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Attempted reactions of methoxyallene with dimethyl 2-arylcyclopropane 1,1-dicarboxylates (D-A cyclopropanes); dual catalytic activity of scandium triflate $Sc(OTf)_3$ and unexpected formation of the MeOH adducts

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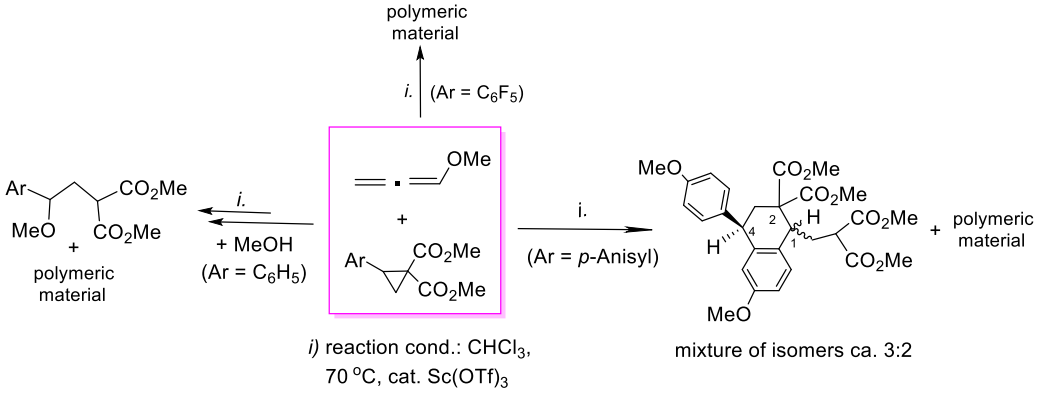
Dedicated to Prof. Thomas J. J. Mueller in recognition of his outstanding achievements in organic and materials chemistry

Received 02-11-2026 **Accepted** 05-12-206 **Published on line** 05-17-2026

Abstract

Dimethyl 2-arylcyclopropane 1,1-dicarboxylates do not react with methoxyallene under typical ring-opening reaction conditions ($CHCl_3$, 70°C, cat. amounts of $Sc(OTf)_3$). Instead, the regioselective formation of the MeOH adducts with starting cyclopropanes was observed. The $Sc(OTf)_3$ induced polymerization of methoxyallene is postulated as the initial process which occurred upon partial extrusion of MeOH. The latter is subsequently trapped by the activated D-A cyclopropane yielding the corresponding dimethyl 2-(2-methoxyethyl)malonate derivatives in good yields. Under the applied conditions, the 2-anisyl substituted cyclopropane dicarboxylate underwent (3+3) cyclodimerization and a 3:2 mixture of isomeric, six-membered dimers, was isolated in 50% yield.

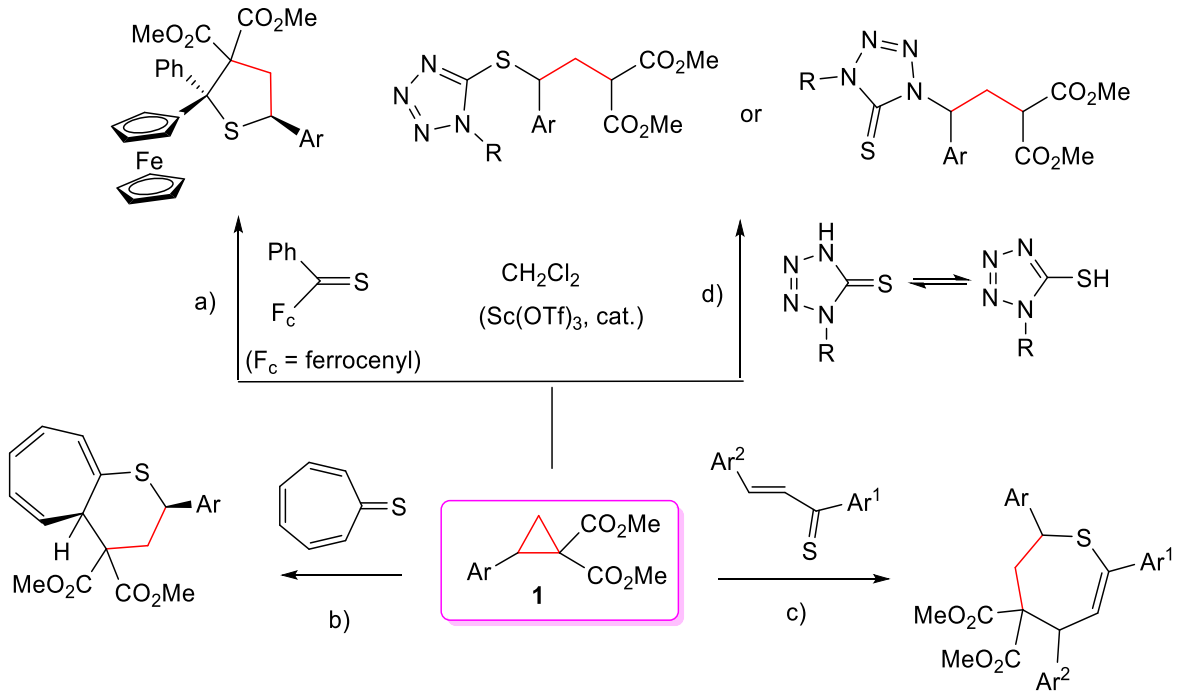


Keywords: D-A Cyclopropanes, ring opening reactions, methoxyallene, Lewis acids, polymerization

