Photochemical Synthesis of Prochiral Dialkyl 3,3-Dialkylcyclopropene-1,2-dicarboxylates with Facial Shielding Substituents and Related Substrates

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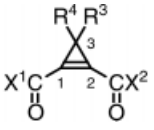
Keywords: Alkynes / Cyclopropenes / Oxadiazolines / Pyrazoles / Strained molecules

Different types of cyclopropene-1,2-dicarboxylates **1** have been obtained by photochemical methods from the corresponding pyrazoles **11**, **12**, or **13**. These pyrazoles were synthesized by 1,3-dipolar cycloadditions of alkynes **8** or **9** with either preformed diazoalkanes or diazoalkanes generated photochemically in situ, by use of oxadiazolines as diazoalkane precursors. The numerous substrates have clearly established the scope and limitations of the syntheses of the precursors and the cyclopropenes by the different routes; even prochiral and enantiomerically pure chiral derivatives could be synthesized. Numerous precursors and cyclopropenes could be characterized by X-ray crystal structure analyses, which revealed interesting structural features and allowed unequivocal assignment of different diastereomers or constitutional isomers. Some of the photochemical reactions produced unique side-products; the crystal structure analyses were absolutely crucial for unambiguous structural assignment here.

Introduction

We recently investigated the formation of *trans*-5-palladatricyclo[4.1.0.0^{2,6}]heptanes[1] through an oxidative cyclization of two cyclopropenes at a Pd^0 centre. For that purpose we needed to prepare two series of dialkyl 3,3-dialkylcyclopropene-1,2-dicarboxylates **1**.

In one series, the alcohol component of the ester groups is derived from enantiomerically pure (discounting cases of achiral alcohols) α- or β-hydroxy carboxylates. The cyclopropenes each bear two methyl groups at the 3-position of the cyclopropene (**1α** for two identical alcohols in the ester groups, **1β** for two different ones). These allowed enantiomerically pure palladacycles to be synthesized highly stereoselectively; the stereoselectivity is based on a regioselective reaction of the coordinated strained olefin.[2] Another interesting result obtained with these substrates was the synthesis of the first stable palladepanes, stable palladacycloheptanes that do not reductively eliminate cyclohexane derivatives.[3] For both **1α** and **1β** it was possible to prepare not only esters but also amides (Scheme 1).



1α $X^1 = X^2$; $R^3 = R^4 = CH_3$

1β $X^1 \neq X^2$; $R^3 = R^4 = CH_3$

1γ $X^1 = X^2$; $R^3 = R^4 \neq CH_3$ or $R^3 \neq R^4$

Scheme 1. Different types of cyclopropene-1,2-dicarboxylates **1**

In the second series, we needed to place two substituents other than methyl − often two substituents with different steric demands, or even chiral substituents − at the 3-position of the cyclopropene (**1γ**, with, for example, R^4 bulkier than R^3). With such substrates we were studying an entirely different stereochemical question: the facial selection during the oxidative cyclization (and not the regioselection mentioned above) resulting in the palladacycles.[4] Lastly, combination of this approach with use of esters of chiral alcohols was conceivable. Here we present the scope and limitation of our synthetic route to these classes of cyclopropenes.

Results and Discussion

There are numerous ways to synthesize cyclopropenes.[5] Many of these methods, such as formation of the double bond by elimination with a strong base, are not compatible with the presence of α-chiral ester groups or esters with carboxylate leaving groups in β-position. We therefore chose to form the cyclopropenes by a route based on earlier work by Franck-Neumann et al., who prepared doubly acceptor-substituted cyclopropenes such as **1** by means of photochemical reactions of pyrazoles **11**, **12**, or **13**.[6] These pyrazoles were obtained by 1,3-dipolar cycloadditions of acetylenedicarboxylates **8** or **9** with diazoalkanes **10**.[7] While several simple dialkyl derivatives of **8** were commercially available, the synthesis of chiral derivatives in particular remained a challenge. Fortunately, just as we began our investigation, Charlton et al. published a method for the preparation of such substrates.[8] In analogy with Charlton's results, "protection" of the triple bond of the relatively electron-rich dipotassium acetylenedicarboxylate (prepared in situ from the monopotassium salt **2** and KOH) by bromine, followed by the formation of the diacid dichloride **4** from the diacid **3** with PCl_5 in pentane (Scheme 2), esterification (to **5**, Scheme 3) and subsequent removal of the "protecting

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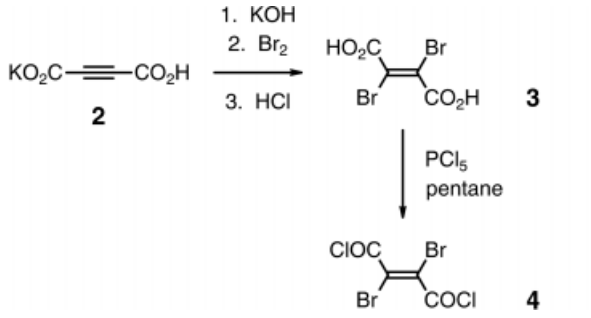
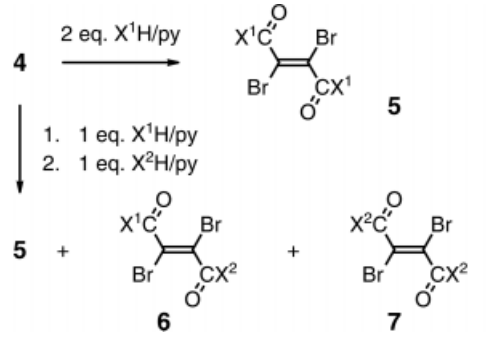
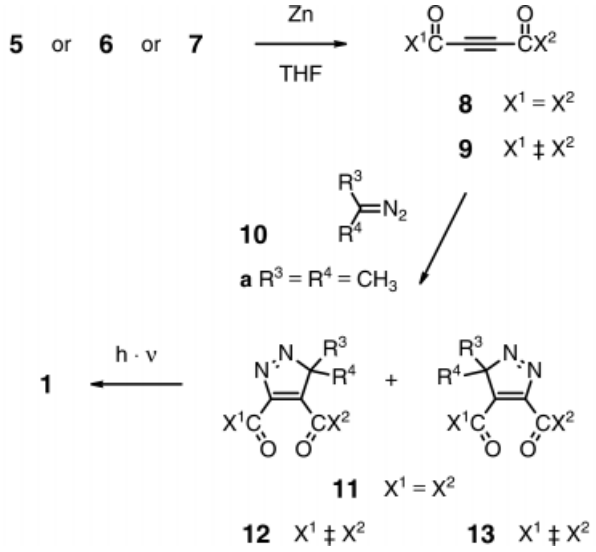
group'' with zinc also proved superior to other methods in our case (Scheme 4).



Scheme 2. Synthesis of the diacid dichloride **4**

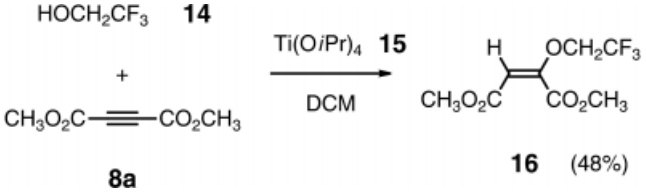


Scheme 3. Esterification of **4**



Scheme 4. Synthesis of **1**

In addition to the other methods discussed by Charlton et al., we also examined a transesterification.[9] However, the activation of the carboxylate carbon atom towards nucleophilic attack also activated the Michael system towards nucleophilic attack (Scheme 5). Hence, the enol ether **16** was produced from **14** and **8a** with Ti(O*i*Pr)$_4$ (**15**).



Scheme 5. Catalysed addition of trifluoroethanol to **8a**

The (*E*) configuration of the double bond in **16** was established by X-ray crystal structure analysis[10] (Figure 1) and is probably the result of thermodynamic control, providing a stereoelectronically favourable (*E*) arrangement of the alkoxy donor and the ester group as a π-acceptor. Because of steric repulsion between O(2) and C(5), the molecule shows a small deviation from planarity. The observed O(2)···C(5) distance of 2.782(1) Å is slightly shorter than the van der Waals contact distance. The angle between the plane of the methoxycarbonyl group labelled O(3), O(4), C(5), and C(6) and the plane of the C(3)−C(4) double bond is 67°, and so the other methoxycarbonyl group and the alkoxy group are in conjugation. This large value is required in order to avoid steric repulsion between O(3) and O(5). The observed O(3)···O(5) distance of 2.787(1) Å corresponds to the van der Waals contact distance between O atoms. The crystal packing shows an intermolecular distance of 2.35(1) Å between O(4) and H(7A) of a neighbouring molecule, which approaches the van der Waals contact distance between O and H and may be characterized as a weak, electrostatic interaction.

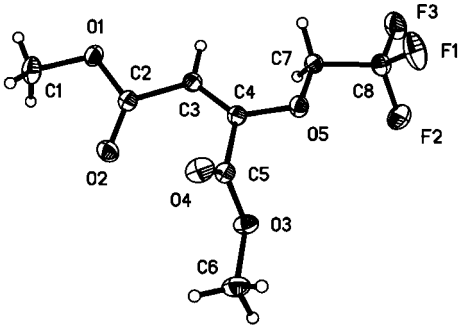


Figure 1. X-ray crystal structure of **16** (ORTEP plot)

Synthesis of Cyclopropenes 1α

By following the Charlton route and then applying Franck-Neumann's sequence, we obtained the results shown in Table 1.

The yields of the first step, the synthesis of **5**, range from 10 to 88%. One possible explanation for the large fluctuation in the yields is that the sequence from **2** to **4** was always performed without any purification, and so the quality of **4** was variable. X-ray crystal structure analyses were obtained for the dibromides **5j**, **5k**, and **5m**.[10] These showed an interesting feature; the central unit in the crystal

Table 1. Synthesis of dibromofumarates **5**, acetylenedicarboxylates **8**, pyrazoles **11**, and cyclopropenes **1α** with $X^1 = X^2$ and $R^3 = R^4 = CH_3$

	$X^1 = X^2$	Yields [%] of **5**	**8**	**11**	**1α**
a	OCH_3	–	–[a]	–[b]	92[c]
b	OCH_2CH_3	–	–[a]	66[d]	76[d]
c	OCH_2CF_3	–	–[e]	36[d]	54[d]
d	$OCH_2CH_2CH_3$	82	90	75	90
e	O*t*Bu	–	–[a]	65[f]	76[f]
f	OPh	81[g]	62[h]	66[g]	16
g	$OCH_2CH{=}CH_2$	84	94	91	91
h	$OCH_2C{\equiv}CH$	82	70	85	82
i	$OCH_2CH_2OCH_3$	65	85	53	91
j	$OCH_2CO_2CH_3$	88	51	50	89
k	$OCH_2C(CH_3)_2CO_2CH_3$	54	91	38	89
l	$OCH_2C(=O)N(-CH_2CH_2-CH_2CH_2CH_2-)$	29	–[i]	–	–
m	$N(CH_2CH_2CH_2CH_3)_2$	75	88	80	95
n	$N(-CH_2CH_2CH_2CH_2-)$	42	97	–[i]	–
o	(*S*)-$OCH(CH_3)CO_2CH_2CH_3$	55[j]	65[j]	60	96
p	(*R*)-$OCH(CH_3)CO_2C(CH_3)_3$	10	75	55	96
q	(*S*)-$OCH(CH_3)CO_2CH_3$	50	55	64	75
r	(*S*)-$OCH(CH_3)CO_2CH(CH_3)_2$	31	59	65	75
s	(*S*)-$OCH(C_6H_5)CO_2CH_3$	68[j]	–[i]	–	–
t	(*S*)-$OCH(CO_2CH_3)CH_2CO_2CH_3$	51	68	70	44

[a] Commercially available. [b] Ref.[6] [c] Even with 20 g of **11a**. [d] Ref.[1c] [e] Ref.[30] [f] Ref.[31] [g] Ref.[1b] [h] Ref.[32] [i] Reaction failed. [j] Ref.[8]

was always disordered, as shown, for example, in Figure 2 for **5j**. The molecule is centrosymmetric, with a crystallographic inversion centre at the midpoint of the C=C double bond. The angle between the plane of the C=C double bond and the plane of the nearest carboxylate group is 85.6(1)°. The angle between the planes of the two adjacent carboxylate groups is 77.6(1)°. The molecule has no short intramolecular steric interactions. The C=C double bond has a different orientation in about 16% of the molecules. The positions of the bromine atoms exactly coincide for both conformations! The carbon atom C(2) should have slightly different positions in the two conformations, but only one position for C(2) can be identified within the experimental resolution. The crystal packing shows stacks of molecules in the crystallographic 0,1,−1 direction, with rather short intermolecular contact distances of 3.035(2) Å between Br and O(3) of neighbouring molecules, about 0.3 Å shorter than the van der Waals contact distance between O and Br.

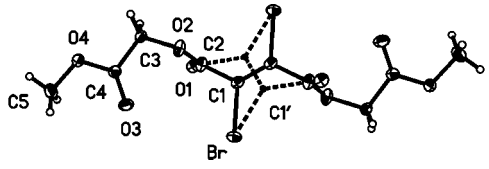


Figure 2. X-ray crystal structure and disordering of **5j** (ORTEP plot)

Compound **5k** is also centrosymmetric, with a crystallographic inversion centre at the midpoint of the C=C double bond (Figure 3). The angle between the plane of the C=C double bond and the plane of the adjacent carboxylate group is 54°. The shortest intramolecular contact distances are Br···O(1′) 3.190(3) Å and Br···O(2) 3.094(3) Å. Those distances are slightly shorter than the van der Waals contact distance of 3.35 Å calculated from the van der Waals radii of O and Br reported by Pauling. Again, two different orientations are found for the C=C double bond, and the Br positions exactly coincide for both conformations, while the carbon atom C(2) should once more have slightly different positions for both conformations, but only one position for it can be found within experimental resolution. The crystal packing shows a rather short intermolecular contact distance of 3.092(3) Å between Br(1) and O(3) of a neighbouring molecule. This is about 0.25 Å shorter than the generally accepted van der Waals contact distance of 3.35 Å between Br and O.

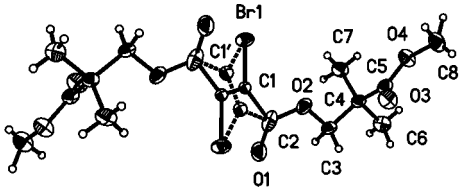


Figure 3. X-ray crystal structure and disordering of **5k** (ORTEP plot)

Similar disorder was observed in the solid-state structure of **5m** (Figure 4). The structure contains two crystallographically independent molecules. Each molecule has a crystallographic inversion centre at the midpoint of the C=C double bond. The two molecules have different conformations for the dibutylamino groups, but are otherwise rather similar. The angle between the plane of the C=C double bond and the plane of the amide bond is 85.4° for molecule 1 and 81.9° for molecule 2. The geometry around the N atom in molecule 1 is perfectly planar (sum of valence angles: 359.9°), that in molecule 2 shows a very small deviation from planarity (sum of valence angles: 358.8°). The structure shows no short intra- or intermolecular contacts.

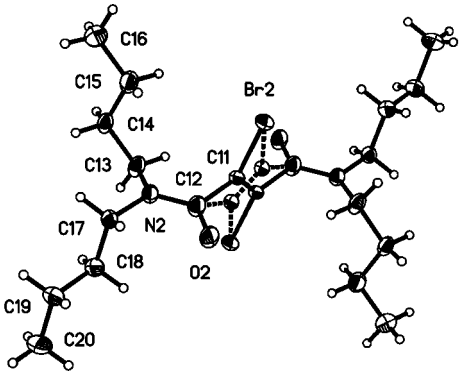


Figure 4. X-ray crystal structure and disordering of **5m** (ORTEP plot)

The next step, the 1,2-elimination to **8**, worked much better, yields ranging from 51 to 97%! The major problem

with this elimination was that substrate and product were usually not distinguishable by TLC, so monitoring of the progress of the reaction and separation from unconverted starting material were not easy. Any remaining dibromide **5** would reduce the yield of the next step, since the dibromide would not react with the diazoalkane **10a**, but an excess of **10a** would slowly add to the pyrazole **11**.

Here, crystal structures were obtained from **8h**, **8n**, and (*S*,*S*)-**8o**.[10] In **8h**, the molecule has a crystallographic inversion centre at the midpoint of the C(1)≡C(1′) triple bond (Figure 5). The central acetylenedicarboxylate group is planar, while the angle between the plane of the propynyloxy group and the plane of the central group is 6.0(3)°. The molecule shows no short intramolecular contacts. The crystal packing consists of short intermolecular C−H···O interactions between the C(5)−H(5) group and oxo oxygen atom O(1) in a neighbouring molecule. The intermolecular H(5)···O(1) distance of 2.33(2) Å is slightly shorter than the van der Waals contact distance. Each molecule is connected to four neighbouring molecules.

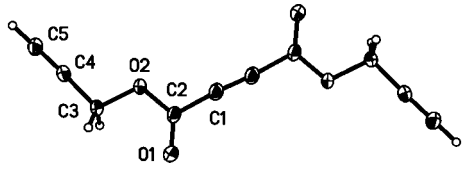


Figure 5. X-ray crystal structure of **8h** (ORTEP plot)

If amide moieties rather than esters are situated at the ends of the alkyne, the donor capacity of this ligand is increased. In such a case, we were able to isolate the $ZnBr_2$ complex of **8n** from the elimination reaction (Figure 6). The molecules form infinite chains in the crystallographic *b* direction. The five-membered rings have approximate envelope conformations. One ring can occupy two possible conformations and thus contains disordered C atoms. There are no short intra- or intermolecular contacts.

In the enantiomerically pure (*S*,*S*)-**8o** (Figure 7), the dimensions of the acetylenedicarboxylate group are similar to those found in other structures containing this group.[11] The angle between the planes of the two carboxylate groups attached to the central acetylene group is 67.2(1)°. The angles between the carboxylate plane of the lactate group and the plane of the adjacent carboxylate group are 71.4(1)° and 75.6(1)°, respectively. The molecule shows a small deviation from an exact twofold symmetry, possibly due to crystal packing effects. One terminal ethyl group has a *trans* orientation, the other a *gauche* conformation. The molecule shows no short intramolecular distances. The crystal packing shows a distance of 2.40(2) Å between O(2) and H(4) of a neighbouring molecule, which equals the van der Waals contact distance. This contact may be classified as a weak, electrostatic interaction. Other intermolecular distances are considerably longer.

With pure **8**, yields of **11** of over 60% were obtained in most cases. Remarkable are examples **11g** and **11h**; the reactions nicely obey the Sustmann classification,[12] the diazoalkane selectively reacting with the electron-poor triple

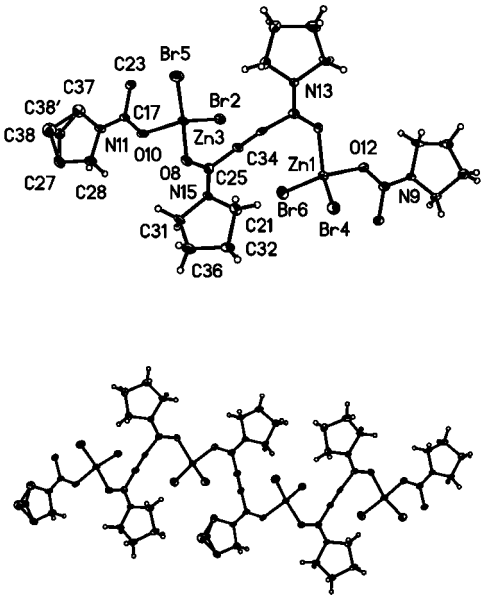


Figure 6. X-ray crystal structure and coordination polymer of **8n**·$ZnBr_2$ (ORTEP plot)

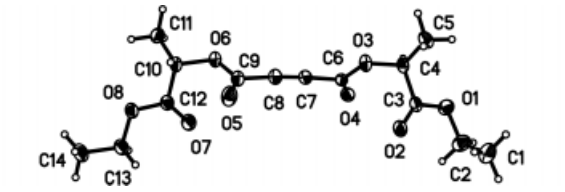


Figure 7. X-ray crystal structure of (*S*,*S*)-**8o** (ORTEP plot)

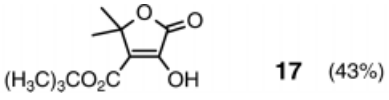
bond and ignoring the two electron-rich double bonds or triple bonds in the ester moiety. Since all pyrazoles bear two geminal substituents, no subsequent aromatization through an H-shift (van Alphen−Hüttel rearrangement)[13] was observed.

Finally, the photoreaction in most cases gave high yields of the cyclopropenes. Again, no problems occurred with the allyl or propargyl esters in **11g** and **11h**. The formation of the cyclopropene from the intermediate vinylcarbene was more effective than an intramolecular addition of the vinylcarbene to the double or triple bond available at an attractive distance (possibility of the formation of a five-membered ring). Significant problems occurred only with **11c**, in which photolability of the halide may cause the problem, and with **11f**, in which the aromatic ring absorbs the light and undergoes excitation.

A photochemical step is often a bottleneck in a synthesis, but here we were able to work with high concentrations of the pyrazoles. Up to 20 g of the pyrazoles in only 100 mL of ether could be used and high yields were still obtained. Most of the cyclopropenes are thus easily available in multigram quantities.

With the cyclopropenes **1α*o*−r** and **1αt**, enantiomerically pure palladacycles were obtained.[2] One possible explanation for the high diastereoselectivity of the formation of the palladacycles would have been a U-shaped conformation of the side chain of the ester. Neither force-field calculations

nor the solid-state structure of **8o** support the theory of such a conformation, however. The crystal structure of the cyclopropene **1αa** is discussed later. Another interesting feature is the reactivity of **1αe**. In an fruitless effort to obtain single crystals of **1αe**, a solution in ether was slowly concentrated at room temperature. The remaining oil was left in the fumehood for one year, after which colourless crystals had separated. NMR clearly showed that a new compound, **17**, had been formed (Scheme 6). Its structure was unequivocally established by crystal structure analysis (Figure 8).[10] The compound crystallises with two independent molecules in the asymmetric unit; these form hydrogen-bonded dimers. A least-squares fit of all non-H atoms of the two molecules (rmsd = 0.109 Å) shows that there are only minor differences between them. Furthermore, there is one intramolecular hydrogen bond per molecule from the hydroxy group to the acyclic carbonyl O atom. The pathway for the formation of **17** is unknown, but by inspection of the product one can only guess that one side bond of the cyclopropene is oxidatively cleaved and one molecule of *tert*-butyl alcohol is lost in the formation of the lactone.



Scheme 6. Oxidation product formed from **1αe**

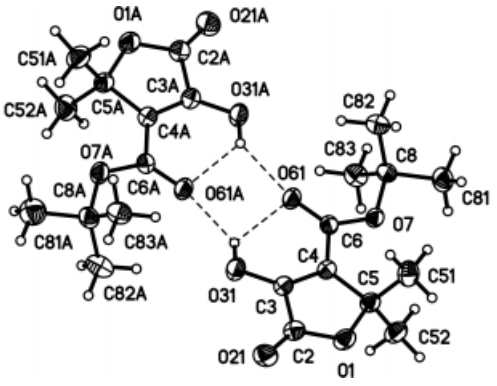


Figure 8. X-ray crystal structure of the dimers of **17** (ORTEP plot)

Synthesis of Cyclopropenes 1β

We also prepared acetylenedicarboxylates with two different substituents in the ester group, by treatment of **4** with only 1 equiv. of the first alcohol X^1H and subsequent application of a small excess of a second alcohol X^2H. A statistical ratio of the three conceivable diesters **5**, **6**, and **7** was thus obtained. Elimination of **6** provided **9**, and treatment with **10a** now produced two constitutional isomers **12** and **13**, both of which afforded the same cyclopropene **1β** upon irradiation. Those results are shown in Table 2.

