile.[28]

To shed more light on the mechanism of the dienes **6** formation, we synthesized cyclopropane **1l**-d_2 deuterated at the C(3) position of three-membered ring and investigated its transformations induced by the treatment with $GaCl_3$. We found that after 30 minutes the reaction mixture contained dienes **6a**-d_2, **6a**-d_1, and **7**-d_2 in a ratio of *ca*. 1:0.37:0.32 together with oligomerization products (Scheme 4), with isomeric diene **7** being absent in the reaction mixture after reflux for 1 h. We believe that the coordination of $GaCl_3$ to ester group(s) induced heterolysis of C(1)–C(2) bond in three-membered ring producing 1,3-zwitter-ionic intermediate of **Z** type. Deuteride shift in this intermediate afforded diene **A** with unconjugated C–C double bonds. Then it underwent isomerization to more stable products **6** and **7** through 1,5-shift of proton or deuterium from CHD moiety to the carbonyl oxygen atom affording trienols **B** and **C** respectively.[29] In accordance with the general principle that heavier isotopes have lower mobility, proton migration proceeded faster than deuterium migration. The complexation of

$GaCl_3$ to **B** or **C** is accompanied by deprotonation producing enolates **D** and **E** containing, respectively, two or one deuterium atom. These enolates are protonated at benzyl or malonyl carbon atoms furnishing dienes **6a** and **7**. Dienes **6a** are more stable possibly due to stereoelectronic effects of *ortho*-nitro group. As a result, **7**-d_2 was still present in the reaction mixture as minor isomer after 0.5 h but was not observed after 1 h. According to the proposed mechanism, compound **7**-d_1 should also be present in the reaction mixture obtained after reflux for 0.5 h. However, the precision of integral measurements for different signals of minor product **7** did not allow us to determine unambiguously the relative content of **7**-d_1 in the studied mixture.

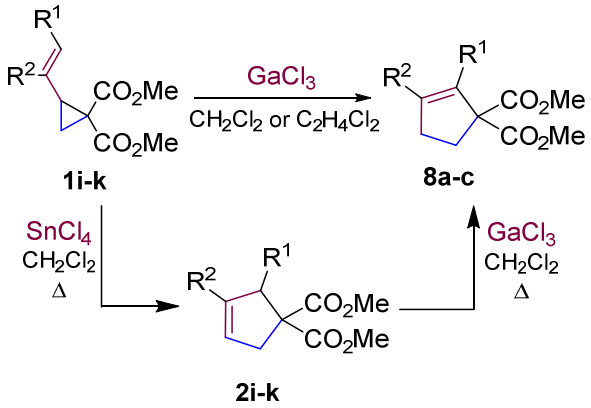
Scheme 4. $GaCl_3$-Induced Isomerization of 1l-d_2



We found that the Lewis acid-induced isomerization of cyclopropanes **1i-k** containing trisubstituted double bond can produce not only the corresponding cyclopentenes **2** but also isomeric products **8** (Table 4). The reaction chemoselectivity can be switched by a simple

modification of the reaction conditions. Specifically, the treatment of the solution of cyclopropanes **1i-k** in CH_2Cl_2 with $GaCl_3$ under reflux led to the formation of 2,3-substituted cyclopent-2-ene-1,1-dicarboxylates **8a-c** instead of cyclopent-3-ene-1,1-dicarboxylates obtained in reactions initiated by $SnCl_4$. ^1H NMR monitoring of $GaCl_3$-initiated process provided clear evidence that cyclopentenes **2** are intermediates in the formation of cyclopentenes **8**. Evidently, the last step in the compounds **8a-c** formation is the isomerization of cyclopentene **2** with trisubstituted double bond into more stable cyclopentene **8** containing tetrasubstituted double bond. This conclusion was unambiguously supported by control experiments which showed that cyclopentenes **2i**,**k** isomerize into cyclopentenes **8a**,**c** under mild conditions in the presence of $GaCl_3$.

Table 4. $GaCl_3$-Assisted Isomerization of Cyclopropanes 1i-k and Cyclopentenes 2i-k to Cyclopentenes 8a-c[a,b]

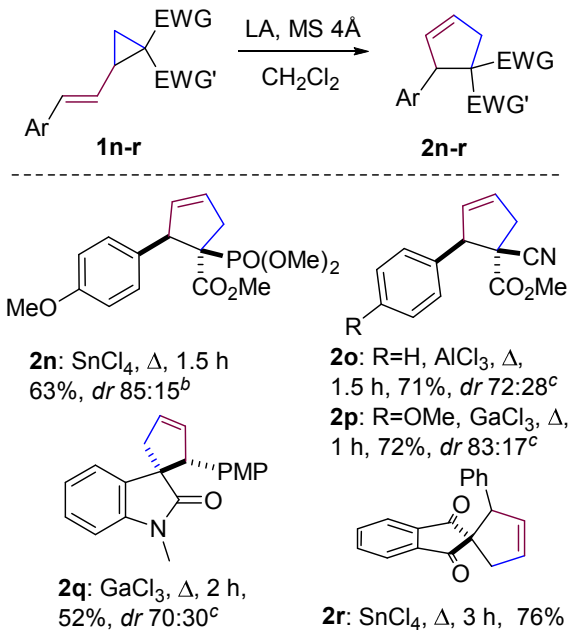


Entry	**1,2**	R^1	R^2	mol% of $GaCl_3$	T [°C]	t [h]	**8**	Yield [%][a]
1	**1i**	Ph	Me	100	83	0.5	**a**	72
2	**2i**	Ph	Me	200	20	7	**a**	85
3	**1j**	4-FC_6H_4	Me	200	20	6.5[c]	**b**	75
4	**1k**	2-Th	Bn	100	20	14[c]	**c**	67
5	**2k**	2-Th	Bn	100	20	14	**c**	70

[a] Isolated yields. [b] Reaction was performed in DCM or DCE (0.07 M). [c] Reaction mixture was heated under reflux for 0.5 h after stirring at room temperature.

Donor-acceptor cyclopropanes bearing two ester groups as acceptors and diverse donors (aryl, hetaryl, alkenyl, silylmethyl, amino groups *etc*.) are intensively studied as both model substrates and powerful building blocks in organic synthesis. Oppositely, donor-acceptor cyclopropanes with other combinations of acceptor groups are underinvestigated. Herein, we decided to explore Lewis acid-induced VCR for substrates bearing diverse acceptor groups. We found that this isomerization has a general character and proceed with the same efficiency for cyclopropanes bearing ester, keto, cyano and phosphoryl groups (Table 5). Moreover, 1'-methyl-2-(4-methoxystyryl)spiro[cyclopropane-1,3'-oxindole] **1q** underwent isomerization to the corresponding spiro[cyclopent-3-ene-1,3'-oxindole] **2q** in reasonable yield and diastereoselectivity.[30] Similarly, D-A cyclopropane **1r**, obtained from indane-1,3-dione, rearranged into the corresponding spiro[cyclopentene-3,2'-indane-1,3-dione] **2r**. This result is in contrast to the earlier reported isomerization of 1,1-diacyl-2-vinylcyclopropanes and related substrates to dihydrofurans under catalysis with Cu(I) chloride and various transition metal complexes.[31]

Table 5. **Variation of Electron-Withdrawing Groups**[a]



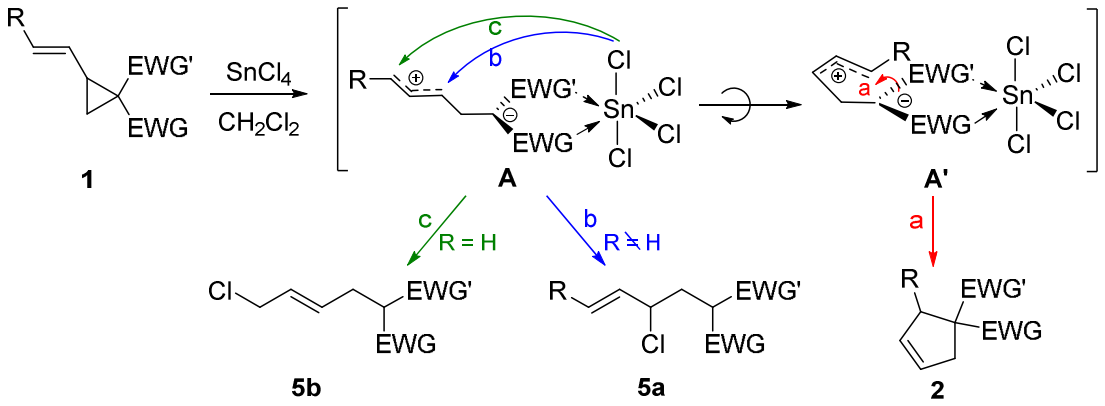
[a] Isolated yields. [b] Diastereomeric ratio was determined by NMR analysis of the reaction mixture. [c] Diastereomeric ratio was deduced from the weight ratio of isolated isomers.

It is noteworthy that isomerization of cyclopropanes **1n-q** bearing two different electron-withdrawing groups into the corresponding cyclopentenes proceeded with reasonable diastereoselectivity which did not depend on the isomeric composition of cyclopropanes **1**. Thus, substrates **1o**,**p**, used as single isomers with *cis*-arrangement of aromatic substituent and cyano group, afforded cyclopentenes **2o,p** as a mixture of two diastereomers in a ratio of 72:28 and 83:17 respectively. To better understanding of the studied process, we studied isomerization of both diastereomers of **1n** and found that they produced cyclopentene **2n** with identical *cis*:*trans* ratio. The same was also true for **1q**-to-**2q** rearrangement. This unambiguously supports the hypothesis of the intermediate formation of zwitter-ion of **Z** type during the transformation of **1** into **2** and is consistent with the thermodynamic control of the cyclization step affording the equilibrium mixture of diasteromers.

Based on the obtained results, we proposed the following mechanism for these transformations (Scheme 5). First, the coordination of Lewis acid to acceptor substituent(s) induces cyclopropane ring opening to give a zwitter-ionic species **A** containing stabilized electrophilic and nucleophilic centers. After rotation to the conformation **A'** this zwitter-ion

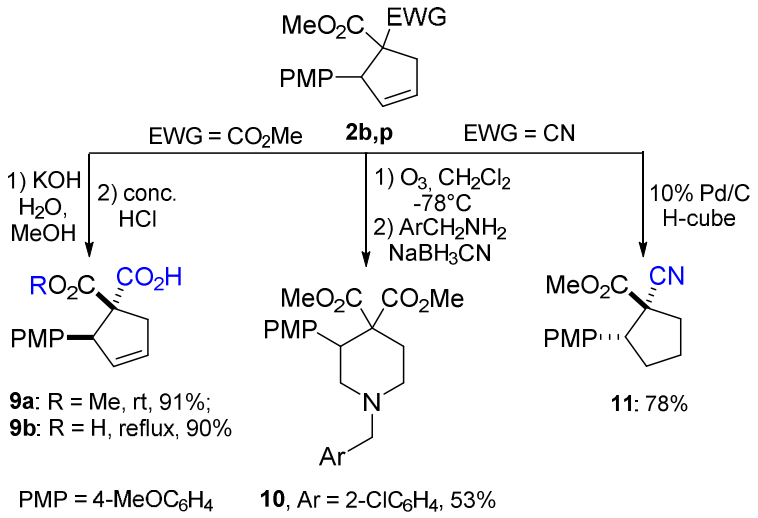
undergoes 1,5-cyclization to cyclopentene **2** through nucleophilic attack of the malonate anion onto the remote atom of the allylic cation moiety (Scheme 5, path *a*). Oppositely, when allyl cation is not stabilized (**1i**,**m**), it abstracts chloride ion from $SnCl_4$ affording **5a** or **5b** (Scheme 5, paths *b* and *c*) or undergoes isomerization to dienes **6** (**7**) (see Scheme 4).

Scheme 5. Proposed Mechanism



Easy modifiability of (het)aryl group and electron-withdrawing substituents as well as the C−C double bond in five-membered ring makes the formed cyclopentenes relevant reagents for producing various potentially useful compounds including pharmacological agents. Thus, upon treatment with KOH in aqueous methanol at room temperature followed by acidifying cyclopentene **2b** underwent partial stereoselective saponification yielding hemimalonate **9a** in excellent yield. In comparison, hydrolysis of **2b** under reflux produced smoothly the corresponding diacid **9b**. Moreover, we showed that cyclopentenes **2**, the products of VCR studied, can be transformed to 3-arylpiperidines which are promising substrates for medicinal chemistry and pharmacology due to a broad range of their bioactivities.[32] Namely, piperidine **10** was synthesized by two-step procedure including the ozonolysis of cyclopentene **2b** followed by the reductive amination of the formed dialdehyde with 2-chlorobenzylamine and $NaBH_3CN$. Finally, we demonstrated that **2p** can be easily and selectively reduced to the corresponding cyclopentane **11** (Scheme 6).

Scheme 6. **Post-modifications of Cyclopentenes 2**



Conclusion

In conclusion, we demonstrated that 2-styrylcyclopropane-1,1-diesters and their heterocyclic analogs in the presence of Lewis acid undergo isomerization to the corresponding 2-(het)arylcyclopent-3-ene-1,1-diesters under mild reaction conditions in moderate to high yields. Unlike most of reported methods for vinylcyclopropane-to-cyclopentene rearrangement under mild reaction conditions, this protocol does not involve the use of noble metal-based catalysts. Post-modifications of the obtained cyclopentenes were conducted to demonstrate possible extensions of the practical utility of the title reaction. We deem that the Lewis acid-initiated VCR would not only serve as a tool for the formation of simple cyclopentene-based compounds but also provide a potential route to useful complex structures containing cyclopentene motif.

Experimental section

General Information

NMR spectra were acquired on Bruker Avance 600, Bruker Avance 500 and Bruker Avance 400 spectrometers at room temperature, if not specified otherwise; the chemical shifts δ were measured in ppm with respect to solvent ($CDCl_3$: δ_H = 7.27 ppm; δ_C = 77.0 ppm). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; dd, double doublet. Coupling constants (J) are in Hertz. The structures of synthesized compounds were elucidated with the aid of 1D NMR (^1H, ^{13}C) and 2D NMR (COSY ^1H-^1H, HSQC and HMBC

^{1}H-^{13}C, NOESY ^{1}H-^{1}H) spectroscopy. Infrared spectra were recorded on Thermo Nicolet IR200 FT-IR and Agilent FTIR Cary 630 spectrometers with ATR (Attenuated Total Reflectance) module. ESI mass spectra were recorded using Shimadzu LCMS-8040 instrument, equipped with dual ion source (DUIS) in electrospray positive mode (interface voltage – 4,5 kV, nebulizer gas flow – 2 L/min, drying gas flow – 15 L/min, desolvation line temperature – 250°C, heat block temperature – 400 °C. GC-MS were recorded on the Thermo Focus DSQ II mass spectrometer. High resolution and accurate mass measurements were carried out using a BrukermicrOTOF-Q^{TM} ESI-TOF (Electro Spray Ionization/Time of Flight) and Thermo Scientific* LTQ Orbitrap mass spectrometers. Elemental analyses were performed with Fisons EA-1108 CHNS elemental analyser instrument. Melting points (mp) are uncorrected and were measured on Electrothermal 9100 capillary melting point apparatus. Analytical thin layer chromatography (TLC) was carried out with silica gel plates (silica gel 60, F_{254}, supported on aluminium); the revelation was done by UV lamp (365 nm). All reactions were carried out using freshly distilled and dry solvents. Column chromatography was performed on silica gel 60 (230–400 mesh, Merck). NaH (60% dispersion in mineral oil), Lewis acids used, trimethylsulfoxonium iodide, 3-arylprop-2-enals **3** are available commercially except for compounds **3j**, obtained according to reported procedure,[33] and **3k**, synthesis of which is given below. Perdeuterated Corey ylide and cyclopropanes **1a**,**b**,**m** were synthesized by published procedures.[14a,34,35] Other 2-substituted cyclopropane-1,1-diesters **1** were prepared by Knoevenagel/Corey-Chaykovsky reactions sequence from the corresponding aldehydes analogously to described procedures.[35,36] All experiments were carried out under an argon atmosphere using freshly distilled and dry solvents.

(2*Z*)-2-Benzyl-3-(thiophen-2-yl)prop-2-enal (**3k**). To a cooled (0 °C) solution of freshly distilled thiophene-2-carbaldehyde (2.80 g, 25 mmol) and 3-phenylpropanal (3.35 g, 25 mmol) in 25 mL of methanol 10% NaOH methanolic solution (4 mL) was added dropwise under vigorous stirrinng. The mixture was brought to room temperature and stirred at this temperature for 4 h. The solution was then rendered acidic to litmus by the addition of 10% aqueous HCl and

extracted with diethyl ether. The organic layer was separated, dried and evaporated under reduced pressure to give brown oil. The final residue was purified by column chromatography (SiO_2, eluent – petroleum ether : diethyl ether) to yield **3k** as yellow oil (3.37 g, 59% yield). R_f = 0.30 (petroleum ether : ethyl acetate, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.10 (s, 2H, CH_2Ph), 7.15 (dd, ^3J = 5.0 Hz, ^3J = 3.8 Hz, 1H, Th), 7.19–7.35 (m, 5H, CH, Ph), 7.42 (d, ^3J = 3.8 Hz, 1H, Th), 7.57 (d, ^3J = 5.0 Hz, 1H, Th), 7.63 (br.s, 1H, CH=), 9.67 (s, 1H, CHO); ^{13}C NMR (126 MHz, $CDCl_3$): δ 30.6 (CH_2Ph), 126.3 (CH), 127.9 (CH), 128.3 (2×CH), 128.5 (2×CH), 131.5 (CH), 133.7 (CH), 137.48 (C), 137.52 (C), 137.8 (C), 143.1 (CH=), 194.2 (CHO); IR (film) 1671, 1614 cm^{-1}; HRMS (ESI/Q-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{13}OS$ 229.0682; Found 229.0684.

General procedure A (Knoevenagel condensation). To a solution of aldehyde (5 mmol) and dimethyl malonate (0.66 g, 5 mmol) in toluene (15 mL) glacial acetic acid (0.06 mL, 1 mmol) and piperidine (0.01 mL, 0.1 mmol) were added. The mixture was refluxed with the Dean-Stark trap until water separation was finished (2–6 h). Upon cooling, water (20 mL) was added to the mixture and the organic layer was separated. The aqueous phase was extracted with ether (3×10 mL). The combined organic fractions were washed with water (3×10 mL), dried with Na_2SO_4, concentrated *in vacuo*. The purification by column chromatography (SiO_2) afforded the target alkenes.

Dimethyl 2-[(2*E*)-3-(4-chlorophenyl)prop-2-en-1-ylidene]malonate (4c). General Procedure A; white solid (1.35 g, 96% yield); mp 87–88 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.83 (s, 3H, CH_3O), 3.90 (s, 3H, CH_3O), 7.00 (d, ^3J = 15.5 Hz, 1H, CH=), 7.24 (dd, ^3J = 15.5 Hz, ^3J = 12.0 Hz, 1H, CH=), 7.35 (d, ^3J = 8.3 Hz, 2H, CH, Ar), 7.43 (d, ^3J = 8.3 Hz, 2H, CH, Ar), 7.54 (d, ^3J = 12.0 Hz, 1H, CH=); ^{13}C NMR (126 MHz, $CDCl_3$): δ 52.25 (CH_3O), 52.31 (CH_3O), 123.7 (CH), 124.5 (C), 128.9 (2×CH), 129.1 (2×CH), 134.0 (C), 135.7 (C), 143.4 (CH=), 145.7 (CH=), 165.0 (*C*O_2Me), 165.5 (*C*O_2Me); IR (film) 1720, 1618 cm^{-1}; HRMS (ESI/Q-TOF) *m/z*: $[M + H]^+$ Calcd

for $C_{14}H_{13}ClO_4$ 281.0575; Found 281.0575; Anal. Calcd for $C_{14}H_{13}ClO_4$: C, 59.90; H, 4.67. Found: C, 60.03; H, 4.37.