Cite as *Arkivoc* **2026** (3) 202612561
DOI: to be inserted by editorial office

Introduction

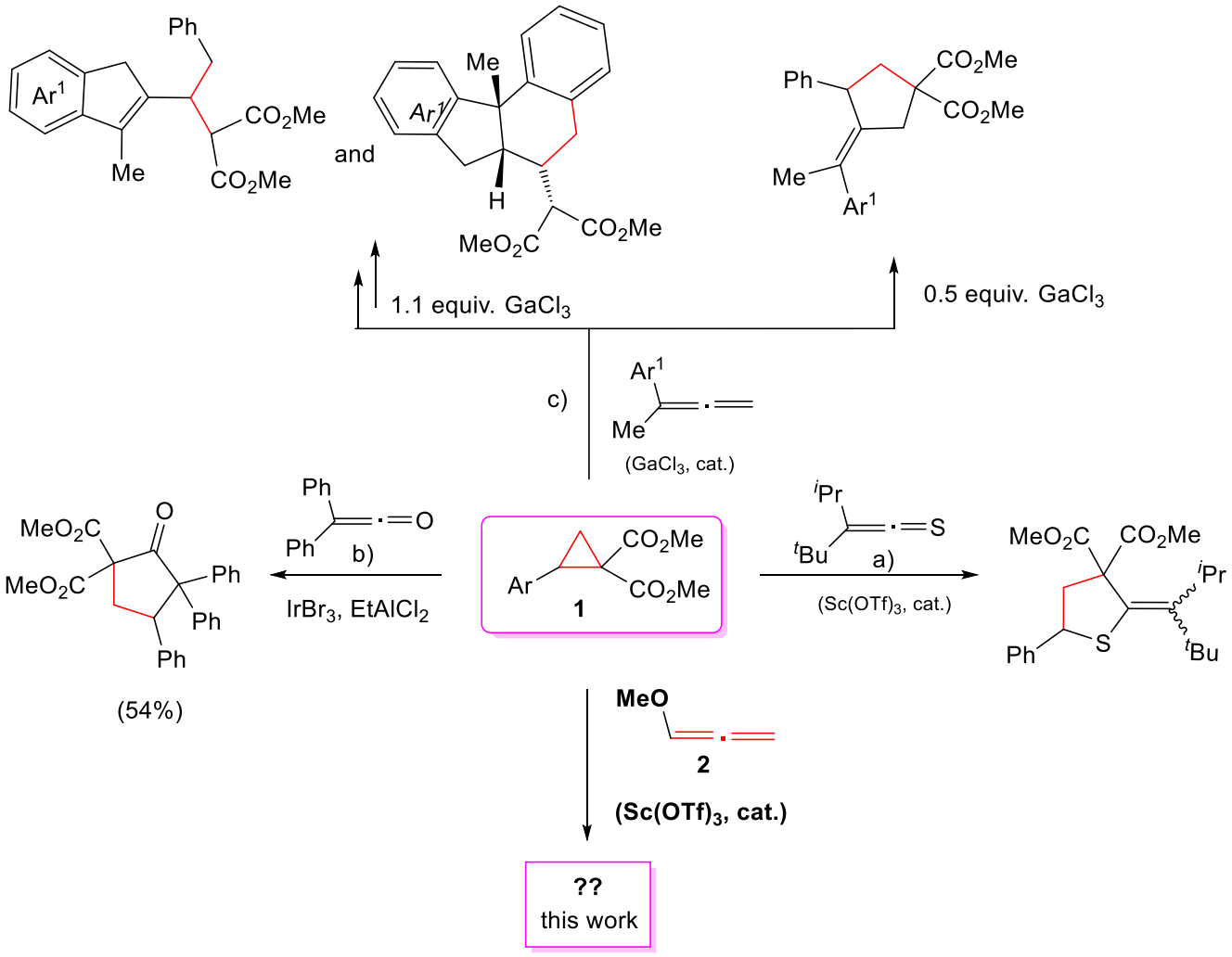
Dimethyl 2-arylcyclopropane-1,1-dicarboxylates (**1**) constitute a prominent class of so called D-A cyclopropanes (Donor-Acceptor Cyclopropanes), which in recent years are in the focus of interest of numerous research groups working in the field of modern organic synthesis[1--5] (including asymmetric methodology [6]) and interested in studying mechanisms of multi-step organic reactions leading to heterocyclic [7] and carbocyclic compounds.[8--10] In the presence of a Lewis acid, which activates the strained three-membered ring *via* chelation of the ester groups, D-A cyclopropanes **1** undergo ring opening reactions leading to cyclic or acyclic products. For example, thiocarbonyl compounds, containing the nucleophilic S-atom of the C=S functionality, were shown to undergo easily cycloaddition reactions with cyclopropanes **1** yielding the five-[11], six-[12] or seven-membered[13] sulfur heterocycles (Scheme 1). In this series, the ring size was constructed by using the appropriate thiocarbonyl substrates (thioketones, tropothione or thiochalcones, respectively). Notably, the enolizable heterocyclic thiones, e.g. 1*H*-tetrazole 5-thiones, were reported to yield in reactions with D-A cyclopropanes **1** either *N*- or *S*-adducts, depending on the substituent Ar [14,15] (Scheme 1).



Scheme 1. Representative cycloaddition and insertion reactions of D-A cyclopropanes **1** with thiocarbonyl compounds, acting as reactive nucleophiles, and leading to: a) ferrocenyl substituted thiolanes;[11] b) bicyclic thiopyrane derivatives;[12] c) functionalized tetrahydrothiepines;[13] d) *N*- and *S*-insertion products derived from 1*H*-tetrazole-5-thione.[14,15]

In the context of the presented study, special attention is focused on reactions with cumulenes. In the case of thioketenes, the respective (3+2) cycloaddition reactions were observed upon chemoselective involvement of the C=S bond in the formation of the *exo*-methylene functionalized thiolanes [16] (Scheme 2). Notably, a similar reaction of D-A cyclopropanes **1** with the *in situ* generated ketenes yielded highly substituted cyclopentanones.[17,18]

On the other side, widely studied cycloadditions of D-A cyclopropanes **1** with alkenes or alkynes lead to diverse carbocyclic products.[8] Conjugated dienes[9] as well as allenes[19] were also used in reactions with D-A cyclopropanes. Remarkably, in the latter case a more complicated reaction course was observed. Thus, in a recent work, it was demonstrated that the type of the carbocyclic product, obtained from 1-methyl-1-phenylallene in the $GaCl_3$ catalyzed reaction, was strongly dependent on the ratio of the Lewis acid and the starting D-A cyclopropane (Scheme 2).[19]



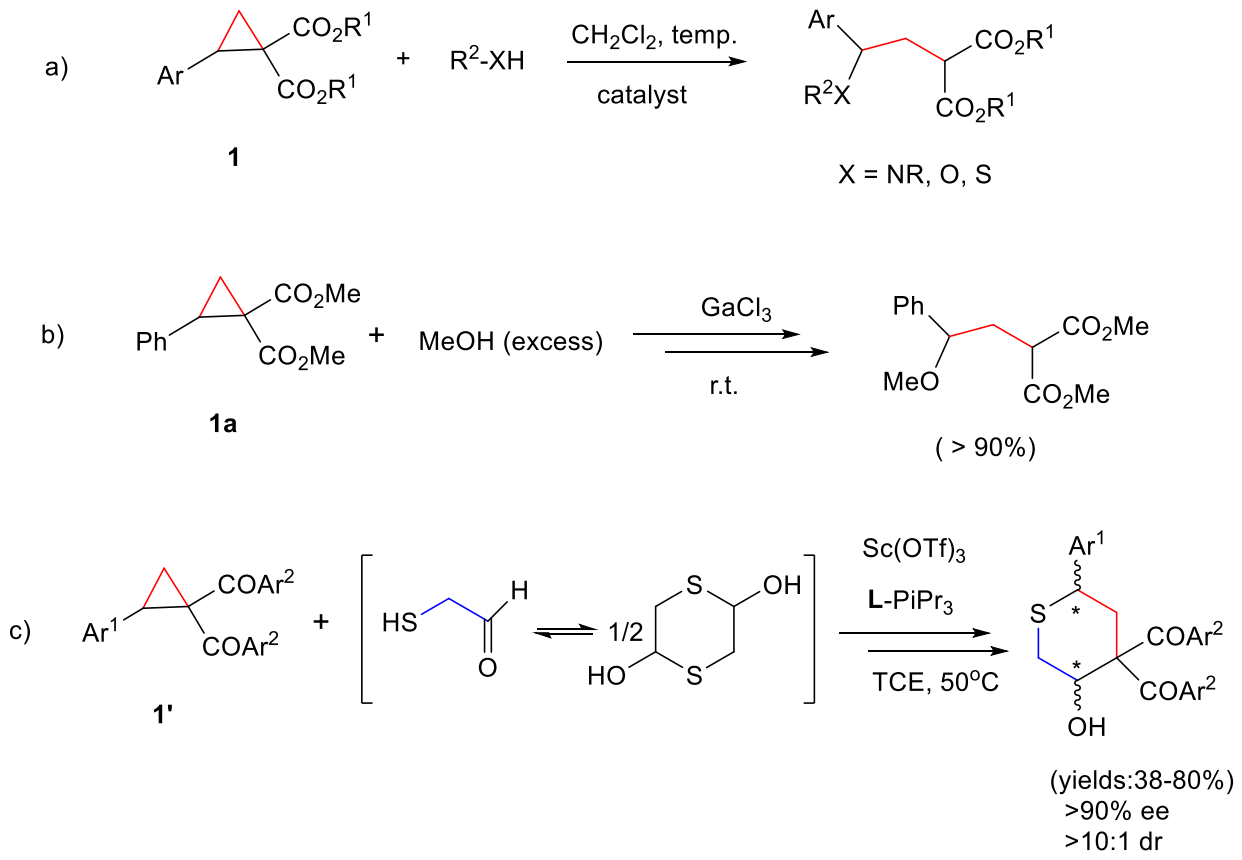
Scheme 2. Selected cycloaddition/annulation reactions of D-A cyclopropanes **1** with various cumulenes: a) thioketenes;[16] b) ketenes,[17,18] and c) 1-aryl-1-methylallenes.[19]