The low yields stem from the statistical product distribution, which delivers a yield of at best 50% of the unsymmetrical **6**, while the reasons for the strong fluctuation in the yield of **6** are probably analogous to those discussed above for **5**. Again, the eliminations gave yields clearly above 50%. Amazingly, though, the elimination failed with the methyl salicylate derived **6h** and the amide **6i**.

A crystal structure analysis was obtained for the unsymmetrical alkyne **9f** (Figure 9).[10] The structure contains two crystallographically independent molecules, related by a pseudo-translation. The conformations of both molecules are very similar, differing mainly in the relative orientation of the terminal methoxycarbonyl group. The six-membered ring has a chair conformation. The geometry around the nitrogen atom is perfectly planar and the torsion angle about the amide C−N bond is about 5°. The angle between the plane of the amide group and the plane of the adjacent carboxylate group is 86.7(1)° for molecule I and 83.5(1)° for molecule II. The angle between the planes of the two carboxylate groups attached to the triple bond is 72.7(1)° for molecule I and 72.4(1)° for molecule II. The shortest intramolecular contact distances are: O(1)···H(1B) 2.34(2) Å, O(3)···H(7B) 2.43(2) Å, O(4)···H(12C) 2.41(2) Å, O(6)···H(13B) 2.35(2) Å, and O(8)···H(19B) 2.43(2) Å. Those distances approach the van der Waals contact distance of 2.4 Å. The crystal structure shows a number of intermolecular O···H contacts that approach the van der Waals contact distance and may be classified as weak, electrostatic interactions: O(1)···H(19A) 2.40(2) Å,

Table 2. Synthesis of dibromofumarates **6**, alkynes **9**, pyrazoles **12** and **13** and cyclopropenes **1β** with $X^1 \neq X^2$ and $R^3 = R^4 = CH_3$

	X^1	X^2	**6**	**9**	Yields [%] of **12** + **13**	**1β**
a	OCH_3	$OCH_2CH{=}CH_2$	33	69	80	77
b	OCH_3	$OCH_2C{\equiv}CH$	27	81	78	–[a]
c	OCH_3	$OCH_2CH_2OCH_3$	33	87	82	95
d	OCH_3	$OCH_2CO_2CH_3$	49	68	42	94
e	OCH_3	$OCH_2C(CH_3)_2CO_2CH_3$	29	77	54	77
f	OCH_3	$OCH_2C(=O)N(-CH_2CH_2CH_2CH_2CH_2-)$	28	74	81	70
g	OCH_3	$OCH_2C(=O)N(CH_3)_2$	25	81	40	63
h	OCH_3	OC_6H_4-2-(CO_2CH_3)	3	–[a]	–	–
i	OCH_3	$N(-CH_2CH_2CH_2CH_2-)$	27	–[a]	–	–
j	OCH_3	(*S*)-$OCH(CH_3)CO_2CH_3$	50	55	56	81
k	$OCH_2CO_2CH_3$	$OCH_2C(CH_3)_2CO_2CH_3$	27	99	66	86

[a] Reaction failed.

O(2)···H(13B) 2.50(2) Å, O(3)···H(1A) 2.49(2) Å, and O(6)···H(7A) 2.39(2) Å.

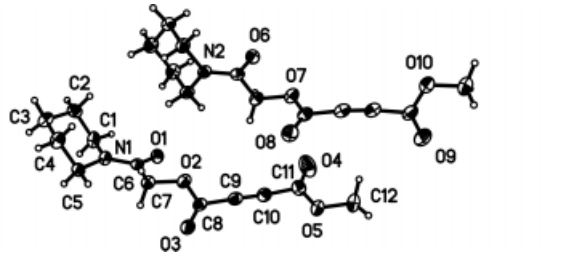


Figure 9. X-ray crystal structure of **9f** (ORTEP plot)

Subsequent 1,3-dipolar cycloaddition delivered mixtures of **12** and **13**. These compounds could often be separated, and unambiguous assignment of the two constitutional isomers was possible with the aid of crystal structure analyses, as in the cases of **12e**, **12f**, and **13k**.[10]

In **12e** (Figure 10), the pyrazole ring is approximately planar. The angle between the plane of the pyrazole ring and the plane of the carboxylate group attached to C(3) is 58.1(1)°. The angle between the plane of the pyrazole ring and the plane of the carboxylate group attached to C(4) is 21.2(1)°. The molecule shows no short intramolecular contact distances. The dimensions of the 3,3-dimethylpyrazole group agree well with values reported for this group in other crystal structures.[14] The crystal packing shows a rather short intermolecular distance of 2.35(2) Å between O(3) and H(11A) of a neighbouring molecule, which approaches the van der Waals contact distance between O and H. Several other intermolecular O···H and N···H distances are about 2.65 Å or more.

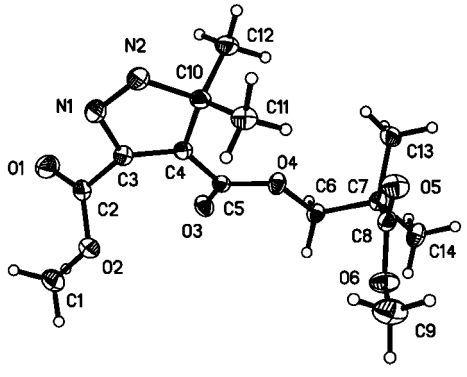


Figure 10. X-ray crystal structure of **12e** (ORTEP plot)

In the solid-state structure of **12f** (Figure 11), the six-membered ring was found to be disordered over two possible conformations. The occupancy factor of the major ring conformation [labelled N(3), C(11), C(12), C(13), C(14), and C(15)] refined to 0.715(3). The occupancy factor of the minor conformation is thus 0.285(3).

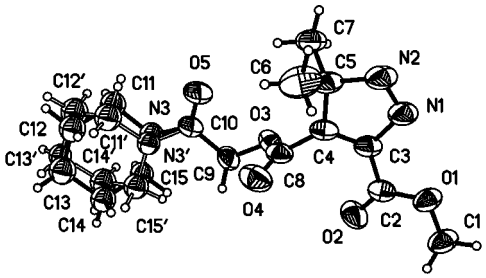


Figure 11. X-ray crystal structure of **12f** (ORTEP plot)

The five-membered ring of **13k** is perfectly planar (Figure 12). The angle between the plane of the five-membered ring and the plane of the carboxylate group attached to C(5) is 87.7(1)°, while the angle between the plane of the five-membered ring and the plane of the carboxylate group attached to C(9) is 3.9(3)°. This carboxylate group is thus almost coplanar with the five-membered ring. Consequently, the C(9)−C(10) bond is significantly shorter than the corresponding C(4)−C(5) bond, due to resonance. An intramolecular distance of 2.51(2) Å between O(8) and C(3A) is about 0.1 Å longer than the van der Waals contact distance between O and H and may be classified as a weak, electrostatic interaction between the side chains.

Finally, the chemoconvergent photochemical step delivered **1β** in high yields.

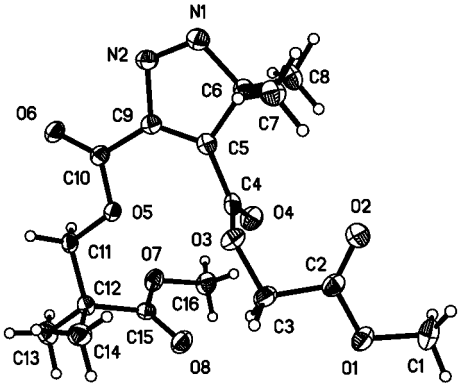


Figure 12. X-ray crystal structure of **13k** (ORTEP plot)

Cyclopropenes with only one ester group were also prepared. 1,3-Dipolar cycloaddition of **10** with the commercially available ethyl phenylpropynoate delivered **18**; assignment of the constitutional isomers was possible with the aid of the crystal structure analysis of **18b**[10] (Figure 13). The carboxylate and the pyrazole are twisted by 28.2(1)°, the pyrazole and phenyl group by 36.9°. Photolysis of the pyrazoles delivered the cyclopropenes **19** (Scheme 7).

Synthesis of Cyclopropenes 1γ

The third class of cyclopropenes comprises those bearing two different substituents at their 3-positions. Here we applied a modification of Warkentin's photochemical route[15] to diazo compounds, in which we used diethyl ether instead of benzene as solvent and thus obtained the cyclopropene

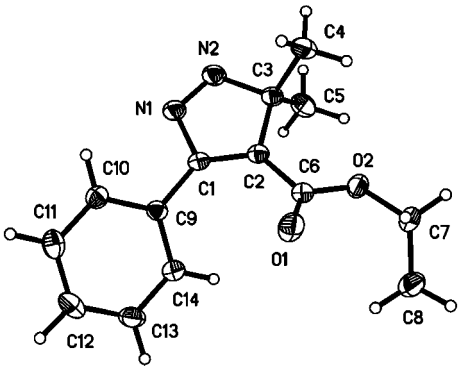
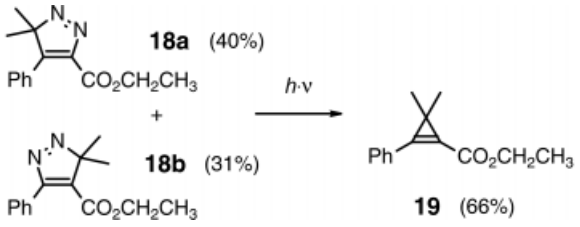
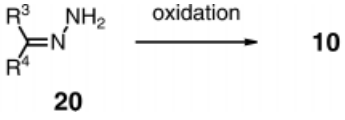


Figure 13. X-ray crystal structure of **18b** (ORTEP plot)



Scheme 7. Synthesis of cyclopropene **19**

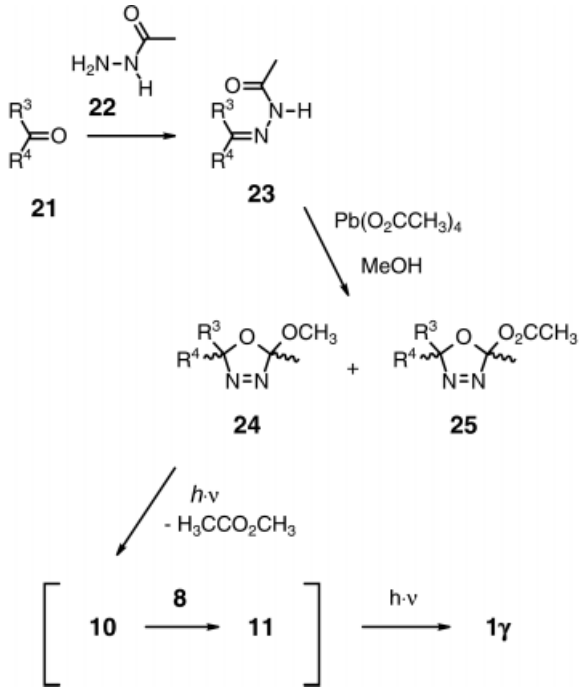
instead of the pyrazole in a one-pot procedure. This procedure is a useful alternative to the oxidation of hydrazones **20**, which works well for 2-diazopropane but is far from being a general method (Scheme 8).



Scheme 8. Oxidation of hydrazones **20** to diazoalkanes **10**

In the first step, the yields of *N*-acetylhydrazones **23** (obtained from ketones **21** and *N*-acetylhydrazone **22**, Scheme 9, Table 3) were usually high. Again, detailed structural information was available from crystal structure analyses of **23b**, **23c**, **23d**, **23e**, and **23g**.[10]

In **23b** (Figure 14), the acetylhydrazine group is almost planar. The angle between the *N*-acetyl group and the plane of the N(2)=C(3) double bond is 1.7°. The cyclohexane ring has a chair conformation, while the side group at C(5) is in an equatorial position. The C(5)−H(5) bond is coplanar with the C(3)=N(2) double bond [torsion angle H(5)−C(5)−C(3)−N(2) 0.3(8)°], resulting in an N(2)···H(5) distance of 2.36(1) Å, slightly shorter than the van der Waals contact distance of 2.5 Å between N and H. The intramolecular N(2)···H(1A) distance of 2.5 Å equals the van der Waals contact distance. The molecules crystallize as centrosymmetric dimers with hydrogen bonding between the amide groups, with N(1)−H(01)···O hydrogen bond dimensions of N(1)−H(01) 0.91(1) Å, H(01)···O 2.01(1) Å, N(1)···O 2.919(1) Å and angle N(1)−H(01)−O 172(1)°. The dimers are stabilized by an additional weak, electrostatic interaction between O and H(4A), with an O···H(4A) distance of 2.48(1) Å.



Scheme 9. Synthesis of cyclopropenes **1** by Warkentin's oxadiazoline route

Table 3. Synthesis of acetylhydrazones **23**, oxadiazolines **24**, acetates **25**, and cyclopropenes **1γ** with $X^1 = X^2$; R^3 and $R^4 \neq CH_3$

			Yields [%] of			
	R^3	R^4	**23**	**24**	**25**	**1γ**[a]
With $X^1 = X^2 = OCH_3$						
a	$(CH_2)_5CH_3$	$(CH_2)_5CH_3$	77	85	14	69
b	CH_3	$CH(-CH_2CH_2CH_2CH_2CH_2-)$	91	61	9	64
c	CH_3	$C(CH_3)_3$	99[b]	30[b]	–	54
d			84	59	6	40
e			–[c]	44	–	–[d]
f	CH_3	adamantyl	–[e]	–[e]	–	4[f]
g			69	28	11	–[g]
With $X^1 = X^2 = (S)$-$OCH(CH_3)CO_2CH_2CH_3$						
h	CH_3	$CH(-CH_2CH_2CH_2CH_2CH_2-)$	91	61	9	48

[a] Yields based on recovered starting material. [b] Compare ref.[15] [c] Prepared according to ref.[33] [d] Compound **26** is formed. [e] Ref.[20] [f] Several other products were isolated. [g] Only other products were obtained.

In **23c**, the structure contains two crystallographically independent molecules related by a non-crystallographic glide plane. This interesting pseudosymmetry operation is not continuous in the *c* direction but is only approximately valid within a bilayered structure with a thickness of half of the *c* axis.[16]

Compound **23d** crystallises with four independent molecules in the asymmetric unit. Molecules A and D are nearly

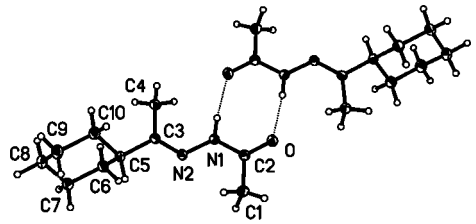


Figure 14. X-ray crystal structure of the dimers of **23b** (ORTEP plot)

identical, as are molecules B and C. The main difference between A/D and B/C is the orientation of the isopropyl group with respect to the cyclohexyl ring (Figure 15). In A and D the H atoms H(2) and H(21) are in an antiperiplanar orientation, but in B and C these two H atoms are in a anticlinal relationship. Two pairs at a time (A/B and C/D) form hydrogen-bonded dimers. It is also noteworthy that the structure is a merohedral twin, pretending orthorhombic symmetry but in fact being monoclinic.

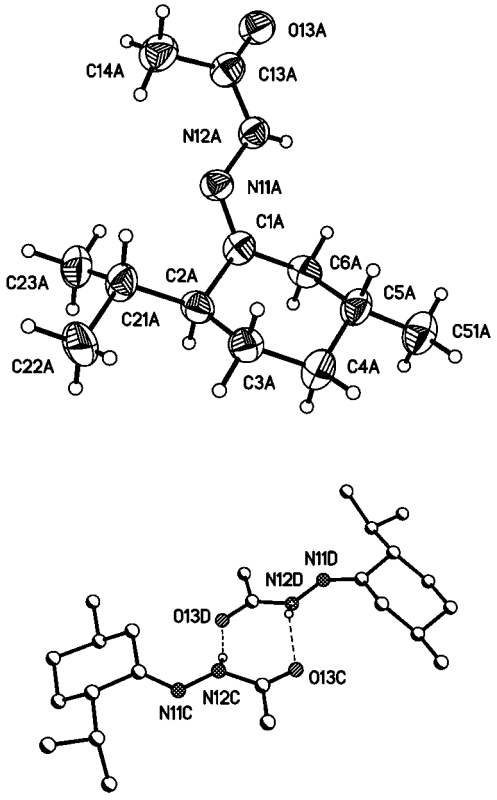


Figure 15. X-ray crystal structure and dimers of **23d** (ORTEP plot)

Compound **23e** crystallises with two molecules in the asymmetric unit. A least-squares fit of the seven atoms of the norbornane skeleton (rmsd = 0.02 Å) shows that there are only minor differences between these two molecules. A similar structure was found in the Cambridge Crystallographic Database, in the form of (1*R*)-(+)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidenehydrazinecarboxamide.[17] The terminal methyl group of **23e** is replaced in this compound by an amino group. This exchange does not markedly change the conformation of the molecule, with the exception that the carbonyl O atom in **23e** (Figure 16) is *trans* to the imine nitrogen atom, whereas the carbonyl O atom is *cis* to the imine nitrogen atom in the other compound. The molecules form hydrogen-bonded chains along the crystallographic *a* axis.

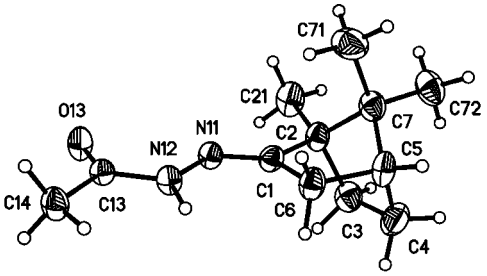


Figure 16. X-ray crystal structure of **23e** (ORTEP plot)

Compound **23g** crystallises with two molecules in the asymmetric unit (Figure 17). A least-squares fit of the adamantyl skeleton (rmsd = 0.015 Å) shows that there are only minor differences between these two molecules. As in **23e**, the carbonyl O atom is *cis* to the imine N atom. The packing motif is similar to that of **23e**; the molecules crystallize in hydrogen-bonded chains along the crystallographic *a* axis, but the hydrogen bonds are slightly different. Whereas the distances between the H atom and the carbonyl O atom and the imine N atom of an adjacent molecule in **23e** are significantly different, these distances are more similar in **23g**.

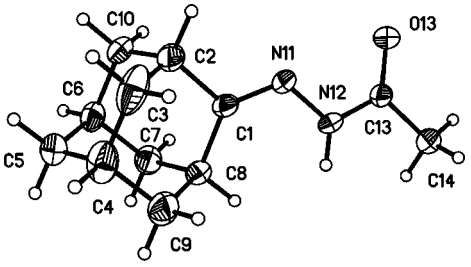


Figure 17. X-ray crystal structure of **23g** (ORTEP plot)

Oxidation of compounds **23** with lead tetraacetate in methanol provided compounds **24**; the acetates **25** were occasionally observed minor side-products. For $R^3 \neq R^4$, a mixture of the two possible diastereomers (each of **24** and **25**) was formed, if one of the substituents already contained a stereogenic centre, even four diastereomers. In the next step, however, all of these diastereomers of **24** chemoconvergently delivered the same diazoalkane **10**. The oxadiazolines could be conveniently purified by column chromatography. From one derivative, namely **24g**, single crystals were obtained[10] (Figure 18). Here the oxadiazole ring is approximately planar. Its dimensions are similar to those found in crystal structures of other oxadiazole derivatives.[18] The shortest intramolecular contacts are: O(1)···H(10A) 2.49 Å and O(1′)···H(7A) 2.52 Å. There are no other significant intra- or intermolecular contacts.

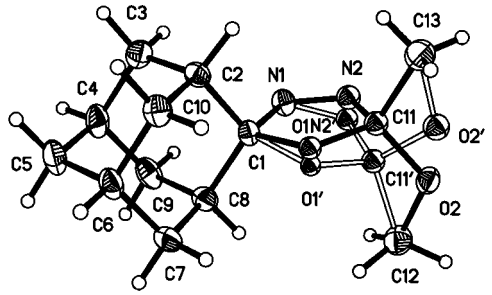
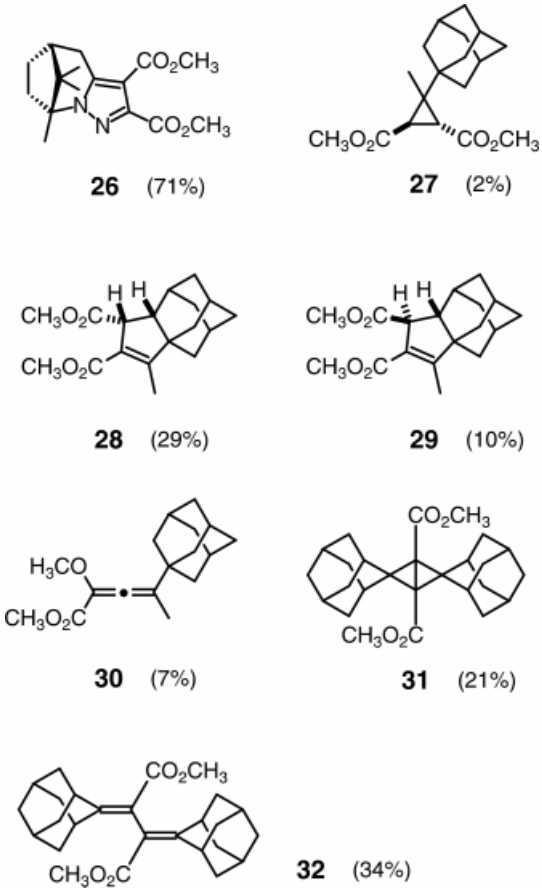


Figure 18. X-ray crystal structure of **24g** (ORTEP plot)

Finally, irradiation of compounds **24** in the presence of an excess of the acetylenedicarboxylate then delivered **1γ**, in most cases in reasonable yield for the three-step, one-pot conversion of **24** → **10** → **11** → **1γ**. Crystal structures of compounds **1** are discussed later. Remarkable is the fact that under these conditions the transformation of **11** into **1γ** is the major reaction pathway even for groups that stabilize a positive charge, such as *t*Bu, and which would thus allow isomerization to the *N*-alkylpyrazoles through the corresponding cation and an aromatic anion. Such isomerizations have previously been observed by Warkentin et al.[19] In our case, the formation of such a product was only observed in the case of the strained **24e**, giving the ring-expanded **26** (Scheme 10). The connectivity in **26** was established by a crystal structure analysis. Because of an interesting pseudosymmetry this has been published elsewhere.[20] Several products were formed on treatment of **24f**; only 4% of the desired **1γf** could be isolated.

Another product was the cyclopropane **27**. Its crystal structure analysis[10] (Figure 19) shows that the two carboxylate side chains are *trans*-oriented. There is a short intramolecular contact between the C(4)−H(4B) bond and oxo oxygen atom O(2), with a H(4B)···O(2) distance of 2.44 Å. The molecule shows a short, repulsive, intramolecular steric interaction between atoms H(10A) and C(7), with a H···C distance of only 2.45 Å. The bond angles C(10)−C(9)−C(1) [114.7(1)°], C(9)−C(1)−C(3) [125.0(1)°], and C(1)−C(3)−C(7) [127.4(1)°] are larger than related bond angles because of this steric interaction. How **27** is formed remains open.