Dimethyl 2-[(2*E*)-3-(3-chlorophenyl)prop-2-en-1-ylidene]malonate (4d). General Procedure A; orange solid (1.24 g, 88% yield); R_f = 0.52 (petroleum ether : ethyl acetate; 4:1); mp 68–69 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.84 (s, 3H, CH_3O), 3.92 (s, 3H, CH_3O), 6.98 (d, ^3J = 15.4 Hz, 1H, CH=), 7.24 (d, ^3J = 11.6 Hz, 1H, CH=), 7.30–7.40 (m, 3H, CH, Ar), 7.48–7.50 (m, 1H, CH, Ar), 7.54 (dd, ^3J = 15.4 Hz, ^3J = 11.6 Hz, 1H, CH=); ^{13}C NMR (126 MHz, $CDCl_3$): δ 52.41 (CH_3O), 52.45 (CH_3O), 124.5 (CH), 125.1 (C), 126.0 (CH), 127.5 (CH), 129.7 (CH), 130.1 (CH), 134.9 (C), 137.4 (C), 143.1 (CH=), 145.4 (CH=), 165.0 (CO_2Me), 165.5 (CO_2Me); IR (film) 1717, 1614 cm^{-1}; LC-MS *m/z* 281 $[M + H]^+$. Anal. Calcd for $C_{14}H_{13}ClO_4$: C, 59.90; H, 4.67. Found: C, 59.95; H, 4.68.

Dimethyl 2-[(2*E*)-3-(2-methoxyphenyl)prop-2-en-1-ylidene]malonate (4e). General Procedure A; orange solid (1.20 g, 87% yield); mp 91–92 °C (lit. 92 °C[37]); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.82 (s, 3H, CH_3O), 3.87 (s, 3H, CH_3O), 3.90 (s, 3H, CH_3O), 6.89 (d, ^3J = 8.3 Hz, 1H, CH, Ar), 6.95 (dd, ^3J = 7.7 Hz, ^3J = 7.3 Hz, 1H, CH, Ar), 7.32 (dd, ^3J = 15.5 Hz, ^3J = 11.2 Hz, 1H, CH=), 7.28–7.34 (m, 1H, CH, Ar), 7.44 (br.d, ^3J = 15.5 Hz, 1H, CH=), 7.55 (dd, ^3J = 7.7 Hz, ^4J = 1.5 Hz, 1H, CH, Ar), 7.61 (d, ^3J = 11.2 Hz, 1H, CH=); ^{13}C NMR (126 MHz, $CDCl_3$): δ 52.2 (CH_3O), 52.3 (CH_3O), 55.5 (CH_3O), 111.2 (CH), 120.8 (CH), 123.2 (C, Ar), 123.7 (CH), 124.6 (C, Ar), 128.0 (CH), 131.2 (CH), 140.4 (CH), 147.3 (CH), 157.9 (C, Ar), 165.3 (CO_2Me), 165.9 (CO_2Me); IR (film) 1737, 1699, 1260 cm^{-1}; LC-MS *m/z* 277 $[M + H]^+$. Anal. Calcd for $C_{15}H_{16}O_5$: C, 65.21; H, 5.84. Found: C, 65.44; H, 5.83.

Dimethyl 2-{(2*E*)-3-[4-(dimethylamino)phenyl]prop-2-en-1-ylidene}malonate (4f). General Procedure A; red-orange solid (1.14 g, 79% yield); mp 127–128 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.02 (s, 6H, 2×CH_3N), 3.80 (s, 3H, CH_3O), 3.88 (s, 3H, CH_3O), 6.65–6.66 (m, 2H, CH, Ar), 7.00 (d, ^3J = 15.3 Hz, 1H, CH=), 7.15 (dd, ^3J = 15.3 Hz, ^3J = 11.7 Hz, 1H, CH=), 7.40–7.41 (m, 2H, CH, Ar), 7.60 (d, ^3J = 11.7 Hz, 1H, CH=); ^{13}C NMR (151 MHz, $CDCl_3$): δ 40.1

(2×CH_3N), 52.0 (CH_3O), 52.1 (CH_3O), 111.9 (2×CH, Ar), 118.8 (CH=), 120.0 (C), 123.6 (C), 129.8 (2×CH, Ar), 146.8 (CH=), 148.5 (CH=), 151.7 (C), 165.8 (*C*O_2Me), 166.2 (*C*O_2Me); HRMS (ESI/Q-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{20}NO_4$ 290.1387; Found 290.1387. Anal. calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.51; H, 6.67; N, 4.65.

Dimethyl 2-[(2E)-3-(thiophen-2-yl)prop-2-en-1-ylidene]malonate (4g). General Procedure A; yellow solid (0.77 g, 61% yield); R_f = 0.64 (petroleum ether : ethyl acetate; 4:1); mp 64–65 °C (lit. 68 °C[37]; 64–65 °C[38]); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.82 (s, 3H, CH_3O), 3.90 (s, 3H, CH_3O), 7.05 (dd, ^3J = 4.9 Hz, ^3J = 3.7 Hz, 1H, Th), 7.07 (dd, ^3J = 15.3 Hz, ^3J = 11.6 Hz, 1H, CH=), 7.18 (d, ^3J = 15.3 Hz, 1H, CH=), 7.21 (d, ^3J = 3.7 Hz, 1H, Th), 7.38 (d, ^3J = 4.9 Hz, 1H, Th), 7.52 (d, ^3J = 11.6 Hz, 1H, CH=); ^{13}C NMR (126 MHz, $CDCl_3$): δ 52.2 (CH_3O), 52.3 (CH_3O), 122.6 (CH), 123.2 (C), 128.1 (CH), 128.4 (CH), 130.0 (CH), 137.4 (CH), 141.0 (C), 146.0 (CH), 165.2 (*C*O_2Me), 165.7 (*C*O_2Me); HRMS (ESI/Q-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{13}O_4S$ 253.0529; Found 253.0530.

Dimethyl 2-[(2*E*)-3-(furan-2-yl)prop-2-en-1-ylidene]malonate (4h). General Procedure A; yellow solid (839 mg, 71% yield); mp 89–90 °C (lit. 91 °C[37]; 88-90 °C[38]); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.81 (s, 3H, CH_3O), 3.89 (s, 3H, CH_3O), 6.45 (dd, ^3J = 3.4 Hz, ^3J = 1.8 Hz, 1H, Fu), 6.57 (d, ^3J = 3.4 Hz, 1H, Fu), 6.80 (d, ^3J = 15.2 Hz, 1H, CH=), 7.11 (dd, ^3J = 15.2 Hz, ^3J = 12.0 Hz, 1H, CH=), 7.47 (br.d, ^3J = 1.8 Hz, 1H, Fu), 7.50 (d, ^3J = 12.0 Hz, 1H, CH=); ^{13}C NMR (126 MHz, $CDCl_3$): δ 52.27 (CH_3O), 52.31 (CH_3O), 112.5 (CH), 113.9 (CH), 121.5 (C), 123.8 (C), 130.9 (CH), 144.6 (CH), 145.5 (CH), 151.9 (C), 165.1 (*C*O_2Me), 165.7 (*C*O_2Me); IR (film) 1729, 1609, 1470 cm^{-1}; LC-MS *m/z* 237 $[M+H]^+$. Anal. Calcd for $C_{12}H_{12}O_5$: C, 61.01; H, 5.12. Found: C, 61.18; H, 5.13.

Dimethyl 2-[(2*E*)-3-phenyl-2-methylprop-2-en-1-ylidene]malonate (**4i**). General Procedure A; (1.07 g, 82% yield). Spectral data (NMR, IR) are consistent with the reported ones.[39] Compound **4i** was used in synthesis of cyclopropane **1o** without additional purification.

Dimethyl 2-[(2*E*)-3-(4-fluorophenyl)-2-methylprop-2-en-1-ylidene]malonate (4j). General Procedure A; yellow solid (1.09 g, 78% yield); R_f = 0.46 (petroleum ether : diethyl ether; 2:1); mp 82–83 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.99 (d, ^4J = 0.8 Hz, 3H, CH_3), 3.82 (s, 3H, CH_3O), 3.86 (s, 3H, CH_3O), 6.92 (br.s, 1H, CH=), 7.07 (dd, $^3J_{HF}$ = 8.7 Hz, ^3J = 8.5 Hz, 2H, CH, Ar), 7.32 (dd, ^3J = 8.5 Hz, $^4J_{HF}$ = 5.4 Hz, 2H, CH, Ar), 7.45 (q, ^4J = 0.8 Hz, 1H, CH=); ^{13}C NMR (126 MHz, $CDCl_3$): δ 14.5 (CH_3), 52.45 (CH_3O), 52.52 (CH_3O), 115.5 (d, $^2J_{CF}$ = 22 Hz, 2×CH, Ar), 123.6 (C), 131.4 (d, $^3J_{CF}$ = 8 Hz, 2×CH, Ar), 132.2 ($^4J_{CF}$ = 3 Hz, C, Ar), 132.6 (C), 140.9 (CH=), 147.4 (CH=), 162.4 (d, $^1J_{CF}$ = 249 Hz, C, Ar), 165.0 (*C*O_2Me), 167.4 (*C*O_2Me); IR (KBr) 1727, 1691, 1264 cm^{-1}; LC-MS *m/z* 279 $[M+H]^+$. Anal. Calcd for $C_{15}H_{15}FO_4$: C, 64.74; H, 5.43. Found: C, 64.63; H, 5.75.

Dimethyl 2-[2-benzyl-3-(thiophen-2-yl)prop-2-en-1-ylidene]malonate (4k). General Procedure A; yellow solid (1.22 g, 71% yields), isolated as mixture of isomers, **A**:**B** = 59:41; R_f = 0.60 (petroleum ether : ethyl acetate 4:1); mp 35–38 °C; ^{1}H NMR (500 MHz, $CDCl_3$): 3.43 (s, 3H, CH_3O, **A**), 3.68 (s, 2H, C*H*$_2$Ph, **B**), 3.77 (s, 3H, CH_3O, **B**), 3.79 (s, 3H, CH_3O, **A**), 3.85 (s, 3H, CH_3O, **B**), 4.08 (s, 2H, C*H*$_2$Ph, **A**), 6.65 (br.s, 1H, CH=, **B**), 7.02–7.41 (m, 9H+8H, CH, **A**, **B**), 7.54 (d, ^4J = 0.7 Hz, 1H, CH= **A**), 8.04 (br.s, 1H, CH=, **B**); ^{13}C NMR (126 MHz, $CDCl_3$): δ 34.8 (C*H*$_2$Ph, **A**), 40.6 (C*H*$_2$Ph, **B**), 52.1 (CH_3O, **A**), 52.5 (CH_3O+CH_3O, **A**, **B**), 52.7 (CH_3O, **A**), 126.4 (CH, **A**), 126.6 (CH, **B**), 127.57 (CH, **A**), 126.62 (CH, **B**), 128.0 (2×CH, A), 128.4 (CH, **B**), 128.5 (2×CH, **A**), 128.6 (2×CH, **B**), 129.2 (CH+2×CH, **A**, **B**), 130.0 (CH, **B**), 130.6 (CH, **B**), 131.4 (CH, **A**), 131.6 (C, **A**), 131.9 (C, **B**), 132.8 (C, **A**), 134.7 (C, **B**), 135.3 (CH, **A**), 136.8 (C, **A**), 138.3 (C, **B**), 138.6 (C, **A**), 139.2 (C, **B**), 142.3 (CH, **B**), 146.3 (CH, **A**), 164.9 (*C*O_2Me, **B**), 165.0 (*C*O_2Me, **A**), 166.6 (*C*O_2Me, **B**), 167.0 (*C*O_2Me, **A**); IR (film) 1732, 1601 cm^{-1}; HRMS (ESI/Q-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{18}O_4S$ 343.0999; Found 343.1001. Anal. Calcd for $C_{19}H_{18}O_4S$: C, 66.65; H, 5.30. Found: C, 66.47; H, 5.31.

Dimethyl 2-[(2*E*)-3-(2-nitrophenyl)prop-2-en-1-ylidene]malonate (4l). General Procedure A; red-orange solid (1.08 g, 74% yield); mp 114–115 °C (lit. 114 °C[40]); ^{1}H NMR (500 MHz,

$CDCl_3$): δ 3.84 (s, 3H, CH_3O), 3.89 (s, 3H, CH_3O), 7.24 (dd, ^3J = 15.2 Hz, ^3J = 11.6 Hz, 1H, CH=), 7.55 (d, ^3J = 15.2 Hz, 1H, CH=), 7.55–7.59 (m, 1H, CH, Ar), 7.57 (br.d, ^3J = 11.6 Hz, 1H, CH=), 7.62–7.65 (m, 1H, CH, Ar), 7.72 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 1H, CH, Ar), 8.01 (dd, ^3J = 8.2 Hz, ^4J = 1.2 Hz, 1H, CH, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 52.2 (CH_3O), 52.3 (CH_3O), 124.7 (CH), 126.3 (C), 127.4 (CH), 128.6 (CH), 129.8 (CH), 130.9 (C), 133.1 (CH), 138.7 (CH), 144.4 (CH), 147.9 (C), 164.5 (CO_2Me), 165.0 (CO_2Me); HRMS (ESI/Q-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{14}NO_6$ 292.0816; Found 292.0816. Anal. Calcd for $C_{14}H_{13}NO_6$: C, 57.73; H, 4.50; N, 4.81. Found: C, 57.91; H, 4.43; N, 4.65.

Methyl 2-(dimethoxyphosphoryl)-5-(4-methoxyphenyl)penta-2,4-dienoate (4n). General Procedure A. According to ^{1}H NMR data product was formed as a mixture of *(2E,4E)*- and *(2Z,4E)*-isomers in a ratio of 61:39.

((2*E*,4*E*)-4n): yellow solid (832 mg, 51% yield), R_f = 0.35 (ethyl acetate); mp 48–49 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.75 (d, $^3J_{PH}$ = 11.3 Hz, 6H, $(CH_3O)_2$P), 3.79 (s, 3H, CH_3O), 3.84 (s, 3H, CH_3O), 6.88 (br.d, ^3J = 8.8 Hz, 2H, CH, Ar), 7.03 (d, ^3J = 15.0 Hz, CH=), 7.48 (br.d, ^3J = 8.8 Hz, 2H, CH, Ar), 7.65–7.80 (m, 2H, 2CH=); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 51.9 (CH_3O), 52.8 (d, $^2J_{PC}$ = 5.9 Hz, $(CH_3O)_2$P), 55.3 CH_3O), 114.2 (2×CH, Ar), 115.4 (d, $^1J_{PC}$ = 189 Hz, C=), 122.0 (d, $^3J_{PC}$ = 19 Hz, CH=), 128.1 (C, Ar), 129.9 (2×CH, Ar), 147.3 (CH=), 157.1 (d, $^2J_{PC}$ = 7.0 Hz, CH=), 161.4 (C, Ar), 165.1 (d, $^2J_{PC}$ = 14.2 Hz, CO_2Me); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 19.6 (doublet of septets, $^3J_{PH}$ = 23 Hz, $^2J_{PH}$ = 13 Hz); IR (film) 1715, 1600, 1246 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{15}H_{20}O_6P$ 327.0992; Found 327.0993. Anal. Calcd for $C_{15}H_{19}O_6P$: C, 55.22; H, 5.87. Found: C, 55.25; H, 5.77.

((2*Z*,4*E*)-4n): yellow solid (587 mg, 36% yield); R_f = 0.45 (ethyl acetate); mp 74–75 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.78 (d, $^3J_{PH}$ = 11.3 Hz, 6H, $(CH_3O)_2$P), 3.81 (s, 3H, CH_3O), 3.82 (s, 3H, CH_3O), 6.89 (br.d, ^3J = 8.8 Hz, 2H, CH, Ar), 7.05 (d, ^3J = 14.4 Hz, 1H, CH=), 7.51 (br.d, ^3J = 8.8 Hz, 2H, CH, Ar), 8.00–8.18 (m, 2H, 2CH=); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 52.2 (CH_3O), 52.6 (d, $^2J_{PC}$ = 5.7 Hz, $(CH_3O)_2$P), 55.3 (CH_3O), 114.2 (2×CH, Ar), 115.4 (d, $^1J_{PC}$ = 188

Hz, C=), 122.5 (d, $^3J_{PC}$ = 5 Hz, CH=), 128.3 (C, Ar), 130.0 (2×CH, Ar), 147.8 (CH=), 158.7 (d, $^2J_{PC}$ = 7 Hz, CH=), 161.4 (C, Ar), 166.2 (d, $^2J_{PC}$ = 15 Hz, *C*O_2Me); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 16.9 (doublet of septets, $^3J_{PH}$ = 46 Hz, $^2J_{PH}$ = 11 Hz); IR (film) 1714, 1600, 1255 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{15}H_{20}O_6P$ 327.0992; Found 327.0994. Anal. Calcd for $C_{15}H_{19}O_6P$: C, 55.22; H, 5.87. Found: C, 55.39; H, 5.94.

Methyl (2*E*,4*E*)-2-cyano-5-phenylpenta-2,4-dienoate (**4o**). To a solution of cinnamaldehyde (1.32 g, 10 mmol) and methyl cyanoacetate (0.99 g, 10 mmol) in methanol (9 mL) piperidine (0.01 mL, 0.1 mmol) was added at vigorous stirring. The product precipitates immediately after piperidine addition. The precipitate was filtered, washed with hexane and dried to constant weight. Yellow solid (1.64 g, 77% yield). NMR spectral data are consistent with published ones.[41,42] Compound **4o** was used in synthesis of cyclopropane **1o** without additional purification.

Methyl (2*E*,4*E*)-2-cyano-5-(4-methoxyphenyl)penta-2,4-dienoate (4p) was synthesized analogously to **4o** from 4-methoxycinnamaldehyde (1.62 g, 10 mmol) and methyl cyanoacetate (0.99 g, 10 mmol). Yellow solid (1.98 g, 93% yield). R_f = 0.40 (petroleum ether : ethyl acetate; 5:1); mp 114–115 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.87 (s, 3H, CH_3O), 3.88 (s, 3H, CH_3O), 6.94 (d, ^3J = 8.4 Hz, 2H, 2×CH), 7.14 (dd, ^3J = 11.4 Hz, ^3J = 15.4 Hz, 1H, CH=), 7.23 (d, ^3J = 15.4 Hz, 1H, CH=), 7.55 (d, ^3J = 8.4 Hz, 2H, 2×CH), 7.98 (d, ^3J = 11.4 Hz, 1H, CH=); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 53.0 (CH_3O), 55.6 (CH_3O), 102.2 (C), 114.8 (2×CH, Ar), 115.0 (C), 120.9 (CH=), 127.6 (C), 130.6 (2×CH, Ar), 149.2 (CH=), 156.2 (CH=), 162.4 (C), 163.2 (C). HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{14}H_{14}NO_3$ 244.0968; Found 244.0972. Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39. Found: C, 68.91; H, 5.25.