Reactions with various R^1–XH nucleophiles (X = R^2N, O, S) with D-A cyclopropanes **1**, leading to the ring opening and formation of chiral R^1X- substituted derivatives of malonic acid, have also been studied (Scheme 3). Thus, reactions with secondary amines lead to chiral, amino functionalized malonates, and in most of the reported reactions of this type, the final products were obtained in high yields with complete regioselectivity. Notably, some asymmetric reactions of this type have recently also been reported (Scheme 3).[5,20] In contrast to amines, reactions of D-A cyclopropanes **1** with alcohols are scarcely reported.[21,22] Finally, 1,3-additions of thiols onto the D-A cyclopropanes **1** were shown to yield the corresponding sulfane derivatives with complete

regioselectivity and in high yields.[21,24] Notably, in the reactions with thiophenols, CaI_2 in C_6H_5F solution was proved as the most efficient catalyst.[23]

In a single report the ring opening of **1a** with MeOH in the presence of $GaCl_3$ as a catalyst was reported to yield the corresponding adduct in 92%; however, there are no experimental details presented in the short publication (Scheme 3).[24]

Moreover, the stereoselective synthesis of a tetrahydrothiopyran derivative *via* a cascade of reactions starting with the nucleophilic S-attack of mercaptoacetaldehyde onto cyclopropanes **1'** deserves special attention (Scheme 3).[25]



Scheme 3. a) General scheme of ring opening reactions of D-A cyclopropanes **1** using aliphatic amines,[20] alcohols,[21,22] and thiols;[23] b) the reported example of the ring opening of D-A cyclopropane **1a** with MeOH in the presence of gallium chloride;[24] c) (3+3) annulation of D-A cyclopropanes **1'** with mercaptoacetaldehyde.[25]

Methoxyallene (**2**) is considered as an exceptional representative of cumulenes which has found a plethora of useful applications as a starting compound in syntheses of various carbo- and heterocyclic compounds,[26] including some bioactive carbohydrate mimetics.[27,28] However, in contrast to some aryl/alkyl substituted allenes, it has never been tested in reactions with a representative of D-A cyclopropanes.

In the context of the present work, it is worth mentioning that methoxyallene (**2**) as well as other alkoxyallenes were reported to undergo polymerization upon treatment with diverse Lewis acids, such as $NiCl_2/AlEt_3$, $CoCl_2/AlEt_3$, $TiCl_4$, $VOCl_3$, $FeCl_3/AlEt_3$, $PdCl_2$, etc,[29] or with $BF_3{\cdot}Et_2O$, and different structures, depending on the type of the Lewis acid used in the reaction, were proposed for the obtained polymers.[30] However, proposals were based on the assumption that the MeO functionality was stoichiometrically incorporated in the polymeric

chain. Notably, $Sc(OTf)_3$ has never been applied as an initiator in the reported polymerization processes of any alkoxyallene.

The goal of the present work was the examination of the behavior of methoxyallene (**2**) under conditions typical for reactions of dialkyl 2-arylcyclopropane-1,1-dicarboxylates **1**, i.e. in a neutral solvent and in the presence of a Lewis acid. In analogy to our earlier studies performed with D-A cyclopropanes **1**,[10-15] scandium triflate $Sc(OTf)_3$, used in cat. amounts, should be applied for activation of the strained cyclopropane ring. Noteworthy, the same catalyst has been applied for (3+2) cycloadditions of D-A cyclopropanes **1** with some ethylene derivatives.[31]

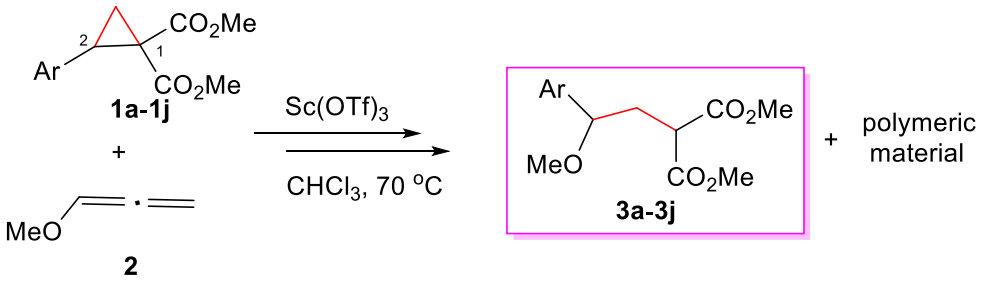
Results and Discussion

In a test experiment dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (**1a**) was dissolved in $CDCl_3$ with equimolar amounts of methoxyallene (**2**). Unexpectedly, after addition of cat. amounts of $Sc(OTf)_3$, immediate formation of a black suspension was observed; subsequently, the reaction solution was heated at 70°C for 4h. Examination of the reaction progress by ^{1}H NMR demonstrated that after this time both substrates were completely consumed. Two singlets attributed to the ester OMe fragments appeared at 3.74 and 3.71 ppm, and the third high-field shifted signal, found at 3.17 ppm, suggested the presence of a new OMe fragment. To our surprise no signals which could be attributed to the =CH(OMe) or $=CH_2$ in the anticipated (3+2) cycloadducts onto the allene system were found in the spectrum. The chromatographic separation (PLC plates, SiO_2, CH_2Cl_2/MeOH mixture (7:3)) led to isolation of a less polar oily material as well as a more polar fraction obtained as a viscous oil from the bottom line. It was soluble in acetone and precipitated after addition of hexane forming a colorless, amorphous solid identified as a typica, polymeric material with very complicated pattern of signals in the ^{1}H NMR spectrum registered in $CDCl_3$ solution. In the course of the described study, its structure was not in focus of the interest. Finally, the black material formed as a suspension in the reaction mixture was completely insoluble in organic solvents used in the course of the workup and left unchanged on the start-line.

The structure of the less polar, colorless product was elucidated based on the collected spectroscopic data. Thus, the ^{1}H NMR of this pure fraction revealed the presence of the above mentioned three OMe signals along with three multiplets located in narrow regions 4.16–4.12, 3.64–3.60 and 2.34–2.20 ppm, respectively, and the ratio of intensities was established to 1:1:2. On the other hand, the ^{13}C NMR demonstrated the presence of three signals of the OMe groups at 56.8, 52.5 and 48.7 ppm, respectively. Finally, the HRMS (ESI) confirmed the molecular mass *m/e* = 265.1080, which corresponded $[M–H]^-$ for a compound with the formula $C_{14}H_{18}O_5$. All these data suggested that the isolated product corresponds to an, 1:1 adduct of **1a** and MeOH, i.e. the methoxy functionalized malonate **3a** (Scheme 4). In fact, this compound was obtained by a completely different method described in an earlier publication.[32] The reported spectroscopic data (^{1}H and ^{13}C NMR) fitted well with those registered in our laboratory.

The yield of **3a** calculated after isolation as a pure sample was unsatisfactory (41%) and, therefore, the next optimization experiment was performed starting with the molar ratio of the starting materials (**2**/**1a**) changed to 2.5:1. Also, in this case the reaction was finished after 4h heating at 70°C and the ^{1}H NMR of the crude mixture was registered. Notably, along with the signals of the formed **3a** mentioned above, an additional, intense singlet at 3.50 ppm indicated the presence of the in situ formed and not consumed MeOH. Apparently, the latter was released from **2** in the initial step of the reaction. This time, the chromatographic workup led to **3a** as a pure, oily material in the high yield of 80%.

Based on this observation, further reactions of **2** with D-A cyclopropanes **1b**,**c** were also carried out starting with a molar ratio 2.5:1 of the substrates **2** and **1b** (or **1c**), and in both cases substantial increase of the yields of the isolated MeOH adducts **3b** and **3c**, respectively, was observed (Table 1). The series of experiments with **2** and D-A cyclopropanes **1d**–3**j** was performed starting with equimolar amounts of both substrates, and in all cases the anticipated adducts **3d**–**3j** were isolated in yields <50% (see Table 1).