The next two products were formed by insertion of the intermediate vinylcarbene into a nearby C−H bond of the adamantyl cage. Compound **28** (Figure 20) is the diastereomer with a *syn* arrangement[10] of the two hydrogen atoms on the newly formed C−C bond, **29** (Figure 21) that with an *anti* arrangement.[10] In the solid state, the cyclopentene ring of **28** adopts a twist conformation, with C(21), C(23), and C(11) in a common plane and C(1) and C(2) deviating from this plane by −0.392 Å and 0.126 Å, respectively. The ester group attached to C(23) is coplanar with the double bond, with the carbonyl O atom *cis* to C(21). The other ester group is nearly perpendicular to the cyclopentene ring. The dihedral angle between these two moieties is 72.2°. The torsion angle involving the two tertiary H atoms at the cyclopentene ring is −31.8°. While the two chiral centres in



Scheme 10. Side products obtained in the synthesis of **1γ**

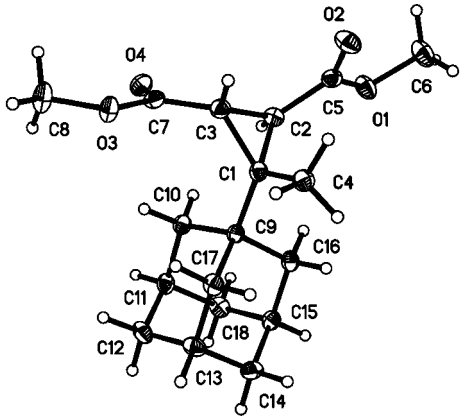


Figure 19. X-ray crystal structure of **27** (ORTEP plot)

the cyclopentene ring of **28** have different configurations, these two centres in **29** have the same configuration. This is also expressed in the H(1)−C(1)−C(11)−H(11) torsion angle of 164.2°, compared to −31.8° in **28**. The cyclopentene ring adopts an envelope conformation, with C(2), C(21), C(23), and C(11) in a common plane (rmsd = 0.017 Å) and C(1) deviating from this plane by −0.57 Å. The ester group attached to C(23) is coplanar with the double bond, with the carbonyl O atom *cis* to C(21). The other

ester group is nearly perpendicular to the cyclopentene ring. The dihedral angle between these two moieties is 74.1°.

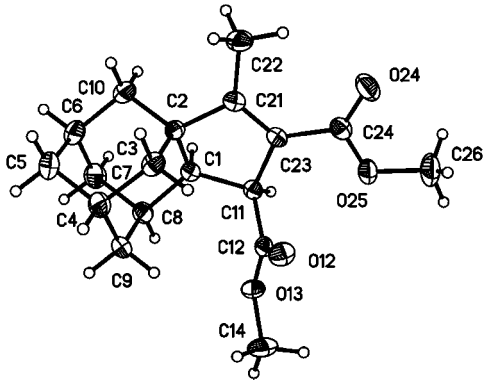


Figure 20. X-ray crystal structure of **28** (ORTEP plot)

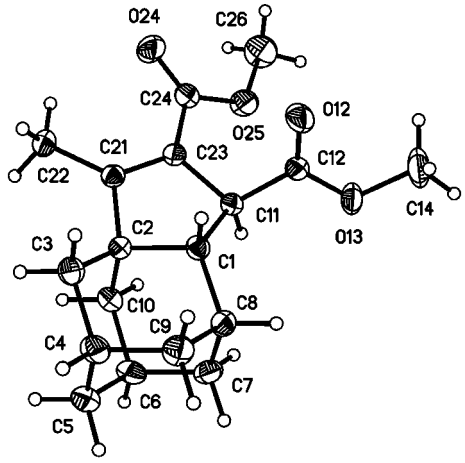


Figure 21. X-ray crystal structure of **29** (ORTEP plot)

The fifth product was the allene **30**[10] (Figure 22). Here, loss of CO was accompanied by a 1,2-shift of the methoxy group at the intermediate vinylcarbene.[1c] The C−C bond lengths in the allene group are 1.314(3) Å and are in good agreement with values found for other allenes. The angle between the plane through C(1), C(11), C(12), and C(17) and the plane through C(12), C(13), O(2), and C(15) is 87.4°.

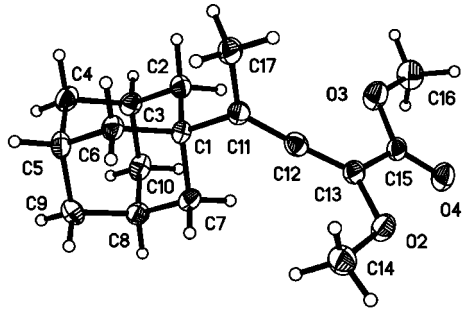


Figure 22. X-ray crystal structure of **30** (ORTEP plot)

On irradiation of **24g**, no cyclopropene was produced, but the double-addition product **31** was obtained. Its crystal structure[21] (Figure 23) shows that the dimensions of the bicyclo[1.1.0]butane group reflect those observed by Padwa et al.[22] However, there is a very short, intramolecular, repulsive H···H interaction between the two adamantyl groups; the H(8)···H(18) distance is only 1.76(2) Å! This steric interaction results in deformation of the bond angles at atoms C(7) and C(17). The C(8)−C(7)−C(4), C(8)−C(7)−C(3), C(18)−C(17)−C(3), and C(18)−C(17)−C(4) angles are about 10° larger than the corresponding C(14)−C(7)−C(4), C(14)−C(7)−C(3), C(24)−C(17)−C(3), and C(24)−C(17)−C(4) angles. One could thus view **31** as a bicyclobutane with enhanced strain.

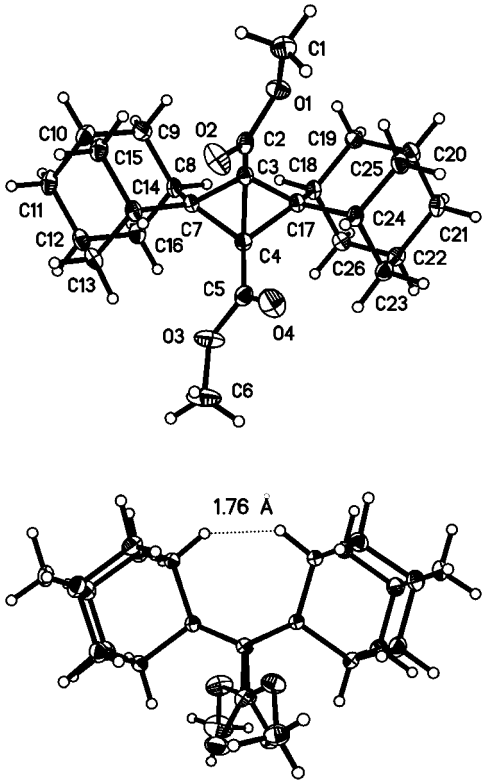


Figure 23. X-ray crystal structure and intramolecular interactions of **31** (ORTEP plot)

The ring-opening product of **31**, the 1,3-diene **32**, was also obtained. Again, the structural assignment was established by X-ray crystal structure analysis. Because of an interesting phase-transition at low temperature, this analysis has been published elsewhere.[23]

Structures of the Cyclopropenes

Single-crystal structure analyses of **1αa** and **1γf** were obtained,[10] and the structures of the known cyclopropenes **33**,[24] **34**,[25] and **35**[26] were also investigated.[10] For **1αa** (Figure 24), the entire molecule lies on a crystallographic mirror plane, with the exception of the methyl groups C(8) and C(8′). Consequently, the cyclopropene ring and the two carboxylic groups are perfectly coplanar. The dimensions of the cyclopropene group are in good agreement with results found for other cyclopropene structures, with a double bond length of about 1.30 Å and single bond lengths of

1.52 Å. The bond angles in the three-membered ring, of about 51° and 65°, are also quite normal. Both C=O double bonds have *s-trans* conformations with respect to the C=C double bond.

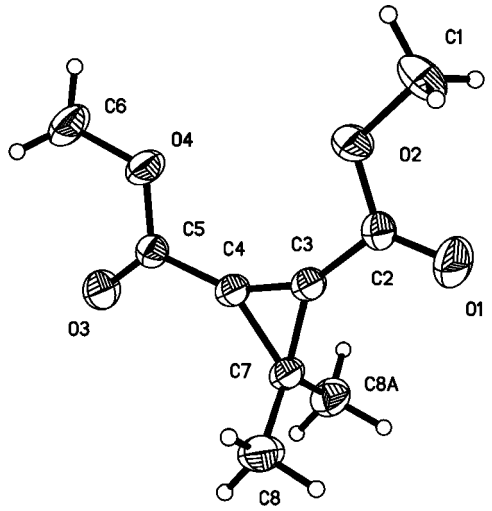


Figure 24. X-ray crystal structure of **1αa** (ORTEP plot)

In **1γf** (Figure 25), the C=C double bond [1.305(5) Å] has a value typical for cyclopropenes (1.294 Å). Whereas one C=O double bond is *cis* to the cyclic double bond [dihedral angle C(31)−C(21)−C(22)−O(22): −26.6(9)°], the other has a *trans* conformation [dihedral angle C(21)−C(31)−C(32)−O(32): −163.0(6)°]. This feature was also found in the one comparable structure, with at least one ester group attached to a cyclopropene ring, retrieved from the Cambridge Crystallographic Database.[27]

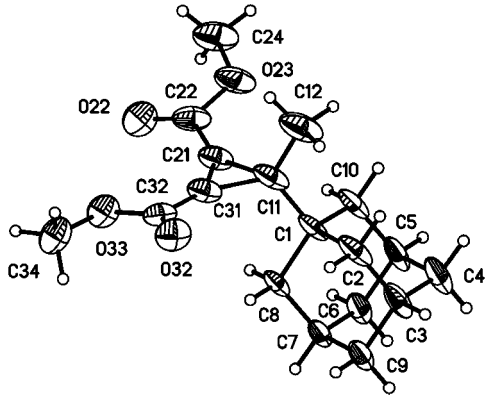
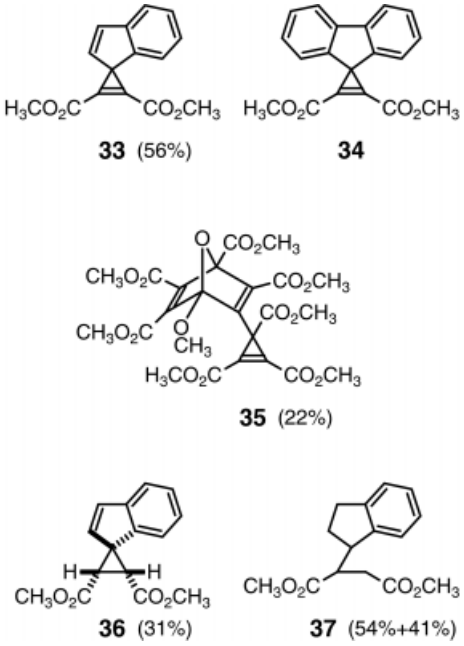


Figure 25. X-ray crystal structure of **1γf** (ORTEP plot)

The structure of **33** (Scheme 11, Figure 26) contains two crystallographically independent molecules. The dimensions of both molecules are very similar. The main differences between the molecules are found in the orientations of the methoxycarbonyl side chains. The indene groups show small deviations from planarity. The angle between the planes of the five- and the six-membered rings is 2.0°. The five-membered ring is approximately planar, with C(1) 0.034 Å outside the plane through atoms C(2), C(3), C(4), and C(9), and atom C(16) 0.018 Å outside the plane through atoms C(17), C(18), C(19), and C(24). The angle between the plane of the three-membered cyclopropene ring and the indene plane is 87.2° for both molecules. The C=C double bond length in the cyclopropene ring is 1.287(2) Å in molecule 1 and 1.288(2) Å in molecule 2. This bond length is significantly shorter than the standard C=C double bond length of 1.33 Å. Similar short bond lengths have been observed in a number of other structures containing cyclopropene rings. The molecules show no short intramolecular contacts. The crystal packing shows a number of weak, intermolecular, electrostatic interactions between O and H atoms, with O···H distances of 2.4 Å and longer.



Scheme 11. Cyclopropene-1,2-dicarboxylates from the literature and hydrogenation products of **33**

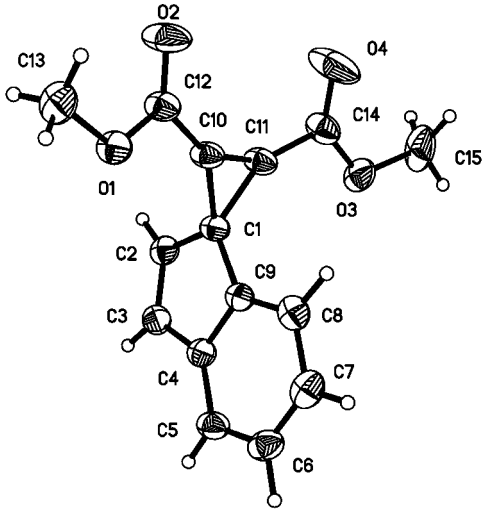


Figure 26. X-ray crystal structure of **33** (ORTEP plot)

In the solid state, **34** (Figure 27) shows approximate C_2 symmetry with the ester groups displaying the largest deviations from perfect C_2 symmetry. The almost planar [rmsd = 0.04 Å] fluorene moiety is nearly perpendicular to the cyclopropene ring. The dihedral angle between the two ring systems is 87.18(8)°. In **33** and **34**, both C=O double bonds have *s-cis* conformations with respect to the C=C double bond of the cyclopropene.

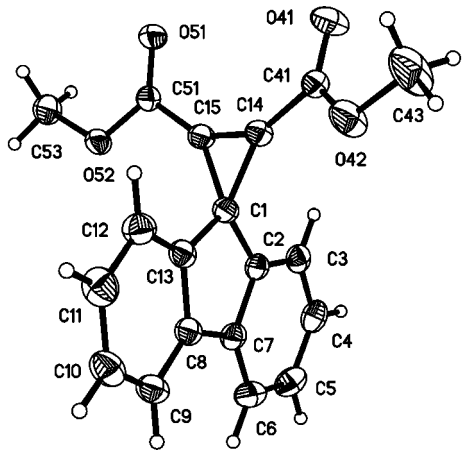


Figure 27. X-ray crystal structure of **34** (ORTEP plot)

The 7-oxabicyclo[2.2.1]heptadiene ring of **35** (Figure 28) has the expected boat configuration. The angle between the C(3)−C(2)−C(1)−C(6) plane and the C(3)−C(4)−C(5)−C(6) plane is 68.1(1)°. The C(1)−C(2) and C(4)−C(5) double bonds show significant deviations from planarity; atoms C(16) and C(7) deviate 0.19 and 0.15 Å from the C(3)−C(2)−C(1)−C(6) plane in a direction away from the oxa bridge, while atoms C(20) and C(22) deviate 0.21 and 0.26 Å from the C(3)−C(4)−C(5)−C(6) plane, also in a direction away from the oxa bridge. These deviations from planarity may result from steric repulsions between the side chains of the 7-oxabicyclo[2.2.1]heptadiene group. The molecule shows a considerable number of intramolecular steric contacts: O(1)···O(10) 2.726(2) Å, O(2)···C(1) 2.775(3) Å, O(3)···C(9) 2.899(3) Å, O(8)···C(3) 2.913(3) Å, O(8)···C(18) 2.843(3) Å, O(9)···C(10) 2.771(3) Å, O(11)···C(4) 2.889(3) Å, O(11)···C(20) 2.865(3) Å, O(14)···C(4) 2.842(3) Å, O(14)···C(20) 2.852(3) Å, O(16)···C(12) 2.837(3) Å, and O(16)···C(8) 2.801(3) Å. Slightly smaller deviations of the double bonds from planarity have been observed in a related compound in which the side chain attached to C(1) is slightly less bulky.[28] Once more, the C=C double bond, at 1.286(4) Å, is considerably shorter than a normal C=C double bond. Atoms C(12) and C(14) deviate 0.12 and 0.28 Å from the plane of the cyclopropene group. The crystal packing shows a considerable number of intermolecular, weak, electrostatic interactions between O and H atoms. The shortest intermolecular O···H contact distance is 2.43(3) Å between O(3) and H(13A), only slightly longer than the van der Waals contact distance of 2.4 Å. Other intermolecular O···H distances range from 2.50 Å and upwards. In **35**, one ester group C=O double bond and the C=C double bond have *s-cis* conformations, while the other C=O double bond is *s-trans*.

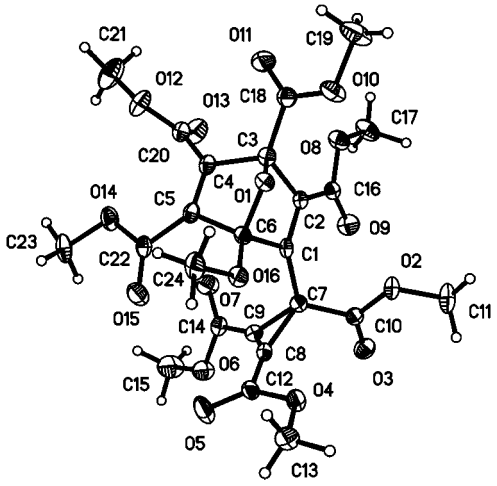


Figure 28. X-ray crystal structure of **35** (ORTEP plot)

Attempted selective hydrogenation of the double bond in the indenylidene part of **33** was not successful. With a small amount of dihydrogen, compound **36** was mainly formed, its configuration established by a ROESY spectrum. An excess of H_2 not only hydrogenated the second double bond but also cleaved the benzylic C−C single bond of the cyclopropane. Compound **37** was thus formed as a mixture of two diastereomers, which is in accordance with the literature.[29]

Conclusion

The photochemical routes to cyclopropenes that we have investigated allow the synthesis of cyclopropenes with chiral ester groups at their double bonds and different substituents in their 3-positions. The last, photochemical step is in most cases the most efficient of the whole sequence and the reactions can conveniently be performed with highly concentrated solutions; up to 20 g of product can hence be obtained from a normal-sized photolysis apparatus. This makes many of the cyclopropenes described here readily available. On the other hand, one has to go through the whole sequence again for each new substituent; a divergent synthetic approach would be more desirable than this parallel synthesis. For cyclopropenes we still lack such a strategy, but for the metallacycles mentioned in the introduction (our true goal) we are now successfully investigating such divergent routes, in which we modify the ester groups in the metallacyles by positional selective transesterification. The major limitations for the photochemical step were the requirement of a good solubility in the solvent diethyl ether and the exclusion of neighbouring C−H bonds that permit efficient insertion of the intermediate vinyl carbene.

Experimental Section

General Remarks: ^1H and ^{13}C NMR spectra were recorded with a Bruker AM 250 spectrometer. Chemical shifts (in δ units, ppm) are reported downfield from $SiMe_4$ for ^1H and ^{13}C NMR. The assignments s ($C_{quat.}$), d (CH), t (CH_2), and q (CH_3) for the ^{13}C NMR signals are based on DEPT 135 and DEPT 90 spectra. Mass spectra (EI) were obtained with a Varian MAT 711 or 112S spectrometer; for FAB^+ spectrometry a DMSO/*m*-nitrobenzyl alcohol matrix and xenon bombardment was used. Infrared spectra were measured with a Perkin−Elmer 1600 spectrometer. Elemental analysis were carried out with a Foss−Heraeus CHN-O-Rapid instrument, high-resolution mass spectra were recorded with a MAT 711 machine, and melting points were measured with a Kofler hot-stage instrument and are uncorrected. Dibromofumaroyl dichloride (**4**),[8] diazopropane (**10a**),[7] *N*,*N*-dimethylglycolamide,[34] glycolpiperidide,[32] 1-acetyl-2-[1,2,2-trimethylpropylidene]hydrazine (**23c**),[15] 1-acetyl-2-[1-(1-adamantyl)-1-ethylidene]hydrazone (**23f**),[19] 2-methoxy-2,5-dimethyl-5-(2,2-dimethylethyl)-(Δ^3)-1,3,4-oxadiazoline (**24c**),[15] 2-acetoxy-2,5-dimethyl-5-(2,2-dimethylethyl)-(Δ^3)-1,3,4-oxadiazoline (**25c**),[15] **24f**,[19] **33**,[35] **34**,[25] and **35**[36] were prepared as described elsewhere. Column chromatography was conducted on Merck silica gel 60, with hexane/ethyl acetate or hexane/ethyl acetate/dichloromethane (DCM) as eluent.

General Procedures

1. Esterification of the Dibromofumaroyl Dichloride: A solution of the alcohol or amine and pyridine in CCl_4 (50 mL for 40 mmol of **4** or the amount necessary to dissolve the substrate) was added slowly at 0 °C to a solution of **4** in CCl_4 (100 mL for 40 mmol of **4**). In the case of the unsymmetrical substrates **6**, 1 equiv. of the first alcohol or amine together with 1 equiv. of pyridine was added, followed by 1 equiv. of the second alcohol together with 1 equiv. of pyridine. After normal hydrolytic workup, the crude product was purified as described in the individual experiments.

2. Elimination to Give the Acetylenedicarboxylates: A solution of the substrate **5** or **6** in THF (100 mL for 10 mmol of substrate) and zinc powder was heated to reflux under argon for 3.5 h. After normal hydrolytic workup, the crude product was purified as described in the individual experiments.

3. 1,3-Dipolar Cycloaddition to the Acetylenedicarboxylates: A solution of **10a** was synthesized according to ref.[7] We assumed a quantitative yield of **10a** and used this to calculate the concentrations of the solutions of **10a** in diethyl ether that were obtained. The real concentrations were probably lower and the yields reported for **11** or **12/13** are in fact the yields for the two-step conversion of the acetone hydrazone to either of these compounds. The cold (−78 °C) solution of **10a** was added to a precooled (−20 °C to −30 °C) solution of the substrate **8** or **9** in DCM (50 mL for 20 mmol, or the amount necessary to dissolve the substrate). After normal hydrolytic workup, the crude product was purified as described in the individual experiments.

4. Photochemical Synthesis of the Cyclopropenes 1α and 1β: In analogy with a procedure reported by Franck-Neumann,[6] solutions of the pyrazole in 100 mL of absolute, deoxygenated ether were irradiated with a Heraeus TQ150 mercury lamp in a normal glass apparatus. After consumption of the starting material (checked by TLC), the solvent was removed in vacuo and the crude product was purified by column chromatography as described in the individual experiments.

5. Synthesis of the Oxadiazolines 24: The oxadiazolines were synthesized as described by Warkentin et al. The products were purified by column chromatography on silica gel.[15]

6. Synthesis of the Cyclopropenes 1γ: A solution of the oxadiazoline **24** and 1.2−3 equiv. of **8** in 100 mL of diethyl ether was irradiated for 6−10 h with a Heraeus TQ150 mercury lamp in a normal glass apparatus. The solvent was removed under vacuum and the products were separated by column chromatography on silica gel. Yields are based on the amounts of consumed oxadiazoline, taking reisolated **24** into account.