3-[(2*E*)-3-(4-Methoxyphenyl)prop-2-en-1-ylidene]-1-methylindolin-2-one (4q). NaOH (0.54 g, 13.5 mmol, 2 equiv.) was added at 0 °C to a stirred solution of *N*-methyloxindole (1.0 g, 6.8 mmol) and 4-methoxycinnamaldehyde (1.65 g, 10.1 mmol, 1.5 equiv.) in aq. EtOH (1:1, 27 mL). The reaction mixture was stirred at room temperature for 2 h, poured into H_2O (20 mL) and

extracted with ethyl acetate (3×15 mL). The combined organic fractions were washed with water (3×10 mL), dried with Na_2SO_4 and concentrated *in vacuo*. Product **4q** was purified by column chromatography to yield yellowish solid (733 mg, 37% yield; *E*/*Z* ratio 72:28). R_f = 0.54 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.22 (s, 3H+3H, CH_3N, **A**, **B**), 3.82 (s, 3H+3H, CH_3O, **A**, **B**), 6.75 (d, ^3J = 7.8 Hz, 1H, Ar, **B**), 6.79 (d, ^3J = 7.8 Hz, 1H, Ar, **A**), 6.86 (br. d, ^3J = 8.7 Hz, 2H, Ar, **B**), 6.90 (br. d, ^3J = 8.7 Hz, 2H, Ar, **A**), 6.89–6.92 (m, 1H, **B**), 6.95–7.09 (m, 2H+2H, **A**, **B**), 7.18–7.27 (m, 1H+1H, **A**, **B**), 7.39 (d, ^3J = 7.5 Hz, 1H, Ar, **B**), 7.49 (br. d, ^3J = 8.7 Hz, 2H, Ar, **A**), 7.43–7.53 (m, 2H, **A**), 7.52 (br. d, ^3J = 8.7 Hz, 2H, Ar, **B**), 7.66 (br. d, ^3J = 7.5 Hz, 1H, Ar, **A**), 8.45 (dd, ^3J = 15.6 Hz, ^3J = 11.5 Hz, CH=, **B**); ^{13}C NMR (126 MHz, $CDCl_3$): δ 25.6 (CH_3N, **B**), 26.0 (CH_3N, **A**), 55.36 (CH_3O, **B**), 55.39 (CH_3O, **A**), 107.8 (CH, **B**), 108.0 (CH, **A**), 114.3 (2×CH, **B**), 114.5 (2×CH, **A**), 118.9 (CH, **B**), 121.4 (CH, **A**), 121.7 (CH, **B**), 121.9 (CH, **A**), 122.3 (C, **B**), 122.57 (C, **A**), 122.62 (CH, **B**), 123.2 (CH, **A**), 124.2 (C, **A**), 124.3 (C, **B**), 127.9 (C, **B**), 128.3 (CH, **B**), 128.5 (CH, **A**), 129.0 (C, **A**), 129.2 (2×CH, **A**), 129.3 (2×CH, **B**), 136.2 (CH, **A**), 136.4 (CH, **B**), 142.3 (C, **B**), 142.7 (CH, **B**), 143.5 (C, **A**), 144.0 (CH, **A**), 160.8 (C, **B**), 161.0 (C, **A**), 167.5 (C, **B**), 168.7 (C, **A**); IR (film) 1701, 1590 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{19}H_{18}NO_2$ 292.1332; Found 292.1335.

(E)-2-(3-phenylprop-2-en-1-ylidene)indane-1,3-dione (**4r**). To a solution of cinnamaldehyde (1.32 g, 10 mmol) and indane-1,3-dione (1.46 g, 10 mmol) in benzene (10 mL) piperidine (0.01 mL, 0.1 mmol) was added at vigorous stirring. The product precipitates after piperidine addition. The precipitate was filtered, washed with hexane and dried to constant weight. Brown solid (1.77 g, 68% yield). Mass spectral data (NMR, IR) are consistent with published ones.[43]

General procedure B (Corey–Chaykovsky cyclopropanation). To a stirred suspension of NaH (60% in oil) in dry DMF or DMSO trimethylsulfoxonium iodide was added in a single portion under argon atmosphere at room temperature. Vigorous evolution of hydrogen lasted *ca.* 15 min, after which the reaction mixture was stirred for additional 25 min. Then a solution of electrophilic alkene in dry DMF or DMSO (3 mL) was added dropwise under conditions

specified. The resulted mixture was stirred at indicated temperature for the time specified, poured into ice cooled saturated aq. NH_4Cl (10 mL) and extracted with ethyl acetate (3×8 mL). The combined organic fractions were washed with water (5×5 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The final residue was purified by column chromatography (SiO_2, eluent – petroleum ether: ethyl acetate) to yield cyclopropanes **1**.

Dimethyl 2-[(*E*)-2-(4-chlorophenyl)ethenyl]cyclopropane-1,1-dicarboxylate (1c). General Procedure B: Suspension of NaH (45 mg, 1.13 mmol) and trimethylsulfoxonium iodide (240 mg, 1.09 mmol) in DMF (5 mL), 40 min, room temperature. Alkene **4c** (300 mg, 1.07 mmol) in dry DMF (3 mL) was added. Reaction mixture was stirred at room temperature for 1.5 h. Product **1c** was obtained as yellowish solid (212 mg, 67% yield). R_f = 0.61 (petroleum ether : diethyl ether; 2:1); mp 88–89 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.67 (dd, ^2J = 5.0 Hz, ^3J = 9.0 Hz, 1H, CH_2), 1.81 (dd, ^2J = 5.0 Hz, ^3J = 7.6 Hz, 1H, CH_2), 2.70 (ddd, ^3J = 9.0 Hz, ^3J = 7.6 Hz, ^3J = 8.6 Hz, 1H, CH), 3.70 (s, 3H, CH_3O), 3.73 (s, 3H, CH_3O), 5.77 (dd, ^3J = 15.8 Hz, ^3J = 8.6 Hz, 1H, CH=), 6.56 (d, ^3J = 15.8 Hz, 1H, CH=), 7.18–7.24 (m, 4H, CH, Ar); ^{13}C NMR (151 MHz, $CDCl_3$): δ 21.2 (CH_2), 31.4 (CH), 36.0 (C), 52.6 (CH_3O), 52.7 (CH_3O), 125.3 (CH=), 127.3 (2×CH, Ar), 128.7 (2×CH, Ar), 132.5 (CH=), 133.2 (C, Ar), 135.2 (C, Ar), 167.8 (*C*O_2Me), 169.7 (*C*O_2Me); IR (film) 1723 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{15}H_{16}ClO_4$ 295.0732; Found 295.0736. Anal. Calcd for $C_{15}H_{15}ClO_4$: C, 61.13; H, 5.13. Found: C, 61.03; H, 5.30.

Dimethyl 2-[(*E*)-2-(3-chlorophenyl)ethenyl]cyclopropane-1,1-dicarboxylate (1d). General Procedure B: Suspension of NaH (86 mg, 2.15 mmol) and trimethylsulfoxonium iodide (472 mg, 2.15 mmol) in DMF (4.5 mL), 40 min, room temperature. Alkene **4d** (520 mg, 1.85 mmol) in dry DMF (4.5 mL) was added in a single portion at 0 °C. Reaction mixture was stirred for 45 min and allowed to warm up slowly to room temperature. Product **1d** was obtained as yellowish liquid (375 mg, 69% yield). R_f = 0.64 (petroleum ether : diethyl ether; 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.72 (dd, ^2J = 5.0 Hz, ^3J = 8.9 Hz, 1H, CH_2), 1.86 (dd, ^2J = 5.0 Hz, ^3J = 7.6 Hz, 1H, CH_2), 2.75 (ddd, ^3J = 8.9 Hz, ^3J = 8.8 Hz, ^3J = 7.6 Hz, 1H, CH), 3.76 (s, 3H, CH_3O), 3.78 (s, 3H,

CH_3O), 5.84 (dd, ^3J = 15.9 Hz, ^3J = 8.8 Hz, 1H, CH=), 6.59 (d, ^3J = 15.9 Hz, 1H, CH=), 7.16–7.25 (m, 3H, CH, Ar), 7.29 (br.s, Ar, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.2 (CH_2), 31.2 (CH), 36.0 (C), 52.6 (CH_3O), 52.7 (CH_3O), 124.2 (CH), 125.9 (CH), 126.2 (CH), 127.4 (CH), 129.7 (CH), 132.4 (CH), 134.4 (C, Ar), 138.4 (C, Ar), 167.7 (CO_2Me), 169.7 (CO_2Me); IR (film) 1730 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{15}H_{16}ClO_4$ 295.0732. Found 295.0733. Anal. Calcd for $C_{15}H_{15}ClO_4$: C, 61.13; H, 5.13. Found: C, 61.11; H, 5.17.

Dimethyl 2-[(*E*)-2-(2-methoxyphenyl)ethenyl]cyclopropane-1,1-dicarboxylate (1e). General Procedure B. Suspension of NaH (520 mg, 13 mmol) and trimethylsulfoxonium iodide (2.87 g, 13 mmol) in DMF (29 mL), 40 min, room temperature. Alkene **4e** (3.00 g, 10.9 mmol) in dry DMF (30 mL) was added in a single portion at 0 °C. The resulted mixture was stirred for 1 h and allowed to warm up to room temperature. Product **1e** was obtained as yellowish liquid (2.40 g, 76% yield). R_f = 0.53 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.70 (dd, ^2J = 5.0 Hz, ^3J = 9.1 Hz, 1H, CH_2), 1.86 (dd, ^2J = 5.0 Hz, ^3J = 7.6 Hz, 1H, CH_2), 2.78 (ddd, ^3J = 9.1 Hz, ^3J = 8.7 Hz, ^3J = 7.6 Hz, 1H, CH), 3.74 (s, 3H, CH_3O), 3.76 (s, 3H, CH_3O), 3.83 (s, 3H, CH_3O), 5.84 (dd, ^3J = 16.0 Hz, ^3J = 8.7 Hz, 1H, CH=), 6.87 (ddd, ^3J = 8.1 Hz, ^3J = 7.6 Hz, ^4J = 0.7 Hz, 1H, CH, Ar), 6.91 (dd, ^3J = 7.6 Hz, ^4J = 0.7 Hz, 1H, CH, Ar), 6.97 (d, ^3J = 16.0 Hz, 1H, CH=), 7.21 (ddd, ^3J = 8.1 Hz, ^3J = 7.6 Hz, ^4J = 1.7 Hz, 1H, CH, Ar), 7.31 (dd, ^3J = 7.6 Hz, ^4J = 1.7 Hz, 1H, CH, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.3 (CH_2), 32.2 (CH), 36.1 (C), 52.5 (CH_3O), 52.6 (CH_3O), 55.4 (CH_3O), 110.9 (CH), 120.6 (CH), 125.2 (CH), 125.8 (C, Ar), 126.7 (CH), 128.7 (CH), 128.8 (CH), 156.5 (C, Ar), 168.0 (CO_2Me), 170.0 (CO_2Me); IR (film) 1730 cm^{-1}; LC-MS *m/z* 291 $[M + H]^+$. Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.20; H, 6.25. Found: C, 66.23; H, 6.29.

Dimethyl 2-{(*E*)-2-[4-(dimethylamino)phenyl]ethenyl}cyclopropane-1,1-dicarboxylate (1f). General Procedure B. Suspension of NaH (88 mg, 2.20 mmol) and trimethylsulfoxonium iodide (480 mg, 2.18 mmol) in DMSO (12 mL), 40 min, room temperature. Solution of alkene **4f** (600 mg, 2.07 mmol) in dry DMSO (8 mL) was added dropwise. Reaction mixture was stirred for 1 h.

Product **1f** was obtained as yellow liquid (385 mg, 61% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.67 (dd, ^2J = 4.9 Hz, ^3J = 9.2 Hz, 1H, CH_2), 1.85 (dd, ^2J = 4.9 Hz, ^3J = 7.6 Hz, 1H, CH_2), 2.75 (ddd, ^3J = 9.2 Hz, ^3J = 7.6 Hz, ^3J = 8.6 Hz, 1H, CH), 2.94 (s, 6H, 2×NCH_3), 3.72 (s, 3H, CH_3O), 3.76 (s, 3H, CH_3O), 5.60 (dd, ^3J = 15.7 Hz, ^3J = 8.6, 1H, CH=), 6.55 (d, ^3J = 15.7 Hz, 1H, CH=), 6.64–6.65 (br.d, ^3J = 8.8 Hz, 2H, CH, Ar), 7.19–7.21 (br.d, ^3J = 8.8 Hz, 2H, CH, Ar); ^{13}C NMR (151 MHz, $CDCl_3$): δ 21.3 (CH_2), 32.3 (CH), 36.0 (C), 40.4 (2×CH_3), 52.6 (CH_3O), 52.7 (CH_3O), 112.3 (2×CH, Ar), 119.7 (CH=), 125.2 (C), 127.2 (2×CH, Ar), 133.9 (CH=), 150.1 (C, Ar), 168.1 (CO_2Me), 170.1 (CO_2Me); HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{17}H_{22}NO_4$ 304.1544. Found 304.1545. Anal. Calcd for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98; N, 4.62. Found: C, 67.17; H, 7.21; N, 4.54.

Dimethyl 2-[(*E*)-2-(thiophen-2-yl)ethenyl]cyclopropane-1,1-dicarboxylate (1g). General Procedure B. Suspension of NaH (161 mg, 4.03 mmol) and trimethylsulfoxonium iodide (890 mg, 4.05 mmol) in DMF (7.0 mL), 40 min, room temperature. Solution of alkene **4g** (850 mg, 3.37 mmol) in dry DMF (1 mL) was added in a single portion at 0 °C. The resulted mixture was stirred for 15 min at the same temperature. Product **1g** was obtained as yellow oil (682 mg, 76% yield). R_f = 0.53 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.63 (dd, ^2J = 5.0 Hz, ^3J = 9.0 Hz, 1H, CH_2), 1.78 (dd, ^2J = 5.0 Hz, ^3J = 7.6 Hz, 1H, CH_2), 2.65 (ddd, ^3J = 9.0 Hz, ^3J = 8.6 Hz, ^3J = 7.6 Hz, 1H, CH), 3.68 (s, 3H, CH_3O), 3.70 (s, 3H, CH_3O), 5.63 (dd, ^3J = 15.7 Hz, ^3J = 8.6 Hz, 1H, CH=), 6.69 (d, ^3J = 15.7 Hz, 1H, CH=), 6.86 (d, ^3J = 3.5 Hz, 1H, Th), 6.88 (dd, ^3J = 5.0 Hz, ^3J = 3.5 Hz, 1H, Th), 7.06 (d, ^3J = 5.0 Hz, 1H, Th); ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.0 ($^1J_{CH}$ = 166 Hz, CH_2), 31.2 ($^1J_{CH}$ = 166 Hz, CH), 36.0 (C), 52.5 ($^1J_{CH}$ = 148 Hz, CH_3O), 52.6 ($^1J_{CH}$ = 148 Hz, CH_3O), 124.1 (2×CH), 125.4 ($^1J_{CH}$ = 167 Hz, CH), 126.8 ($^1J_{CH}$ = 156 Hz, CH), 127.4 ($^1J_{CH}$ = 168 Hz, CH), 141.7 (C, Th), 167.7 (CO_2Me), 169.7 (CO_2Me); IR (Nujol) 1740, 1680 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{13}H_{15}O_4S$ 267.0686; Found 267.0689. Anal. Calcd for $C_{13}H_{14}O_4S$: C, 58.63; H, 5.30; S, 12.04. Found: C, 58.39; H, 5.05; S, 12.14.

Dimethyl 2-[(*E*)-2-(furan-2-yl)ethenyl]cyclopropane-1,1-dicarboxylate (1h). General Procedure B. Suspension of NaH (407 mg, 10.2 mmol) and trimethylsulfoxonium iodide (2.24 g, 10.2 mmol) in DMF (25 mL), 40 min, room temperature. Solution of alkene **4h** (2.0 g, 8.5 mmol) in dry DMF (2 mL) was added in a single portion at 0 °C. Reaction mixture was stirred at 0 °C for 45 min. Product **1h** was obtained as orange oil (1.80 g, 85% yield). R_f = 0.76 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.69 (dd, ^2J = 5.0 Hz, ^3J = 9.1 Hz, 1H, CH_2), 1.83 (dd, ^2J = 5.0 Hz, ^3J = 7.5 Hz, 1H, CH_2), 2.69 (ddd, ^3J = 9.1 Hz, ^3J = 8.9 Hz, ^3J = 7.5 Hz, 1H, CH), 3.75 (s, 3H, CH_3O), 3.76 (s, 3H, CH_3O), 5.75 (dd, ^3J = 15.7 Hz, ^3J = 8.9 Hz, 1H, CH=), 6.19 (d, ^3J = 3.3 Hz, 1H, Fu), 6.34 (dd, ^3J = 3.3 Hz, ^3J = 1.8 Hz, 1H, Fu), 6.43 (d, ^3J = 15.7 Hz, 1H, CH=), 7.30 (d, ^3J = 1.8 Hz, 1H, Fu); ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.3 (CH_2), 31.5 (CH), 36.2 (C), 52.6 (CH_3O), 52.7 (CH_3O), 107.7 (CH), 111.2 (CH), 122.0 (CH), 123.1 (CH), 141.9 (CH), 152.2 (C, Fu), 167.7 (CO_2Me), 169.9 (CO_2Me); IR (Nujol) 1730 cm^{-1}; LC-MS *m/z* 251 $[M + H]^+$. Anal. Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.32; H, 5.75.

Dimethyl 2-[(*E*)-1-phenylprop-1-en-2-yl]cyclopropane-1,1-dicarboxylate (1i). General Procedure B. Suspension of NaH (895 mg, 22.4 mmol) and trimethylsulfoxonium iodide (4.92 g, 22.4 mmol) in DMF (47 mL), 40 min, room temperature. Solution of alkene **4i** (4.85g, 18.7 mmol) in dry DMF (2 mL) was added dropwise at 0 °C. Reaction mixture was stirred at 0 °C for 45 min. Product **1i** was obtained as orange oil (4.19 g, 82% yield). R_f = 0.73 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.58 (dd, ^2J = 5.1 Hz, ^3J = 8.9 Hz, 1H, CH_2), 1.94 (s, 3H, CH_3), 2.09 (dd, ^2J = 5.1 Hz, ^3J = 8.1 Hz, 1H, CH_2), 2.73 (dd, ^3J = 8.9 Hz, ^3J = 8.1 Hz, 1H, CH), 3.68 (s, 3H, CH_3O), 3.79 (s, 3H, CH_3O), 6.32 (br. s, 1H, CH=), 7.18–7.24 (m, 3H, CH, Ar), 7.28–7.35 (m, 2H, CH, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 18.58 (CH_3), 18.60 (CH_2), 36.4 (C), 36.6 (CH), 52.5 (CH_3O), 52.8 (CH_3O), 126.6 (CH), 127.6 (CH), 128.2 (2×CH, Ar), 128.9 (2×CH, Ar), 131.9 (C), 137.4 (C), 167.5 (CO_2Me), 170.6 (CO_2Me); HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{16}H_{19}O_4$ 275.1278; Found 275.1279. Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 70.26; H, 6.50.