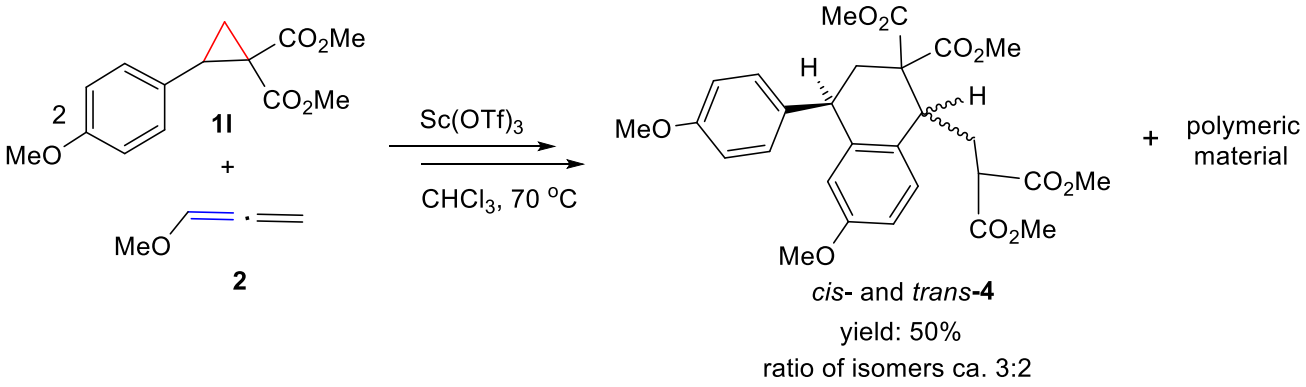
Scheme 4. The $Sc(OTf)_3$ catalysed, attempted reactions of D-A cyclopropanes **1a–1j** with methoxyallene (**2**); ring opening via the insertion of the in situ generated MeOH.

Table 1. Reactions of D-A cyclopropanes **1** with methoxyallene (**2**); reaction conditions and yields of isolated dimethyl malonate derivatives **3**.

Product **3**	Ar	Molar ratio **1**:**2**	Reaction time (h)	Yields (%) of isolated dimethyl malonates **3**
a	C_6H_5	1:1	4	41
		1:2.5	4	80
b	*p*-ClC_6H_4	1:1	52	33
		1:2.5	4	67
c	*p*-$CF_3C_6H_4$	1:1	4	26
		1:2.5	4	72
d	*o*-$CH_3C_6H_4$	1:1	4	43
e	*p*-$CH_3C_6H_4$	1:1	4	38
f	*p*-$C_6H_5C_6H_4$	1:1	4	32
g	*p*-BrC_6H_4	1:1	15	39
h	*p*-FC_6H_4	1;1	4	53
i	*m*-$NO_2C_6H_4$	1:1	32	32
j	*p*-$NO_2C_6H_4$	1:1	35	38
k	C_6F_5	1:1	>100	0
		1:2.5	>100	0

In the case of D-A cyclopropane **1k** bearing the C_6F_5 substituent, irrespective of the molar ratio of starting compounds, no formation of the MeOH adduct was observed, and extension of the reaction time led to slow decomposition of the starting cyclopropane.

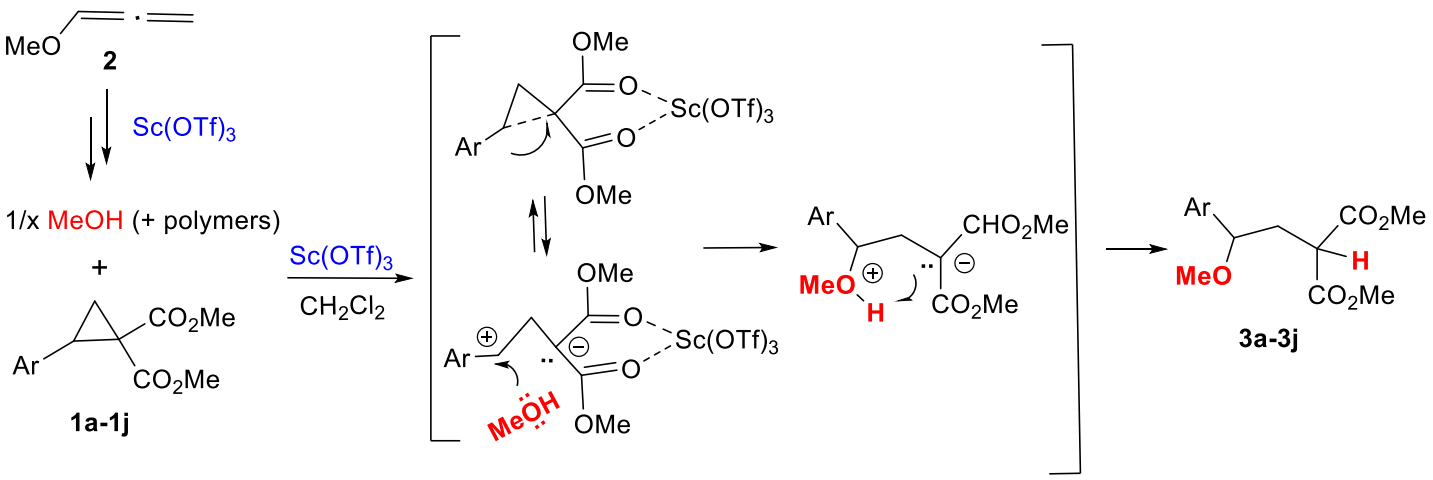
Unexpectedly, a completely different result was obtained in the experiments starting with methoxyallene (**2**) and D-A cyclopropane **1l**, bearing the *p*-anisyl ring at the C(2) atom. Irrespective of the molar ratio of substrates (1:1 or 2.5:1), the crude mixtures, isolated after preliminary separation of the polymeric material on a short chromatographic column, revealed in the ^{1}H NMR spectrum a very similar composition of both samples and demonstrated formation of a complicated mixture of products completely different from those observed in reactions with **1a**–**1j**. The spectrum suggested the presence of two isomeric compounds with sets of 12 singlets, attributed to diagnostic MeO groups, located in the region between 3.83 and 3.26 ppm. Attempted chromatographic separation (PLC, SiO_2) led to the isolation of a viscous oil which could be identified as a ca. 3:2 mixture of two isomeric dimers **4**. The most intense, characteristic absorptions of the MeO groups for the major component were found at 3.82, 3.71, 3.705, 3.70, 3.47 and 3.26 ppm, and at 3.83, 3.74, 3.65, 3.64, 3.45 and 3.27 ppm, respectively, for the minor one. In addition, eight signals attributed to C=O groups were found in the ^{13}C NMR at 172.8, 170.8, 168.6 and 168.5 ppm (major), and 172.2, 170.7, 169.1 and 168.5 ppm (minor), respectively. Finally, the anticipated molecular mass for the dimeric compounds **4** ($C_{28}H_{32}O_{10}$) was confirmed by HRMS, which revealed the exact mass corresponding to $[M+H]^+$ = 529.2075. Further attempts to separate these two isomeric compounds by standard, preparative layer chromatography were unsuccessful, however.



Scheme 5. (3+3) Cycloannulation of the D-A cyclopropane **1l** leading to ca. 3:2 mixture of isomeric dimers **4**.