Synthesis of Symmetrical Diesters 5

Dipropyl (*E*)-2,3-Dibromobut-2-enedioate (5d): The crude product obtained from dibromofurmaroyl dichloride (**4**, 10.9 g, 35.1 mmol), 1-propanol (4.22 g, 70.2 mmol) and pyridine (5.55 g, 70.2 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 8:1). Compound **5d** (10.3 g, 82%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 8:1) = 0.57. IR (film): $\tilde{\nu}$ = 2971, 2881, 1738, 1464, 1389, 1310, 1235, 1055, 999, 925, 904 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.01 (t, *J* = 7.4 Hz, 6 H), 1.70−1.84 (m, 4 H), 4.26 (t, *J* = 6.6 Hz, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 10.18 (q, 2 C), 21.59 (t, 2 C), 68.55 (t, 2 C), 112.50 (s, 2 C), 162.20 (s, 2 C). MS (80 eV): *m*/*z* (%) = 358 (6) [M^+], 317 (13), 299 (16), 275 (46), 257 (28), 43 (100). $C_{10}H_{14}Br_2O_4$ (358.0): calcd. C 33.55, H 3.94; found C 33.26, H 3.97.

Diallyl (*E*)-2,3-Dibromobut-2-enedioate (5g): The crude product obtained from **4** (11.9 g, 38.2 mmol), allyl alcohol (6.62 g, 114 mmol), and pyridine (6.05 g, 76.5 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 8:1). Compound **5g** (11.4 g, 84%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 3:1) = 0.53. IR (film): $\tilde{\nu}$ = 1739, 1451, 1424, 1360, 1229, 1042, 989, 937 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 4.76−4.79 (m, 4 H), 5.24−5.47 (m, 4 H), 5.84−6.34 (m, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 67.29 (t, 2 C), 112.56 (s, 2 C), 119.65 (t, 2 C), 130.39 (d, 2 C), 161.69 (s, 2 C). $C_{10}H_{10}Br_2O_4$ (354.0): calcd. C 33.93, H 2.85; found C 34.10, H 2.99.

Dipropargyl (*E*)-2,3-Dibromobut-2-enedioate (5h): The crude product obtained from **4** (11.3 g, 36.5 mmol), propargyl alcohol (4.13 g, 73.7 mmol), and pyridine (5.77 g, 72.9 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 8:1). Compound **5h** (10.5 g, 82%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 1:1) = 0.39. IR (film): $\tilde{\nu}$ = 3296, 2953, 2132, 1744, 1436, 1369, 1221, 1048, 1030, 994, 950 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.55 (t, *J* = 2.4 Hz, 2 H), 4.84 (d, *J* = 2.5 Hz, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 54.15 (d, 2 C), 75.77 (t, 2 C), 76.32 (s, 2 C), 112.59 (s, 2 C), 161.09 (s, 2 C). MS (80 eV): *m*/*z* (%) = 350 (16) [M^+], 295 (100), 257 (32), 39 (51). $C_{10}H_6Br_2O_4$ (350.0): calcd. C 34.32, H 1.73; found C 35.01, H 1.84.

Bis(2-methoxyethyl) (*E*)-2,3-Dibromobut-2-enedioate (5i): The crude product obtained from **4** (15.3 g, 49.3 mmol), glycol monomethyl ether (7.70 g, 98.6 mmol) and pyridine (7.80 g, 98.6 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 9:1). Compound **5i** (12.5 g, 65%) was obtained as a colourless oil; R_f (hexane/ethyl acetate, 1:1) = 0.42. IR (film): $\tilde{\nu}$ = 2932, 1740, 1449, 1233, 1200, 1131, 1031 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.40 (s, 6 H), 3.67 (t, *J* = 4.7 Hz, 4 H), 4.43 (m, *J* = 4.8 Hz, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 58.89 (q, 2 C), 65.75 (t, 2 C), 69.63(t, 2

C), 112.57 (s, 2 C), 161.99 (s, 2 C). MS (FAB$^+$): *m/z* (%) = 391 (20) [M + H$^+$], 359 (10), 315 (15), 59 (100). $C_{10}H_{14}Br_2O_6$ (390.0): calcd. C 30.80, H 3.62; found C 31.05, H 3.70.

Bis(methoxycarbonylmethyl) (*E*)-2,3-Dibromobut-2-enedioate (5j): The crude product obtained from **4** (12.0 g, 38.5 mmol), methyl glycolate (6.95 g, 77.1 mmol), and pyridine (6.10 g, 77.1 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 5:1). Compound **5j** (14.2 g, 88%) was obtained as a colourless solid. M.p. 115 °C; R_f (hexane/ethyl acetate, 1:1) = 0.51. IR (film): $\tilde{\nu}$ = 3021, 2965, 2860, 1743, 1444, 1381, 1215, 1061, 1027, 975, 895 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.81 (s, 6 H), 4.81 (s, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 52.42 (q, 2 C), 62.03 (t, 2 C), 112.72 (s, 2 C), 161.29 (s, 2 C), 166.65 (s, 2 C). MS (70 eV): *m/z* (%) = 418 (1) [M$^+$], 387 (5), 337 (60), 329 (18), 73 (100). $C_{10}H_{10}Br_2O_8$ (418.0): calcd. C 28.74, H 2.41; found C 28.64, H 2.48.

Bis(2-methoxycarbonyl-2-methylpropyl) (*E*)-2,3-Dibromobut-2-enedioate (5k): The crude product obtained from **4** (11.6 g, 37.2 mmol), methyl 3-hydroxy-2,2-dimethylpropionate (9.83 g, 74.4 mmol) and pyridine (5.59 g, 74.4 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 9:1). Compound **5k** (10.1 g, 54%) was obtained as a colourless solid. M.p. 47 °C; R_f (hexane/ethyl acetate, 2:1) = 0.45. IR (film): $\tilde{\nu}$ = 2982, 2955, 2883, 1736, 1627, 1469, 1368, 1255, 1191, 1155, 1015, 916 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.18 (s, 12 H), 3.60 (s, 6 H), 4.22 (s, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.11 (q, 4 C), 42.42 (s, 2 C), 52.04 (q, 2 C), 72.13 (t, 2 C), 112.75 (s, 2 C), 161.56 (s, 2 C), 175.19 (s, 2 C). $C_{16}H_{22}Br_2O_8$ (502.2).

Bis(2-oxo-2-piperidin-1-ylethyl) (*E*)-2,3-Dibromobut-2-enedioate (5l): The crude product obtained from **4** (4.88 g, 15.7 mmol), 1-(2-hydroxyacetyl)piperidine (4.50 g, 31.4 mmol), and pyridine (2.48 g, 31.4 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 1:5). Compound **5l** (2.38 g, 29%) was obtained as a yellow oil. R_f (hexane/ethyl acetate, 1:10) = 0.51. IR (film): $\tilde{\nu}$ = 2950, 2867, 1739, 1648, 1472, 1448, 1428, 1270, 1239, 1220, 1047, 1001, 904 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.64 (m, 6 H), 3.33 (t, *J* = 5.3 Hz, 4 H), 3.57 (t, *J* = 5.5 Hz, 4 H), 4.91 (s, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 24.13 (t, 2 C), 25.16 (t, 2 C), 25.84 (t, 2 C), 43.25 (t, 2 C), 45.53 (t, 2 C), 63.21 (t, 2 C), 112.78 (s, 2 C), 162.87 (s, 2 C), 161.51 (s, 2 C). MS (FAB$^+$): *m/z* (%) = 525 (7) [M + H$^+$], 481 (1), 435 (1), 154 (100). $C_{18}H_{24}Br_2N_2O_6$ (524.2): calcd. C 41.24, H 4.61, N 5.34; found C 41.47, H 4.85, N 5.41.

(*E*)-2,3-Dibromo-*N*,*N*-dibutylbut-2-enediamide (5m): The crude product obtained from **4** (12.0 g, 38.5 mmol) and dibutylamine (21.9 g, 170 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 20:1). Compound **5m** (14.3 g, 75%) was obtained as a slightly yellow solid. M.p. 43 °C; R_f (hexane/ethyl acetate, 3:1) = 0.70. IR (film): $\tilde{\nu}$ = 2958, 2933, 2872, 1652, 1462, 1428, 1377, 1294, 1256, 1224, 1195, 1152, 1101, 1034, 934 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.94 (t, *J* = 7.3 Hz, 12 H), 1.35 (t of brq, *J* = 7.7 Hz, 8 H), 1.60 (t of brt, *J* = 7.8 Hz, 8 H), 3.28−3.31 (m, 8 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.63 (q, 4 C), 19.96 (t, 2 C), 20.04 (t, 2 C), 28.80 (t, 2 C), 30.06 (t, 2 C), 44.15 (t, 2 C), 48.01 (t, 2 C), 110.38 (s, 2 C), 163.00 (s, 2 C). MS (80 eV): *m/z* (%) = 496 (14) [M$^+$], 453 (25), 415 (71), 368 (22), 355 (100). $C_{20}H_{36}Br_2N_2O_2$ (496.3): calcd. C 48.40, H 7.31, N 5.64; found C 48.40, H 7.19, N 5.74.

(*E*)-2,3-Dibromo-1,4-dipyrrolidin-1-ylbut-2-ene-1,4-dione (5n): The crude product obtained from **4** (4.88 g, 15.7 mmol), pyrrolidine (2.23 g, 31.4 mmol), and pyridine (2.48 g, 31.4 mmol) according to the general procedure was purified by column chromatography on silica gel [(i) hexane/ethyl acetate, 4:1; (ii) hexane/ethyl acetate, 1:10; (iii) ethyl acetate]. Compound **5n** (2.50 g, 42%) was obtained as a slightly yellow solid; M.p. 223 °C; R_f (hexane/ethyl acetate, 1:1) = 0.08. IR (film): $\tilde{\nu}$ = 2972, 2950, 2879, 1643, 1426, 1340, 1253, 1226, 1188 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.90 (m, 8 H), 3.41 (m, 8 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 24.19 (t, 2 C), 25.59 (t, 2 C), 45.61 (t, 2 C), 46.92 (t, 2 C), 110.90 (s, 2 C), 161.28 (s, 2 C). MS (80 eV): *m/z* (%) = 380 (1) [M$^+$], 379 (1), 341 (1), 311 (20), 202 (71), 70 (100). $C_{12}H_{16}Br_2N_2O_2$ (380.1): calcd. C 37.92, H 4.24, N 7.37; found C 38.57, H 4.42, N 7.24.

Bis[(*S*)-1-ethoxycarbonylethyl] (*E*)-2,3-Dibromobut-2-enedioate [(*S*,*S*)-5o]: The crude product obtained from **4** (5.00 g, 16.1 mmol), ethyl (*S*)-lactate (3.44 g, 29.1 mmol), and pyridine (2.30 g, 29.1 mmol) according to the general procedure was purified by washing with ethyl acetate. Compound (*S*,*S*)-**5o** (3.79 g, 55%) was obtained as a colourless oil; R_f (hexane/ethyl acetate, 3:1) = 0.45. IR (film): $\tilde{\nu}$ = 2979, 2935, 1743, 1623, 1594, 1455, 1371, 1316, 1225, 1163, 1090, 1045, 843 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.28 (t, *J* = 7.1 Hz, 6 H), 1.58 (d, *J* = 7.1 Hz, 6 H), 4.22 (q, *J* = 7.1 Hz, 4 H), 5.22 (q, *J* = 7.1 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.92 (q, 2 C), 16.52 (q, 2 C), 61.63 (t, 2 C), 70.83 (d, 2 C), 112.49 (s, 2 C), 161.21 (s, 2 C), 169.14 (s, 2 C).

Bis[(*R*)-1-*tert*-butoxycarbonylethyl] (*E*)-2,3-Dibromobut-2-enedioate [(*R*)-5p]: The crude product obtained from **4** (5.31 g, 17.1 mmol), *tert*-butyl (*R*)-lactate (4.93 g, 33.7 mmol), and pyridine (2.67 g, 33.7 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 12:1) and subsequently by semipreparative HPLC (hexane/methyl acetate, 10:0.2 + 50% DCM). Compound (*R*)-**5p** (891 mg, 10%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 5:1) = 0.35. IR (film): $\tilde{\nu}$ = 2981, 2938, 1742, 1624, 1596, 1456, 1370, 1316, 1225, 1160, 1092, 1045, 845 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.47 (s, 18 H), 1.54 (d, *J* = 7.1 Hz, 6 H), 5.08 (q, *J* = 7.1 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.42 (q, 2 C), 27.72 (q, 6 C), 71.33 (d, 2 C), 82.44 (q, 2 C), 130.44 (s, 2 C), 160.28 (s, 2 C), 168.25 (s, 2 C). MS (70 eV): *m/z* (%) = 457 (3) [M$^+$ − O*t*Bu], 401 (15), 57 (100) [O*t*Bu]. HRMS (80 eV): $C_{14}H_{26}{}^{79}Br_2O_8$ [M$^+$ − O*t*Bu]: calcd. 454.93413; found 454.93403. $[\alpha]_D^{20}$ = +24.5 (*c* = 1.0, $CHCl_3$).

Bis[(*S*)-1-methoxycarbonylethyl] (*E*)-2,3-Dibromobut-2-enedioate [(*S*,*S*)-5q]: The synthesis and data of this compound have been reported.[8]

Bis[(*S*)-1-isopropoxycarbonylethyl] (*E*)-2,3-Dibromobut-2-enedioate [(*S*,*S*)-5r]: The crude product obtained from **4** (7.15 g, 23.0 mmol), isopropyl (*S*)-lactate (6.00 g, 45.4 mmol), and pyridine (3.59 g, 45.4 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 8:1). Compound (*S*,*S*)-**5r** (3.49 g, 31%) was obtained as a colourless oil; R_f (hexane/ethyl acetate, 3:1) = 0.40. IR (film): $\tilde{\nu}$ = 2984, 2941, 2879, 1746, 1595, 1454, 1377, 1247, 1211, 1090, 1043, 987, 930, 864, 832 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.21 (d, *J* = 4.8 Hz, 6 H), 1.23 (d, *J* = 4.8 Hz, 6 H), 1.53 (d, *J* = 7.1 Hz, 6 H), 4.95−5.17 (m, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.43 (q, 4 C), 21.45 (q, 2 C), 69.40 (d, 2 C), 70.97 (d, 2 C), 112.41 (s, 2 C), 161.17 (s, 2 C), 168.63 (s, 2 C). MS (80 eV): *m/z* (%) = 443 (6) [M$^+$ − O*i*Pr], 423 (2) [M$^+$ − Br]. HRMS (70 eV): $C_{16}H_{22}{}^{79}BrO_8$ [M$^+$ − Br]: calcd. 421.049; found 421.049. $[\alpha]_D^{20}$ = +24.0 (*c* = 6.25, $CHCl_3$).

Bis[methoxycarbonyl(phenyl)methyl] (*E*)-2,3-Dibromobut-2-enedioate [(*S*,*S*)-5s]: The crude product obtained from **4** (16.3 g, 5.07 mmol), isopropyl (*S*)-lactate (5.42 g, 32.6 mmol), and pyridine

(2.58 g, 32.6 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 2.5:1). Compound (*S*,*S*)-**5s** (6.31 g, 68%) was obtained as a colourless oil; R_f (hexane/ethyl acetate, 1:1) = 0.37. IR (film): $\tilde{\nu}$ = 2956, 2850, 1747, 1456, 1437, 1351, 1215, 1175, 1029, 734 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.77 (s, 3 H), 6.08 (s, 1 H), 7.36−7.44 (m, 3 H), 7.47−7.53 (m, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 52.75, 76.24, 112.99, 127.55 (2 C), 128.77 (2 C), 129.52, 132.37, 161.15, 167.80. MS (80 eV): *m*/*z* (%) = 570 (80), 237 (100). $[\alpha]_D^{20}$ = −1.790 (*c* = 1.75).

Bis[(*S*)-1,2-bis(methoxycarbonyl)ethyl] (*E*)-2,3-Dibromobut-2-enedioate [(*S*,*S*)-5t]: The crude product obtained from **4** (5.97 g, 19.2 mmol), dimethyl (*S*)-maleate (6.16 g, 38.0 mmol), and pyridine (3.01 g, 38.0 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 3:2) and subsequent semipreparative HPLC (hexane/methyl acetate, 10:0.5). Compound (*S*,*S*)-**5t** (5.45 mg, 51%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 1:1) = 0.30. IR (film): $\tilde{\nu}$ = 2956, 1744, 1438, 1376, 1288, 1214, 1174, 1050 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.98 (d, *J* = 5.1 Hz, 2 H), 2.99 (d, *J* = 5.1 Hz, 2 H), 3.74 (s, 6 H), 3.82 (s, 6 H), 5.66 (dd, *J* = 5.2 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 35.46 (t, 2 C), 52.19 (q, 2 C), 52.81 (q, 2 C), 70.19 (d, 2 C), 112.57 (s, 2 C), 160.73 (s, 2 C), 167.83 (s, 2 C), 168.84 (s, 2 C). MS (70 eV): *m*/*z* (%) = 563 (70) [M + H^+], 531 (65) [M^+ − OMe)], 483 (100). HRMS (70 eV): $C_{15}H_{15}Br_2O_{11}$ [M^+ − OMe]: calcd. 528.898; found 528.898. $[\alpha]_D^{20}$ = −28.7 (*c* = 1.95, $CHCl_3$).

Synthesis of the Alkynes 8

Dipropyl But-2-ynedioate (8d): The crude product obtained from **5d** (8.00 g, 22.3 mmol) and zinc (9.04 g, 138 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 8:1). Compound **8d** (3.98 g, 90%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 8:1) = 0.56. IR (film): $\tilde{\nu}$ = 2973, 2883, 1724, 1466, 1392, 1349, 1256, 1057, 1036, 1027, 925, 903 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.97 (t, *J* = 7.4 Hz, 6 H), 1.70 (tq, *J* = 7.5, 6.8 Hz, 4 H), 4.19 (t, *J* = 6.6 Hz, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 10.02 (q, 2 C), 21.50 (t, 2 C), 68.31 (t, 2 C), 74.51 (s, 2 C), 151.80 (s, 2 C). MS (80 eV): *m*/*z* (%) = 198 (3) [M^+], 157 (8), 115 (95), 43 (100). $C_{10}H_{14}O_4$ (198.2): calcd. C 60.59, H 7.12; found C 59.92, H 7.20.

Diallyl But-2-ynedioate (8g): The crude product obtained from **5g** (10.2 g, 28.8 mmol) and zinc (10.4 g, 159 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 3:1). Compound **8g** (5.24 g, 94%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 3:1) = 0.53. IR (film): $\tilde{\nu}$ = 3090, 1725, 1650, 1451, 1425, 1363, 1248, 1176, 1089, 1036, 992, 936 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 4.65−4.76 (m, 4 H), 5.25−5.42 (m, 4 H), 5.83−6.00 (m, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 67.12 (t, 2 C), 74.51 (s, 2 C), 119.91 (t, 2 C), 130.17 (d, 2 C), 152.24 (s, 2 C). $C_{10}H_{10}O_4$ (194.2): calcd. C 61.85, H 5.19; found C 62.04, H 5.19.

Dipropargyl But-2-ynedioate (8h): The crude product obtained from **5h** (2.00 g, 5.71 mmol) and zinc (2.25 g,, 34.4 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 8:1). Compound **8h** (758 mg, 70%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 8:1) = 0.76. IR (film): $\tilde{\nu}$ = 3296, 2956, 2133, 1736, 1438, 1373, 1248, 1048, 998, 942 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.57 (t, *J* = 2.4 Hz, 2 H), 4.79 (d, *J* = 2.5 Hz, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 53.92 (t, 2 C), 74.54 (s, 2 C), 75.54 (d, 2 C), 76.42 (s, 2 C), 150.54 (s, 2 C). $C_{10}H_6O_4$ (190.2): calcd. C 63.16, H 3.18; found C 62.28, H 3.31.

Bis(2-methoxyethyl) But-2-ynedioate (8i): The crude product obtained from **5i** (12.5 g, 32.0 mmol) and zinc (12.9 g, 197 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 5:1). Compound **8i** (6.23 g, 85%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 1:1) = 0.43. IR (film): $\tilde{\nu}$ = 2988, 2933, 2891, 2844, 2822, 1725, 1450, 1370, 1256, 1200, 1131, 1101, 1046 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.35 (s, 6 H), 3.59 (t, *J* = 4.7 Hz, 4 H), 4.34 (t, *J* = 4.7 Hz, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 58.79 (q, 2 C), 65.46 (t, 2 C), 69.46 (t, 2 C), 74.68 (s, 2 C), 151.45 (s, 2 C). MS (FAB^+): *m*/*z* (%) = 231 (33) [M + H^+], 199 (23), 137 (8), 59 (100). $C_{10}H_{14}O_6$ (230.2): calcd. C 52.17, H 6.13; found C 52.06, H 6.08.

Bis(methoxycarbonylmethyl) But-2-ynedioate (8j): The crude product obtained from **5j** (15.8 g, 37.8 mmol) and zinc (15.0 g, 229 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate/DCM, 4:1:1). Compound **8j** (4.96 g, 51%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 1:1) = 0.61. IR (film): $\tilde{\nu}$ = 2959, 2361, 1735, 1434, 1382, 1283, 1211, 1079, 1028 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.73 (s, 6 H), 4.69 (s, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 52.46 (q, 2 C), 61.84 (t, 2 C), 74.88 (s, 2 C), 150.64 (s, 2 C), 165 (s, 2 C). MS (70 eV): *m*/*z* (%) = 227 (39) [M^+ − OMe], 199 (5), 111 (21), 169 (100). − $C_{10}H_{10}O_8$ (258.2): calcd. C 46.52, H 3.90; found C 46.66, H 4.09.

Bis(2-methoxycarbonyl-2-methylpropyl) But-2-ynedioate (8k): The crude product obtained from **5k** (9.20 g, 18.3 mmol) and zinc (7.30 g, 112 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 7:1). Compound **8k** (5.68 g, 91%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 2:1) = 0.44. IR (film): $\tilde{\nu}$ = 2959, 2361, 1735, 1434, 1382, 1283, 1211, 1079, 1028 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.18 (s, 12 H), 3.67 (s, 6 H), 4.20 (s, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 21.97 (q, 4 C), 42.19 (s, 2 C), 52.05 (q, 2 C), 71.69 (t, 2 C), 74.57 (s, 2 C), 151.22 (s, 2 C), 175.09 (s, 2 C). MS (70 eV): *m*/*z* (%) = 342 (1) [M^+], 327 (3), 311 (20), 283 (23), 115 (100).

***N*,*N*,*N*′,*N*′-Tetrabutylbut-2-ynediamide (8m):** The crude product obtained from **5m** (13.9 g, 28.0 mmol) and zinc (15.4 g, 236 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate/DCM, 5:1:1). Compound **8m** (8.30 g, 88%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 3:1) = 0.35. IR (film): $\tilde{\nu}$ = 2959, 2932, 2873, 1637, 1466, 1426, 1378, 1294, 1256, 1228, 1196, 1112 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.91 (t, *J* = 7.0 Hz, 6 H), 0.93 (t, *J* = 7.3 Hz, 6 H), 1.32 (t of brq, *J* = 7.3 Hz, 8 H), 1.55 (t of brt, *J* = 7.3 Hz, 8 H), 3.35 (t, *J* = 7.8 Hz, 4 H), 3.51 (t, *J* = 7.7 Hz, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.57 (q, 4 C), 19.68 (t, 2 C), 19.96 (t, 2 C), 29.17 (t, 2 C), 30.80 (t, 2 C), 44.36 (t, 2 C), 48.57 (t, 2 C), 80.71 (s, 2 C), 152.46 (s, 2 C). MS (80 eV): *m*/*z* (%) = 336 (5) [M^+], 321 (3), 307 (7), 293 (32), 128 (100). $C_{20}H_{36}N_2O_2$ (336.5): calcd. C 71.38, H 10.78, N 8.32; found C 71.12, H 10.75, N 8.21.