Dimethyl 2-[(*E*)-1-(4-fluorophenyl)prop-1-en-2-yl]cyclopropane-1,1-dicarboxylate (1j). General Procedure B. Suspension of NaH (145 mg, 3.6 mmol) and trimethylsulfoxonium iodide (798 mg, 3.6 mmol) in DMSO (7 mL), 40 min, room temperature. Solution of alkene **4j** (835 mg, 3.0 mmol) in DMSO (6 mL) was added portionwise. Reaction mixture was stirred for additional 1.5 h. Product **1j** was obtainied as colorless oil (570 mg, 65% yield). R_f = 0.47 (petroleum ether : diethyl ether; 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.58 (dd, ^2J = 5.2 Hz, ^3J = 8.9 Hz, 1H, CH_2), 1.90 (s, 3H, CH_3), 2.08 (dd, ^2J = 5.2 Hz, ^3J = 8.1 Hz, 1H, CH_2), 2.71 (dd, ^3J = 8.9 Hz, ^3J = 8.1 Hz, 1H, CH), 3.68 (s, 3H, CH_3O), 3.79 (s, 3H, CH_3O), 6.26 (br. s, 1H, CH=), 6.99–7.03 (m, 2H, CH, Ar), 7.14 (dd, ^3J = 8.7 Hz, $^4J_{HF}$ = 5.5 Hz, 2H, CH, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 18.40 (CH_3), 18.44 (CH_2), 36.2 (C), 36.3 (CH), 52.4 (CH_3O), 52.7 (CH_3O), 115.0 (d, $^2J_{CF}$ = 21 Hz, 2×CH, Ar), 126.5 (CH=), 130.4 (d, $^3J_{CF}$ = 8 Hz, 2×CH, Ar), 131.9 (C), 133.3 (d, $^4J_{CF}$ = 3 Hz, C, Ar), 161.3 (d, $^1J_{CF}$ = 246 Hz, C, Ar), 167.4 (CO_2Me), 170.5 (CO_2Me); IR (film) 1730 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* $[M + Na]^+$ Calcd for $C_{16}H_{17}FNaO_4$ 315.1004; Found 315.1005. Anal. Calcd for $C_{16}H_{17}FO_4$: C, 65.74; H, 5.86. Found: C, 65.77; H, 6.02.

Dimethyl 2-[3-phenyl-1-(thiophen-2-yl)prop-1-en-2-yl]cyclopropane-1,1-dicarboxylate (1k). General Procedure B. Suspension of NaH (154 mg, 3.9 mmol) and trimethylsulfoxonium iodide (0.85 g, 3.9 mmol) in DMF (8 mL), 40 min, room temperature. Solution of alkene **4k** (1.10 g, 3.2 mmol) was added in a single portion at 0 °C. Reaction mixture was stirred for 45 min at 0 °C. Product **1k** was obtained as yellow liquid (811 mg, 70% yield); ratio of ***Z***:***E*** isomers = 65:35 (**A**:**B**). R_f = 0.58 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.55 (dd, ^2J = 5.2 Hz, ^3J = 8.9 Hz, 1H, CH_2, **A**), 1.63 (dd, ^2J = 5.2 Hz, ^3J = 9.5 Hz, 1H, CH_2, **B**), 2.06 (dd, ^2J = 5.2 Hz, ^3J = 8.5 Hz, 1H, CH_2, **B**), 2.09 (dd, ^2J = 5.2 Hz, ^3J = 8.2 Hz, 1H, CH_2, **A**), 2.64 (dd, ^3J = 8.9 Hz, ^3J = 8.2 Hz, 1H, CH, **A**), 2.99 (dd, ^3J = 9.5 Hz, ^3J = 8.5 Hz, 1H, CH, **B**), 3.45 (AB-system, ^2J = 16.2 Hz, 2H, CH_2Ph, **B**), 3.59 (d, ^2J = 16.2 Hz, 1H, CH_2Ph, **A**), 3.66 (s, 3H, CH_3O, **B**), 3.70 (s, 3H, CH_3O, **A**), 3.74 (s, 3H, CH_3O, **A**), 3.83 (s, 3H, CH_3O, **B**), 4.18 (d, ^2J = 16.2 Hz, 1H, CH_2Ph, **A**), 6.56 (br.s, 1H, CH=, **A**), 6.69 (br.s, 1H, CH=, **B**), 7.00–7.06 (m, 2H+2H, CH,

Ar, **A**, **B**), 7.24–7.36 (m, 6H+6H, CH, Ar, **A**, **B)**; ^{13}C NMR (126 MHz, $CDCl_3$): δ 18.7 (CH_2, **A**), 21.5 (CH_2, **B**), 31.0 (CH, **B**), 34.4 (CH, **A**), 36.2 (C, **B**), 36.7 (C, **A**), 38.1 (CH_2Ph, **A**), 43.1 (CH_2Ph, **B**), 52.5 (CH_3O+CH_3O, **A**, **B**), 52.57 (CH_3O, **A**), 52.60 (CH_3O, **B**), 121.6 (CH, **A**), 125.2 (CH, **A**), 125.8 (CH, **B**), 126.29 (CH, **B**), 126.33 (CH, **A**), 126.5 (CH, **B**), 126.7 (CH, **B**), 126.9 (CH, **A**), 127.5 (CH, **B**), 127.7 (CH, **A**), 128.4 (2×CH, **B**), 128.5 (2×CH, **A**), 128.7 (2×CH, **A**), 129.0 (2×CH, **B**), 131.9 (C, **B**), 132.8 (C, **A**), 138.0 (C, **A**), 138.9 (C, **B**), 139.2 (C, **A**), 139.5 (C, **B**), 167.2 (*C*O_2Me, **A**), 167.6 (*C*O_2Me, **B**), 169.9 (*C*O_2Me, **A**), 170.0 (*C*O_2Me, **B**); IR (film) 1727 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{20}H_{21}O_4S$ 357.1155; Found 357.1159. Anal. Calcd for $C_{20}H_{20}O_4S$: C, 67.39; H, 5.66. Found: C, 67.35; H, 5.71.

Dimethyl 2-[(*E*)-2-(2-nitrophenyl)ethenyl]cyclopropane-1,1-dicarboxylate (1l). Suspension of NaH (49 mg, 1.23 mmol) and trimethylsulfoxonium iodide (272 mg, 1.24 mmol) in DMF (2 mL) was stirred at room temperature for 40 min. The formed ylide was added dropwise to the solution of alkene **4l** (300 mg, 1.03 mmol) in dry DMF (2 mL). (Beware! This order of reactants addition is crucial for the synthesis of **1l**. When alkene **4l** was added to the ylide solution, product was formed in trace amounts only.) The reaction mixture was stirred for 20 min at 0 °C. Product **1l** was obtained as yellow solid (182 mg, 58% yield). Mp 93–94 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.75 (dd, ^2J = 5.0 Hz, ^3J = 8.9 Hz, 1H, CH_2), 1.87 (dd, ^2J = 5.0 Hz, ^3J = 7.5 Hz, 1H, CH_2), 2.80 (ddd, ^3J = 8.9 Hz, ^3J = 8.7 Hz, ^3J = 7.5 Hz, 1H, CH), 3.73 (s, 3H, CH_3O), 3.74 (s, 3H, CH_3O), 5.86 (dd, ^3J = 15.7 Hz, ^3J = 8.7 Hz, 1H, CH=), 7.14 (d, ^3J = 15.7 Hz, 1H, CH=), 7.39 (ddd, ^3J = 8.8 Hz, ^3J = 8.2 Hz, ^4J = 1.3 Hz, 1H, Ar), 7.47 (dd, ^3J = 7.9 Hz, ^4J = 1.3 Hz, 1H, Ar), 7.54 (ddd, ^3J = 8.8 Hz, ^3J = 7.9 Hz, ^4J = 1.0 Hz, 1H, Ar), 7.92 (dd, ^3J = 8.2 Hz, ^4J = 1.0 Hz, 1H, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.3 (CH_2), 31.1 (CH), 36.1 (C), 52.7 (CH_3O), 52.8 (CH_3O), 124.5 (CH), 128.1 (CH), 128.5 (CH), 128.8 (CH), 130.5 (CH), 132.2 (C, Ar), 133.0 (CH), 147.5 (C, Ar), 167.8 (*C*O_2Me), 169.5 (*C*O_2Me); HRMS (ESI/Q-TOF) *m/z* $[M + Na]^+$ Calcd for $C_{15}H_{15}NNaO_6$ 328.0792; Found 328.0796. Anal. Calcd for $C_{15}H_{15}NO_6$: C, 59.02; H, 4.95; N, 4.59. Found: C, 58.79; H, 5.05; N, 4.41.

Dimethyl 3,3-dideuterio-2-[(*E*)-2-(2-nitrophenyl)ethenyl]cyclopropane-1,1-dicarboxylate (1l-d_2) was synthesized by the same procedure from alkene **4l** (292 mg, 1.0 mmol) and $(CD_3)_3SOI$ (254 mg, 1.16 mmol). Product **1l**-d_2 was obtained as yellow solid (176 mg, 58%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.80 (d, ^3J = 8.9 Hz, 1H, CH), 3.78 (s, 3H, CH_3O), 3.79 (s, 3H, CH_3O), 5.86 (dd, ^3J = 15.6 Hz, ^3J = 8.7 Hz, 1H, CH=), 7.15 (d, ^3J = 15.6 Hz, 1H, CH=), 7.40 (ddd, ^3J = 8.5 Hz, ^3J = 8.0 Hz, ^4J = 1.4 Hz, 1H, Ar), 7.47 (dd, ^3J = 8.0 Hz, ^4J = 1.4 Hz, 1H, Ar), 7.54 (ddd, ^3J = 8.5 Hz, ^3J = 8.0 Hz, ^4J = 1.4 Hz, 1H, Ar), 7.92 (dd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, 1H, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 20.9 (CD_2), 31.1 (CH), 36.1 (C), 52.7 (CH_3O), 52.8 (CH_3O), 124.5 (CH), 128.1 (CH), 128.5 (CH), 128.8 (CH), 130.5 (CH), 132.2 (C, Ar), 133.0 (CH), 147.5 (C, Ar), 167.8 (CO_2Me), 169.5 (CO_2Me).

Methyl 1-(dimethoxyphosphoryl)-2-[(*E*)-2-(4-methoxyphenyl)ethenyl]cyclopropanecarboxylate (1n). General Procedure B. Suspension of NaH (44 mg, 1.1 mmol) and trimethylsulfoxonium iodide (242 mg, 1.1 mmol) in DMF (2 mL), 40 min, room temperature. Solution of (2*E*,4*E*)-**4n** (300 mg, 0.92 mmol) was added in a single portion at 0 °C. The resulted mixture was stirred for 45 min at 0 °C. According to ^{1}H NMR data for the reaction mixture, product **1n** was formed as a diastereomeric mixture in 56:44 ratio. After purification by column chromatography cyclopropanes (**1*R**,2*S**)-1n** (117 mg, 37% yield) and (**1*R**,2*R**)-1n** (93 mg, 30% yield) were isolated. The same mixture was also obtained from (2*Z*,4*E*)-**4n**.

(**1*R**,2*S**)-1n** was obtained as yellow liquid. R_f = 0.45 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.75–1.83 (m, 1H, CH_2), 1.80–1.87 (m, 1H, CH_2), 2.57–2.65 (m, 1H, CH), 3.71 (s, 3H, CH_3O), 3.74 (s, 3H, CH_3O), 3.77 (d, $^3J_{PH}$ = 11.0 Hz, 3H, (CH_3O)P), 3.78 (d, $^3J_{PH}$ = 11.3 Hz, 3H, (CH_3O)P), 5.80 (dd, ^3J = 15.9 Hz, ^3J = 9.2 Hz, 1H, CH=), 6.59 (d, ^3J = 15.9 Hz, 1H, CH=), 6.78 (br.d, ^3J = 8.5 Hz, 2H, CH, Ar), 7.21 (br.d, ^3J = 8.5 Hz, 2H, CH, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 19.2 (d, $^2J_{PC}$ = 3 Hz, CH_2), 26.8 (d, $^1J_{PC}$ = 189 Hz, C), 30.5 (d, $^2J_{PC}$ = 2 Hz, CH), 52.7 (CH_3O), 53.3 (d, $^2J_{PC}$ = 6 Hz, (CH_3O)P), 53.5 (d, $^2J_{PC}$ = 6 Hz, (CH_3O)P), 55.2 (CH_3O), 114.0 (2×CH, Ar), 121.7 (d, $^3J_{PC}$ = 1 Hz, CH=), 127.3 (2×CH, Ar), 129.4 (C, Ar),

133.8 (CH=), 159.3 (C, Ar), 168.0 (d, $^{2}J_{PC}$ = 7 Hz, *C*O_2Me); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 24.6–25.1 (m); IR (film) 1726, 1250 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* = $[M + H]^+$ Calcd for $C_{16}H_{22}O_6P$ 341.1149; Found 341.1150. Anal. Calcd for $C_{16}H_{21}O_6P$: C, 56.47; H, 6.22. Found: C, 56.27; H, 6.32.

(1*R,2*R**)-1n** was obtained as yellow liquid. R_f = 0.58 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.79 (ddd, ^{2}J = 4.6 Hz, $^{3}J_{PH}$ = 14.3 Hz, ^{3}J = 7.6 Hz, 1H, CH_2), 1.95 (dd, ^{2}J = 4.6 Hz, ^{3}J = 8.9 Hz, $^{3}J_{PH}$ = 7.7 Hz, 1H, CH_2), 2.43–2.50 (m, 1H, CH), 3.67 (d, $^{3}J_{PH}$ = 11.3 Hz, 3H, (CH_3O)P), 3.70 (s, 3H, CH_3O), 3.72 (s, 3H, CH_3O), 3.73 (d, $^{3}J_{PH}$ = 11.3 Hz, 3H, (CH_3O)P), 6.26 (dd, ^{3}J = 15.9 Hz, ^{3}J = 9.5 Hz, 1H, CH=), 6.57 (d, ^{3}J = 15.9 Hz, 1H, CH=), 6.77 (br.d, ^{3}J = 8.9 Hz, 2H, CH, Ar), 7.25 (br.d, ^{3}J = 8.9 Hz, 2H, CH, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.2 (CH_2), 27.0 (d, $^{1}J_{PC}$ = 195 Hz, C), 33.9 (d, $^{2}J_{PC}$ = 3 Hz, CH), 52.7 (CH_3O), 52.9 (d, $^{2}J_{PC}$ = 6 Hz, $(CH_3O)_2$P), 53.4 (d, $^{2}J_{PC}$ = 6 Hz, $(CH_3O)_2$P), 55.2 (CH_3O), 114.0 (2×CH, Ar), 124.0 (d, $^{3}J_{PC}$ = 4 Hz, CH=), 127.3 (2×CH, Ar), 129.6 (C, Ar), 133.3 (CH=), 159.2 (C, Ar), 169.9 (d, $^{2}J_{PC}$ = 7 Hz, *C*O_2Me); ^{31}P NMR (202.5 MHz, $CDCl_3$,): δ = 24.9–25.3 (m); IR (film) 1724, 1254 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{16}H_{22}O_6P$ 341.1149; Found 341.1151. Anal. Calcd for $C_{16}H_{21}O_6P$: C, 56.47; H, 6.22. Found: C, 56.24; H, 6.37.

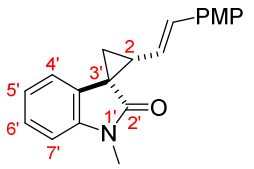
Methyl (1*R,2*S**)-1-cyano-2-[(*E*)-2-phenylethenyl]cyclopropane-1-carboxylate (1o)**. General Procedure B. Suspension of NaH (43 mg, 1.07 mmol) and trimethylsulfoxonium iodide (240 mg, 1.09 mmol) in DMF (2 mL), 40 min, room temperature. Solution of alkene **4o** (211 mg, 0.99 mmol) in dry DMF (0.5 mL) was added in a single portion at 0 °C. The resulted mixture was stirred for 15 min at 0 °C. According to ^{1}H NMR data for the reaction mixture, product **1o** was formed as a diastereomeric mixture in 65:35 ratio. After purification by column chromatography cyclopropane **(1*R**,2*S**)-1o** was isolated as colorless oil (146 mg, 65% yield). R_f = 0.62 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.79 (dd, ^{2}J = 5.1 Hz, ^{3}J = 7.9 Hz, 1H, CH_2), 2.11 (dd, ^{2}J = 5.1 Hz, ^{3}J = 8.9 Hz, 1H, CH_2), 2.74 (ddd, ^{3}J = 8.9 Hz, ^{3}J = 8.7 Hz, ^{3}J = 7.9 Hz, 1H, CH), 3.88 (s, 3H, CH_3O), 5.97 (dd, ^{3}J = 15.7 Hz, ^{3}J = 8.7 Hz, 1H, CH=),

6.79 (d, ^3J = 15.7 Hz, 1H, CH=), 7.27–7.42 (m, 5H, CH, Ph); ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.2 (CH_2), 24.5 (CH), 34.2 (C), 53.5 (CH_3O), 116.7 (CN), 123.2 (CH), 126.4 (2×CH, Ar), 128.2 (CH, Ar), 128.6 (2×CH, Ar), 135.8 (C, Ar), 135.9 (CH), 167.6 (CO_2Me); IR (KBr) 2245, 1740 cm^{-1}; LC-MS *m/z* 228 $[M + H]^+$; HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{14}H_{14}NO_2$ 228.1019; Found 228.1020. Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.91; H, 5.69; N, 6.18.

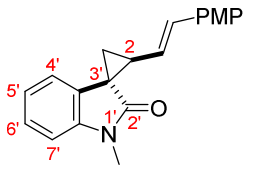
Methyl (1*R,2*S**)-1-cyano-2-[(*E*)-2-(4-methoxyphenyl)ethenyl)cyclopropane-1-carboxylate (1p)**. General Procedure B. Suspension of NaH (104 mg, 2.60 mmol) and trimethylsulfoxonium iodide (624 mg, 2.84 mmol) in DMF (6.0 mL), 40 min, room temperature. The mixture was ice-cooled to 0 °C and a solution of alkene **4p** (575 mg, 2.36 mmol) in dry DMF (3 mL) was added in a single portion. The resulting mixture was stirred for 15 min. Cyclopropane **1q** was isolated by column chromatography as a mixture of two isomers **1*R**,2*S****:**1*R**,2*R**** in a ratio of 94:6; yellow oil (430 mg, 71%). R_f = 0.77 (petroleum ether : ethyl acetate; 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) for major isomer: δ 1.76 (dd, ^2J = 5.2 Hz, ^3J = 7.6 Hz, 1H, CH_2), 2.08 (dd, ^2J = 5.2 Hz, ^3J = 8.2 Hz, 1H, CH_2), 2.72 (ddd, ^3J = 8.5 Hz, ^3J = 8.2 Hz, ^3J = 7.6 Hz, 1H, CH), 3.81 (s, 3H, CH_3O), 3.84 (s, 3H, CH_3O), 5.82 (dd, ^3J = 15.6 Hz, ^3J = 8.5 Hz, 1H, CH=), 6.71 (d, ^3J = 15.6 Hz, 1H, CH=), 6.87 (br. d, ^3J = 8.5 Hz, 2H, Ar), 7.33 (br. d, ^3J = 8.5 Hz, 2H, Ar); ^{13}C NMR (126 MHz, $CDCl_3$) for major isomer: δ 21.2 (CH_2), 24.5 (CH), 34.6 (C), 53.5 (CH_3O), 55.2 (CH_3O), 114.0 (2×CH, Ar), 116.8 (CN), 120.8 (CH=), 127.6 (2×CH, Ar), 128.6 (C, Ar), 135.3 (CH=), 159.6 (C, Ar), 167.6 (CO_2Me); IR (Nujol) 2244, 1737 cm^{-1}; GC-MS (EI, 70 eV) *m/z* (%) 257 (84) $[M]^+$, 256 (18), 230 (19), 225 (19), 224 (34), 198 (91), 197 (100), 196 (36), 183 (58), 182 (42), 171 (41), 146 (26), 131 (26), 127 (27), 115 (28), 103 (18), 63 (17). Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 70.29; H, 5.58; N, 5.28.