Notably, formation of a mixture of identical dimeric compounds **4** was reported in an earlier publication.[33] However, in the reported case, separation of the major isomer, identified as *cis*-**4**, was achieved by fractional crystallization and its structure was confirmed by X-ray analysis.[33]

The interpretation of the obtained results deserves a comment. They showed that in most of the performed experiments, the observed reactions were initiated by a rapid extrusion of MeOH and subsequent polymerization of the starting **2**. Remarkably, after addition of a little portion of the catalyst, immediate formation of a black suspension, very likely consisting of elemental carbon [C], was observed. Apparently, ca. 60% of **2** was incorporated in the structure of a polymeric material without elimination of MeOH. The studied D-A cyclopropanes **1** were not reactive enough to trap **2** before it underwent this rapid conversion (Scheme 6).

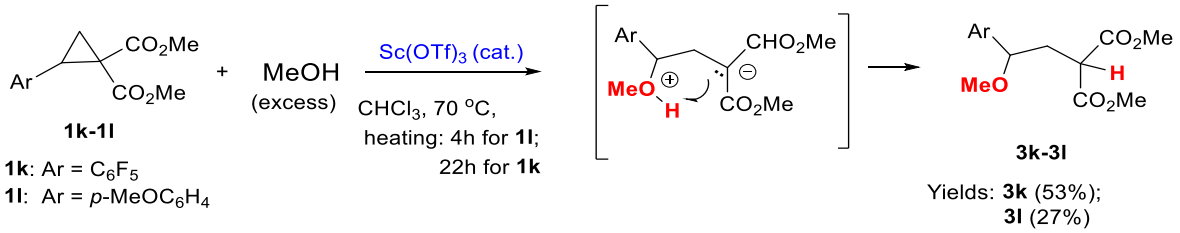


Scheme 6. The insertion reaction of the *in situ* generated MeOH with the activated D-A cyclopropanes **1**; mechanistic presentation of the reaction pathway.

Apparently, the ring opening reaction with the extruded MeOH, leading to adducts **1a**–**3j**, was a slower process; actually, D-A cyclopropanes **1** played the role of trapping reagents for the MeOH initially extruded from **2**.

Remarkably, in the experiments with equimolar amounts of starting materials, the yields of trapping products **3** were always estimated <50%. However, in experiments with the 2.5-fold molar ratio of **2**, the yields of isolated products **3** could be remarkably enhanced (>70%).

In the final stage of the study, D-A cyclopropanes **1k**-**1l**, which did not lead to the MeOH adducts in the attempted reactions with **2**, were tested in the ring-opening reactions performed in $CHCl_3$ solution at 70°C with added MeOH in the presence of cat. amounts of $Sc(OTf)_3$. The molar ration of MeOH and cyclopropane **1k** (or **1l**) was 2:1 (Scheme 7).



Scheme 7. The MeOH insertion reaction onto D-A cyclopropanes **1k** and **1l**.

Whereas reaction with **1k** required 22h of heating, the anisyl-analogue **1l** was completely consumed after 4h under the same conditions. However, the yield of isolated trapping product **3l** was significantly lower (27%) then in the case of **3k** (53%).

The observed difference in the reactivity of **1k** and **1l** deserves also a brief comment. They point out that the reactivity of the strained cyclopropanes **1** depends to some extent on the type of substituent Ar, which is of importance for the activating chelation of the ester groups by the Lewis acid (in this case $Sc(OTf)_3$). Whereas the electron-rich anisyl group (Ar = *p*-$MeOC_6H_4$) enables a strong chelation of the ester groups in **1l**, which apparently is competitive to the similar chelation of $Sc(OTf)_3$ with **2**, and therefore enables better polarization of the C(1)–C(2) bond leading to (3+3) cycloannulation, the electron withdrawing substituent C_6F_5 does not

support an efficient chelation. Apparently, in the reaction with methoxyallene (**2**), the Lewis acid is strongly coordinated with the latter, and maybe with the polymeric product formed therefrom. In the absence of **2,** not only **1l** but also **1k** was enough activated to undergo the reaction with MeOH leading to adducts **3l** and **3k**, respectively.

Conclusions

The present study shows that the electron-rich methoxyallene (**2**) behaves differently than aryl/alkyl substituted allenes toward D-A cyclopropanes **1**, and under typical reaction conditions, in the presence of cat. amounts of $Sc(OTf)_3$, it undergoes a fast polymerization reaction, which is initiated by partial elimination of MeOH. The latter acts as an O-nucleophile and reacts with activated **1** yielding the corresponding 2-methoxyethyl functionalized dimethyl malonates **3**. Competitive chelation of the catalyst by the electron-rich **2** can lead to some side reactions such as dimerization of **1l** or non-activation of **1k**, which finally prevent the reaction with MeOH. Remarkably, the behavior of D-A cyclopropanes **1** is determined by the type of the Ar substituent attached to the C(2)-atom.

The structure of the polymeric material formed under the presented conditions remains unknown at the moment and deserves further studies by a group interested in the chemistry of polymers formed from alkoxyallenes.

Experimental Section

General. Melting points were determined on a Stuart SMP30 apparatus with automatic temperature monitoring and are uncorrected. The ^1H, ^{13}C, and ^{19}F NMR spectra were measured on a Bruker Avance III (working at 600 MHz, 151 MHz and 565 MHz, for ^1H, ^{13}C and ^{19}F NMR, respectively). Chemical shifts are reported relative to solvent residual peaks (^1H NMR: δ= 7.26 ppm [$CHCl_3$], ^{13}C NMR = 77.16 ppm [$CDCl_3$], and to $CFCl_3$ for ^{19}F NMR δ= 0 ppm). All spectra were registered in $CDCl_3$ solution. Coupling constants *J* are given in Hz. The HRMS spectra were measured using a SynaptG2-Si mass spectrometer (Waters) equipped with an ESI source and quadrupole-time-of-flight mass analyzer instrument.

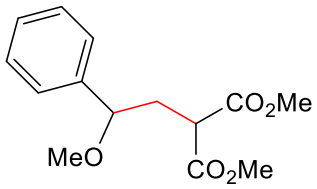
Starting materials. D-A Cyclopropanes **1a**–**1k** were prepared according to the published procedure starting with dimethyl diazomalonate and the corresponding styrene derivate; dirhodium tetraacetate ($Rh_2(OAc)_4$) was applied to catalyze decomposition of the carbenoid precursor.[34] Methoxyallene (**2**) was prepared following a known procedure comprising isomerization of methyl propargyl ether in the presence of potassium *tert*-butanolate in DMSO solution at 80°C.[35] During the storage at ambient conditions, **2** undergoes a slow polymerization and therefore its purification via distillation is recommended.

1. Attempted reactions of methoxyallene (**2**) *with D-A cyclopropanes* **1a–1j** *in the presence of cat. amounts of scandium triflate Sc(OTf)₃ – general procedure*: To a stirred solution of the corresponding D-A-cyclopropane **1** (0.25 mmol) in 0.5 mL $CHCl_3$ a cat. amount of scandium triflate $Sc(OTf)_3$ (ca. 5 mg, 0.01 mmol) was added at room temp. and subsequently a portion of 19 mg (0.27 mmol) (method **A**) [or 44 mg (0.62 mmol) (method **B**)] of freshly distilled methoxyallene (**2**) was added. In both methods, addition of **2** led to the formation of a black suspension (elemental carbon?). The stirred heterogenous mixture was heated in a thick-walled screwed tube

for 4–52 h. Next, the crude reaction mixture was separated by preparative layer chromatography using 20x20 cm plates coated with silca gel and using CH_2Cl_2 as an eluent. In some cases, a more polar solvent was added to CH_2Cl_2 (see separation methods presented for each compound **3**). All products were isolated as colorless, viscous oils.

A more polar fraction identified as a polymeric material could be isolated from the crude mixture using CH_2Cl_2 as an eluent. The isolated, viscous oil was disssolved in a portion of acetone (5 ml) and precipitated upon addition of hexane (5 ml). The colorless, polymeric, solid material was filtered off (40 mg) but it has not been identified within the presented project. The most polar fraction forming a black zone at the bottom line, did not move under the applied conditions.