1,4-Dipyrrolidin-1-ylbut-2-yne-1,4-dione (8n): The crude product obtained from **5n** (2.50 g, 6.58 mmol), zinc (2.70 g, 41.3 mmol), and iodine (100 mg, 394 μmol) according to the general procedure was purified by column chromatography on silica gel (ethyl acetate/methanol, 10:1). Compound **8n** (1.40 g, 97%) was obtained as a colourless oil. R_f (ethyl acetate/methanol, 10:1) = 0.26. IR (film): $\tilde{\nu}$ = 2974, 2880, 1644, 1633, 1434, 1338, 1253, 1226, 1192, 1117,

1082 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.86−2.01 (m, 8 H), 2.58−3.54 (m, 4 H), 3.69−3.74 (m, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 24.32 (t, 2 C), 25.09 (t, 2 C), 45.81 (t, 2 C), 48.37 (t, 2 C), 80.48 (s, 2 C), 150.84 (s, 2 C). MS (80 eV): *m/z* (%) = 220 (2) [M^+], 151 (6), 70 (100). $C_{12}H_{16}N_2O_2$ (220.3): calcd. C 65.43, H 7.32, N 12.72; found C 65.21, H 7.30, N 12.62.

Bis[(*S*)-1-ethoxycarbonylethyl] But-2-ynedioate [(*S*,*S*)-8o]: The crude product obtained from (*S*,*S*)-**5o** (3.60 g, 7.59 mmol) and zinc (2.98 g, 45.6 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 5:1). Compound (*S*,*S*)-**8o** (1.56 g, 65%) was obtained as a colourless solid. M.p. 79−80 °C; R_f (hexane/ethyl acetate, 3:1) = 0.45. IR (film): $\tilde{\nu}$ = 2987, 2940, 1730, 1450, 1381, 1348, 1260, 1206, 1092, 1049, 1018, 910, 856 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.29 (t, *J* = 7.1 Hz, 6 H), 1.56 (d, *J* = 7.1 Hz, 6 H), 4.24 (q, *J* = 7.1 Hz, 4 H), 5.19 (q, *J* = 7.1 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.87 (q, 2 C), 16.52 (q, 2 C), 61.72 (t, 2 C), 70.72 (d, 2 C), 74.75 (s, 2 C), 150.68 (s, 2 C), 168.90 (s, 2 C). $C_{14}H_{18}O_8$ (314.3): calcd. C 53.50, H 5.77; found C 53.31, H 5.74. $[\alpha]_D^{20}$ = −9.8 (*c* = 1.2, $CHCl_3$).

Bis[(*R*)-1-*tert*-butoxycarbonylethyl] But-2-ynedioate [(*R*,*R*)-8p]: The crude product obtained from (*R*,*R*)-**5p** (870 mg, 1.64 mmol) and zinc (644 mg, 9.85 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 30:1). Compound (*R*,*R*)-**8p** (456 mg, 75%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 5:1) = 0.35. IR (film): $\tilde{\nu}$ = 2981, 2940, 2879, 1731, 1457, 1370, 1355, 1316, 1261, 1228, 1160, 1133, 1093, 1049, 911, 869, 845, 740 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.40 (s, 18 H, Me), 1.45 (d, 7.1 Hz, 6 H), 4.99 (q, 7.1 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.46 (q, 2 C), 27.70 (q, 6 C), 71.20 (d, 2 C), 74.71 (s, 2 C), 82.69 (s, 2 C), 150.79 (s, 2 C), 168.01 (s, 2 C). MS (70 eV): *m/z* (%) = 313 (4) [$M^+ - C_4H_9$], 57 (100) [C_4H_9]. HRMS (80 eV): $C_{14}H_{17}O_8$ [$M^+ - C_4H_9$]: calcd. 313.0924; found: 313.0925. $[\alpha]_D^{20}$ = +16.8 (*c* = 2.05, $CHCl_3$).

Bis[(*S*)-1-methoxycarbonylethyl] But-2-ynedioate [(*S*,*S*)-8q]: The synthesis of and data for this compound have been reported.[8]

Bis[(*S*)-1-isopropoxycarbonylethyl] But-2-ynedioate [(*S*,*S*)-8r]: The crude product obtained from (*S*,*S*)-**5r** (3.45 g, 6.87 mmol) and zinc (2.70 g, 41.3 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate/DCM, 5:0.1:2). Compound (*S*,*S*)-**8r** (1.39 g, 59%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 5:1) = 0.50. IR (film): $\tilde{\nu}$ = 2986, 2942, 2881, 1732, 1455, 1378, 1378, 1340, 1309, 1261, 1213, 1146, 1090, 1048, 1010 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.24 (d, *J* = 5.9 Hz, 6 H), 1.26 (d, *J* = 5.9 Hz, 6 H), 1.53 (d, *J* = 5.7 Hz, 6 H), 5.01−5.19 (m, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.12 (q, 2 C), 21.05 (q, 2 C), 21.08 (q, 2 C), 69.22 (d, 2 C), 70.54 (d, 2 C), 74.37 (s,2 C), 150.37 (s, 2 C), 168.10 (s, 2 C). MS (70 eV): *m/z* (%) = 283 (71) [M^+ − O*i*Pr], 43 (100). $C_{16}H_{22}O_8$ (342.3): calcd. C 56.14, H 6.48; found C 55.92, H 6.38. $[\alpha]_D^{20}$ = +3.7 (*c* = 1.0, $CHCl_3$).

Bis[(*S*)-1,2-bis(methoxycarbonyl)ethyl] But-2-ynedioate [(*S*,*S*)-8t]: The crude product obtained from (*S*,*S*)-**5t** (2.40 g, 4.27 mmol) and zinc (1.69 g, 25.8 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 3:2). Compound (*S*,*S*)-**8t** (1.17 g, 68%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 3:2) = 0.20. IR (film): $\tilde{\nu}$ = 2958, 1738, 1731, 1439, 1377, 1359, 1264, 1219, 1177, 1054 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.95 (d, *J* = 6.0 Hz, 4 H), 3.74 (s, 6 H), 3.79 (s, 6 H), 5.61 (dd, *J* = 6.0 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 35.36 (t, 2 C), 52.24 (q, 2 C), 52.93 (q, 2 C), 69.93 (d, 2 C), 74.92 (s, 2 C), 150.20 (s, 2 C), 167.60 (s, 2 C), 168.82 (s, 2 C). MS (70 eV): *m/z* (%) = 371 (2) [M^+ − OMe], 241 (95), 59 (100). HRMS (70 eV): *m/z* (%) = $C_{15}H_{15}O_{11}$ ([M^+ − OMe]): calcd. 371.0614; found 371.0615. $[\alpha]_D^{20}$ = −11.9 (*c* = 1.1, $CHCl_3$).

Synthesis of the Pyrazoles 11

Dipropyl 3,3-Dimethyl-3*H*-pyrazole-4,5-dicarboxylate (11d): The crude product obtained from **8d** (3.55 g, 17.9 mmol) and a solution of **10a** in ether (29.8 mL, 21.1 mmol, 0.63 M) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 5:1). Compound **11d** (3.60 g, 75%) was obtained as a yellow oil. R_f (hexane/ethyl acetate, 5:1) = 0.23. IR (film): $\tilde{\nu}$ = 2971, 2939, 2881, 1732, 1637, 1459, 1395, 1326, 1263, 1171, 1105, 1059, 1018 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.97 (t, *J* = 7.4 Hz, 3 H), 1.00 (t, *J* = 7.3 Hz, 3 H), 1.56 (s, 6 H), 1.74 (m, 4 H), 4.25 (t, *J* = 6.7 Hz, 2 H), 4.34 (t, *J* = 6.6 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 10.14 (q, 2 C), 19.93 (q, 2 C), 21.64 (t), 21.70 (t), 67.58 (t, 2 C), 97.04 (s), 144.66 (s), 152.99 (s), 160.43 (s), 162.52 (s). MS (80 eV): *m/z* (%) = 268 (1) [M^+], 253 (1), 240 (4), 199 (42), 112 (100). $C_{13}H_{20}N_2O_4$ (268.3): calcd. C 58.19, H 7.51, N 10.44; found C 58.39, H 7.79, N 10.28.

Di-*tert*-butyl 3,3-Dimethyl-3*H*-pyrazole-4,5-dicarboxylate (11e): The synthesis and data of this compound have been reported.[31]

Diallyl 3,3-Dimethyl-3*H*-pyrazole-4,5-dicarboxylate (11g): The crude product obtained from **8g** (7.96 g, 41.0 mmol) and a solution of **10a** in ether (65.1 mL, 0.63 M, 41.0 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 5:1). Compound **11g** (9.82 g, 91%) was obtained as a yellow oil. R_f (hexane/ethyl acetate, 5:1) = 0.27. IR (film): $\tilde{\nu}$ = 3088, 2986, 2939, 1732, 1635, 1454, 1425, 1369, 1321, 1252, 1170, 1119, 1045, 1022, 995, 966, 940 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.57 (s, 6 H), 4.75−4.88 (m, 4 H), 5.29−5.46 (m, 4 H), 5.86−6.08 (m, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.90 (q, 2 C), 66.49 (t, 2 C), 97.26 (s), 119.44 (t), 119.51 (t), 130.69 (d), 130.86 (d), 144.46 (s), 152.85 (s), 159.90 (s), 162.00 (s). $C_{13}H_{16}N_2O_4$ (264.3): calcd. C 59.08, H 6.10, N 10.60; found C 58.86, H 6.30, N 10.42.

Dipropargyl 3,3-Dimethyl-3*H*-pyrazole-4,5-dicarboxylate (11h): The crude product obtained from **8h** (2.55 g, 13.4 mmol) and a solution of **10a** in ether (18.5 mL, 0.74 M, 13.7 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 3:1). Compound **11h** (2.95 g, 85%) was obtained as a yellow oil. R_f (hexane/ethyl acetate, 3:1) = 0.19. IR (film): $\tilde{\nu}$ = 3288, 2988, 2940, 2874, 2131, 1738, 1634, 1435, 1379, 1318, 1236, 1167, 1120, 1052, 1004, 969, 909 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.58 (s, 6 H), 2.56 (d, *J* = 2.5 Hz, 2 H), 4.88 (d, *J* = 2.5 Hz, 2 H), 4.96 (d, *J* = 2.5 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.89 (q, 2 C), 53.32 (t, 2 C), 76.06 (d, 2 C), 76.29 (s), 76.42 (s), 97.75 (s), 144.01 (s), 152.79 (s), 159.23 (s), 161.41 (s). $C_{13}H_{12}N_2O_4$ (260.2): calcd. C 60.00, H 4.65, N 10.76; found C 59.59, H 4.81, N 10.08.

Bis(2-methoxyethyl) 3,3-Dimethyl-3*H*-pyrazole-4,5-dicarboxylate (11i): The crude product obtained from **8i** (5.82 g, 25.3 mmol) and a solution of **10a** in ether (27.0 mL, 954 mM, 25.8 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 2:1). Compound **11i** (4.00 g, 53%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 1:1) = 0.27. IR (film): $\tilde{\nu}$ = 2985, 2996, 2891, 2845, 2822, 2093, 1731, 1635, 1453, 1406, 1374, 1321, 1260, 1201, 1171, 1123, 1053 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.57 (s, 6 H), 3.37 (s, 3 H), 3.39 (s, 3 H), 3.64 (t, *J* = 4.7 Hz, 2 H), 3.71 (t, *J* = 4.8 Hz, 2

H), 4.43 (t, J = 4.8 Hz, 2 H), 4.51 (t, J = 4.9 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.76 (q, 2 C), 58.55 (q), 58.63 (q), 64.54 (t), 64.71 (t), 69.62 (t), 69.67 (t), 97.16 (s), 144.34 (s), 153.09 (s), 160.13 (s), 162.18 (s). MS (80 eV): m/z (%) = 300 (1) [M^+], 255 (1), 59 (100). $C_{13}H_{20}N_2O_6$ (300.3): calcd. C 51.99, H 6.71, N 9.33; found C 51.77, H 6.88, N 9.12.

Bis(methoxycarbonylmethyl) 3,3-Dimethyl-3*H*-pyrazole-4,5-dicarboxylate (11j): The crude product obtained from **8j** (4.92 g, 19.1 mmol) and a solution of **10a** in ether (10.2 mL, 1.89 M, 19.2 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 1:2). Compound **11j** (3.11 g, 50%) was obtained as a yellow oil. R_f (hexane/ethyl acetate, 1:2) = 0.64. IR (film): $\tilde{\nu}$ = 2988, 2959, 2860, 1748, 1640, 1437, 1382, 1330, 1226, 1120, 1076, 1031, 960 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.62 (s, 6 H), 3.77 (s, 6 H), 4.82 (s, 2 H), 4.88 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.77 (q, 2 C), 52.26 (q), 52.29 (q), 61.36 (t), 61.49 (t), 98.24 (s), 143.06 (s), 154.71 (s), 159.07 (s), 162.01 (s), 166.89 (s), 167.00 (s). MS (70 eV): m/z (%) = 328 (1) [M^+], 297 (12), 285 (3), 269 (3), 253 (23), 93 (100). $C_{13}H_{16}N_2O_8$ (328.3): calcd. C 47.56, H 4.91, N 8.53; found C 47.53, H 5.00, N 8.63.

Bis(2-methoxycarbonyl-2-methylpropyl) 3,3-Dimethyl-3*H*-pyrazole-4,5-dicarboxylate (11k): The crude product obtained from **8k** (4.99 g, 14.6 mmol) and a solution of 2-diazopropane **10a** in ether (7.90 mL, 1.89 M, 14.9 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 3:1). Compound **11k** (2.30 g, 38%) was obtained as a yellow oil. R_f (hexane/ethyl acetate, 1:1) = 0.62. IR (film): $\tilde{\nu}$ = 2983, 2954, 2882, 1734, 1638, 1463, 1396, 1371, 1318, 1257, 1156, 1111, 1047, 971 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.23 (s, 6 H), 1.26 (s, 6 H), 1.52 (s, 6 H), 3.66 (s, 3 H), 3.68 (s, 3 H), 4.30 (s, 2 H), 4.39 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.76 (q, 2 C), 22.10 (q, 2 C), 22.12 (q, 2 C), 42.31 (s), 42.37 (s), 51.98 (q, 2 C), 71.17 (t), 72.38 (t), 97.27 (s), 144.27 (s), 152.96 (s), 159.85 (s), 161.84 (s), 175.27 (s), 175.37 (s). MS (70 eV): m/z (%) = 412 (1) [M^+], 397 (1), 381 (8), 284 (4), 115 (100). $C_{19}H_{28}N_2O_8$ (412.4): calcd. C 55.33, H 6.84, N 6.79; found C 55.09, H 6.96, N 6.52.

***N*,*N*,*N*′,*N*′-Tetrabutyl-3,3-dimethyl-3*H*-pyrazole-4,5-dicarboxamide (11m):** The crude product obtained from **8m** (7.81 g, 23.2 mmol) and a solution of **10a** in ether (25.0 mL, 954 mM, 23.8 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 4:1). Compound **11m** (7.55 g, 80%) was obtained as a yellow oil. R_f (hexane/ethyl acetate, 1:1) = 0.59. IR (film): $\tilde{\nu}$ = 2960, 2932, 2873, 1650, 1462, 1378, 1314, 1256, 1225, 1190, 1155, 1100, 948 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.72−0.89 (m, 12 H), 1.03−1.56 (m, 16 H), 1.44 (s, 6 H), 2.99−3.39 (m, 8 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.36 (q), 13.53 (q, 2 C), 13.61 (q), 19.62 (t), 19.83 (t, 2 C), 19.95 (t), 20.89 (q, 2 C), 28.99 (t), 29.45 (t), 30.51 (t), 30.97 (t), 43.20 (t), 45.25 (t), 48.04 (t), 48.30 (t), 96.19 (s), 145.13 (s), 151.16 (s), 161.80 (s), 163.62 (s). MS (80 eV): m/z (%) = 406 (4) [M^+], 391 (14), 264 (100). $C_{23}H_{42}N_4O_2$ (406.6): calcd. C 67.94, H 10.41, N 13.78; found C 67.74, H 10.49, N 13.56.

Bis[(*S*)-1-ethoxycarbonylethyl] 3,3-Dimethyl-3*H*-pyrazole-4,5-dicarboxylate [(*S*,*S*)-11o]: The crude product obtained from (*S*,*S*)-**8o** (1.34 g, 4.26 mmol) and a solution of **10a** in ether (7.50 mL, 570 mM, 4.28 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 3:1). Compound (*S*,*S*)-**11o** (983 mg, 60%) was obtained as a yellow oil. R_f (hexane/ethyl acetate, 3:1) = 0.20. IR (film): $\tilde{\nu}$ = 2987, 2941, 1746, 1637, 1454, 1257, 1210, 1095 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.26 (t, J = 7.2 Hz, 3 H), 1.27 (t, J = 7.2 Hz, 3 H), 1.53 (d, J = 7.1 Hz, 3 H), 1.59 (s, 6 H), 1.61 (d, J = 7.1 Hz, 3 H), 4.21 (q, J = 7.2 Hz, 4 H), 5.30 (m, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.90 (q), 13.94 (q), 16.46 (q), 16.75 (q), 19.70 (q), 19.86 (q), 61.50 (t), 61.60 (t), 69.94 (d), 70.10 (d), 97.97 (s), 143.25 (s), 155.05 (s), 159.12 (s), 162.04 (s), 169.43 (s), 169.51 (s). MS (70 eV): m/z (%) = 385 (3) [M^+ + H], 121 (82), 94 (100), 73 (55). $C_{17}H_{24}N_2O_8$ (384.4): calcd. C 53.12, H 6.29, N 7.29; found C 53.15, H 6.28, N 7.44. $[\alpha]_D^{20}$ = −6.5 (c = 1.8, $CHCl_3$).

Bis[(*R*)-1-*tert*-butoxycarbonylethyl] 3,3-Dimethyl-3*H*-pyrazole-4,5-dicarboxylate [(*R*,*R*)-11p]: The crude product obtained from (*R*,*R*)-**8p** (505 mg, 1.36 mmol) and a solution of **10a** in ether (2.5 mL, 570 mM, 1.43 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 5:1). Compound (*R*,*R*)-**11p** (330 mg, 55%) was obtained as a yellow oil. R_f (hexane/ethyl acetate, 3:1) = 0.33. IR (film): $\tilde{\nu}$ = 2982, 2939, 2878, 1742, 1637, 1593, 1455, 1370, 1314, 1258, 1229, 1161, 1096, 1049, 917, 878, 846, 742 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.47 (s, 9 H), 1.48 (s, 9 H), 1.50 (d, J = 7.0 Hz, 3 H), 1.56 (d, J = 7.0 Hz, 3 H), 1.61 (s, 3 H), 1.64 (s, 3 H), 5.15 (q, J = 7.0 Hz, 1 H), 5.23 (q, J = 7.0 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.48 (q), 16.65 (q), 19.80 (q), 19.89 (q), 27.74 (s), 27.79 (s), 70.44 (d), 70.53 (d), 82.30 (s), 82.40 (s), 97.84 (s), 143.70 (s), 154.90 (s), 159.26 (s), 161.93 (s), 168.56 (s, 2 C). MS (70 eV): m/z (%) = 367 (2) [M^+ − OtBu], 57 (100) [tBu]. $C_{21}H_{32}N_2O_8$ (440.5): calcd. C 57.26, H 7.32, N 6.36; found C 57.52, H 7.43, N 6.66. $[\alpha]_D^{20}$ = −19.8 (c = 1.24, $CHCl_3$).

Bis[(*S*)-1-methoxycarbonylethyl] 3,3-Dimethyl-3*H*-pyrazole-4,5-dicarboxylate [(*S*,*S*)-11q]: The crude product obtained from (*S*,*S*)-**8q** (2.75 g, 9.61 mmol) and a solution of **10a** in ether (12.8 mL, 756 mM, 9.68 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 2:1). Compound (*S*,*S*)-**11q** (2.19 g, 64%) was obtained as a yellow oil. R_f (hexane/ethyl acetate, 2:1) = 0.20. IR (film): $\tilde{\nu}$ = 2993, 2957, 1748, 1636, 1594, 1454, 1381, 1361, 1303, 1257, 1219, 1170, 1134, 1097, 1054, 1014, 975 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.55 (d, J = 7.1 Hz, 3 H), 1.60 (s, 6 H), 1.63 (d, J = 7.1 Hz, 3 H), 3.77 (s, 6 H), 5.31 (q, J = 7.1 Hz, 1 H), 5.39 (q, J = 7.1 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.47 (q), 16.78 (q), 19.69 (q), 19.86 (q), 52.39 (q), 52.42 (q), 69.82 (d), 69.98 (d), 98.03 (s), 143.40 (s), 154.98 (s), 159.10 (s), 162.03 (s), 169.96 (s, 2 C). MS (70 eV): m/z (%) = 356 (1) [M^+], 325 (3) [M^+ − OMe], 94 (100). $C_{15}H_{20}N_2O_8$ (356.3): calcd. C 50.56, H 5.66, N 7.86; found C 50.78, H 5.88, N 7.61. $[\alpha]_D^{20}$ = −6.9 (c = 2.26, $CHCl_3$).

Bis[(*S*)-1-isopropoxycarbonylethyl] 3,3-Dimethyl-3*H*-pyrazole-4,5-dicarboxylate [(*S*,*S*)-11r]: The crude product obtained from (*S*,*S*)-**8r** (1.36 g, 3.97 mmol) and a solution of **10a** in ether (7.00 mL, 570 mM, 3.99 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 4:1). Compound (*S*,*S*)-**11r** (1.06 g, 65%) was obtained as a yellow oil. R_f (hexane/ethyl acetate, 3:1) = 0.50. IR (film): $\tilde{\nu}$ = 2985, 2940, 2880, 1742, 1634, 1599, 1454, 1377, 1362, 1256, 1215, 1170, 1134, 1094, 1051, 934, 876, 803, 750 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.23 (d, J = 6.2 Hz, 3 H), 1.24 (d, J = 6.5 Hz, 3 H), 1.25 (d, J = 6.5 Hz, 3 H), 1.26 (d, J = 6.5 Hz, 3 H), 1.51 (d, J = 7.1 Hz, 3 H), 1.59 (d, J = 7.1 Hz, 3 H), 1.59 (s, 3 H), 1.63 (s, 3 H), 5.06 (m, 2 H), 5.23 (q, J = 7.1 Hz, 1 H), 5.29 (q, J = 7.1 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.42 (q), 16.67 (q), 19.72 (q), 19.87 (q), 21.45 (q, 2 C), 21.51 (q, 2 C), 69.26 (d), 69.39 (d), 70.09 (d), 70.25 (d), 97.90 (s), 143.32 (s), 154.95 (s), 159.15 (s), 162.0 (s), 168.95 (s), 169.04 (s). MS (70 eV): m/z (%) = 412 (1) [M^+], 353 (13) [M^+ − OiPr]. $C_{19}H_{28}N_2O_8$ (412.4): calcd. C 55.33, H 6.84, N

6.79; found C 55.77, H 6.93, N 6.67. $[\alpha]_D^{20} = -4.0$ (c = 4.76, $CHCl_3$).