(*E*)-2-[2-(4-Methoxyphenyl)ethenyl]-1'-methylspiro[cyclopropane-1,3'-indolin]-2'-one (1q). General Procedure B. Suspension of NaH (70 mg, 1.75 mmol) and trimethylsulfoxonium iodide (385 mg, 1.75 mmol) in DMF (4.5 mL), 40 min, room temperature. The mixture was ice-cooled

to 0 °C and a solution of alkene **4q** (432 mg, 1.48 mmol) in DMF (1 mL) was added dropwise. The resulting mixture was stirred for 1 h 40 min and allowed to warm up to room temperature. According to ^{1}H NMR data, the ratio of diastereomers in the reaction mixture was 54:46. After purification by column chromatography cyclopropanes (**1*R***,2*R***)-1q** (119 mg, 27%) and (**1*R***,2*S***)-1q** (101 mg, 22%) were isolated.



(**1*R***,2*R***)-1q**; yellowish oil; R_f = 0.50 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.02 (dd, ^2J =4.9 Hz, ^3J = 8.9 Hz, 1H, CH_2), 2.09 (dd, ^2J = 4.9 Hz, ^3J =7.9 Hz, 1H, CH_2), 2.65 (ddd, ^3J = 9.2 Hz, ^3J = 8.9 Hz, ^3J = 7.9 Hz, 1H, CH), 3.29 (s, 3H, CH_3N), 3.81 (s, 3H, CH_3O), 6.53 (d, ^3J = 15.7 Hz, 1H, CH=), 6.60 (dd, ^3J = 15.7 Hz, ^3J = 9.2 Hz, 1H, CH=), 6.85 (d, ^3J = 8.5 Hz, 2H, Ar), 6.89 (br. d, ^3J = 7.9 Hz, 1H, H$^{7'}$), 6.90 (br. d, ^3J = 7.6 Hz, 1H, H$^{4'}$), 7.06–7.09 (m, 1H, Ar), 7.26–7.29 (m, 1H, Ar), 7.34 (d, ^3J = 8.5 Hz, 2H, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 24.9 (CH_2), 26.4 (NMe), 34.1 (C), 37.4 (CH), 55.2 (CH_3O), 107.8 (CH), 113.9 (2×CH), 117.8 (CH), 121.9 (CH), 123.8 (CH=), 126.7 (CH), 127.3 (2×CH), 129.9 (C), 130.3 (C), 131.2 (CH=), 143.3 (C), 158.9 (C), 174.6 (CO); IR (film) 1711 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* [M + H]$^+$ Calcd for $C_{20}H_{20}NO_2$ 306.1489; Found 306.1492. Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27. Found: C, 78.29; H, 6.07.



(**1*R***,2*S***)-1q**; yellowish oil; R_f = 0.36 (petroleum ether:ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.80 (dd, ^2J =4.6 Hz, ^3J = 7.6 Hz, 1H, CH_2), 2.17 (dd, ^2J = 4.6 Hz, ^3J =8.9 Hz, 1H, CH_2), 2.80 (ddd, ^3J = 8.9 Hz, ^3J = 7.9 Hz, ^3J = 7.6 Hz, 1H, CH), 3.32 (s, 3H, CH_3N), 3.81 (s, 3H, CH_3O), 6.10 (dd, ^3J = 15.9 Hz, ^3J = 7.9 Hz, 1H, CH=), 6.63 (d, ^3J = 15.9 Hz, 1H, CH=), 6.86 (d, ^3J = 8.5 Hz, 2H, Ar), 6.92 (br. d, ^3J = 7.9 Hz, 1H, H$^{7'}$), 7.01–7.05 (m, 2H, H$^{4'}$, H$^{5'}$), 7.26–7.29 (m, 1H, H$^{6'}$), 7.30 (br. d, ^3J = 8.5 Hz, 2H, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 23.4 (CH_2), 26.5 (NMe), 33.9 (C), 35.4 (CH), 55.2 (CH_3O), 108.0 (C(7′)H), 113.9 (2×CH), 120.7 (C(4′)H), 121.6 (C(5′)H), 122.9 (CH=), 126.6 (C(6′)H), 127.2 (2×CH), 127.5 (C(3′a)), 129.5 (C), 133.2 (CH=), 144.0 (C(7′a)), 159.2

(C), 176.0 (C(2′)); HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{20}H_{20}NO_2$ 306.1489; Found 306.1490.

(*E*)-2-(2-Phenylethenyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (1r). To a stirred suspension of NaH (93 mg, 2.32 mmol) in dry DMF (10 mL) trimethylsulfoxonium iodide (535 mg, 2.43 mmol) was added in a single portion under argon atmosphere at room temperature. Vigorous evolution of hydrogen lasted *ca.* 10 min, after which the reaction mixture was stirred for additional 25 min. Then the resulting solution was added dropwise to the solution of alkene **4r** (576 mg, 2.1 mmol) in DMF (4 mL) at 0 °C. The resulting solution was stirred for 20 min at 0 °C, poured into cold ammonium chloride solution (10 mL) and extracted with ethyl acetate (5×5 mL). The combined organic fractions were washed with water (6×5 mL), dried with Na_2SO_4 and concentrated *in vacuo*. Cyclopropane **1r** was isolated by column chromatography as yellow solid (0.479 g, yield 88%). Mp 110–111 °C; R_f = 0.62 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.13 (dd, ^2J =4.0 Hz, ^3J = 7.6 Hz, 1H, CH_2), 2.25 (dd, ^2J = 4.0 Hz, ^3J = 8.5 Hz, 1H, CH_2), 3.01 (ddd, ^3J = 9.6 Hz, ^3J = 8.5 Hz, ^3J = 7.6 Hz, 1H, CH), 6.47 (dd, ^3J = 15.7 Hz, ^3J = 9.6 Hz, 1H, CH=), 6.62 (d, ^3J = 15.7 Hz, 1H, CH=), 7.20–7.45 (m, 5H, CH, Ar), 7.73–7.80 (m, 2H, CH, Ar), 7.78–7.98 (m, 2H, CH, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 24.8 (CH_2), 40.5 (CH), 42.8 (C), 122.3 (2×CH), 124.7 (CH), 126.2 (2×CH), 127.6 (CH), 128.5 (2×CH, Ar), 133.5 (CH), 134.6 (CH), 134.7 (CH), 136.5 (C, Ar), 141.7 (C, Ar), 142.4 (C, Ar), 196.9 (CO), 197.6 (CO); IR (KBr) 1735, 1705 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{19}H_{15}O_2$ 275.1067; Found 275.1067. Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 83.17; H, 5.16.

General procedure C (vinylcyclopropane – cyclopentene rearrangement). Lewis acid ($GaCl_3$, $AlCl_3$, $Ni(ClO_4)_2$, $Sc(OTf)_3$, 1M solution of $SnCl_4$ in CH_2Cl_2) was added to 0.07 M solution of cyclopropane **1** in CH_2Cl_2 (or $C_2H_4Cl_2$) and molecular sieves 4 Å at the specified temperature under argon atmosphere. Then the reaction mixture was stirred for the specified time

at room temperature or under reflux and quenched in accordance with one of three procedures given below.

Procedure **C1**. The reaction mixture was poured into saturated aqueous $NaHCO_3$ solution (20 mL) and extracted with CH_2Cl_2 (3×10 mL). The combined organic fractions were washed with aqueous $NaHCO_3$ solution (2×10 mL), with water (2×10 mL) and dried with anhydrous Na_2SO_4. The solvent was evaporated under vacuum. The final residue was purified by column chromatography (SiO_2, eluent – petroleum ether : ethyl acetate) to yield cyclopentene **2.**

Procedure **C2**. The reaction mixture was acidified to pH ca. 3 with 5% aqueous HCl and extracted with CH_2Cl_2 (3×10 mL). The organic layer was washed with water (2×10 mL) and dried with anhydrous Na_2SO_4; the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (SiO_2, eluent – petroleum ether : ethyl acetate, 10:1 to 2:1) to afford cyclopentene **2**.

Procedure **C3**. The mixture was filtered through a pad of silica gel; the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2, eluent – petroleum ether : ethyl acetate, 10:1 to 2:1) to afford cyclopentene **2.**

Dimethyl 2-phenylcyclopent-3-ene-1,1-dicarboxylate (2a).[44] General procedure C2. $GaCl_3$ (88 mg, 0.5 mmol) was added to the solution of **1a** (130 mg, 0.5 mmol) in DCE (7 mL) in a single portion at room temperature. The resulting mixture was stirred for 1 h at room temperature. Product **2a** was obtained as colorless oil (108 mg, 83% yield). R_f = 0.55 (petroleum ether : ethyl acetate; 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.77–2.85 (m, 1H, CH_2), 3.08 (s, 3H, CH_3O), 3.50 (ddd, ^2J = 17.5 Hz, ^3J = 4.4 Hz, ^4J = 2.1 Hz, 1H, CH_2), 3.76 (s, 3H, CH_3O), 4.90 (br.s, 1H, CH), 5.71 (ddd, ^3J = 6.5 Hz, ^3J = 4.4 Hz, ^3J = 2.3 Hz, 1H, CH=), 5.89 (ddd, ^3J = 6.5 Hz, ^3J = 4.4 Hz, ^4J = 2.1 Hz, 1H, CH=), 7.15–7.40 (m, 5H, Ph); ^{13}C NMR (101 MHz, $CDCl_3$): δ 40.4 ($^1J_{CH}$ = 134 Hz, CH_2), 51.7 ($^1J_{CH}$ = 147 Hz, CH_3O), 52.7 ($^1J_{CH}$ = 147 Hz, CH_3O), 57.2 ($^1J_{CH}$ = 136 Hz, CH), 65.0 (C), 127.1 (CH), 127.8 (2×CH), 128.6 (CH), 128.9 (2×CH), 131.9 (CH), 138.8 (C), 169.7 (CO_2Me), 172.5 (CO_2Me); IR (film) 1739, 1603 cm^{-1}; GC-MS (EI, 70 eV) *m*/*z* (%) 260 (20)

$[M]^+$, 228 (9), 201 (12), 200 (100), 197 (16), 172 (19), 169 (16), 168 (21), 157 (10), 142 (15), 141 (73), 139 (11), 128 (10), 115 (20). Anal. Calcd for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20. Found: C, 69.37; H, 6.25.

Compound **2a** was also obtained by General procedure C1 using $SnCl_4$ as an initiator: 1M solution of $SnCl_4$ in CH_2Cl_2 (0.8 mL, 1.1 equiv.) was added to the solution of **1a** (260 mg, 0.7 mmol) in CH_2Cl_2 (10 mL) at room temperature; the reaction mixture was refluxed for 2 h. Product **2a** was obtained in 63% yield (164 mg).

Dimethyl 2-(4-methoxyphenyl)cyclopent-3-ene-1,1-dicarboxylate (2b).[14a] General procedure C1. 1M solution of $SnCl_4$ in CH_2Cl_2 (0.55 mL, 1.1 equiv.) was added to the solution of **1b** (145 mg, 0.5 mmol) in CH_2Cl_2 (6.5 mL) at room temperature; the reaction mixture was refluxed for 1.5 h. Product **2b** was obtained as colorless crystals (126 mg, 87% yield). Mp 73–74 °C (lit: 68–70 °C[14a]); R_f = 0.71 (petroleum ether : ethyl acetate; 4:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.77 (dddd, ^2J = 17.7 Hz, ^3J = 2.5 Hz, ^4J = 2.0 Hz, ^4J = 1.0 Hz, 1H, H^a-5), 3.16 (s, 3H, CH_3O), 3.46 (ddd, ^2J = 17.7 Hz, ^3J = 4.3 Hz, ^4J = 2.2 Hz, 1H, H^b-5), 3.76 (s, 3H, CH_3O), 3.77 (s, 3H, CH_3O), 4.84 (br.s, 1H, CH), 5.68–5.70 (m, 1H, CH=), 5.84–5.86 (m, 1H, CH=), 6.80 (d, ^3J = 8.8 Hz, 2H, Ar), 7.10 (d, ^3J = 8.8 Hz, 2H, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 40.2 (CH_2), 51.8 (CH_3O), 52.7 (CH_3O), 55.1 (CH_3O), 56.2 (CH), 64.9 (C), 113.2 (2×CH), 128.3 (CH), 129.9 (2×CH), 130.6 (C), 132.2 (CH), 158.7 (C), 169.9 (*C*O_2Me), 172.6 (*C*O_2Me); IR (KBr) 1730, 1610 cm^{-1}; GC-MS (EI, 70 eV) *m*/*z* (%) 290 (20) $[M]^+$, 231 (13), 230 (100), 227 (11), 199 (12), 198 (16), 171 (39), 128 (10), 127 (6). Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25. Found: C, 65.91; H, 6.15.

Compound **2b** was also prepared using following procedures.

General procedure C2. $Ni(ClO_4)_2 \cdot 6H_2O$ (44 mg, 0.12 mmol) was added to the solution of **1b** (174 mg, 0.6 mmol) in CH_2Cl_2 (9 mL) in a single portion at room temperature. The resulting mixture was stirred for 4 h at room temperature. Product **2b** was obtained in 95% yield (165 mg).

General procedure C3. $Sc(OTf)_3$ (25 mg, 0.05 mmol) was added to the solution of **1b** (145 mg, 0.5 mmol) in CH_2Cl_2 (7 mL) in a single portion at room temperature. The resulting mixture was stirred for 4 h at room temperature. Product **2b** was obtained in 91% yield (132 mg).

Dimethyl 2-(4-chlorophenyl)cyclopent-3-ene-1,1-dicarboxylate (2c). General procedure C2. $GaCl_3$ (88 mg, 0.5 mmol)was added to the solution of **1c** (147 mg, 0.05 mmol) in DCE (7 mL) in a single portion at room temperature. The resulting mixture was stirred for 1 h at room temperature. Product **2c** was obtained as colorless oil (137 mg, 93% yield). R_f = 0.64 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.79 (dddd, ^2J = 17.6 Hz, ^3J = 2.1 Hz, ^4J = 3.2 Hz, ^4J = 1.2 Hz, 1H, H^a-5), 3.15 (s, 3H, CH_3O), 3.45 (ddd, ^2J = 17.6 Hz, ^3J = 4.5 Hz, ^4J = 2.4 Hz, 1H, H^b-5), 3.76 (s, 3H, CH_3O), 4.86–4.87 (m, 1H, H-2), 5.66 (ddd, ^3J = 6.4 Hz, ^3J = 4.5 Hz, ^3J = 2.1 Hz, 1H, H-4), 5.87–5.89 (ddd, ^3J = 6.4 Hz, ^3J = 4.4 Hz, ^4J = 2.4 Hz, 1H, H-3), 7.12 (br.d, ^3J = 8.5 Hz, 2H, Ar), 7.22 (br.d, ^3J = 8.5 Hz, 2H, Ar); ^{13}C NMR (151 MHz, $CDCl_3$): δ 40.5 (CH_2), 52.0 (CH_3O), 53.0 (CH_3O), 56.3 (CH), 65.0 (C), 128.1 (2×CH), 129.3 (CH), 130.0 (2×CH), 131.6 (CH), 133.1 (C), 137.5 (C), 169.7 (CO_2Me), 172.4 (CO_2Me); IR (film) 1736, 1696, 1595 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* [M + H]$^+$ Calcd for $C_{15}H_{15}ClO_4$ 295.0732; Found 295.0747. Anal. Calcd for $C_{15}H_{15}ClO_4$: C, 61.13; H, 5.13. Found: C, 61.07; H, 5.15.

Dimethyl 2-(3-chlorophenyl)cyclopent-3-ene-1,1-dicarboxylate (2d). General procedure C2. $GaCl_3$ (107 mg, 0.61 mmol) was added to the solution of **1d** (180 mg, 0.61 mmol) in DCE (9 mL) in a single portion at room temperature. The resulting mixture was stirred for 1 h at room temperature. Product **2d** was obtained as white solid (155 mg, 86% yield). Mp 77–78 °C; R_f = 0.45 (petroleum ether : diethyl ether; 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.82 (dddd, ^2J = 17.6 Hz, ^3J = 2.4 Hz, ^4J = 2.1 Hz, ^4J = 1.3 Hz, 1H, H^a-5), 3.19 (s, 3H, CH_3O), 3.48 (ddd, ^2J = 17.6 Hz, ^3J = 4.4 Hz, ^4J = 2.4 Hz, 1H, H^b-5), 3.80 (s, 3H, CH_3O), 4.88 (ddd, ^3J = 4.5 Hz, ^4J = 2.4 Hz, ^4J = 1.3 Hz 1H, H-2), 5.69 (ddd, ^3J = 6.6 Hz, ^3J = 4.4 Hz, ^3J = 2.4 Hz, 1H, H-4), 5.92 (ddd, ^3J = 6.6 Hz, ^3J = 4.5 Hz, ^4J = 2.1 Hz, 1H, H-3), 7.07–7.12 (m, 1H, Ar), 7.20 (br.s, 1H, Ar), 7.20–7.22 (m, 2H, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 40.5 (CH_2), 52.0 (CH_3O), 53.0 (CH_3O), 56.6 (CH),

65.1 (C), 127.1 (CH), 127.4 (CH), 129.1 (CH), 129.2 (CH), 129.5 (CH), 131.3 (CH), 133.9 (C), 141.2 (C), 169.6 (CO_2Me), 172.3 (CO_2Me); IR (film) 1731, 1696, 1593 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{15}H_{15}ClO_4$ 295.0732; Found 295.0725. Anal. Calcd for $C_{15}H_{15}ClO_4$: C, 61.13; H, 5.13. Found: C, 60.96; H, 5.07.

Alternatively, compound **2d** was prepared using General procedure C1. 1M solution of $SnCl_4$ in CH_2Cl_2 (0.8 mL, 1.5 equiv.) was added to the solution of **1d** (160 mg, 0.55 mmol) in CH_2Cl_2 (7 mL) at 0 °C; the reaction mixture was refluxed for 1.5 h. Product **2d** was obtained in 41% yield (91 mg).