Dimethyl 2-(2-methoxy-2-phenylethyl)malonate (3a): colorless oil,[32,36] yield: 53 mg, 80% (method B); CH_2Cl_2 was used as an eluent for chromatographic separation.

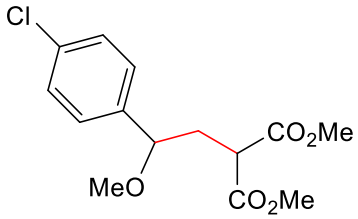


3a

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.3−7.31 (m, 2$C_{sp2}H$), 7.30−7.26 (m, 3 $C_{sp2}H$), 4.16−4.12 (m, $C_{sp3}H$), 3.74 (s, OCH_3), 3.71 (s, OCH_3), 3.64−3.60 (m, $C_{sp3}H$), 3.17 (s, OCH_3), 2.34−2.20 (m, CH_2).

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.8, 169.7 (2 C=O), 141.0 (C_{sp2}), 128.5 (2C_{sp2}H), 127.8 (C_{sp2}H), 126.5 (2C_{sp2}H), 81.3 (C_{sp3}H), 56.8 (CO_2CH_3), 52.5 (C_{sp3}H), 52.4 (CO_2CH_3), 48.7 (OCH_3), 37.2 (CH_2).

HRMS (ESI) $C_{14}H_{18}O_5$ requires 266.2897, found 265.1080 $[M–H]^-$.



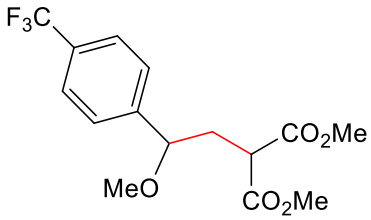
3b

Dimethyl 2-(2-(4-chlorophenyl)-2-methoxyethyl)malonate (**3b**): colorless oil,[36,37] yield 50 mg (67%) (method B); CH_2Cl_2 was used as an eluent for chromatographic separation.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, $^3J_{H,H}$ = 12Hz, 2$C_{sp2}H$), 7.21 (d, $^3J_{H,H}$ = 12Hz, 2$C_{sp2}H$), 4.14−4.10 (m, $C_{sp3}H$), 3.73, 3.70 (2s, 2CO_2CH_3), 3.61−3.57 (m, $C_{sp3}H$), 3.14 (s, OCH_3), 2.28−2.16 (m, CH_2).

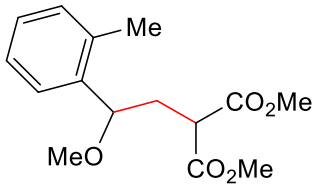
^{13}C NMR (150 MHz, $CDCl_3$) δ 169.7, 169.6 (2C=O), 139.6, 133.6 (2C_{sp2}), 128.7, 127.9 (2C_{sp2}H), 80.7 (C_{sp3}H), 56.8 (C_{sp3}H), 52.5, 52.4 (2CO_2CH_3), 48.5 (OCH_3), 37.1 (CH_2).

HRMS (ESI) $C_{14}H_{17}O_5Cl$ requires 300.7348, found 299.0682 $[M–H]^-$.



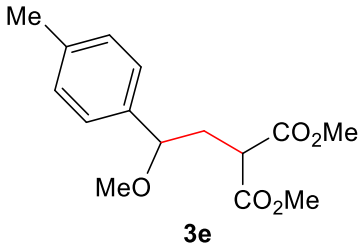
3c

Dimethyl 2-(2-methoxy-2-(4-trifluoromethyl)phenylethyl)malonate (**3c**): colorless oil, yield: 60 mg (72%) (method B); CH_2Cl_2 was used as an eluent for chromatographic separation.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, $^3J_{H,H}$ = 12Hz, 2$C_{sp2}H$), 7.41 (d, $^3J_{H,H}$ = 12Hz, 2$C_{sp2}H$), 4.25−4.21 (m, $C_{sp3}H$), 3.75, 3.70 (2s, 2CO_2CH_3), 3.65−3.61 (m, $C_{sp3}H$), 3.18 (s, OCH_3), 2.26−2.22 (m, CH_2).
^{13}C NMR (150 MHz, $CDCl_3$) δ 169.6, 169.5 (2C=O), 130.1 (q, $^2J_{C-F}$ = 30Hz, C_{sp2}), 126.7 (C_{sp2}), 125.5 (q, $^3J_{C-F}$ = 3.2Hz, 2C_{sp2}H), 124.1 (q, $^1J_{C-F}$ = 273Hz, CF_3), 80.8 (C_{sp3}H), 57.1 (C_{sp3}H), 52.5, 52.4 (2CO_2CH_3), 48.5 (OCH_3), 37.1 (CH_2).
^{19}F NMR (565 MHz, $CDCl_3$) δ −62.5
HRMS (ESI) $C_{15}H_{17}F_3O_5$ requires 334.2877, found 333.0951 $[M–H]^-$.



3d

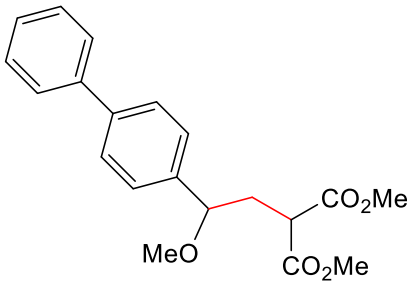
Dimethyl 2-(2-methoxy-2-(*o*-tolyl))ethyl)malonate (**3d**): colorless oil, yield: 36 mg (51%) (method A); CH_2Cl_2 was used as an eluent for chromatographic separation.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, $^3J_{H.H}$ = 6Hz, $C_{sp2}H$), 7.22–7.18 (m, $C_{sp2}H$), 7.17–7.14 (m, $C_{sp2}H$), 7.12 (d, $^3J_{H.H}$ = 6Hz, $C_{sp2}H$), 4.43–4.39 (m, $C_{sp3}H$), 3.77, 3.70 (2s, 2CO_2CH_3), 3.76–3.72 (m, $C_{sp3}H$), 3.16 (s, OCH_3), 2.32 (s, CH_3), 2.25–2.12 (m, CH_2).
^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 169.8 (2C=O), 139.1, 135.3 (2C_{sp2}), 130.5, 127.3, 126.2, 125.5 (4C_{sp2}H), 77.7, 52.4 (2C_{sp3}H), 56.7, 52.4 (2CO_2CH_3), 48.6 (OCH_3), 36.1 (CH_2), 18.7 (CH_3).
HRMS (ESI) $C_{15}H_{20}O_5$ requires 280.3163, found 279.1228 $[M–H]^-$.



3e

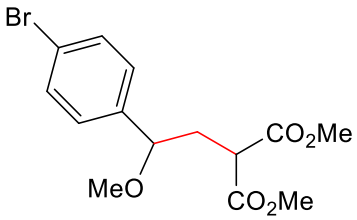
Dimethyl 2-(2-methoxy-2-(*p*-tolyl))ethyl)malonate (**3e**): colorless oil,[36,37] yield: 27 mg (38%) (method A); CH_2Cl_2 was used as an eluent for chromatographic separation.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (d, $^3J_{H,H}$ = 6Hz, 2$C_{sp2}H$), 7.15 (d, $^3J_{H,H}$ = 6Hz, 2$C_{sp2}H$), 4.13−4.08 (m, $C_{sp3}H$), 3.73, 3.71 (2s, CO_2CH_3), 3.63−3.58 (m, $C_{sp3}H$), 3.15 (s, OCH_3), 2.33 (s, CH_3), 2.30−2.18 (m, CH_2).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 169.7 (2C=O), 137.0, 137.5 (2C_{sp2}), 129.2, 126.5 (4C_{sp2}H), 81.1, 52.4 (2C_{sp3}H), 56.6, 52.4 (2CO_2CH_3), 48.7 (OCH_3), 37.2 (CH_2), 21.1 (CH_3).
HRMS (ESI) $C_{15}H_{20}O_5$ requires 280.3163, found 303.1209 $[M+Na]^+$.