Bis[(*S*)-1,2-bis(methoxycarbonyl)ethyl] 3,3-Dimethyl-3*H*-pyrazole-4,5-dicarboxylate [(*S*,*S*)-11t]: The crude product obtained from (*S*,*S*)-**8t** (1.19 g, 2.96 mmol) and a solution of **10a** in ether (4.00 mL, 756 mM, 3.02 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate/DCM, 3:2:2). Compound (*S*,*S*)-**11t** (978 mg, 70%) was obtained as a yellow oil. R_f (hexane/ethyl acetate, 1:1) = 0.20. IR (film): $\tilde{\nu}$ = 2975, 1744, 1439, 1364, 1222, 1171, 1114, 1055 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.61 (s, 6 H), 2.99 (d, J = 5.8 Hz, 2 H), 3.05 (d, J = 6.1 Hz, 2 H), 3.71 (s, 3 H), 3.72 (s, 3 H), 3.80 (s, 6 H), 5.67 (t, J = 5.9 Hz, 1 H), 5.76 (t, J = 6.1 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.62 (q), 19.77 (q), 35.30 (t), 35.54 (t), 52.08 (q, 2 C), 52.76 (q, 2 C), 69.36 (d), 69.54 (d), 98.22 (s), 143.25 (s), 154.72 (s), 161.37 (s), 168.04 (s), 168.23 (s), 169.02 (s), 169.22 (s) one s hidden by signal overlap. MS (FAB^+): m/z (%) = 473 [M^+]. $[\alpha]_D^{20} = -5.2$ (c = 1.0, $CHCl_3$).

Syntheses of the Cyclopropenes 1α

Dipropyl 3,3-Dimethylcycloprop-1-ene-1,2-dicarboxylate (1αd): The crude product obtained from **11d** (2.60 g, 9.69 mmol) was purified by column chromatography on silica gel (hexane/ethyl acetate, 7:1). Compound **1αd** (2.10 g, 90%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 5:1) = 0.58. IR (film): $\tilde{\nu}$ = 2969, 1718, 1239, 1104, 1062, 1033, 934 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.98 (t, J = 7.4 Hz, 6 H), 1.40 (s, 6 H), 1.73 (m, 4 H), 4.20 (t, J = 6.7 Hz, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 10.98 (q, 2 C), 22.47 (t, 2 C), 26.11 (q, 2 C), 31.81 (t, 2 C), 67.81 (s), 132.73 (s, 2 C), 160.91 (s, 2 C). MS (80 eV): m/z (%) = 240 (2) [M^+], 225 (8), 199 (54), 180 (32), 112 (100). $C_{13}H_{20}O_4$ (240.3): calcd. C 64.98, H 8.39; found C 64.99, H 8.52.

Diallyl 3,3-Dimethylcycloprop-1-ene-1,2-dicarboxylate (1αg): The crude product obtained from **11g** (9.40 g, 35.6 mmol) was purified by column chromatography on silica gel (hexane/ethyl acetate, 8:1). Compound **1αg** (7.68 g, 91%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 5:1) = 0.48. IR (film): $\tilde{\nu}$ = 3086, 2946, 1833, 1719, 1648, 1450, 1372, 1248, 1086, 992, 933 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.42 (s, 6 H), 4.74 (dt, J = 15.6, 1.4 Hz, 4 H), 5.26−5.42 (m, 4 H), 5.91−6.04 (m, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.32 (q, 2 C), 31.32 (s), 65.89 (t, 2 C), 118.60 (t, 2 C), 131.15 (d, 2 C), 132.15 (s, 2 C), 159.48 (s, 2 C). MS (FAB^+): m/z (%) = 731 (1) [3 M + Na^+], 495 (14) [2 M + Na^+], 473 (3) [2 M + H^+], 41 (100). $C_{13}H_{16}O_4$ (236.3): calcd. C 66.09, H 6.83; found C 65.80, H 6.84.

Dipropargyl 3,3-Dimethylcycloprop-1-ene-1,2-dicarboxylate (1αh): The crude product obtained from **11h** (701 mg, 2.69 mmol) was purified by column chromatography on silica gel (hexane/ethyl acetate, 8:1). Compound **1αh** (514 mg, 82%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 2:1) = 0.55. IR (film): $\tilde{\nu}$ = 3287, 2941, 2130, 1739, 1438, 1372, 1217, 1082, 994 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.13 (s, 6 H), 2.54 (t, J = 2.5 Hz, 2 H), 4.84 (d, J = 2.5 Hz, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.20 (q, 2 C), 31.86 (s), 52.77 (t, 2 C), 75.48 (d, 2 C), 76.49 (s, 2 C), 132.43 (s, 2 C), 158.74 (s, 2 C).

Bis(2-methoxyethyl) 3,3-Dimethylcycloprop-1-ene-1,2-dicarboxylate (1αi): The crude product obtained from **11i** (4.00 g, 13.3 mmol) was purified by column chromatography on silica gel (hexane/ethyl acetate, 3:1). Compound **1αi** (3.29 g, 91%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 1:1) = 0.42. IR (film): $\tilde{\nu}$ = 2951, 2972, 2892, 2821, 1834, 1715, 1454, 1371, 1247, 1201, 1131, 1106, 1059 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.37 (s, 6 H), 3.36 (s, 6 H), 3.63 (t, J = 4.5 Hz, 4 H), 4.35 (t, J = 4.8 Hz, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.27 (q, 2 C), 31.36 (s), 58.82 (q, 2 C), 64.50 (t, 2 C), 69.86 (t, 2 C), 131.38 (s, 2 C), 159.84 (s, 2 C). MS (80 eV): m/z (%) = 544 (1) [2 M^+], 272 (1) [M^+], 258 (2), 185 (24), 59 (100). $C_{13}H_{20}O_6$ (272.3): calcd. C 57.34, H 7.40; found C 57.18, H 7.40.

Bis(methoxycarbonylmethyl) 3,3-Dimethylcycloprop-1-ene-1,2-dicarboxylate (1αj): The crude product obtained from **11j** (2.60 g, 7.92 mmol) was purified by column chromatography on silica gel (hexane/ethyl acetate, 2:1). Compound **1αj** (2.11 g, 89%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 1:1) = 0.57. IR (film): $\tilde{\nu}$ = 3008, 2959, 2865, 1837, 1727, 1437, 1380, 1286, 1206, 1048, 1028 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.43 (s, 6 H), 3.76 (s, 6 H), 4.75 (s, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.23 (q, 2 C), 31.88 (s), 52.21 (q, 2 C), 61.17 (t, 2 C), 132.85 (s, 2 C), 158.82 (s, 2 C), 167.15 (s, 2 C). MS (70 eV): m/z (%) = 300 (2) [M^+], 285 (14), 257 (8), 253 (22), 121 (100). $C_{13}H_{16}O_8$ (300.3): calcd. C 52.00, H 5.37; found C 52.05, H 5.46.

Bis(2-methoxycarbonyl-2-methylpropyl) 3,3-Dimethylcycloprop-1-ene-1,2-dicarboxylate (1αk): The crude product obtained from **11k** (1.98 g, 4.80 mmol) was purified by column chromatography on silica gel (hexane/ethyl acetate, 4:1). Compound **1αk** (1.64 g, 89%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 1:1) = 0.81. IR (film): $\tilde{\nu}$ = 2977, 2955, 1853, 1728, 1464, 1394, 1368, 1247, 1154, 1109, 1060, 980 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.25 (s, 12 H), 1.36 (s, 6 H), 3.68 (s, 6 H), 4.27 (s, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.08 (q, 4 C), 25.22 (q, 2 C), 31.25 (s), 42.45 (s, 2 C), 51.92 (q, 2 C), 70.68 (t, 2 C), 132.31 (s, 2 C), 159.41 (s, 2 C), 175.48 (s, 2 C). MS (70 eV): m/z (%) = 384 (1) [M^+], 369 (2), 353 (1), 309 (1), 115 (100). $C_{19}H_{28}O_8$ (384.4): calcd. C 59.36, H 7.34; found C 59.53, H 7.36.

***N*,*N*,*N*′,*N*′-Tetrabutyl-3,3-dimethylcycloprop-1-ene-1,2-dicarboxamide (1αm):** The crude product obtained from **11m** (8.00 g, 19.7 mmol) was purified by column chromatography on silica gel (hexane/ethyl acetate, 4:1). Compound **1αm** (7.05 g, 95%) was obtained as a pale yellow oil. R_f (hexane/ethyl acetate, 3:1) = 0.26. IR (film): $\tilde{\nu}$ = 2959, 2932, 2873, 1798, 1632, 1463, 1426, 1378, 1293, 1257, 1225, 1198, 1112, 1103, 945 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.88 (t, J = 6.7 Hz, 12 H), 1.27 (q of brt, J = 7.3 Hz, 8 H), 1.37 (s, 6 H), 1.51 (t of brt, J = 8.1 Hz, 8 H), 3.35 (t, J = 7.8 Hz, 4 H), 3.38 (t, J = 7.8 Hz, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.63 (q, 2 C), 19.79 (t, 2 C), 20.08 (t, 2 C), 26.04 (q, 4 C), 29.51 (t, 2 C), 30.66 (s), 31.46 (t, 2 C), 44.88 (t, 2 C), 47.51 (t, 2 C), 128.04 (s, 2 C), 160.96 (s, 2 C). MS (80 eV): m/z (%) = 378 (11) [M^+], 363 (4), 251 (46), 128 (100).

Bis[(*S*)-1-ethoxycarbonylethyl] 3,3-Dimethylcycloprop-1-ene-1,2-dicarboxylate [(*S*,*S*)-1αo]: The crude product obtained from (*S*,*S*)-**11o** (500 mg, 1.30 mmol) was purified by column chromatography on silica gel (hexane/ethyl acetate, 4:1). Compound (*S*,*S*)-**1αo** (443 mg, 96%) was obtained as a pale yellow oil. R_f (hexane/ethyl acetate, 3:1) = 0.35. IR (film): $\tilde{\nu}$ = 2985, 2944, 2876, 1836, 1755, 1722, 1456, 1249, 1203, 1095 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.26 (t, J = 7.1 Hz, 6 H), 1.42 (s, 6 H), 1.55 (d, J = 8.1 Hz, 6 H), 4.20 (q, J = 7.1 Hz, 4 H), 5.18 (q, J = 8.1 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.88 (q, 2 C), 16.69 (q, 2 C), 25.28 (q, 2 C), 31.80 (s), 61.37 (d, 2 C), 69.66 (t, 2 C), 132.60 (s, 2 C), 159.04 (s, 2 C), 169.76 (s, 2 C). MS (70 eV): m/z (%) = 357 (3) [M^+ + H], 257 (39), 139 (55), 121 (100), 73 (88). $C_{17}H_{24}O_8$ (356.4): calcd. C 57.30, H 6.79; found C 57.01, H 6.82. $[\alpha]_D^{20} = -3.3$ (c = 2.05, $CHCl_3$).

Bis[(*R*)-1-*tert*-butoxycarbonylethyl] 3,3-Dimethylcycloprop-1-ene-1,2-dicarboxylate [(*R*,*R*)-1αp]: The crude product obtained from (*R*,*R*)-**11p** (301 mg, 683 μmol) was purified by column chromatography on silica gel (hexane/ethyl acetate, 4:1). Compound (*R*,*R*)-**1αp** (270 mg, 96%) was obtained as a pale yellow oil. R_f (hexane/ethyl acetate, 3:1) = 0.55. IR (film): $\tilde{\nu}$ = 2980, 2940, 2877, 1837, 1752, 1747, 1738, 1727, 1716, 1455, 1371, 1313, 1252, 1224, 1161, 1132, 1095, 1058, 935, 876, 847, 731 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.43 (s, 6 H), 1.46 (s, 18 H), 1.52 (d, *J* = 7.0 Hz, 6 H), 5.06 (q, *J* = 7.0 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.75 (q, 2 C), 25.41 (q, 2 C), 27.83 (q, 6 C), 31.72 (s), 70.20 (d, 2 C), 82.17 (s, 2 C), 132.54 (s, 2 C), 159.18 (s, 2 C), 168.95 (s, 2 C). MS (70 eV): *m*/*z* (%) = 413 (1) [M + H^+], 210 (100), 57 (97). HRMS (80 eV): $C_{21}H_{33}O_8$: calcd. 413.2176; found 413.2173. $[\alpha]_D^{20}$ = +12.3 (*c* = 1.04, $CHCl_3$).

Bis[(*S*)-1-methoxycarbonylethyl] 3,3-Dimethylcycloprop-1-ene-1,2-dicarboxylate [(*S*,*S*)-1αq]: The crude product obtained from (*S*,*S*)-**11q** (1.08 g, 3.03 mmol) was purified by column chromatography on silica gel (hexane/ethyl acetate, 2:1). Compound (*S*,*S*)-**1αq** (746 mg, 75%) was obtained as a pale yellow oil. R_f (hexane/ethyl acetate, 2:1) = 0.40. IR (film): $\tilde{\nu}$ = 2994, 2957, 1835, 1760, 1719, 1451, 1438, 1380, 1356, 1310, 1249, 1212, 1133, 1097, 1058, 977, 876, 849, 730 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.43 (s, 6 H), 1.56 (d, *J* = 7.1 Hz, 6 H), 3.76 (s, 6 H), 5.22 (q, *J* = 7.1 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.75 (q, 2 C), 25.28 (q, 2 C), 31.93 (s), 52.32 (q, 2 C), 69.53 (d, 2 C), 132.74 (s, 2 C), 158.99 (s, 2 C), 170.25 (s, 2 C). MS (70 eV): *m*/*z* (%) = 313 (10) [M^+ − CH_3], 121 (100). HRMS (70 eV): $C_{12}H_{14}O_8$ [M^+ − C_3H_6]: calcd. 286.06887; found 286.06879. $[\alpha]_D^{20}$ = −5.1 (*c* = 1.14, $CHCl_3$).

Bis[(*S*)-1-isopropoxycarbonylethyl] 3,3-Dimethylcycloprop-1-ene-1,2-dicarboxylate [(*S*,*S*)-1αr]: The crude product obtained from (*S*,*S*)-**11r** (996 mg, 2.41 mmol) was purified by column chromatography on silica gel (hexane/ethyl acetate, 10:1). Compound (*S*,*S*)-**1αr** (696 mg, 75%) was obtained as a colourless oil. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.24 (d, *J* = 6.3 Hz, 6 H), 1.27 (d, *J* = 6.3 Hz, 6 H), 1.44 (s, 6 H), 1.55 (d, *J* = 7.1 Hz, 6 H), 4.98−5.11 (m, 2 H), 5.15 (d, *J* = 7.1 Hz, 2 H).

Bis[(*S*)-1,2-bis(methoxycarbonyl)ethyl] 3,3-Dimethylcycloprop-1-ene-1,2-dicarboxylate [(*S*,*S*)-1αt]: The crude product obtained from (*S*,*S*)-**11t** (850 mg, 1.80 mmol) was purified by column chromatography on silica gel (hexane/ethyl acetate/DCM, 15:4:10). Compound (*S*,*S*)-**1αt** (352 mg, 44%) was obtained as a colourless oil. R_f (hexane/ethyl acetate/DCM, 15:10:10) = 0.40. IR (film): $\tilde{\nu}$ = 2958, 2855, 1836, 1745, 1732, 1439, 1373, 1289, 1213, 1173, 1108, 1057 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.38 (s, 6 H), 2.93 (d, *J* = 5.5 Hz, 2 H), 2.94 (d, *J* = 5.5 Hz, 2 H), 3.69 (s, 6 H), 3.75 (s, 6 H), 5.58 (t, *J* = 5.6 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.15 (q, 2 C), 32.05 (s), 35.67 (t, 2 C), 52.01 (q, 2 C), 52.66 (q, 2 C), 69.10 (d, 2 C), 132.90 (s, 2 C), 158.33 (s, 2 C), 168.37 (s, 2 C), 169.07 (s, 2 C). MS (70 eV): *m*/*z* (%) = 444 (2) [M^+]. $C_{19}H_{24}O_{12}$ (444.4): calcd. C 51.35, H 5.44; found C 51.45, H 5.60. $[\alpha]_D^{20}$ = −17.7 (*c* = 1.1, $CHCl_3$).

Synthesis of Unsymmetrical Diesters 6

Allyl Methyl (*E*)-2,3-Dibromobut-2-enedioate (6a): The crude product obtained from **4** (63.3 g, 204 mmol), methanol (6.53 g, 204 mmol), and pyridine (16.1 g, 204 mmol), followed by allyl alcohol (12.1 g, 208 mmol) and pyridine (16.1 g, 204 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 40:1). Compound **6a** (22.0 g, 33%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 10:1) = 0.47. IR (film): $\tilde{\nu}$ = 2956, 1739, 1435, 1236, 1044, 1013, 992, 940 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.83 (s, 3 H), 4.71 (dt, *J* = 5.8, 1.5 Hz, 2 H), 5.28 (d, *J* = 23.0 Hz, 1 H), 5.33 (d, *J* = 29.8 Hz, 1 H), 5.82−5.97 (m, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 53.52 (q), 67.26 (t), 112.45 (s), 112.63 (s), 119.62 (t), 130.39 (d), 161.66 (s), 162.43 (s). $C_8H_8Br_2O_4$ (328.0): calcd. C 29.30, H 2.46; found C 29.52, H 2.69.

Methyl Propargyl (*E*)-2,3-Dibromobut-2-enedioate (6b): The crude product obtained from **4** (51.3 g, 165 mmol), methanol (5.29 g, 165 mmol), and pyridine (13.1 g, 166 mmol), followed by propargylic alcohol (9.26 g, 165 mmol) and pyridine (13.1 g, 166 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 35:1). Compound **6a** (14.5 g, 27%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 7:1) = 0.46. IR (film): $\tilde{\nu}$ = 3295, 3008, 2956, 2132, 1738, 1435, 1369, 1229, 1047, 1025, 997 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.58 (t, *J* = 2.5 Hz, 1 H), 3.90 (s, 3 H), 4.87 (d, *J* = 2.5 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 53.59 (q), 54.08 (t), 75.85 (s), 76.28 (d), 111.72 (s), 113.42 (s), 161.19 (s), 162.33 (s). MS (70 eV): *m*/*z* (%) = 326 (15) [M^+], 295 (18), 271 (100), 245 (50), 39 (40). $C_8H_6Br_2O_4$ (325.9): calcd. C 29.48, H 1.86; found C 29.75, H 1.97.

2-Methoxyethyl Methyl (*E*)-2,3-Dibromobut-2-enedioate (6c): The crude product obtained from **4** (66.4 g, 213 mmol), methanol (6.79 g, 212 mmol), and pyridine (16.8 g, 212 mmol) , followed by ethylene glycol monomethyl ether (16.1 g, 212 mmol) and pyridine (16.8 g, 213 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 9:1). Compound **6c** (24.0 g, 33%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 1:1) = 0.52. IR (film): $\tilde{\nu}$ = 2987, 2955, 2892, 2843, 1738, 1450, 1435, 1244, 1131, 1027 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.37 (s, 3 H), 3.65 (m, 2 H), 3.87 (s, 3 H), 4.41 (m, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 53.84 (q), 58.86 (q), 65.76 (t), 65.61 (t), 112.43 (s), 112.64 (s), 161.99 (s), 162.42 (s). MS (70 eV): *m*/*z* (%) = 346 (1) [M^+], 315 (12), 271 (42), 58 (100). $C_8H_{10}Br_2O_5$ (346.0): calcd. C 27.77, H 2.91; found C 27.51, H 3.00.

Methoxycarbonylmethyl Methyl (*E*)-2,3-Dibromobut-2-enedioate (6d): The crude product obtained from **4** (25.0 g, 80.4 mmol), methanol (2.56 g, 79.9 mmol), and pyridine (6.33 g, 80.0 mmol), followed by methyl glycolate (7.40 g, 82.2 mmol) and pyridine (6.33 g, 80.0 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 10:1). Compound **6d** (14.1 g, 49%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 3:1) = 0.31. IR (film): $\tilde{\nu}$ = 3011, 2957, 1744, 1436, 1381, 1259, 1212, 1069, 1034 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.67 (s, 3 H), 3.79 (s, 3 H), 4.70 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 52.32 (q), 53.59 (q), 61.97 (t), 111.24 (s), 113.84 (s), 161.12 (s), 162.41 (s), 166.66 (s). MS (70 eV): *m*/*z* (%) = 271 (100) [M^+ − $CH_2CO_2CH_3$ (Br_2 isotope pattern], 59 (92). $C_8H_8Br_2O_6$ (360.0): calcd. C 26.69, H 2.24; found C 26.75, H 2.43.

2-Methoxycarbonyl-2-methylpropyl Methyl (*E*)-2,3-Dibromobut-2-enedioate (6e): The crude product obtained from **4** (25.0 g, 80.4 mmol), methanol (2.56 g, 79.9 mmol), and pyridine (6.33 g, 80.0 mmol), followed by methyl 3-hydroxy-2,2-dimethylpropionate (10.8 g, 81.7 mmol) and pyridine (6.33 g, 80.0 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 15:1). Compound **6e** (9.36 g, 29%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 2:1) = 0.48. IR (film): $\tilde{\nu}$ = 2969, 2859, 1743, 1443, 1248, 1155, 1015 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.29 (s, 6 H), 3.71 (s, 3 H), 3.91 (s, 3 H), 4.32 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.13 (q, 2 C), 42.44 (s), 52.07 (q), 53.53 (q), 72.14 (t), 112.59 (s), 112.68

(s), 161.54 (s), 162.49 (s), 175.23 (s). MS (70 eV): *m/z* (%) = 402 (3) [M$^+$], 371 (12), 343 (8), 321 (17), 271 (100). $C_{11}H_{14}Br_2O_6$ (402.0): calcd. C 32.86, H 3.51; found C 33.57, H 3.62.

Methyl 2-Oxo-2-(piperidin-1-yl)ethyl (*E*)-2,3-Dibromobut-2-ene-1,4-dioate (6f): The crude product obtained from **4** (34.2 g, 110 mmol), methanol (3.52 g, 110 mmol), and pyridine (8.70 g, 110 mmol), followed by glycolate pyrrolidide (15.7 g, 110 mmol) and pyridine (8.70 g, 110 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate/DCM, 15:1:1; then hexane/ethyl acetate/DCM, 1:2:0.5). Compound **6f** (12.8 g, 28%) was obtained as a colourless solid. M.p. 35 °C; R_f (hexane/ethyl acetate, 3:1) = 0.10. IR (film): $\tilde{\nu}$ = 2941, 2858, 1742, 1666, 1463, 1446, 1242, 1223, 1008 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.60−1.69 (m, 6 H), 3.33 (brt, 2 H), 3.56 (brt, 2 H), 3.89 (s, 3 H), 4.89 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 24.15 (t), 25.12 (t), 26.09 (t), 43.01 (t), 45.50 (t), 53.49 (q), 63.16 (t), 111.95 (s), 113.48 (s), 161.43 (s), 162.62 (s), 162.85 (s). MS (80 eV): *m/z* (%) = 413 (1) [M$^+$], 354 (6), 332 (38), 112 (100).