Dimethyl 2-(2-methoxyphenyl)cyclopent-3-ene-1,1-dicarboxylate (2e). General procedure C1. 1M solution of $SnCl_4$ in CH_2Cl_2 (0.8 mL, 1.5 equiv.) was added to the solution of **1e** (160 mg, 0.55 mmol) in CH_2Cl_2 (7 mL) at 0 °C; the reaction mixture was refluxed for 1.5 h. Product **2e** was obtained as white solid (144 mg, 90% yield). Mp 59–60 °C; R_f = 0.56 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.77 (dddd, ^2J = 17.5 Hz, ^3J = 2.5 Hz, ^4J = 2.1 Hz, ^4J = 0.7 Hz, 1H, H^a-5), 3.10 (s, 3H, CH_3O), 3.52–3.63 (m, 1H, H^b-5), 3.77 (s, 3H, CH_3O), 3.88 (s, 3H, CH_3O), 5.44 (ddd, ^3J = 4.4 Hz, ^4J = 2.1 Hz, ^4J = 0.7 Hz, 1H, H-2), 5.60–5.64 (m, 1H, H-4), 5.83 (ddd, ^3J = 6.4 Hz, ^3J = 4.4 Hz, ^4J = 2.1 Hz, 1H, H-3), 6.83 (br.d, ^3J = 7.5 Hz, 1H, CH, Ar), 6.86 (dd, ^3J = 8.1 Hz, ^3J = 7.9 Hz, ^4J = 0.9 Hz, 1H, CH, Ar), 7.00 (dd, ^3J = 8.1 Hz, ^4J = 1.8 Hz, 1H, CH, Ar), 7.17 (dd, ^3J = 7.9 Hz, ^3J = 7.5 Hz, ^4J = 1.8 Hz, 1H, CH, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 41.3 (CH_2), 49.3 (CH_3O), 51.7 (CH_3O), 52.8 (CH_3O), 55.6 (CH), 64.3 (C), 110.4 (CH), 120.2 (CH), 127.7 (C), 127.9 (CH), 128.3 (C), 129.4 (CH), 132.4 (CH), 157.5 (C), 170.2 (CO_2Me), 172.6 (CO_2Me); IR (KBr) 1737, 1598 cm^{-1}; GC-MS (EI, 70 eV) *m/z* (%) 290 (14) $[M]^+$, 231 (13), 230 (100), 227 (21), 199 (22), 171 (21), 170 (8), 169 (15), 128 (16), 127 (11), 115 (8), 91 (5). 77 (6).Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.20; H, 6.25. Found: C, 66.05; H, 6.29.

General procedure C2. $Ni(ClO_4)_2 \cdot 6H_2O$ (44 mg, 0.12 mmol) was added to the solution of **1e** (174 mg, 0.6 mmol) in CH_2Cl_2 (9 mL) in a single portion at room temperature. The resulting mixture was stirred for 4 h at room temperature. Product **2e** was obtained in 95% yield (165 mg).

General procedure C3. $Sc(OTf)_3$ (25 mg, 0.05 mmol) was added to the solution of **1e** (145 mg, 0.5 mmol) in CH_2Cl_2 (7 mL) in a single portion at room temperature. The resulting mixture was stirred for 3 h at room temperature. Product **2e** was obtained in 98% yield (142 mg).

Dimethyl 2-[4-(dimethylamino)phenyl]cyclopent-3-ene-1,1-dicarboxylate (2f). General procedure C1. 1M solution of $SnCl_4$ in CH_2Cl_2 (0.42 mL, 1.1 equiv.) was added to the solution of **1f** (110 mg, 0.38 mmol) in CH_2Cl_2 (5 mL) at –40 °C; the reaction mixture was warmed to 10 °C for 2 h. Product **2f** was obtained as yellowish solid (87 mg, 79% yield). Mp 80–81 °C; R_f = 0.49 (petroleum ether : ethyl acetate; 5:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.76 (dddd, ^2J = 17.7 Hz, ^3J = 2.5 Hz, ^4J = 2.0 Hz, ^4J = 1.0 Hz, 1H, H^a-5), 2.91 (s, 6H, 2×CH_3), 3.18 (s, 3H, CH_3O), 3.46 (ddd, ^2J = 17.7 Hz, ^3J = 4.3 Hz, ^4J = 2.2 Hz, 1H, H^b-5), 3.76 (s, 3H, CH_3O), 4.80 (ddd, ^3J = 4.5 Hz, ^4J = 2.2 Hz, ^4J = 1.0 Hz, 1H, H-2), 5.69 (ddd, ^3J = 6.7 Hz, ^3J = 4.3 Hz, ^3J = 2.5 Hz, 1H, H-4), 5.83 (ddd, 1H, ^3J = 6.7 Hz, ^3J = 4.5 Hz, ^4J = 2.0 Hz, H-3), 6.65 (br.d, ^3J = 8.7 Hz, 2H, Ar), 7.03 (br.d, ^3J = 8.7 Hz, 2H, Ar); ^{13}C NMR (151 MHz, $CDCl_3$,): δ 40.2 ($^1J_{CH}$ = 134 Hz, 2×CH_3), 40.5 ($^1J_{CH}$ = 133 Hz, CH_2), 51.8 ($^1J_{CH}$ = 147 Hz, CH_3O), 52.7 ($^1J_{CH}$ = 147 Hz, CH_3O), 56.2 ($^1J_{CH}$ = 136 Hz, CH), 64.9 (C), 112.1 (2×CH), 126.2 (C), 127.8 (CH), 129.5 (2×CH), 132.5 (CH), 149.8 (C), 170.0 (CO_2Me), 172.8 (CO_2Me); IR (film) 1735, 1620 cm^{-1}. Anal. Calcd for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98; N, 4.62. Found: C, 67.09; H, 7.12; N, 4.48.

Alternatively, compound **2f** was prepared by following procedures.

General procedure C3. $Sc(OTf)_3$ (30 mg, 0.06 mmol) was added to the solution of **1f** (182 mg, 0.6 mmol) in CH_2Cl_2 (9 mL) in a single portion at room temperature. The resulting mixture was stirred for 3 h at room temperature. Product **2f** was obtained in 94% yield (171 mg).

Compound **1f** (121 mg, 0.4 mmol) underwent column chromatography on silica gel (bed height 6 cm) and eluted with petroleum ether – ethyl acetate mixture (5:1). Product **2f** was isolated in 98% yield (118 mg).

Dimethyl 2-(thiophen-2-yl)cyclopent-3-ene-1,1-dicarboxylate (2g). General procedure C2. $Ni(ClO_4)_2 \cdot 6H_2O$ (276 mg, 0.75 mmol) was added to the solution of **1g** (200 mg, 0.75 mmol) in trifluorotoluene (10 mL) in a single portion at room temperature. The resulting mixture was stirred for 3 h at 60 °C. Product **2g** was obtained as yellowish oil (142 mg, 71% yield). R_f = 0.60 (petroleum ether : ethyl acetate; 5:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.81 (dddd, ^2J = 17.5 Hz, ^3J = 2.5 Hz, ^4J = 1.9 Hz, ^4J = 0.9 Hz, 1H, H^a-5), 3.34 (s, 3H, CH_3O), 3.50 (ddd, ^2J = 17.5 Hz, ^3J = 4.5 Hz, ^4J = 2.3 Hz, 1H, H^b-5), 3.78 (s, 3H, CH_3O), 5.12 (ddd, ^3J = 4.3 Hz, ^4J = 2.3 Hz, ^4J = 0.9 Hz, 1H, H-2), 5.79 (ddd, ^3J = 5.9 Hz, ^3J = 4.5 Hz, ^3J = 2.5 Hz, 1H, H-4), 5.88 (ddd, ^3J = 5.9 Hz, ^3J = 4.3 Hz, ^4J = 1.9 Hz, 1H, H-3), 6.84 (br.d, ^3J = 3.5 Hz, 1H, CH, Th), 6.93 (dd, ^3J = 5.0 Hz, ^3J = 3.5 Hz, 1H, CH, Th), 7.17 (d, ^3J = 5.0 Hz, ^4J = 0.9 Hz, 1H, CH, Th); ^{13}C NMR (126 MHz, $CDCl_3$): δ 39.6 ($^1J_{CH}$ = 135 Hz, CH_2), 51.6 ($^1J_{CH}$ = 139 Hz, CH), 52.2 ($^1J_{CH}$ = 147 Hz, CH_3O), 53.0 ($^1J_{CH}$ = 147 Hz, CH_3O), 65.2 (C), 124.8 ($^1J_{CH}$ = 187 Hz, CH), 126.3 ($^1J_{CH}$ = 166 Hz, CH), 126.7 ($^1J_{CH}$ = 167 Hz, CH), 129.1 ($^1J_{CH}$ = 166 Hz, CH), 132.0 ($^1J_{CH}$ = 169 Hz, CH), 141.8 (C, Th), 169.5 (CO$_2$Me), 172.2 (CO$_2$Me); IR (Nujol) 1730, 1670 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* [M + H]$^+$ Calcd for $C_{13}H_{15}O_4S$ 267.0686; Found 267.0679.

Alternatively, compound **2g** was prepared by General procedure C1. 1M solution of $SnCl_4$ in CH_2Cl_2 (0.65 mL, 1.1 equiv.) was added to the solution of **1g** (133 mg, 0.5 mmol) in CH_2Cl_2 (6.5 mL) at –40 °C; the reaction mixture was warmed to 10 °C for 2 h. Product **2g** was obtained in 32% yield (43 mg).

Dimethyl 2-(furan-2-yl)cyclopent-3-ene-1,1-dicarboxylate (2h). General procedure C3. $Ni(ClO_4)_2 \cdot 6H_2O$ (59 mg, 0.16 mmol) was added to the solution of **1h** (200 mg, 0.8 mmol) in CH_2Cl_2 (13 mL) in a single portion at room temperature. The reaction mixture was refluxed for 70 min. Product **2h** was obtained as yellowish oil (102 mg, 51%). R_f = 0.66 (petroleum ether :

ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.76–2.83 (m, 1H, H^a-5), 3.42 (s, 3H, CH_3O), 3.50 (ddd, ^2J = 17.5 Hz, ^3J = 4.8 Hz, ^4J = 2.4 Hz, 1H, H^b-5), 3.78 (s, 3H, CH_3O), 4.97–4.99 (m, 1H, H-2), 5.68 (ddd, ^3J = 5.8 Hz, ^3J = 4.5 Hz, ^3J = 2.2 Hz, 1H, H-4), 5.86 (ddd, ^3J = 5.8 Hz, ^3J = 4.5 Hz, ^4J = 2.3 Hz, 1H, H-3), 6.09 (br.d, ^3J = 3.2 Hz, 1H, CH, Fu), 6.28 (dd, ^3J = 3.2 Hz, ^3J = 1.8 Hz, 1H, CH, Fu), 7.33 (d, ^3J = 1.8 Hz, ^4J = 0.8 Hz, 1H, CH, Fu); ^{13}C NMR (126 MHz, $CDCl_3$): δ 40.1 (CH_2), 50.6 (CH), 52.5 (CH_3O), 52.9 (CH_3O), 63.9 (C), 107.7 (CH), 110.3 (CH), 129.3 (CH), 129.5 (CH), 142.0 (CH), 152.8 (C, Th), 169.8 (CO_2Me), 172.0 (CO_2Me); IR (Nujol) 1736 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{13}H_{15}O_5$ 251.0914; Found 251.0914.

Dimethyl 3-methyl-2-phenylcyclopent-3-ene-1,1-dicarboxylate (2i). General procedure C1. 1M solution of $SnCl_4$ in CH_2Cl_2 (0.8 mL, 1.45 equiv.) was added to the solution of **1i** (151 mg, 0.55 mmol) in CH_2Cl_2 (7 mL) at 0 °C; the reaction mixture was refluxed for 3 h. Product **2i** was obtained as colorless oil (101 mg, 67% yield). R_f = 0.55 (petroleum ether : diethyl ether; 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.59–1.61 (m, 3H, CH_3), 2.71–2.79 (m, 1H, H^a-5), 3.15 (s, 3H, CH_3O), 3.48 (dddd, ^2J = 17.3 Hz, ^3J = 4.8 Hz, ^4J = 2.5 Hz, ^5J = 1.9 Hz, 1H, H^b-5), 3.77 (s, 3H, CH_3O), 4.57 (br.s, 1H, H-2), 5.51 (ddd, ^3J = 4.8 Hz, ^3J = 3.1 Hz, ^4J = 1.5 Hz, 1H, H-4), 7.12–7.16 (m, 2H, Ph), 7.18–7.31 (br.d, 3H, Ph); ^{13}C NMR (126 MHz, $CDCl_3$): δ 15.2 (CH_3), 39.5 (CH_2), 51.8 (CH_3O), 52.8 (CH_3O), 60.4 (CH), 65.9 (C), 122.8 (CH), 127.2 (CH), 128.1 (2×CH), 129.1 (2×CH), 138.0 (C), 140.9 (C), 169.9 (CO_2Me), 172.8 (CO_2Me); IR (film) 1736, 1601 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{16}H_{19}O_4$ 275.1278; Found 275.1282. Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 69.98; H, 6.63.

Alternatively, compound **2i** was prepared by the same procedure using 1M solution of $TiCl_4$ in CH_2Cl_2 (0.75 mL, 1.25 equiv.) and the solution of **1i** (133 mg, 0.6 mmol) in CH_2Cl_2 (6.75 mL). Product **2i** was obtained in 71% yield (117 mg).

Dimethyl 2-(4-fluorophenyl)-3-methylcyclopent-3-ene-1,1-dicarboxylate (2j). General procedure C1. 1M solution of $SnCl_4$ in CH_2Cl_2 (1.0 mL, 1.5 equiv.) was added to the solution of **1j** (193 mg, 0.66 mmol) in CH_2Cl_2 (8.5 mL) at 0 °C; the reaction mixture was refluxed for 2 h.

Product **2j** was obtained as colorless liquid (154 mg, 80% yield). R_f = 0.73 (petroleum ether : diethyl ether; 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.56 (br.s, 3H, CH_3), 2.70–2.75 (m, 1H, CH_2), 3.17 (s, 3H, CH_3O), 3.43 (ddd, ^2J =17.4 Hz, ^3J = 4.6 Hz, ^4J = 2.4 Hz, 1H, CH_2), 3.74 (s, 3H, CH_3O), 4.55 (br.s, 1H, CH), 5.46–5.48 (m, 1H, CH=), 6.94 (dd, ^3J = 8.5 Hz, $^3J_{HF}$ = 9.2 Hz, 2H, CH, Ar), 7.14 (dd, ^3J = 8.5 Hz, $^4J_{HF}$ = 5.8 Hz, 2H, CH, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 14.9 (CH_3), 39.3 (CH_2), 51.8 (CH_3O), 52.7 (CH_3O), 59.5 (CH), 65.6 (C), 114.8 (d, $^2J_{CF}$ = 21 Hz, 2×CH, Ar), 122.9 (CH=), 130.6 (d, $^3J_{CF}$ = 7 Hz, 2×CH, Ar), 133.5 (d, $^4J_{CF}$ = 3 Hz, C, Ar), 140.6 (C), 161.9 (d, $^1J_{CF}$ = 246 Hz, C, Ar), 169.6 (CO_2Me), 172.5 (CO_2Me); IR (film) 1736, 1605 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{16}H_{18}FO_4$ 293.1184; Found 293.1188. Anal. Calcd for $C_{16}H_{17}FO_4$: C, 65.74; H, 5.86. Found: C, 65.70; H, 5.83.

Dimethyl 3-benzyl-2-(thiophen-2-yl)cyclopent-3-ene-1,1-dicarboxylate (2k). General procedure C1. 1M solution of $SnCl_4$ in CH_2Cl_2 (0.7 mL, 1.4 equiv.) was added to the solution of **1k** (179 mg, 0.5 mmol) in CH_2Cl_2 (6.5 mL) at 0 °C; the reaction mixture was refluxed for 1.5 h. Product **2k** was obtained as white solid (125 mg, 70% yield). Mp 97–98 °C; R_f = 0.58 (petroleum ether : ethyl acetate; 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.74–2.81 (m, 1H, CH_2), 3.22 (ddd, ^2J =16.0 Hz, ^4J = 5.3 Hz, ^4J = 2.8 Hz, 1H, CH_2, Bn), 3.38 (s, 3H, CH_3O), 3.40 (d, ^2J =16.0 Hz, 1H, CH_2, Bn), 3.46–3.56 (m, 1H, CH_2), 3.74 (s, 3H, CH_3O), 4.84 (br.s, 1H, CH), 5.33–5.35 (m, 1H, CH=), 6.86 (ddd, ^3J = 3.5 Hz, ^4J = 1.2 Hz, ^4J = 0.6 Hz, 1H, CH, Th), 6.97 (dd, ^3J = 5.1 Hz, ^3J = 3.5 Hz, 1H, CH, Th), 7.13–7.17 (m, 2H, CH, Ar), 7.20–7.34 (m, 4H, CH, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 36.0 (CH_2), 38.4 (CH_2), 52.2 (CH_3O), 52.9 (CH_3O), 53.3 (CH), 65.9 (C), 123.6 (CH), 125.0 (CH), 126.2 (CH), 126.8 (2×CH), 128.2 (2×CH), 129.2 (2×CH), 138.7 (C), 140.9 (C), 145.6 (C), 169.4 (CO_2Me), 172.1 (CO_2Me); IR (film): 1731, 1621 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{20}H_{21}O_4S$ 357.1155; Found 357.1159. Anal. Calcd for $C_{20}H_{20}O_4S$: C, 67.39; H, 5.66. Found: C, 67.79; H, 5.54.

Methyl 1-(dimethoxyphosphoryl)-2-(4-methoxyphenyl)cyclopent-3-ene-1-carboxylate (2n). General procedure C1. 1M solution of $SnCl_4$ in CH_2Cl_2 (0.7 mL, 1.4 equiv.) was added to the

solution of **1n** (170 mg, 0.5 mmol) in CH_2Cl_2 (6.5 mL) at 0 °C; the reaction mixture was refluxed for 1.5 h. Product **2n** was obtained as colorless liquid (107 mg, 63% yield) as a mixture of isomers **(1*R**,2*S**)-2n** and **(1*R**,2*R**)-2n** in a ratio of 85:15. R_f = 0.41 (ethyl acetate).

(1*R,2*S**)-2n**: ^{1}H NMR (500 MHz $CDCl_3$,): δ = 2.95–3.03 (m, 1H, H^a-5), 3.17 (s, 3H, CH_3O), 3.38–3.45 (m, 1H, H^b-5), 3.78 (s, 3H, CH_3O), 3.81 (d, $^3J_{PH}$ = 10.7 Hz, 3H, $(CH_3O)P$), 3.87 (d, $^3J_{PH}$ = 10.4 Hz, 3H, $(CH_3O)P$), 4.61 (br.d, $^3J_{PH}$ = 20.5 Hz, 1H, H-2), 5.61 (ddd, ^3J = 7.8 Hz, ^3J = 4.3 Hz, ^3J = 2.1 Hz, 1H, H-4), 5.88 (ddd, ^3J = 7.8 Hz, ^3J = 4.4 Hz, ^4J = 2.2 Hz, 1H, H-3), 6.79–6.82 (m, 2H, CH, Ar), 7.10–7.12 (m, 2H, CH, Ar); ^{13}C NMR (151 MHz, $CDCl_3$): δ 38.8 (CH_2), 51.9 (CH_3O), 53.0 (d, $^2J_{PC}$ = 7 Hz, CH_3O), 54.4 (d, $^2J_{PC}$ = 6 Hz, CH_3O), 55.2 (CH_3O), 56.7 (d, $^2J_{PC}$ = 3 Hz, CH), 58.4 (d, $^1J_{PC}$ = 143 Hz, C), 113.3 (2×CH, Ar), 129.8 (d, $^3J_{PC}$ = 5 Hz, CH=), 130.0 (2×CH, Ar), 131.0 (d, $^3J_{PC}$ = 5 Hz, CH=), 131.3 (C, Ar), 158.9 (C, Ar), 169.8 (CO$_2$Me).