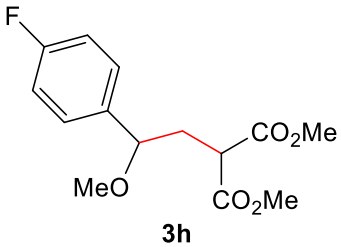
3f

Dimethyl 2-(2-(biphenyl-4-yl)-2-methoxyethyl)malonate (**3f**): colorless oil, yield: 27 mg (32%) (method A); CH_2Cl_2 was used as an eluent for chromatographic separation.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61−7.55 (m, 4$C_{sp2}H$), 7.45−7.40 (m, 2C_{sp2}H), 7.38–7.31 (m, 3C_{sp2}H), 4.23−4.19 (m, $C_{sp3}H$), 3.76, 3.73 (2s, CO_2CH_3), 3.69−3.64 (m, $C_{sp3}H$), 3.22 (s, OCH_3), 2.40−2.25 (m, CH_2).
^{13}C NMR (151 MHz, $CDCl_3$) δ 169.8, 169.7 (2C=O), 140.8, 140.7, 140.0 (3C_{sp2}), 128.7, 127.2, 127.0, 125.9, 127.3 (for 9C_{sp2}H), 81.0, 52.5 (2C_{sp3}H), 56.8, 52.4 (2CO_2CH_3), 48.7 (OCH_3), 37.1 (CH_2).
HRMS (ESI) $C_{20}H_{22}O_5$ requires 342.3857, found 341.1393 $[M–H]^-$.



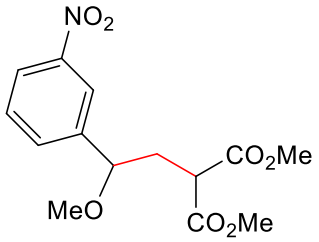
3g

Dimethyl 2-(2-(4-bromophenyl)-2-methoxyethyl)malonate (**3g**): colorless oil, yield: 34 mg (39%) (method A); CH_2Cl_2 was used as an eluent for chromatographic separation.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, $^3J_{H,H}$ = 12Hz, 2$C_{sp2}H$), 7.16 (d, $^3J_{H,H}$ = 12Hz, 2$C_{sp2}H$), 4.13−4.09 (m, $C_{sp3}H$), 3.73, 3.70 (2s, CO_2CH_3), 3.61−3.57 (m, CH), 3.15 (s, OCH_3), 2.28−2.14 (m, CH_2).
^{13}C NMR (151 MHz, $CDCl_3$) δ 169.7, 169.6 (2C=O), 140.2 (C_{sp2}), 131.7, 128.2 (2C_{sp2}H), 121.7 (C_{sp2}), 80.7 (C_{sp3}H), 56.9 (C_{sp3}H), 52.50, 52.52 (2CO_2CH_3), 48.5 (OCH_3), 37.1 (CH_2).
HRMS (ESI) $C_{14}H_{17}BrO_5$ requires 345.1858, found 345.0161 $[M]^+$, 343.0182 $[M–2H]^{-2}$.



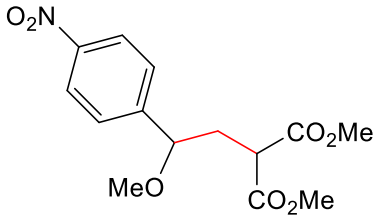
3h

Dimethyl 2-(2-(4-fluorophenyl)-2-methoxyethyl)malonate (**3h**): colorless oil, yield: 27 mg (53%) (method A). A mixture of CH_2Cl_2 and MeOH (99:1) was used as an eluent for chromatographic separation.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26−7.22 (m, 2$C_{sp2}H$), 7.04−6.99 (m, 2$C_{sp2}H$), 4.14−4.11 (m, $C_{sp3}H$), 3.73, 3.70 (2s, 2CO_2CH_3), 3.61−3.57 (m, $C_{sp3}H$), 3.14 (s, OCH_3), 2.30−2.16 (m, CH_2).
^{13}C NMR (150 MHz, $CDCl_3$) δ 169.8, 169.6 (2*C*=O), 163.2 (d, $^1J_{C,F}$ = 246Hz, C_{sp2}F), 136.8 (d, $^4J_{C,F}$ = 3Hz, C_{sp2}), 128.1 (d, $^3J_{C,F}$ = 8Hz, 2C_{sp2}), 115.4 (d, $^2J_{C,F}$ = 21Hz, 2C_{sp2}), 80.6 (C_{sp3}H), 56.7 (C_{sp3}H), 52.5, 52.4 (2CO_2CH_3), 48.6 (OCH_3), 37.2 (CH_2).
^{19}F NMR (565MHz, $CDCl_3$) δ −114.6
HRMS (ESI) $C_{14}H_{17}FO_5$ requires 284.2802, found 283.0983 [M–H]$^-$.



3i

Dimethyl 2-(2-methoxy-3-nitrophenyl)ethyl)malonate (**3i**): colorless oil,[36] yield: 25 mg (32%) (method A). A mixture of CH_2Cl_2 and hexane (8:2) was used as an eluent for chromatographic separation.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (s, $C_{sp2}H$), 8.17−8.12 (m, $C_{sp2}H$), 7.63 (d, $^3J_{H,H}$ = 6Hz, $C_{sp2}H$), 7.55−7.50 (m, $C_{sp2}H$), 4.31−4.26 (m, $C_{sp3}H$), 3.76, 3.71 (2s, 2CO_2CH_3), 3.66−3.62 (m, $C_{sp3}H$), 3.20 (s, OCH_3), 2.27−2.23 (m, CH_2).
^{13}C NMR (151 MHz, $CDCl_3$) δ 169.5, 169.4 (2*C*=O), 148.6, 143.7 (2C_{sp2}), 132.5, 129.6. 122.9, 121.4 (4C_{sp2}H), 80.4 (C_{sp3}H), 57.2 (C_{sp3}H), 52.6, 52.5 (2CO_2CH_3), 48.4 (OCH_3), 37.1 (CH_2).
HRMS (ESI) $C_{14}H_{17}NO_7$ requires 311.2873, found 310.0934 [M–H]$^-$.

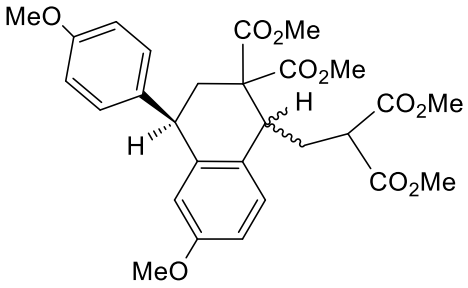


3j

Dimethyl 2-(2-methoxy-4-nitrophenyl)ethyl)malonate (**3j**): colorless oil, yield: 30 mg (38%) (method A); CH_2Cl_2 was used as an eluent for chromatographic separation.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, $^3J_{H,H}$ = 12Hz, 2$C_{sp2}H$), 7.48 (d, $^3J_{H,H}$ = 12Hz, 2$C_{sp2}H$), 4.30−4.27 (m, $C_{sp3}H$), 3.75, 3.70 (2s, CO_2CH_3), 3.66−3.61 (m, C $_{sp3}H$), 3.19 (s, OCH_3), 2.26−2.20 (m, CH_2).
^{13}C NMR (151 MHz, $CDCl_3$) δ 169.5, 169.4 (2*C*=O), 148.8, 147.7.6 (2C_{sp2}), 127.2, 123.9 (2C_{sp2}H), 80.5 (C_{sp3}H), 57.3 (C_{sp3}H), 52.6, 52.5 (2CO_2CH_3), 48.3 (OCH_3), 37.0 (CH_2).
HRMS (ESI) $C_{14}H_{17}NO_7$ requires 311.2873, found 310.0934 [M–H]$^-$.