Dimethylcarbamoylmethyl Methyl (*E*)-2,3-Dibromobut-2-enedioate (6g): The crude product obtained from **4** (23.0 g, 74.6 mmol), methanol (1.77 g, 55.2 mmol), and pyridine (4.37 g, 55.2 mmol), followed by *N*,*N*-dimethylglycolamide (9.40 g, 91.1 mmol) and pyridine (7.27 g, 91.9 mmol), according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate/DCM, 2:5:2). Compound **6g** (5.16 g, 25%) was obtained as a yellow oil. R_f (hexane/ethyl acetate, 1:10) = 0.37. IR (film): $\tilde{\nu}$ = 2955, 1738, 1666, 1547, 1433, 1236, 1155, 1059, 1031 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.98 (s, 3 H), 2.99 (s, 3 H), 3.90 (s, 3 H), 4.90 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 35.50 (q), 35.71 (q), 53.51 (q), 62.97 (t), 111.86 (s), 113.56 (s), 161.45 (s), 162.63 (s), 164.61 (s). MS (FAB$^+$): *m/z* (%) = 374 (50) [M + H$^+$], 271 (25), 219 (72).

2-Methoxycarbonylphenyl Methyl (*E*)-2,3-Dibromobut-2-enedioate (6h): The crude product obtained from **4** (671 mg, 2.16 mmol), methanol (69.2 mg, 2.16 mmol) and pyridine (171 mg, 2.16 mmol), followed by methyl 2-hydroxybenzoate (wintergreen oil, 329 mg, 2.16 mmol), and pyridine (171 mg, 2.16 mmol), according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 12:1). Compound **6h** (22.8 mg, 3%) was obtained as a colourless solid. M.p. 114 °C; R_f (hexane/ethyl acetate, 3:1) = 0.34. IR (film): $\tilde{\nu}$ = 2954, 1754, 1726, 1608, 1593, 1486, 1452, 1438, 1272, 1236, 1186, 1084, 1002 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.90 (s, 3 H), 3.95 (s, 3 H), 7.26 (dd, *J* = 1.2, 8.1 Hz, 1 H), 7.39 (dt, *J* = 1.2, 7.6 Hz, 1 H), 7.61 (dt, *J* = 1.8, 7.6 Hz, 1 H), 8.06 (dd, J = 1.6, 7.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 52.36 (q), 53.61 (q), 111.54 (s), 115.15 (s), 123.02 (d), 123.19 (s), 126.80 (d), 132.01 (d), 133.83 (d), 149.13 (s), 159.81 (s), 162.82 (s), 164.51 (s). MS (FAB$^+$): *m/z* (%) = 422 (1) [M$^+$], 332 (1), 301 (3), 181 (100).

Methyl (*E*)-2,3-Dibromo-4-oxo-4-(pyrrolidin-1-yl)but-2-enoate (6i): The crude product obtained from **4** (19.6 g, 63.1 mmol), pyrrolidine (4.50 g, 63.3 mmol), and pyridine (4.99 g, 63.1 mmol), followed by methanol (2.03 g, 63.4 mmol) and pyridine (4.99 g, 63.1 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 1:10). Compound **6i** (5.80 g, 27%) was obtained as a colourless solid. M.p. 56 °C; R_f (ethyl acetate/DCM, 1:1) = 0.15. IR (film): $\tilde{\nu}$ = 2954, 2879, 2361, 2343, 1735, 1648, 1560, 1542, 1508, 1430, 1339, 1252, 1191, 1066, 1030, 1015, 911 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.96 (m, 4 H), 3.39 (m, 2 H), 3.53 (m, 2 H), 3.87 (s, 3 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 24.17 (t), 25.58 (t), 45.58 (t), 46.70 (t), 53.41 (q), 108.49 (s), 117.92 (s), 161.79 (s), 161.95 (s). MS (80 eV): *m/z* (%) = 339 (8) [M$^+$], 69 (100), 310 (15), 271 (45), 181 (54). $C_9H_{11}Br_2NO_3$ (340.9): calcd. C 31.70, H 3.25, N 4.11; found C 31.96, H 3.45, N 3.88.

(*S*)-1-Methoxycarbonylethyl Methyl (*E*)-2,3-Dibromobut-2-enedioate [(*S*)-6j]: The crude product obtained from **4** (19.8 g, 63.7 mmol), methanol (2.03 g, 63.4 mmol), and pyridine (5.01 g, 63.3 mmol), followed by methyl (*S*)-lactate (6.60 g, 63.3 mmol) and pyridine (5.02 g, 63.5 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 7:1). Compound (*S*)-**6j** (11.8 g, 50%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 4:1) = 0.25. IR (film): $\tilde{\nu}$ = 3000, 2956, 2850, 1742, 1602, 1445, 1380, 1353, 1310, 1246, 1131, 1093, 1044, 1003, 893, 843, 805, 752, 723 cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 1.57 (d, *J* = 7.1 Hz, 3 H), 3.76 (s, 3 H), 3.88 (s, 3 H), 5.23 (q, *J* = 7.1 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.58 (q), 52.50 (q), 53.61 (q), 70.71 (d), 111.93 (s), 113.33 (s), 161.21 (s), 162.55 (s), 169.67 (s). MS (80 eV): *m/z* (%) = 374 (1) [M$^+$], 343 (4) [M$^+$ − OMe], 271 (100). $C_9H_{10}Br_2O_6$ (374.0): calcd. C 28.90, H 2.70; found C 29.16, H 2.75.

Methoxycarbonylmethyl 2-Methoxycarbonyl-2-methylpropyl (*E*)-2,3-Dibromobut-2-enedioate (6k): The crude product obtained from **4** (37.1 g, 119 mmol), methyl glycolate (10.7 g, 119 mmol), and pyridine (9.38 g, 119 mmol), followed by methyl 3-hydroxy-2,2-dimethylpropionate (15.9 g, 120 mmol) and pyridine (9.38 g, 119 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 13:1). Compound **6k** (14.8 g, 27%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 2:1) = 0.44. IR (film): $\tilde{\nu}$ = 2980, 2956, 1767, 1754, 1745, 1731, 1474, 1461, 1454, 1439, 1380, 1209, 1155, 1070, 1038, 980, 954 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.23 (s, 6 H), 3.65 (s, 3 H), 3.75 (s, 3 H), 4.27 (s, 2 H), 4.75 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.09 (q, 2 C), 42.42 (s), 52.03 (q), 52.30 (q), 61.96 (t), 72.14 (t), 111.39 (s), 113.91 (s), 161.19 (s), 161.19 (s), 166.59 (s), 175.15 (s). MS (70 eV): *m/z* (%) = 460 (1) [M$^+$], 429 (8), 401 (4), 381 (40), 329 (62), 73 (100). $C_{13}H_{16}Br_2O_8$ (460.1): calcd. C 33.94, H 3.51; found C 34.17, H 3.63.

Synthesis of the Alkynes 9

Allyl Methyl But-2-ynedioate (9a): The crude product obtained from **6a** (7.00 g, 21.3 mmol) and zinc (8.30 g, 127 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 13:1). Compound **9a** (2.47 g, 69%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 10:1) = 0.50. IR (film): $\tilde{\nu}$ = 2958, 1727, 1437, 1362, 1263, 1039, 995, 942 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.83 (s, 3 H), 4.71 (dt, *J* = 5.9, 1.3 Hz, 2 H), 5.28−5.42 (m, 2 H), 5.83−5.98 (m, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 53.25 (q), 67.11 (t), 74.45 (s), 74.52 (s), 119.88 (t), 130.18 (d), 151.23 (s), 152.00 (s). $C_8H_8O_4$ (168.2): calcd. C 57.14, H 4.80; found C 56.88, H 4.68.

Methyl Propargyl But-2-ynedioate (9b): The crude product obtained from **6b** (6.92 g, 21.2 mmol) and zinc (8.30 g, 127 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 11:1). Compound **9b** (2.85 g, 81%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 7:1) = 0.52. IR (film): $\tilde{\nu}$ = 3295, 2960, 1727, 1437, 1370, 1266, 1045, 1009 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.56 (t, *J* = 2.5 Hz, 1 H), 3.84 (s, 3 H), 4.81 (d, *J* = 2.6 Hz, 2 H). ^{13}C NMR (CDCl3, 62.9 MHz): δ = 53.34 (q), 55.81 (t), 73.77 (s), 75.26 (s), 75.60 (d), 76.29 (s), 150.72 (s), 152.81 (s).

2-Methoxyethyl Methyl But-2-ynedioate (9c): The crude product obtained from **6c** (24.0 g, 69.4 mmol) and zinc (27.6 g, 422 mmol)

according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 5:1). Compound **9c** (11.2 g, 87%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 1:1) = 0.57. IR (film): $\tilde{\nu}$ = 2956, 1723, 1437, 1368, 1263, 1130, 1045 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.32 (s, 3 H), 3.56 (t, J = 4.6 Hz, 2 H), 3.37 (s, 3 H), 4.31 (t, J = 4.7 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 53.22 (q), 58.82 (q), 65.49 (t), 69.47 (t), 74.50 (s), 74.65 (s), 152.47 (s), 151.97 (s). MS (FAB^+): *m/z* (%) = 187 (5) [M + H^+], 155 (15) [M^+ − OCH_3], 126 (9), 111 (30), 59 (100). $C_8H_{10}O_5$ (186.2): calcd. C 51.61, H 5.41; found C 50.94, H 5.49.

Methoxycarbonylmethyl Methyl But-2-ynedioate (9d): The crude product obtained from **6d** (13.4 g, 37.2 mmol) and zinc (14.8 g, 226 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 7:1). Compound **9d** (5.07 g, 68%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 7:1) = 0.42. IR (film): $\tilde{\nu}$ = 2982, 2955, 1736, 1627, 1469, 1368, 1256, 1191, 1155, 1015, 916 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.80 (s, 3 H), 3.87 (s, 3 H), 4.77 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 52.31 (q), 53.32 (q), 61.73 (t), 73.49 (s), 75.50 (s), 150.74 (s), 151.67 (s), 166.38 (s). MS (70 eV): *m/z* (%) = 169 (31) [M^+ − OMe], 141 (16), 126 (12), 111 (100). $C_8H_8O_6$ (200.1): calcd. C 48.01, H 4.03; found C 47.74, H 4.32.

2-Methoxycarbonyl-2-methylpropyl Methyl But-2-ynedioate (9e): The crude product obtained from **6e** (9.36 g, 23.3 mmol) and zinc (9.32 g, 143 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 10:1). Compound **9e** (4.35 g, 77%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 2:1) = 0.47. IR (film): $\tilde{\nu}$ = 2983, 2957, 1731, 1439, 1265, 1155, 1040 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.20 (s, 6 H), 3.66 (s, 3 H), 3.80 (s, 3 H), 4.22 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 21.98 (q, 2 C), 42.23 (s), 52.05 (q), 53.23 (q), 71.70 (t), 74.36 (s), 74.63 (s), 151.21 (s), 151.95 (s), 175.12 (s). MS (FAB^+): *m/z* (%) = 243 (9) [M + H^+], 211 (20) [M^+ − OMe], 183 (19), 115 (100). $C_{11}H_{14}O_6$ (242.2).

Methyl 2-Oxo-2-(piperidin-1-yl)ethyl But-2-ynedioate (9f): The crude product obtained from **6f** (12.6 g, 30.5 mmol) and zinc (12.1 g, 185 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 1:1). Compound **9f** (5.73 g, 74%) was obtained as a pale yellow solid. M.p. 67 °C; R_f (hexane/ethyl acetate, 3:1) = 0.10. IR (film): $\tilde{\nu}$ = 2943, 2859, 1730, 1667, 1463, 1446, 1436, 1254, 1226, 1065, 1013 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.54−1.67 (m, 6 H), 3.28 (m, 2 H), 3.55 (m, 2 H), 3.84 (s, 3 H), 4.85 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 24.11 (q), 25.08 (t), 26.01 (t), 43.03 (t), 45.43 (t), 53.24 (t), 62.95 (t), 74.16 (s), 75.28 (s), 151.16 (s), 151.92 (s), 162.52 (s). MS (80 eV): *m/z* (%) = 253 (9) [M^+], 222 (11), 125 (23), 112 (100). $C_{12}H_{15}NO_5$ (253.3): calcd. C 56.91, H 5.97, N 5.53; found C 56.86, H 6.10, N 5.40.

Dimethylcarbamoylmethyl Methyl But-2-ynedioate (9g): The crude product obtained from **6g** (6.20 g, 16.6 mmol) and zinc (6.62 g, 101 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 1:5). Compound **9g** (2.86 g, 81%) was obtained as a yellow solid. M.p. 57 °C; R_f (hexane/ethyl acetate, 1:5) = 0.35. IR (film): $\tilde{\nu}$ = 2958, 1731, 1667, 1503, 1434, 1261, 1155, 1061, 1016 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.93 (s, 3 H), 2.94 (s, 3 H), 3.81 (s, 3 H), 4.83 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 35.41 (q), 35.55 (q), 53.28 (q), 62.82 (t), 74.09 (s), 75.26 (s), 151.12 (s), 151.88 (s), 164.26 (s). MS (80 eV): *m/z* (%) = 213 (8) [M^+], 182 (12), 72 (100). $C_9H_{11}NO_5$ (213.2).

(*S*)-1-Methoxycarbonylethyl Methyl But-2-ynedioate [(*S*)-9j]: The crude product obtained from (*S*)-dibromo ester (*S*)-**6j** (5.91 g, 15.8 mmol) and zinc (6.20 g, 94.8 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate/DCM, 5:0.1:2). Compound (*S*)-**9j** (1.86 g, 55%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 4:1) = 0.30. IR (film): $\tilde{\nu}$ = 3004, 2960, 2849, 1737, 1631, 1442, 1380, 1353, 1250, 1131, 1094, 1049, 977, 936, 891, 841, 748 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.52 (d, J = 7.1 Hz, 3 H), 3.73 (s, 3 H), 3.82 (s, 3 H), 5.17 (q, J = 7.1 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.50 (q), 52.50 (q), 53.34 (q), 70.49 (d), 73.96 (s), 75.21 (s), 150.73 (s), 151.84 (s), 169.39 (s). MS (70 eV): *m/z* (%) = 183 (11) [M^+ − OMe], 111 (100). $C_9H_{10}O_6$ (214.2): calcd. C 50.47, H 4.71; found C 50.21, H 4.78.

Methoxycarbonylmethyl 2-Methoxycarbonyl-2-methylpropyl But-2-ynedioate (9k): The crude product obtained from **6k** (12.1 g, 26.3 mmol) and zinc (10.5 g, 161 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 4:1). Compound **9k** (7.81 g, 99%) was obtained as a colourless oil. M.p. 174 °C; R_f (hexane/ethyl acetate, 2:1) = 0.45. IR (film): $\tilde{\nu}$ = 2981, 2958, 1766, 1731, 1476, 1439, 1380, 1267, 1157, 1071, 1009, 974, 935 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.23 (s, 6 H), 3.69 (s, 3 H), 3.77 (s, 3 H), 4.26 (s, 2 H), 4.73 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.01 (q, 2 C), 42.24 (s), 52.09 (q), 52.41 (q), 61.76(t), 71.83 (t), 73.85 (s), 75.63 (s), 150.82 (s), 151.04 (s), 166.36 (s), 175.09 (s). MS (70 eV): *m/z* (%) = 300 (2) [M^+], 285 (7), 269 (56), 169 (100). $C_{13}H_{16}O_8$ (300.3): calcd. C 52.00, H 5.37; found C 51.16, H 5.50.

Synthesis of Isomeric Pyrazoles 12 and 13

5-Allyl 4-Methyl and 4-Allyl 5-Methyl 3,3-Dimethyl-3*H*-pyrazole-4,5-dicarboxylate (12a/13a): The crude product obtained from **9a** (2.11 g, 12.5 mmol) and a solution of **10a** in ether (17.0 mL, 0.74 M, 12.6 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 7:1). Compounds **12a/13a** (2.38 g, 80%) were obtained as a yellow oil. R_f (hexane/ethyl acetate, 1:1) = 0.54. IR (film): $\tilde{\nu}$ = 2986, 2955, 1731, 1637, 1453, 1438, 1366, 1327, 1260, 1169, 1118, 1049, 1028, 937 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.55−1.56 (m, 12 H), 3.85 (s, 3 H), 3.86 (s, 3 H), 4.75−4.86 (m, 4 H), 5.27−5.45 (m, 4 H), 5.85−6.06 (m, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.89 (q, 2 C), 19.92 (q, 2 C), 52.73 (q), 52.76 (q), 66.50 (t, 2 C), 97.25 (s, 2 C), 119.44 (t), 119.53 (t), 130.71 (d), 130.86 (d), 144.48 (s, 2 C), 153.05 (s), 153.11 (s), 159.89 (s), 160.65 (s), 161.99 (s), 162.80 (s). MS (80 eV): *m/z* (%) = 238 (1) [M^+], 223 (1), 195 (2), 41 (100). $C_{11}H_{14}N_2O_4$ (238.2): calcd. C 55.46, H 5.92, N 11.76; found C 55.25, H 6.05, N 11.66.

Compounds 12b/13b: The crude product obtained from **9b** (2.50 g, 15.0 mmol) and a solution of **10a** in ether (21.0 mL, 0.74 M, 15.5 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 4:1). Compounds **12b/13b** (2.76 g, 78%) were obtained as a yellow oil. R_f (hexane/ethyl acetate, 1:1) = 0.56. IR (film): $\tilde{\nu}$ = 3283, 2988, 2951, 2130, 1738, 1635, 1436, 1373, 1327, 1258, 1168, 1119, 1053, 1030, 1005 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.56 (s, 6 H), 1.57 (s, 6 H), 2.55 (t, J = 2.4 Hz, 2 H), 3.89 (s, 3 H), 3.97 (s, 3 H), 4.87 (d, J = 2.5 Hz, 2 H), 4.95 (d, J = 2.5 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.83 (q, 2 C), 19.87 (q, 2 C), 52.81 (q), 52.84 (q), 53.19 (t, 2 C), 75.86 (d, 2 C), 76.21 (s), 76.45 (s), 97.43 (s), 97.46 (s), 143.66 (s), 144.71 (s), 152.16 (s), 153.86 (s), 159.35 (s), 160.45 (s), 161.55 (s), 162.56 (s). MS (FAB^+): *m/z* (%) = 237 (84) [M + H^+], 181 (100). $C_{11}H_{12}N_2O_4$ (236.2): calcd. C 55.93, H 5.12, N 11.86; found C 55.72, H 5.20, N 11.63.

Compounds 12c/13c: The crude product obtained from **9c** (8.77 g, 47.1 mmol) and a solution of **10a** in ether (50.0 mL, 954 mM, 47.7 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 3:1). Compounds **12c/13c** (9.89 g, 82%) were obtained as a yellow oil. R_f (hexane/ethyl acetate, 1:1) = 0.30. IR (film): $\tilde{\nu}$ = 2985, 2955, 2938, 2891, 1731, 1635, 1453, 1327, 1264, 1119, 1053 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.50 (s, 6 H), 1.51 (s, 6 H), 3.32 (s, 3 H), 3.34 (s, 3 H), 3.58 (t, J = 4.7 Hz, 2 H), 3.64 (t, J = 4.7 Hz, 2 H), 3.83 (s, 3 H), 3.92 (s, 3 H), 4.39 (t, J = 4.7 Hz, 2 H), 4.46 (t, J = 4.7 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.88 (q, 4 C), 52.71 (q, 2 C), 58.68 (q), 58.75 (q), 64.63 (t), 64.79 (t), 69.74 (t), 69.79 (t), 97.23 (s), 97.29 (s), 144.45 (s, 2 C), 152.99 (s), 153.31 (s), 160.25 (s), 160.64 (s), 162.30 (s), 162.75 (s). MS (80 eV): *m/z* (%) = 256 (1) [M^+], 241 (1), 181 (18), 154 (43), 59 (100). $C_{11}H_{16}N_2O_5$ (256.3): calcd. C 51.56, H 6.29, N 10.93; found C 51.49, H 6.36, N 10.89.

4-(Methoxycarbonylmethyl) 5-Methyl and 5-(Methoxycarbonylmethyl) 4-Methyl 3,3-Dimethyl-3*H*-pyrazole-4,5-dicarboxylate (12d/13d): The crude product obtained from **9d** (4.72 g, 23.6 mmol) and a solution of **10a** in ether (12.5 mL, 1.89 M, 23.6 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 3:1). Compounds **12d/13d** (6.21 g, 42%) were obtained as a yellow oil. R_f (hexane/ethyl acetate, 3:1) = 0.15. IR (film): $\tilde{\nu}$ = 2983, 2884, 1728, 1369, 1258, 1193, 1154, 1039, 978, 939 cm^{-1}. *First isomer:* ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.62 (s, 6 H), 3.80 (s, 3 H), 3.98 (s, 3 H), 4.83 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.77 (q, 2 C), 52.31 (q), 52.80 (q), 61.27 (t), 97.84 (s), 144.26 (s), 153.33 (s), 160.36 (s), 162.65 (s), 166.94 (s). *Second isomer:* ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.58 (s, 6 H), 3.80 (s, 3 H), 3.90 (s, 3 H), 4.90 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.86 (q, 2 C), 52.26 (q), 52.88 (q), 61.46 (t), 97.59 (s), 154.71 (s), 159.36 (s), 162.06 (s), 162.36 (s), 166.88 (s). MS (70 eV): *m/z* (%) = 270 (1) [M^+], 239 (25), 210 (15), 195 (8), 181 (26), 154 (100). $C_{11}H_{14}N_2O_6$ (270.2) (**12d/13d**): calcd. C 48.88, H 5.22, N 10.37; found C 48.96, H 5.32, N 10.12.

4-(Methoxycarbonyl-2,2-dimethylethyl) 5-Methyl and 5-(Methoxycarbonyl-2,2-dimethylethyl) 4-Methyl 3,3-Dimethyl-3*H*-pyrazole-4,5-dicarboxylate (12e/13e): The crude product obtained from **9e** (4.32 g, 17.8 mmol) and a solution of **10a** in ether (9.50 mL, 1.89 M, 18.0 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 4:1). Compound **12e** (1.49 g, 27%) was obtained as a yellow solid and **13e** (1.49 g, 27%) as a yellow oil. Single crystals of **12e** for crystal structure analysis were grown from diethyl ether. Compound **12e:** M.p. 51 °C; R_f (hexane/ethyl acetate, 1:1) = 0.66. IR (film): $\tilde{\nu}$ = 2985, 2956, 1734, 1639, 1448, 1370, 1327, 1258, 1193, 1158, 1113, 1048, 969 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.19 (s, 6 H), 1.49 (s, 6 H), 3.63 (s, 3 H), 3.92 (s, 3 H), 4.26 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.77 (q, 2 C), 22.04 (q, 2 C), 42.26 (s), 51.95 (q), 52.77 (q), 72.37 (t), 97.15 (s), 144.79 (s), 152.12 (s), 160.65 (s), 161.65 (s), 175.19 (s). MS (70 eV): *m/z* (%) = 312 (1) [M^+], 281 (20), 253 (11), 154 (100). $C_{14}H_{20}N_2O_6$ (312.3): calcd. C 53.84, H 6.45, N 8.97; found C 53.75, H 6.49, N 8.76. Compound **13e**: R_f (hexane/ethyl acetate, 1:1) = 0.59. IR (film): $\tilde{\nu}$ = 2984, 2955, 1736, 1636, 1457, 1437, 1328, 1262, 1155, 1106, 1051, 1027 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.19 (s, 6 H), 1.47 (s, 6 H), 3.62 (s, 3 H), 3.81 (s, 3 H), 4.32 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.83 (q, 2 C), 22.05 (q, 2 C), 42.28 (s), 51.93 (q), 52.85 (q), 71.19 (t), 97.41 (s), 143.58 (s), 153.23 (s), 159.81 (s), 162.83 (s), 175.29 (s). MS (70 eV): *m/z* (%) = 312 (1) [M^+], 281 (11), 267 (3), 252 (43), 115 (100). $C_{14}H_{20}N_2O_6$ (312.3).