(1*R,2*R**)-2n**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.09–3.15 (m, 1H, H^a-5), 3.28–3.35 (m, 1H, H^b-5), 3.35 (d, $^3J_{PH}$ = 11.3 Hz, 3H, $(CH_3O)P$), 3.38 (d, $^3J_{PH}$ = 10.7 Hz, 3H, $(CH_3O)P$), 3.79 (s, 3H, CH_3O), 3.84 (s, 3H, CH_3O), 4.62–4.66 (m, 1H, H-2), 5.67–5.70 (m, 1H, CH=), 5.96–5.99 (m, 1H, CH=), 6.84–6.86 (m, 2H, CH, Ar), 7.25–7.27 (m, 2H, CH, Ar); ^{13}C NMR (151 MHz, $CDCl_3$): δ 37.8 (CH_2), 52.8 (d, $^2J_{PC}$ = 7 Hz, CH_3O), 53.0 (d, $^2J_{PC}$ = 7 Hz, CH_3O), 53.2 (CH_3O), 55.2 (CH_3O), 56.7 (d, $^2J_{PC}$ = 3 Hz, CH), 58.6 (d, $^1J_{PC}$ = 143 Hz, C), 113.0 (2×CH, Ar), 129.3 (d, $^3J_{PC}$ = 11 Hz, CH=), 130.0 (2×CH, Ar), 132.4 (d, $^3J_{PC}$ = 10 Hz, CH=), 131.3 (C, Ar), 158.9 (C, Ar), 172.4 (CO$_2$Me).

IR (film): 1733, 1611, 1250 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{16}H_{22}O_6P$ 341.1149; Found 341.1151. Anal. Calcd for $C_{16}H_{21}O_6P$: C, 56.47; H, 6.22. Found: C, 56.11; H, 6.31.

Methyl 1-cyano-2-phenylcyclopent-3-ene-1-carboxylate (**2o**). General procedure C2. $AlCl_3$ (133 mg, 1.0 mmol) was added to the solution of **1o** (159 mg, 0.7 mmol) in CH_2Cl_2 (10 mL) at 0 °C; the reaction mixture was refluxed for 1.5 h. Product **2o** was obtained as as mixture of isomers **(1*R**,2*S**)**:**(1*R**,2*R**)** in a ratio of 72:28 in 71% total yield (113 mg).

(1*R,2*S**)-2o** was isolated as yellowish oil (81 mg, 51% yield). R_f = 0.70 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.14–3.22 (m, 1H, H^a-5), 3.24–3.32 (m, 1H, H^b-5), 3.90 (s, 3H, CH_3O), 4.64–4.67 (m, 1H, H-2), 5.83–5.87 (m, 1H, CH=), 5.96–6.00 (m, 1H, CH=), 7.27–7.31 (m, 2H, Ph), 7.36–7.41 (m, 3H, Ph); ^{13}C NMR (126 MHz, $CDCl_3$): δ 44.0 (CH_2), 53.9 (CH_3O), 54.8 (C), 59.2 (CH), 118.4 (CN), 128.4 (CH), 128.5 (2×CH), 128.7 (2×CH), 128.8 (CH), 131.6 (CH), 137.5 (C, Ar), 169.5 (*C*O_2Me); IR (film): 2245, 1736, 1599 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* [M + H]$^+$ Calcd for $C_{14}H_{14}NO_2$ 228.1019; Found 228.1017. Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.64; H, 5.83; N, 5.92.

(1*R,2*R**)-2o** was isolated as yellowish oil (32 mg, 20% yield). R_f = 0.77 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.98–3.00 (m, 1H, H^a-5), 3.25 (s, 3H, CH_3O), 3.42–3.52 (m, 1H, H^b-5), 4.68–4.71 (m, 1H, H-2), 5.77–5.82 (m, 1H, CH=), 6.05–6.09 (m, 1H, CH=), 7.17–7.20 (m, 2H, Ph), 7.29–7.34 (m, 3H, Ph); ^{13}C NMR (126 MHz, $CDCl_3$): δ 41.6 (CH_2), 52.0 (C), 52.9 (CH_3O), 62.6 (CH), 121.5 (CN), 128.4 (3×CH), 128.8 (2×CH), 130.0 (CH), 130.2 (CH), 136.3 (C), 166.8 (*C*O_2Me); IR (film): 2242, 1750, 1655 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* [M + H]$^+$ Calcd for $C_{14}H_{14}NO_2$ 228.1019; Found 228.1018.

Methyl 1-cyano-2-(4-methoxyphenyl)cyclopent-3-ene-1-carboxylate (**2p**). General procedure C2. $GaCl_3$ (212 mg, 1.2 mmol) was added to the solution of **1p** (308 mg, 1.2 mmol) in CH_2Cl_2 (18 mL) at room temperature; the reaction mixture was refluxed for 1 h. Product **2p** was obtained as as mixture of isomers **(1*R**,2*S**)**:**(1*R**,2*R**)** in a ratio of 83:17 in 72% total yield (222 mg).

(1*R,2*S**)-2p** was isolated as yellowish oil (184 mg, 60% yield). R_f = 0.60 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.14–3.19 (m, 1H, H^a-5), 3.23–3.28 (m, 1H, H^b-5), 3.83 (s, 3H, CH_3O), 3.89 (s, 3H, CH_3O), 4.58–4.61 (m, 1H, H-2), 5.80–5.82 (m, 1H, CH=), 5.94–5.96 (m, 1H, CH=), 6.92 (br. d, ^3J = 8.8 Hz, 2H, Ar), 7.20 (br. d, ^3J = 8.8 Hz, 2H, CH, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 43.7 (CH_2), 53.8 (CH_3O), 54.9 (C), 55.2 (CH_3O), 58.7 (CH), 114.1 (2×CH), 118.5 (CN), 128.5 (CH), 129.4 (C), 129.5 (2×CH), 131.9 (CH), 159.5 (C, Ar), 169.5 (*C*O_2Me); IR (film): 2245, 1743, 1611 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* [M + H]$^+$ Calcd

for $C_{15}H_{16}NO_3$ 258.1125; Found 258.1131. Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 69.66; H, 5.98; N, 5.46.

(1*R*,2R)-2p** was isolated as yellowish oil (36 mg, 12% yield). R_f = 0.67 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.96–3.01 (m, 1H, H^a-5), 3.31 (s, 3H, CH_3O), 3.40–3.45 (m, 1H, H^b-5), 3.80 (s, 3H, CH_3O), 4.64–4.66 (m, 1H, H-2), 5.75–5.78 (m, 1H, CH=), 6.02–6.05 (m, 1H, CH=), 6.85 (br. d, ^3J = 8.7 Hz, 2H, Ar), 7.09 (br. d, ^3J = 8.7 Hz, 2H, CH, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 41.3 (CH_2), 51.8 (C), 52.9 (CH_3O), 55.2 (CH_3O), 62.0 (CH), 113.7 (2×CH), 121.6 (CN), 127.9 (C), 129.5 (CH), 129.8 (2×CH), 130.4 (CH), 159.6 (C), 166.8 (*C*O_2Me). Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 69.70; H, 5.70; N, 5.33.

2-(4-Methoxyphenyl)-1'-methylspiro[cyclopent-3-ene-1,3'-indol]-2'(1'H)-one (**2q**). General procedure C2. $GaCl_3$ (115 mg, 0.66 mmol) was added to solution of **1q** (200 mg, 0.66 mmol) in DCE (9 mL) at room temperature; the reaction mixture was refluxed for 2 h. Product **2q** was obtained as a mixture of isomers ***(1R*,2R*):(1R*,2S*)*** in a ratio of 70:30 in 52% total yield (104 mg).

(*1R*,2R)-2q** was isolated as yellowish oil (72 mg, 36% yield). R_f = 0.44 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.84 (ddd, ^2J = 16.7 Hz, ^3J = 4.7 Hz, ^4J = 2.4 Hz, 1H, H^a-5), 2.86 (s, 3H, CH_3N), 3.06 (ddd, ^2J = 16.7 Hz, ^3J = 4.6 Hz, ^4J = 2.3 Hz, 1H, H^b-5), 3.76 (s, 3H, CH_3O), 4.33–4.35 (m, 1H, H-2), 5.92–5.95 (m, 1H, H-3), 6.12–6.15 (m, 1H, H-4), 6.72 (d, ^3J = 8.7 Hz, 2H, Ar), 6.73 (br. d, ^3J = 7.3 Hz, 1H, H$^{7'}$), 6.85 (br. d, ^3J = 8.7 Hz, 2H, Ar), 7.13 (dd, ^3J = 7.6 Hz, ^3J = 7.3 Hz, 1H, H$^{5'}$), 7.30 (dd, ^3J = 7.6 Hz, ^3J = 7.3 Hz, 1H, H$^{6'}$), 7.43 (d, ^3J = 7.3 Hz, 1H, H$^{4'}$); ^{13}C NMR (126 MHz, $CDCl_3$): δ 25.7 (CH_3N), 42.8 (CH_2), 55.1 (CH_3O), 58.3 (CH), 62.6 (C), 107.5 (CH), 113.1 (2×CH), 122.0 (CH), 122.5 (CH), 127.8 (CH), 128.9 (2×CH), 130.6 (C), 130.7 (CH), 131.9 (CH), 135.4 (C), 143.5 (C), 158.6 (C), 178.1 (CO); HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{20}H_{20}NO_2$ 306.1489; Found 306.1488. Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27. Found: C, 78.40; H, 6.07.

(*1R*,2S)-2q** was isolated as yellowish oil (32 mg, 16% yield). R_f = 0.54 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.71 (ddd, ^2J = 16.3 Hz, ^3J = 3.8 Hz, ^4J = 2.0 Hz, 1H, H^a-5), 3.12 (ddd, ^2J = 16.3 Hz, ^3J = 4.9 Hz, ^4J = 2.6 Hz, 1H, H^b-5), 3.22 (s, 3H, CH_3N), 3.70 (s, 3H, CH_3O), 4.56–4.57 (m, 1H, H-2), 6.01–6.03 (m, 1H, H-3), 6.12–6.14 (m, 1H, H-4), 6.61 (d, ^3J = 8.8 Hz, 2H, Ar), 6.62 (br. d, ^3J = 7.9 Hz, 1H, H$^{7'}$), 6.76 (dd, ^3J = 7.9 Hz, ^3J = 7.5 Hz, 1H, H$^{6'}$), 6.86 (br. d, ^3J = 8.8 Hz, 2H, Ar), 6.89 (d, ^3J = 7.3 Hz, 1H, H$^{4'}$), 7.05 (dd, ^3J = 7.5 Hz, ^3J = 7.3 Hz, 1H, H$^{5'}$); ^{13}C NMR (126 MHz, $CDCl_3$): δ 26.3 (CH_3N), 43.7 (CH_2), 55.1 (CH_3O), 59.2 (C), 59.7 (CH), 107.4 (C(7′)H), 113.1 (2×CH, Ar), 121.8 (C(6')H), 124.0 (C(5')H), 127.4 (C(4')H), 128.9 (2×CH, Ar), 130.5 (C(4)H, 131.1 (C), 132.5 (C), 132.6 (C(3)H), 142.7 (C), 158.2 (C), 180.8 (CO); HRMS (ESI/Q-TOF) *m/z* [M + H]$^+$ Calcd for $C_{20}H_{20}NO_2$ 306.1489; Found 306.1489.

2-Phenylspiro[cyclopent-3-ene-1,2'-indene]-1',3'-dione (2r). General procedure C1. 1M solution of $SnCl_4$ in CH_2Cl_2 (1.0 mL, 1.5 equiv.) was added to the solution of **1r** (181 mg, 0.66 mmol) in CH_2Cl_2 (8.5 mL) at 0 °C; the reaction mixture was refluxed for 3 h. Product **2r** was obtained as beige solid (138 mg, 76% yield). Mp = 102–103 °C; R_f = 0.85 (petroleum ether : diethyl ether; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.89–2.91 (m, 2H, CH_2), 4.46–4.48 (m, 1H, CH), 5.75–5.78 (m, 1H, CH=), 6.05–6.07 (m, 1H, CH=), 6.84–6.88 (m, 2H, CH, Ar), 7.06–7.08 (m, 3H, CH, Ar), 7.51 (d, ^3J = 8.3 Hz, 1H, CH, Ar), 7.65 (dd, ^3J = 8.3 Hz, ^3J = 7.6 Hz, 1H, CH, Ar), 7.75 (d, ^3J = 8.3 Hz, ^3J = 7.6 Hz, 1H, CH, Ar), 7.99 (d, ^3J = 8.3 Hz, 1H, CH, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 38.5 (CH_2), 61.9 (CH), 64.4 (C), 122.9 (CH), 123.0 (CH), 127.2 (CH), 127.9 (2×CH), 128.5 (2×CH), 130.7 (CH, Ar), 130.8 (CH), 135.1 (CH), 135.5 (CH), 137.6 (C, Ar), 141.7 (C, Ar), 142.7 (C, Ar), 200.5 (CO), 203.1 (*C*O_2Me); IR (KBr) 1740, 1705, 1595 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* [M + H]$^+$ Calcd for $C_{19}H_{15}O_2$ 275.1067. Found 275.1070. Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 83.15; H, 5.11.

Dimethyl [(3*E*)-2-chloro-4-(2-nitrophenyl)but-3-en-1-yl]malonate (5a). General procedure C1. 1M solution of $SnCl_4$ in CH_2Cl_2 (0.66 mL, 1.1 equiv.) was added to the solution of **1l** (183

mg, 0.6 mmol) in CH_2Cl_2 (8 mL) at room temperature; the reaction mixture was refluxed for 2 h. Product **5a** was obtained as yellowish oil (94 mg, 46% yield). R_f = 0.70 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.51 (ddd, ^2J = 14.3 Hz, ^3J = 8.4 Hz, ^3J = 6.1 Hz, 1H, CH_2), 2.58 (ddd, ^2J = 14.3 Hz, ^3J = 8.2 Hz, ^3J = 6.0 Hz, 1H, CH_2), 3.74 (dd, ^3J = 8.4 Hz, ^3J = 6.0 Hz, 1H, CH), 3.78 (s, 3H, CH_3O), 3.79 (s, 3H, CH_3O), 4.68 (dddd, ^3J = 8.5 Hz, ^3J = 8.2 Hz, ^3J = 6.1 Hz, ^4J = 0.6 Hz, 1H, CH), 6.18 (dd, ^3J = 15.6 Hz, ^3J = 8.5 Hz, 1H, CH=), 7.16 (dd, ^3J = 15.6 Hz, ^4J = 0.6 Hz, 1H, CH=), 7.47 (ddd, ^3J = 7.9 Hz, ^3J = 5.8 Hz, ^4J = 2.8 Hz, 1H, Ar), 7.61 (br.s, 1H, Ar), 7.62 (dd, ^3J = 5.8 Hz, ^4J = 1.2 Hz, 1H, Ar), 7.99 (br.d, ^3J = 7.9 Hz, 1H, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 36.9 (CH_2), 48.8 (CH), 52.75 (CH_3O), 52.78 (CH_3O), 59.2 (CH), 124.6 (CH), 128.1 (CH), 128.79 (CH), 128.82 (CH), 131.4 (C), 133.2 (CH), 133.3 (CH), 147.8 (C), 168.8 (CO$_2$Me), 168.9 (CO$_2$Me); HRMS ESI-TOF: *m/z* = 342.0737 $[M + H]^+$ (342.0739 calcd for $C_{15}H_{17}ClNO_6$).

Diethyl [(2*E*)-4-chlorobut-2-en-1-yl]malonate (5b). To solution of cyclopropane **1m** (128 mg, 0.6 mmol) in CH_3NO_2 (8 mL) the solution of $SnCl_4$ (172 mg, 0.08 mL, 1.1 equiv.) in CH_3NO_2 (1 mL) was added at -40 °C under argon atmosphere. The reaction mixture was warmed to room temperature for 3 h and then refluxed for 4 h. Then mixture was poured into saturated $NaHCO_3$ solution. Product was extracted with CH_2Cl_2 (3×10 mL), the combined organic fractions were washed with $NaHCO_3$ (2×5 mL), then with water (2×5 mL) and dried with $MgSO_4$. Chloride **5b** was obtained as colourless oil (91 mg, 61% yield). R_f = 0.61 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.21 (t, ^3J = 7.1 Hz, 3H, CH_3), 1.22 (t, ^3J = 7.1 Hz, 3H, CH_3), 2.58–2.61 (m, ^3J = 7.5 Hz, ^3J = 6.5 Hz, 2H, CH_2), 2.58 (t, ^3J = 7.5 Hz, 1H, CH), 3.74 (br.d, ^3J = 6.5 Hz, 2H, CH_2Cl), 4.08–4.20 (m, 4H, 2×CH_2O), 5.63–5.73 (m, 2H, 2×CH=); ^{13}C NMR (126 MHz, $CDCl_3$): δ 14.1 ($^1J_{CH}$ = 127 Hz, 2×CH_3), 31.1 ($^1J_{CH}$ = 132 Hz, CH_2), 44.4 ($^1J_{CH}$ = 156 Hz, CH_2Cl), 51.4 ($^1J_{CH}$ = 133 Hz, CH), 61.4 ($^1J_{CH}$ = 148 Hz, 2×CH_2O), 124.6 (CH), 128.1 (CH), 128.8 (CH), 128.8 (CH), 130.4 (C), 129.0 ($^1J_{CH}$ = 160 Hz, CH), 130.7 ($^1J_{CH}$ = 155 Hz, CH), 168.6 (2×CO$_2$Et); HRMS ESI-TOF: *m/z* = 249.0884 $[M + H]^+$ (249.0888 calcd for $C_{11}H_{18}ClO_4$).

Dimethyl [(*E*)-4-(2-nitrophenyl)but-2-en-1-ylidene]malonate (6a). General procedure C2. $GaCl_3$ (133 mg, 0.66 mmol) was added to solution of **1l** (200 mg, 0.66 mmol) in DCM (11 mL) at room temperature; the reaction mixture was refluxed for 1 h. Product **6a** was obtained as colorless oil (76 mg, 38%). R_f = 0.72 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.80 (s, 3H, CH_3O), 3.85 (s, 3H, CH_3O), 3.88 (dd, ^3J = 6.9 Hz, ^4J = 1.3 Hz, 2H, CH_2), 6.48 (dt, ^3J = 14.9 Hz, ^3J = 6.9 Hz, 1H, CH=), 6.62 (ddt, ^3J = 14.9 Hz, ^3J = 11.9 Hz, ^4J = 1.3 Hz, 1H, CH=), 7.36 (dd, ^3J = 7.6 Hz, ^4J = 1.2 Hz, 1H, Ar), 7.39 (d, ^3J = 11.9 Hz, 1H, CH=), 7.44 (m, ^3J = 8.8 Hz, ^3J = 8.2 Hz, ^4J = 1.2 Hz, 1H, Ar), 7.59 (ddd, ^3J = 8.8 Hz, ^3J = 7.6 Hz, ^4J = 1.2 Hz, 1H, Ar), 7.99 (dd, ^3J = 8.2 Hz, ^4J = 1.2 Hz, 1H, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 36.3 (CH_2), 52.3 (CH_3O), 52.4 (CH_3O), 124.4 (C), 125.0 (CH, Ar), 127.5 (CH=), 128.0 (CH, Ar), 132.1 (CH, Ar), 133.37 (C), 133.40 (CH, Ar), 144.5 (CH=), 145.1 (CH=), 149.0 (C), 164.9 (*C*O_2Me), 165.4 (*C*O_2Me); HRMS ESI-TOF: *m/z* = 306.0971 $[M + H]^+$ (306.0972 calcd for $C_{15}H_{16}NO_6$).