2. *Attempted reaction of dimethyl 2-anisylcyclopropane-1,1-dicarboxylate* (**1l**) *with methoxyallene* (**2**): To a solution of **1l** (53 mg, 0.20 mmol) and **2** (35 mg, 0.50 mmol) in 0.5 ml $CHCl_3$ a cat. amount of $Sc(OTf)_3$ was added (5 mg, 0.01 mmol). Under magnetical stirring the solution was heated in a screwed thick-walled tube in an oil bath at 70°C. The progress of the reaction was tested by TLC, and after 4h no starting **1l** could be detected. The

preparative chromatographic separation was carried out on glass plates coated with silica and CH_2Cl_2/ethyl acetate (95:5) was used as an eluent). A fraction of a colorless oil with a R_f value of ca. 0.5 was isolated as a single product. The ^{1}H NMR examination of this material demonstrated that it consists of two isomeric compounds identified as the known dimer **4** of the starting D-A **1l**. Further attempts to separate the isomeric compounds **4** by standard chromatography were unsuccessful.



cis- and *trans*-**4**

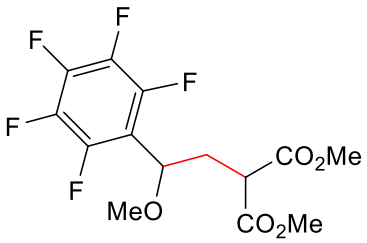
***cis*- and *trans*-Dimethyl 6-methoxy-(3-methoxy-2-(methoxycarbonyl)-3-oxopropyl-4-(4-methoxyphenyl)-3,4-dihydronaphtalene-2,2-(1*H*)-dicarboxylate)** (*cis*- and *trans*-**4**) (unknown assignment of configuration). Isolated as a viscous oil (compare with ref.[33]). Yield: 27 mg (50%).

Selected signals from the spectra: ^{1}H NMR (600 MHz, $CDCl_3$) δ (major) 7.02 (d), 6.96 (d), 6.70−6.67 (m), 3.98−3.94 (m, $C_{sp3}H$), 3.82, 3.71, 3.705, 3.70, 3.47, 3.26 (6s, 6OCH_3); □ (minor) 6.78 (d), 6.72 (d), 6.56−6.51 (m), 4.13 (d, C_{sp3}H), 3.83, 3.74, 3.65, 3.64, 3.45, 3.27 (6s, 6OCH_3).

^{13}C NMR (151 MHz, $CDCl_3$) δ (major) 172.8, 170.8, 168.6, 168.5 (4C=O), 158.2, 158.1 (C_{sp2}O), 132.7, 132.6 (2C_{sp2}), 129.5, 128.4 (for 4C_{sp2}H), 113.6, 113.4, 61.3, 55.09, 55.07, 53.2, 52.6, 52.0, 51.9, 51.7, 49.7 and 42.1 (2$C_{sp3}H_2$); □ (minor) 172.2, 170.7, 169.1, 168.5 (4C=O), 157.7, 157.6 (C_{sp2}O), 133.0, 132.1 (2C_{sp2}), 130.1, 129.2 (for 4C_{sp2}H), 113.0, 112.9, 61.7, 55.0, 54.9, 52.9, 52.7, 52.5, 52.2, 51.8, 51.0, 50.6, 47.3 and 39.9 (2$C_{sp3}H_2$).

HRMS (ESI) $C_{28}H_{32}O_{10}$ requires 528.5477: found 529.2075 $[M+H]^+$, 551.1896 $[M+Na]^+$.

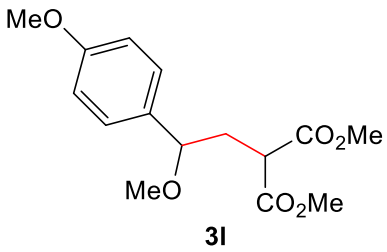
3. *Reactions of D-A cyclopropanes* **1k** *and* **1l** *with MeOH in the presence of scandium triflate Sc(OTf)$_3$ – general procedure*: A magnetically stirred solution of 0.2 mmol of the corresponding cyclopropane **1** and 0.4 mmol (13 mg) MeOH in 0.5 ml $CHCl_3$ was placed in a screwed thick-walled tube, and after additon of catal. amounts of $Sc(OTf)_3$ (ca. 5 mg, 0.01 mmol) was heated in an oil bath at 70°C. The progress of the reaction was monitored by running the ^{1}H NMR spectra and the reaction was completed after 4h in the case of **1l** and after 22h in the case of **1k**, respectively. The crude reaction mixture was separated by PLC (preparative layer chromatography) on 20x20 cm glass plates coated with silica gel and using CH_2Cl_2 as an eluent.



3k

Dimethyl 2-(2-methoxy-2-(perfluorophenyl)ethyl)malonate (3k): colorless oil, yield: 38 mg (53%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.65−4.60 (m, $C_{sp3}H$), 3.75, 3.74 (2s, $2CO_2CH_3$), 3.64−3.59 (m, $C_{sp3}H$), 3.22 (s, OCH_3), 2.70−2.62, 2.31−2.25 (2m, CH_2).
^{13}C NMR (151 MHz, $CDCl_3$) δ 169.2, 169.1 ($2C$=O), 146.3−136.6 (6m, for $5C_{sp2}F$), 113.8−113.4 (m, C_{sp2}), 72.6 ($C_{sp3}H$), 57.5, 52.65, 52.63 ($3OCH_3$), 48.6 ($C_{sp3}H$), 33.7−33.6 (m, CH_2).
^{19}F NMR (565 MHz, $CDCl_3$) δ −142.3/−142.4 (m, $C_{sp2}F$), −153.7/−153.8 (m, $C_{sp2}F$), −161.4/−161.5 (m,$2C_{sp2}F$)
HRMS (ESI) $C_{14}H_{13}F_5O_5$ requires 356.2420, found 379.0589 $[M+H+Na]^+$.



3l

Dimethyl 2-(2-methoxy-2-(4-methoxyphenyl)ethyl)malonate (**3l**): colorless oil, yield: 16 mg (27%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (d, $^{3}J_{H,H}$ = 6 Hz, $2C_{sp2}H$), 6.87 (d, $^{3}J_{H,H}$ = 6 Hz, 2 $C_{sp2}H$), 4.11−4.07 (m, $C_{sp3}H$), 3.80 (OCH_3; *p*-anisyl), 3.73, 3.71 (2s, $2OCH_3$), 3.61−3.57 (m, $C_{sp3}H$), 3.14 (s, OCH_3), 2.34−2.27/2.23−2.17 (2m, CH_2).
^{13}C NMR (150 MHz, $CDCl_3$) δ 169.9, 169.7 (2C=O), 159.3 ($C_{sp2}OCH_3$), 133.0 (C_{sp}^{2}), 127.8, 113.9 (for $4C_{sp2}H$), 80.9 ($C_{sp3}H$), 56.5, 55.2 ($2CO_2CH_3$), 52.5, 52.4 ($2OCH_3$), 48.8 ($C_{sp3}H$), 37.2 (CH_2).
HRMS (ESI) $C_{15}H_{20}O_6$ requires 296.3157, found 319.1161 $[M+Na]^+$.

Acknowledgements

Authors thank prof. Daniel Werz and his collaborators (University of Freiburg) for generous gift of D-A cyclopropanes used in this study. A helpful discussion with prof. H. Heimgartner (University of Zurich), and prof. Z. Witczak (Wilkes University) in the last stage of preparation of this manuscript is also acknowledged.

Supplementary Material

Copies of ^{1}H and ^{13}C NMR spectra of compounds **3a-3l** and **4** are available in the supplementary material file associated with this paper.

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