Dimethyl 2-[(E)-1,2-dideuterio-4-(2-nitrophenyl)but-2-en-1-ylidene]malonate (**6a**-d_2) was obtained as a mixture with *dimethyl 2-[(E)-1-deuterio-4-(2-nitrophenyl)but-2-en-1-ylidene]malonate* (**6a**-d_1) and *dimethyl 2-[(1E,3E)-1,2-dideuterio-4-(2-nitrophenyl)buta-1,3-dien-1-yl]malonate* (**7**-d_2) using General procedure C2 from **1l**-d_2 (176 mg, 0.58 mmol) in DCM (5 mL). $GaCl_3$ (102 mg, 0.58 mmol) was added at room temperature, the reaction mixture was refluxed for 0.5 h. Structures of deuterated products were established by analysis of NMR data.

Product **6a**-d_1. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.80 (s, 3H, CH_3O), 3.85 (s, 3H, CH_3O), 3.86–3.97 (d, ^2J = 7 Hz, 2H, CH_2), 6.44–6.51 (m, 1H, CH=), 6.62 (d, ^3J = 15.0 Hz, 1H, CH=), 7.36 (dd, ^3J = 7.6 Hz, ^4J = 1.1 Hz, 1H, Ar), 7.44 (m, ^3J = 8.8 Hz, ^3J = 8.2 Hz, ^4J = 1.2 Hz, 1H, Ar), 7.57–7.60 (m, 1H, Ar), 7.99 (dd, ^3J = 8.2 Hz, ^4J = 1.2 Hz, 1H, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 36.60 (CH_2), 52.2 (CH_3O), 52.3 (CH_3O), 124.7 (C), 125.0 (CH, Ar), 127.4 (CH=), 127.91 (CH, Ar), 132.0 (CH, Ar), 132.4 (C), 133.3 (CH, Ar), 144.5 (CH=), 144.8 ($^1J_{CD}$ = 24 Hz, CD=), 148.9 (C), 164.9 (*C*O_2Me), 165.4 (*C*O_2Me).

Product **6a**-d_2. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.80 (s, 3H, CH_3O), 3.85 (s, 3H, CH_3O), 3.86–3.97 (d, ^2J = 7 Hz, 2H, CH_2), 6.44–6.51 (m, 1H, CH=), 7.36 (dd, ^3J = 7.6 Hz, ^4J = 1.1 Hz, 1H, Ar), 7.44 (ddd, ^3J = 8.8 Hz, ^3J = 8.2 Hz, ^4J = 1.2 Hz, 1H, Ar), 7.56–7.60 (m, 1H, Ar), 7.99 (br.d, ^3J = 8.2 Hz, ^4J = 1.2 Hz, 1H, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 36.55 (CH_2), 52.2 (CH_3O), 52.3 (CH_3O), 124.7 (C), 125.0 (CH, Ar), 127.1 ($^1J_{CD}$ = 24 Hz, CD=), 127.93 (CH, Ar), 132.0 (CH, Ar), 132.3 (C), 133.4 (CH, Ar), 144.4 (CH=), 144.8 ($^1J_{CD}$ = 24 Hz, CD=), 148.9 (C), 164.9 (*C*O_2Me), 165.4 (*C*O_2Me).

Product **7**-d_2. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.79 (s, 6H, 2×CH_3O), 4.20 (s, H, CH), 6.79 (d, ^3J = 15.6 Hz, 1H, CH=), 7.08 (d, ^3J = 15.6 Hz, 1H, CH=), 7.36–7.40 (m, 1H, Ar), 7.57–7.60 (m, 1H, Ar), 7.65 (br.d, ^3J = 8.2 Hz, 1H, Ar), 7.93 (dd, ^3J = 8.2 Hz, ^4J = 1.2 Hz, 1H, Ar); ^{13}C NMR (126 MHz, $CDCl_3$,): δ 52.9 (2×CH_3O), 54.5 (CH), 124.2 (CH, Ar), 126.4 ($^1J_{CD}$ = 26 Hz, CD=), 127.9 (CH, Ar), 128.2 (CH=), 132.3 (CH, Ar), 132.3 (CH, Ar), 132.4 (CH=), 134.5 ($^1J_{CD}$ = 26 Hz, CD=), 132.4 (C), 147.9 (C), 168.0 (2×*C*O_2Me).

Diethyl [(*E*)-but-2-en-1-ylidene]malonate (6b). General procedure C2. $GaCl_3$ (139 mg, 0.79 mmol) was added to solution of **1m** (168 mg, 0.79 mmol) in DCE (11 mL) at room temperature; the reaction mixture was refluxed for 1 h. Product **6b** was obtained as colorless oil (30 mg, 18%). Spectral data are fully consistent with the reported ones.[45]

General procedure for the synthesis of 2-arylcyclopent-2-ene-1,1-dicarboxylates 8. To a vigorously stirred 0.07 M solution of cyclopropane **1** or cyclopentene **2** in CH_2Cl_2 or $C_2H_4Cl_2$ containing molecular sieves 4Å $GaCl_3$ (100–200 mol%) was added under argon atmosphere. The resulting mixture was stirred at room temperature or refluxed for specified time, poured into 5% aq. solution HCl (9 mL) and extracted with CH_2Cl_2 (3×10 mL). The combined organic fractions were washed with water (2×10 mL), dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, eluent – petroleum ether : ethyl acetate) to yield cyclopentene **8**.

Dimethyl 3-methyl-2-phenylcyclopent-2-ene-1,1-dicarboxylate (8a) was obtained from cyclopropane **1i** (200 mg, 0.73 mmol) and $GaCl_3$ (128 mg, 0.73 mmol); stirred under reflux in DCE (11 mL) for 0.5 h. Product **8a** was obtained as yellowish oil (144 mg, 72%). R_f = 0.72 (diethyl ether : petroleum ether; 1:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.66 (s, 3H, CH_3), 2.51–2.55 (m, 2H, CH_2), 2.60–2.64 (m, 2H, CH_2), 3.62 (s, 6H, 2×CH_3O), 7.17–7.19 (m, 2H, Ph), 7.24–7.26 (m, 1H, Ph), 7.28–7.31 (m, 2H, Ph); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 15.4 (CH_3), 33.53 (CH_2), 36.3 (CH_2), 52.2 (2×CH_3O), 70.5 (C), 126.9 (CH, Ph), 127.7 (2×CH, Ph), 129.7 (2×CH, Ph), 134.5 (C), 136.4 (C), 143.4 (C), 172.1 (2×*C*O_2Me); IR (film) 1740, 1602 cm^{-1}; GC-MS (EI, 70 eV) *m*/*z* (%) 274 (18) $[M]^+$, 242 (19), 215 (22), 214 (55), 183 (22), 156 (19), 155 (100), 154 (25), 153 (35), 141 (18), 129 (15), 128 (18), 115 (25), 77 (12), 59 (30). Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 69.80; H, 6.53.

Alternatively, $GaCl_3$ (84 mg, 0.48 mmol) was added to the solution of cyclopentene **2i** (130 mg, 0.47 mmol) in CH_2Cl_2 (7 mL), the reaction mixture was stirred at room temperature for 1 h, additional portion of $GaCl_3$ (84 mg, 0.48 mmol) was added and stirred for 6 h more. Compound **8a** was obtained in 85% yield (110 mg).

Dimethyl 2-(4-fluorophenyl)-3-methylcyclopent-2-ene-1,1-dicarboxylate (8b) was obtained from cyclopropane **1j** (100 mg, 0.34 mmol) and $GaCl_3$ (60 mg, 0.34 mmol); stirred at room temperature in CH_2Cl_2 (6 mL) for 1 h; additional portion of $GaCl_3$ (60 mg, 0.34 mmol) was added; stirred at room temperature for 5.5 h, then refluxed for 0.5 h. Product **8b** was obtained as colorless oil (75 mg, 75%). R_f = 0.80 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.65 (s, 3H, CH_3), 2.52–2.55 (m, 2H, CH_2), 2.60–2.63 (m, 2H, CH_2), 3.64 (s, 6H, 2×CH_3O), 6.98–7.01 (m, 2H, Ar), 7.15–7.18 (m, 2H, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 15.3 (CH_3), 33.4 (CH_2), 36.1 (CH_2), 52.2 (2×CH_3O), 70.3 (C), 114.6 (d, $^2J_{CF}$ = 21 Hz, 2×CH, Ar), 131.4 (d, $^3J_{CF}$ = 8 Hz, 2×CH, Ar), 132.2 (d, $^4J_{CF}$ = 3 Hz, C, Ar), 133.5 (C), 143.9 (C), 161.9 (d, $^1J_{CF}$ = 246 Hz, C, Ar), 172.0 (2×*C*O_2Me); IR (film): 1731 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* [M +

H]$^+$ Calcd for $C_{16}H_{18}FO_4$ 293.1184; Found 293.1187. Anal. Calcd for $C_{16}H_{17}FO_4$: C, 65.74; H, 5.86. Found: C, 65.69; H, 5.85.

Dimethyl 3-benzyl-2-(thiophen-2-yl)cyclopent-2-ene-1,1-dicarboxylate (8c) was obtained from cyclopropane **1k** (180 mg, 0.51 mmol) and $GaCl_3$ (89 mg, 0.51 mmol); stirred in $C_2H_4Cl_2$ (7 mL) at room temperature for 14 h followed by refluxing for 0.5 h. Product **8c** was obtained as yellowish oil (121 mg, 67% yield, estimated purity is *ca.* 90%). R_f = 0.55 (petroleum ether : ethyl acetate; 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.42–2.48 (m, 2H, CH_2), δ 2.59–2.65 (m, 2H, CH_2), 3.57 (s, 2H, CH_2, Bn), 3.71 (s, 6H, 2×CH_3O), 6.99–7.02 (m, 2H, CH, Ar), 7.16–7.33 (m, 6H, CH, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 32.8 (CH_2), 33.4 (CH_2), 35.5 (CH_2), 51.9 (2×CH_3O), 69.9 (C), 125.2 (CH), 125.7 (CH), 126.0 (CH), 127.3 (CH), 128.0 (2×CH), 128.1 (2×CH), 129.1 (C), 135.7 (C), 138.1 (C), 147.7 (C), 171.1 (2×*C*O_2Me); IR (film): 1731, 1601 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* [M + Na]$^+$ Calcd for $C_{20}H_{20}O_4SNa$ 379.0980; Found 379.0984. Anal. Calcd for $C_{20}H_{20}O_4S$: C, 67.39; H, 5.66. Found: C, 67.31; H, 5.52.

Alternatively, **8c** was obtained from cyclopentene **2k** (180 mg, 0.51 mmol) and $GaCl_3$ (89 mg, 0.51 mmol) in CH_2Cl_2 (7 mL) after stirring at room temperature for 14 h; yield 126 mg (70%).

(1*R,2*R**)-1-(Methoxycarbonyl)-2-(4-methoxyphenyl)cyclopent-3-ene-1-carboxylic acid (9a)**. The solution of **2b** (442 mg, 1.52 mmol) in CH_3OH (0.67 mL) was added to the solution of KOH (514 mg, 9.18 mmol) in water (1.2 mL). The reaction mixture was stirred at 40 °C for 4 h, concentrated under reduced pressure. The residue was taken up in water (10 mL) and washed once with diethyl ether (5 mL). Conc. HCl was added dropwise until aqueous layer became strongly acidic. The precipitate was extracted with diethyl ether (3×5 mL). The combined organic fractions were washed with water (2×5 mL) and dried with anhydrous $CaCl_2$. The solvent was evaporated under reduced pressure to afford **9a** as beige foam (383 mg, 91%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.89–2.95 (m, 1H, CH_2), 3.21 (s, 3H, CH_3O), 3.46–3.52 (m, 1H, CH_2), 3.76 (s, 3H, CH_3O), 4.78–4.79 (m, 1H, CH), 5.67–5.71 (m, 1H, CH=), 5.88–5.91 (m, 1H, CH=), 6.81 (br.d, ^3J = 8.7 Hz, 2H, Ar), 7.10 (br.d, ^3J = 8.7 Hz, 2H, Ar); ^{13}C NMR (126 MHz,

$CDCl_3$): δ 40.1 (CH_2), 51.8 (CH_3O), 54.8 (CH_3O), 56.1 (CH), 64.5 (C), 113.0 (2×CH), 128.2 (CH), 129.6 (2×CH), 130.0 (C), 131.6 (CH), 158.4 (C), 169.5 (CO_2Me), 177.2 (CO_2H); IR (KBr) 1755, 1710, 1610 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{15}H_{17}O_5$ 277.1071; Found 277.1067.

2-(4-Methoxyphenyl)cyclopent-3-ene-1,1-dicarboxylic acid (9b). The solution of **2b** (335 mg, 1.15 mmol) in CH_3OH (1.44 mL) was added to the solution of KOH (1.167 g, 20.8 mmol) in water (2.6 mL). The reaction mixture was refluxed for 3 h, cooled to ambient temperature and concentrated under reduced pressure. The residue was taken up in water (10 mL) and washed once with diethyl ether (5 mL). Conc. HCl was added dropwise until aqueous layer became strongly acidic. The precipitate was extracted with diethyl ether (3×5 mL). The combined organic fractions were washed with water (2×5 mL) and dried with anhydrous $CaCl_2$. The solvent was evaporated under reduced pressure to afford **9b** (300 mg, 99%) as a white foam. ^1H NMR (500 MHz, $CDCl_3$): δ 2.87–2.92 (m, 1H, CH_2), 3.37–3.41 (m, 1H, CH_2), 3.76 (C, 3H, CH_3O), 4.77–4.78 (m, 1H, CH), 5.70 (ddd, ^3J = 5.8 Hz, ^3J = 4.3 Hz, ^4J = 2.1 Hz, 1H, CH=), 5.88 (ddd, ^3J = 5.8 Hz, ^3J = 4.3 Hz, ^4J = 2.2 Hz, 1H, CH=), 6.79 (br.d, ^3J = 8.7 Hz, 2H, Ar), 7.12 (br.d, ^3J = 8.7 Hz, 2H, Ar), 9.94 (br.s, 2H, CO_2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 39.7 (CH_2), 54.7 (CH_3O), 56.1 (CH), 65.3 (C), 113.1 (2×CH), 128.0 (CH), 129.5 (C), 129.6 (2×CH), 131.6 (CH), 158.4 (C), 173.6 (CO_2H), 176.7 (CO_2H); IR (KBr) 1710, 1610 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* $[M + Na]^+$ Calcd for $C_{14}H_{14}NaO_5$ 285.0739; Found 285.0732.

Dimethyl 1-(2-chlorobenzyl)-3-(4-methoxyphenyl)piperidine-4,4-dicarboxylate (10). A solution of dimethyl 2-(4-methoxyphenyl)cyclopent-3-ene-1,1-dicarboxylate **(2c)** (334 mg, 1.15 mmol) in CH_2Cl_2 (11 mL) and methanol (1 mL) was cooled to -78 °C and treated with a steady flow of O_3 until a persistent blue color was evident. The reaction flask was purged with N_2 and dimethyl sulfide (0.18 mL, 2.5 mmol) was added. The solution was warmed to room temperature and stirred for 24 h. The reaction mixture was concentrated to yellowish oil which was dissolved in MeOH (3.5 mL), cooled to 0 °C and treated with 2-chlorobenzylamine (147 mg, 1.04 mmol)

and $NaBH_3CN$ (237 mg, 3.77 mmol). The ice-bath was removed and the reaction mixture was stirred at room temperature overnight. Ethyl acetate (5 mL) and aq sat. $NaHCO_3$ solution (3 mL) were added to the reaction mixture. The organic layer was separated; the aqueous layer was extracted with ethyl acetate (2×3 mL). The combined organic layers were washed with water (2×4 mL) and dried with Na_2SO_4. The solvent was removed in vacuo. Piperidine **10** was isolated by column chromatoraphy as yellow oil (263 mg, 53% yield, estimated purity is *ca.* 90%). R_f = 0.84 (petroleum ether : ethyl acetate; 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.14–2.21 (m, 2H, H^a-5, H^a-6), 2.49 (ddd, ^2J = 14.3 Hz, ^3J = 11.9 Hz, ^3J = 4.3 Hz, 1H, H^b-5), 2.88 (dd, ^2J = 11.6 Hz, ^3J = 4.0 Hz, 1H, H^a-2), 2.90–2.93 (m, 1H, H^b-6), 3.00 (dd, ^2J = 11.6 Hz, ^3J = 3.6 Hz, ^4J = 1.2 Hz, 1H, H^b-2), 3.50 (s, 3H, CH_3O), 3.59 (br.s, 2H, CH_2N), 3.67 (dd, ^3J = 4.0 Hz, ^3J = 3.6 Hz, 1H, H-3), 3.78 (s, 3H, CH_3O), 3.79 (s, 3H, CH_3O), 6.80 (d, ^3J = 8.9 Hz, 2H, Ar), 7.17–7.24 (m, 2H, Ar), 7.36 (dd, ^3J = 7.6 Hz, ^4J = 1.5 Hz, 1H, Ar), 7.43 (d, ^3J = 7.3 Hz, ^4J = 1.8 Hz, 1H, Ar), 7.63 (d, ^3J = 8.9 Hz, 2H, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 27.8 (C(5)H_2), 43.4 (C(3)H), 49.9 (C(6)H_2), 52.0 (CH_3O), 52.6 (CH_3O), 55.1 (CH_3O), 55.7 (C(2)H_2), 57.7 (C), 60.0 (CH_2N), 113.0 (2×CH), 126.5 (CH), 128.3 (CH), 129.5 (CH), 130.9 (2×CH), 131.1 (CH), 133.0 (C), 134.6 (C), 135.9 (C), 158.5 (C), 170.3 (*C*O_2Me), 171.5 (*C*O_2Me); IR (film) 1735 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{23}H_{27}ClNO_5$ 432.1572; Found 432.1574.

Methyl (1*R,2*S**)-1-cyano-2-(4-methoxyphenyl)cyclopentanecarboxylate (11)**. Methanolic solution (0.05 M) of compound **2p** (122 mg, 0.47 mmol) was reduced in H-cube® at 80 °C and 50 bar (5 cycles run) on the 10% Pd/C cartridge. The resulting solution was concentrated and purified *via* flash chromatography to afford **11** as a colorless oil (95 mg, 78% yield). R_f = 0.53 (petroleum ether : ethyl acetate; 5:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.01–2.06 (m, 1H, CH_2), 2.12–2.16 (m, 1H, CH_2), 2.20–2.25 (m, 1H, CH_2), 2.26–2.31 (m, 1H, CH_2), 2.42–2.53 (m, 2H, CH_2), 3.65 (dd, ^3J = 12.2 Hz, ^3J = 7.3 Hz, 1H, CH), 3.76 (s, 3H, CH_3O), 3.81 (s, 3H, CH_3O), 6.90 (br. d, ^3J = 8.5 Hz, 2H, Ar), 7.27 (br. d, ^3J = 8.5 Hz, 2H, CH, Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ 22.5 (CH_2), 30.3 (CH_2), 38.2 (CH_2), 53.5 (CH), 54.3 (CH_3O), 55.3 (CH_3O), 55.9 (C),

114.0 (2×CH), 118.7 (CN), 128.9 (C, Ar), 129.1 (2×CH), 159.5 (C, Ar), 170.0 (*C*O_2Me); IR (film): 2245, 1743 cm^{-1}; HRMS (ESI/Q-TOF) *m/z* $[M + H]^+$ Calcd for $C_{15}H_{18}NO_3$ 260.1281; Found 260.1282. Anal. Calcd for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61. Found: C, 69.22; H, 6.45.

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Supporting information

The supporting information is available free of charge on the ACS Publications website at DOI: Copies of ^1H, ^{13}C and two-dimensional NMR spectra (PDF)

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