5-Methyl 4-(Piperidin-1-ylcarbonylmethyl) and 4-Methyl 5-(Piperidin-1-ylcarbonylmethyl) 3,3-Dimethyl-3*H*-pyrazole-4,5-dicarboxylate (12f/13f): The crude product obtained from **9f** (2.40 g, 9.48 mmol) and a solution of **10a** in diethyl ether (10.0 mL, 954 mM, 9.54 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate/DCM, 1.5:1:2). Compounds **12f/13f** (2.48 g, 81%) were obtained as a yellow solid. R_f (hexane/ethyl acetate, 1:1) = 0.25. IR (film): $\tilde{\nu}$ = 2936, 1734, 1664, 1458, 1355, 1327, 1262, 1117, 1068 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.58−1.69 (m, 6 H), 1.67 (s, 6 H), 3.30 (t, J = 4.9 Hz, 2 H), 3.55 (t, J = 4.9 Hz, 2 H), 3.97 (s, 3 H), 4.94 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.81 (q, 2 C), 24.11 (t), 25.11 (t), 26.02 (t), 43.03 (t), 45.28 (t), 52.73 (q), 62.27 (t), 98.05 (s), 143.66 (s), 155.08 (s), 160.46 (s), 162.58 (s), 162.98 (s). MS (FAB$^+$): 324 (36) [M + H^+], 242 (49), 181 (33), 170 (21), 167 (24). $C_{15}H_{21}N_3O_5$ (323.3): calcd. C 55.72, H 6.55, N 13.00; found C 55.57, H 6.59, N 13.10.

4-(Dimethylcarbamoylmethyl) 5-Methyl and 4-(Dimethylcarbamoylmethyl) 5-Methyl 3,3-Dimethyl-3*H*-pyrazole-4,5-dicarboxylate (12g/13g): The crude product obtained from **9g** (1.26 g, 5.91 mmol) and a solution of **10a** in diethyl ether (6.50 mL, 954 mM, 6.20 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 1:4). Compounds **12g/13g** (664 mg, 40%) were obtained as a yellow oil. R_f (hexane/ethyl acetate, 1:4) = 0.24. IR (film): $\tilde{\nu}$ = 2985, 2953, 2094, 1738, 1871, 1501, 1435, 1327, 1261, 1118, 1066, 1030 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.64 (s, 6 H), 2.96 (s, 3 H), 2.97 (s, 3 H), 3.95 (s, 3 H), 4.92 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.77 (q, 2 C), 35.49 (q, 2 C), 52.71 (q), 62.14 (t), 98.04 (s), 143.64 (s), 154.97 (s), 160.43 (s), 162.56 (s), 164.74 (s). MS (80 eV): *m/z* (%) = 283 (2) [M^+], 268 (4), 240 (5), 72 (100). $C_{12}H_{17}N_3O_5$ (283.3): calcd. C 50.88, H 6.05, N 14.83; found C 50.89, H 6.10, N 15.05.

Compounds (*S*)-12j/(*S*)-13j: The crude product obtained from (*S*)-**9j** (1.69 g, 7.89 mmol) and a solution of **10a** in ether (13.9 mL, 570 mM, 7.92 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 8:1). Compounds (*S*)-**12j**/(*S*)-**13j** (1.26 g, 56%) were obtained as a yellow oil. *First isomer:* R_f (hexane/ethyl acetate, 8:1) = 0.25. IR (film): $\tilde{\nu}$ = 2991, 2955, 1745, 1639, 1451, 1355, 1034, 1263, 1169, 1100, 1053, 1031, 973, 901, 867, 822, 792 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.51 (d, J = 7.1 Hz, 3 H), 1.55 (s, 3 H), 1.57 (s, 3 H), 3.73 (s, 3 H), 3.93 (s, 3 H), 5.28 (q, J = 7.1 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.49 (q), 19.74 (q), 19.82 (q), 52.41 (q), 52.72 (q), 69.70 (d), 97.71 (s), 144.17 (s), 153.44 (s), 160.39 (s), 161.90 (s), 169.89 (s). MS (70 eV): *m/z* (%) = 284 (1) [M^+], 253 (10) [M^+ − OMe], 59 (100). $C_{12}H_{16}N_2O_6$ (284.3): calcd. C 50.71, H 5.67, N 9.85; found C 50.54, H 5.72, N 9.59. *Second isomer:* ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.76 (q), 19.75 (q), 19.85 (q), 52.39 (q), 52.79 (q), 69.84 (d), 97.49 (s), 143.61 (s), 154.11 (s), 159.35 (s), 162.74 (s), 169.91 (s).

Compounds 12k/13k: The crude product obtained from **9k** (4.60 g, 15.3 mmol) and a solution of **10a** in ether (16.0 mL, 954 mM, 15.3 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 2:1). Compound **12k** (1.89 g, 33%) was obtained as a yellow oil and **13k** (1.90 g, 33%) as a yellow solid. Crystals of **13k** for X-ray structure analysis were obtained from diethyl ether. Compound **12k**: R_f (hexane/ethyl acetate, 1:1) = 0.38. IR (film): $\tilde{\nu}$ = 2984, 2958, 1731, 1638, 1454, 1439, 1380, 1326, 1218, 1166, 1120, 1065, 1026, 1010, 968, 953 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.20 (s, 6 H), 1.53 (s, 6 H), 3.64 (s, 3 H), 3.76 (s, 3 H), 4.29 (s, 2 H), 4.86 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.75 (q, 2 C), 22.04 (q, 2

C), 42.28 (s), 51.95 (q), 52.23 (q), 61.51 (t), 71.47 (t), 97.56 (s), 143.45 (s), 154.28 (s), 159.26 (s), 161.71 (s), 166.89 (s), 175.24 (s). MS (80 eV): *m/z* (%) = 370 (1) [M^+], 339 (18), 311 (11), 115 (100). $C_{16}H_{22}N_2O_8$ (370.4): calcd. C 51.89, H 5.99, N 7.56; found C 51.79, H 6.02, N 7.34. Compound **13k:** M.p. 136 °C; R_f (hexane/ethyl acetate, 1:1) = 0.52. IR (film): $\tilde{\nu}$ = 2984, 2956, 1738, 1638, 1439, 1380, 1327, 1252, 1217, 1166, 1121, 1065 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.19 (s, 6 H), 1.56 (s, 6 H), 3.62 (s, 3 H), 3.74 (s, 3 H), 4.32 (s, 2 H), 4.78 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.72 (q, 2 C), 22.06 (q, 2 C), 42.28 (s), 51.97 (q), 52.27 (q), 61.39 (t), 71.38 (t), 98.22 (s), 142.99 (s), 153.79 (s), 159.39 (s), 162.43 (s), 167.11 (s), 175.33 (s). MS (80 eV): *m/z* (%) = 370 (1) [M^+], 339 (19), 252 (16), 242 (13), 115 (100). $C_{16}H_{22}N_2O_8$ (370.4): calcd. C 51.89, H 5.99, N 7.56; found C 51.89, H 6.10, N 7.29.

Synthesis of the Cyclopropenes 1β

1-Allyl 2-Methyl 3,3-Dimethyl-1-cyclopropene-1,2-dicarboxylate (1βa): The crude product obtained from **12a/13a** (1.47 g, 6.17 mmol) was purified by column chromatography on silica gel (hexane/ethyl acetate, 30:1). Compound **1βa** (999 mg, 77%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 6:1) = 0.41. IR (film): $\tilde{\nu}$ = 2910, 1736, 1718, 1430, 1370, 1256, 1223, 1153, 1077, 1021 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.41 (s, 6 H), 3.86 (s, 3 H), 4.75 (dt, *J* = 5.6, 1.4 Hz, 2 H), 5.26−5.43 (m, 2 H), 5.89−6.05 (m, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.36 (q, 2 C), 31.86 (s), 52.40 (q), 65.98 (t), 118.70 (t), 131.16 (d), 132.13 (s), 132.19 (s), 159.60 (s), 160.29 (s). MS (80 eV): *m/z* (%) = 420 (6) [$2M^+$], 379 (7), 167 (41), 141 (53). $C_{11}H_{14}O_4$ (210.2): calcd. C 62.85, H 6.72; found C 62.87, H 6.64.

Compound 1βc: The crude product obtained from **12c/13c** (9.10 g, 35.5 mmol) was purified by column chromatography on silica gel (hexane/ethyl acetate, 4:1). Compound **1βc** (7.70 g, 95%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 1:1) = 0.66. IR (film): $\tilde{\nu}$ = 2954, 1835, 1722, 1454, 1435, 1372, 1248, 1201, 1131, 1107, 1060 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.39 (s, 6 H), 3.39 (s, 3 H), 3.66 (t, *J* = 4.8 Hz, 2 H), 3.84 (s, 3 H), 4.39 (t, *J* = 4.9 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.32 (q, 2c), 31.29 (s), 52.33 (q), 58.88 (q), 64.56 (t), 69.91 (t), 131.96 (s), 132.13 (s), 159.94 (s), 160.28 (s). $C_{11}H_{16}O_5$ (228.2): calcd. C 57.89, H 7.07; found C 58.13, H 7.14.

1-(Methoxycarbonylmethyl) 2-Methyl 3,3-Dimethyl-1-cyclopropene-1,2-dicarboxylate (1βd): The crude product obtained from **12d/13d** (2.14 g, 7.92 mmol) was purified by column chromatography on silica gel (hexane/ethyl acetate, 4:1). Compound **1βd** (1.80 g, 94%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 1:1) = 0.74. IR (film): $\tilde{\nu}$ = 2985, 1837, 1722, 1437, 1378, 1246, 1208, 1106, 1077, 1043 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.40 (s, 6 H), 3.76 (s, 3 H), 3.84 (s, 3 H), 4.75 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.26 (q, 2 C), 31.46 (s), 52.19 (q), 52.43 (q), 62.11 (t), 130.85 (s), 133.96 (s), 158.97 (s), 160.13 (s), 167.22 (s). MS (70 eV): *m/z* (%) = 242 (3) [M^+], 227 (24), 210 (18), 199 (23), 93 (100). $C_{11}H_{14}O_6$ (242.2): calcd. C 54.54, H 5.83; found C 54.52, H 5.92.

1-(1-Methoxycarbonyl-2,2-dimethylethyl) 2-Methyl 3,3-Dimethyl-1-cyclopropene-1,2-dicarboxylate (1βe): The crude product obtained from **12e/13e** (1.00 g, 3.20 mmol) was purified by column chromatography on silica gel (hexane/ethyl acetate, 6:1). Compound **1βe** (700 mg, 77%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 2:1) = 0.69. IR (film): $\tilde{\nu}$ = 2955, 1836, 1721, 1437, 1251, 1153, 1059 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.22 (s, 6 H), 1.35 (s, 6 H), 3.66 (s, 3 H), 3.81 (s, 3 H), 4.24 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.02 (q, 2 C), 25.26 (q, 2 C), 31.15 (s), 42.45 (s), 51.87 (q), 52.29 (q), 70.70 (t), 131.94 (s), 132.56 (s), 159.42 (s), 160.08 (s), 175.45 (s). MS (70 eV): *m/z* (%) = 284 (2) [M^+], 269 (5), 252 (7), 59 (100). $C_{14}H_{20}O_6$ (284.3): calcd. C 59.14, H 7.09; found C 59.25, H 7.11.

1-Methyl 2-(Piperidin-1-ylcarbonylmethyl) 3,3-Dimethyl-1-cyclopropene-1,2-dicarboxylate (1βf): The crude product obtained from **12f/13f** (2.00 g, 6.19 mmol) was purified by column chromatography on silica gel (hexane/ethyl acetate, 2:1; then hexane/ethyl acetate, 1:2). Compound **1βf** (1.28 g, 70%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 1:4) = 0.48. IR (film): $\tilde{\nu}$ = 2946, 2859, 1836, 1720, 1669, 1448, 1247, 1073 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.42 (s, 6 H), 1.46−1.66 (m, 6 H), 3.33 (d of brs, *J* = 5.4 Hz, 2 H), 3.56 (d of brs, *J* = 5.4 Hz, 2 H), 3.85 (s, 3 H), 4.87 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 21.33 (t), 25.23 (t), 25.48 (q, 2 C), 26.21 (t), 31.48 (s), 43.13 (t), 45.67 (t), 52.55 (q), 62.42 (t), 131.48 (s), 133.33 (s), 159.44 (s), 160.39 (s), 163.61 (s). $C_{15}H_{21}NO_5$ (295.3): calcd. C 61.00, H 7.17, N 4.74; found C 60.81, H 7.18, N 4.70.

1-(Dimethylcarbamoylmethyl) 2-Methyl 3,3-Dimethyl-1-cyclopropene-1,2-dicarboxylate (1βg): The crude product obtained from **12g/13g** (660 mg, 2.33 mmol) was purified by column chromatography on silica gel (hexane/ethyl acetate, 1:2). Compound **1βg** (375 mg, 63%) was obtained as a pale yellow oil. R_f (hexane/ethyl acetate, 1:4) = 0.42. IR (film): $\tilde{\nu}$ = 2952, 2870, 1837, 1713, 1681, 1673, 1503, 1435, 1416, 1248, 1156, 1108, 1071 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.95 (s, 6 H), 2.90 (s, 3 H), 2.94 (s, 3 H), 3.77 (s, 3 H), 4.81 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.27 (q, 2 C), 31.24 (s), 35.36 (q), 35.64 (q), 52.32 (q), 62.05 (t), 131.27 (s), 133.08 (s), 159.20 (s), 160.16 (s), 165.17 (s).

(1*S*)-1-Methoxycarbonylethyl 2-Methyl 3,3-Dimethyl-1-cyclopropene-1,2-dicarboxylate [(*S*)-1βj]: The crude product obtained from (*S*)-**12j**/(*S*)-**13j** (1.19 g, 4.19 mmol) was purified by column chromatography on silica gel (hexane/ethyl acetate, 6:1). Compound (*S*)-**1βj** (870 mg, 81%) was obtained as a colourless oil. R_f (hexane/acetone, 2:1) = 0.40. − IR (film): $\tilde{\nu}$ = 2956, 1836, 1758, 1719, 1440, 1372, 1251, 1097, 1057, 979, 902, 827 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.39 (s, 6 H), 1.55 (d, *J* = 7.0 Hz, 3 H), 3.74 (s, 3 H), 3.83 (s, 3 H), 5.20 (q, *J* = 7.1 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.70 (q), 25.28 (q), 25.31 (q), 31.48 (s), 52.29 (q), 52.40 (q), 69.48 (d), 131.27 (s), 133.42 (s), 159.13 (s), 160.19 (s), 170.24 (s). MS (70 eV): *m/z* (%) = 256 (1) [M^+], 59 (100). $C_{12}H_{16}O_6$ (256.3): calcd. C 56.25, H 6.29; found C 56.31, H 6.38.

Compound 1βk: The crude product obtained from **12k/13k** (3.70 g, 9.99 mmol) was purified by column chromatography on silica gel (hexane/ethyl acetate, 4:1). Compound **1βk** (2.95 g, 86%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 1:1) = 0.66. IR (film): $\tilde{\nu}$ = 2956, 2879, 1837, 1767, 1738, 1714, 1440, 1373, 1206, 1155, 1078 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.22 (s, 6 H), 1.37 (s, 6 H), 3.65 (s, 3 H), 3.74 (s, 3 H), 4.24 (s, 2 H), 4.72 (s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.00 (q, 2 C), 25.21 (q, 2 C), 31.50 (s), 42.42 (s), 51.86 (q), 52.14 (q), 61.07 (t), 70.77 (t), 131.42 (s), 133.84 (s), 158.76 (s), 159.21 (s), 167.18 (s), 175.41 (s). MS (80 eV): *m/z* (%) = 342 (2) [M^+], 327 (5), 311 (3), 241 (4), 115 (100). $C_{16}H_{22}O_8$ (342.3): calcd. C 56.14, H 6.48; found C 55.95, H 6.50.

Treatment of 8a with 2,2,2-Trifluoroethanol

Dimethyl (*E*)-2-(2,2,2-Trifluoroethoxy)but-2-enedioate (16): A solution of $TiCl_4$ in DCM (1 M, 9.80 mL, 9.80 mmol) was added to 2,2,2-trifluoroethanol **14** (49.6 mL, 690 mmol). After 12 h, **8a** (13.8 g, 97.1 mmol) was added and the mixture was heated to reflux for 2 h. After 12 h at room temperature, 20 mL of water was added.

Three extractions with 20 mL of DCM each followed, the combined organic phases were dried with sodium sulfate, and the solvent was removed in vacuo. Column chromatography of the crude product on silica gel (hexane/ethyl acetate, 5:1) provided **16** (11.3 g, 48%) as a colourless solid. M.p. 92 °C; R_f (hexane/ethyl acetate, 1:1) = 0.48. IR (film): $\tilde{\nu}$ = 2961, 2908, 2855, 1746, 1721, 1443, 1378, 1297, 1274, 1220, 1166 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.72 (s, 3 H), 3.90 (s, 3 H), 4.21 (q, J = 7.6 Hz, 2 H), 5.28 (s, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 51.78 (q), 53.0 (q), 65.79 (q, $^2J_{C-F}$ = 37.3 Hz), 96.09 (d), 121.99 (q, $^1J_{C-F}$ = 277.7 Hz), 159.0 (s), 162.4 (s), 165.0 (s). MS (FAB$^+$): m/z (%) = 242 (50) [M^+], 235 (22), 174 (18), 157 (100). $C_8H_9F_3O_5$ (242.1): calcd. C 39.68, H 3.75; found C 39.70, H 3.77.

4-Hydroxy-2,2-dimethyl-5-oxo-2,5-dihydrofuran-3-carboxylic Acid (17): Compound **1αe** (1.70 g, 6.33 mmol) was dissolved in diethyl ether (4 mL) in an open flask. After all solvent had evaporated, a viscous oil remained. After about 1 year, **17** (622 mg 43%) had separated as colourless crystals. M.p. 125−128 °C. IR (film): $\tilde{\nu}$ = 3305, 2989, 2938, 1782, 1727, 1682, 1656, 1414, 1372, 1320, 1203, 1151, 1066, 991, 906 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.57 (s, 15 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.7 (q, 2 C), 28.0 (q, 3 C), 83.2 (s), 84.3 (s), 124.5 (s), 151.5 (s), 164.2 (s), 165.0 (s). $C_{11}H_{16}O_5$ (228.2): calcd. C 57.89, H 7.07; found C 57.89, H 6.97.

Synthesis of the Cyclopropene 19

Methyl 3,3-Dimethyl-4-phenyl-3*H*-pyrazole-5-carboxylate (18a) and Methyl 3,3-Dimethyl-5-phenyl-3*H*-pyrazole-4-carboxylate (18b): The crude product obtained from ethyl phenylpropiolate (5.00 g, 28.7 mmol) in DCM (100 mL) and a solution of **10a** in ether (39.0 mL, 0.74 M, 28.9 mmol) according to the general procedure was purified by column chromatography on silica gel (hexane/ethyl acetate, 30:1). Compound **18a** (2.80 g, 40%) was obtained as a red oil and **18b** (2.20 g, 31%) as a yellow solid. Compound **18a**: R_f (hexane/ethyl acetate, 3:1) = 0.40. IR (film): $\tilde{\nu}$ = 2983, 2937, 1721, 1627, 1446, 1338, 1196, 1088, 1029 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.28 (t, J = 7.2 Hz, 3 H), 1.64 (s, 6 H), 4.33 (q, J = 7.1 Hz, 2 H), 7.44−7.52 (m, 3 H), 7.97−8.05 (m, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.77 (q), 20.86 (q, 2 C), 61.10 (t), 97.73 (s), 128.01 (d, 2 C), 129.78 (d, 2 C), 129.97 (d), 140.09 (s, 2 C), 154.79 (s), 163.23 (s). $C_{14}H_{16}N_2O_2$ (244.3): calcd. C 68.83, H 6.60, N 11.47; found C 68.86, H 6.61, N 11.59. Compound **18b**: M.p. 48 °C; R_f (hexane/ethyl acetate, 3:1) = 0.18. IR (film): $\tilde{\nu}$ = 2982, 2935, 1728, 1458, 1368, 1334, 1250, 1210, 1107, 1031 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.23 (t, J = 7.2 Hz, 3 H), 1.50 (s, 6 H), 4.33 (q, J = 7.2 Hz, 2 H), 7.17−7.22 (m, 2 H), 7.41−7.46 (m, 3 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.78 (q), 19.78 (q, 2 C), 61.17 (t), 96.92 (s), 127.03 (d, 2 C), 128.25 (d, 2 C), 129.08 (d), 130.83 (s, 2 C), 161.25 (s), 166.99 (s). $C_{14}H_{16}N_2O_2$ (244.3): calcd. C 68.83, H 6.60, N 11.47; found C 69.00, H 6.70, N 11.29.

Methyl 3,3-Dimethyl-2-phenylcycloprop-1-enecarboxylate (19): The crude product obtained from **18b** (1.80 g, 7.37 mmol) was purified by column chromatography on silica gel (hexane/ethyl acetate, 4:1). Compound **19** (1.05 g, 66%) was obtained as a colourless oil. R_f (hexane/ethyl acetate, 2:1) = 0.54. IR (film): $\tilde{\nu}$ = 2966, 1814, 1698, 1490, 1448, 1367, 1289, 1190, 1050 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.39 (t, J = 7.1 Hz, 3 H), 1.45 (s, 6 H), 4.32 (q, J = 7.1 Hz, 2 H), 7.38−7.49 (m, 3 H), 7.70−7.75 (m, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 14.24 (q), 24.80 (s), 24.99 (q, 2 C), 60.59 (t), 117.09 (s), 127.55 (s), 128.66 (d, 2 C), 130.55 (d), 130.90 (d, 2 C), 141.78 (s), 161.74 (s). MS (80 eV): m/z (%) = 432 (3) [2 M^+], 216 (1), 105 (100). $C_{14}H_{16}O_2$ (216.3): calcd. C 77.75, H 7.46; found C 77.57, H 7.52.

Synthesis of the Acetohydrazides 23

***N*′-(7-Tridecanylidene)acetohydrazide (23a):** Dry Na_2SO_4 (540 mg, 3.80 mmol) and acetohydrazide (**22**) (710 mg, 9.58 mmol) were added to molten 7-tridecanone (**21a**) (2.00 g, 10.1 mmol). The suspension was allowed to cool to room temperature and was stirred for 20 h. The Na_2SO_4 was filtered off and washed several times with a mixture of hexane/ethyl acetate (2:1). The solvent was removed in vacuo. According to the ^1H NMR spectrum of the crude product, the residue was a 2.3:1 mixture of **23a** with 7-tridecanone (**21a**), containing 1.87 g (77%) of acetylhydrazone (**23a**). The mixture was used in the following reaction without further purification.

***N*′-[(*E*)-(1-Cyclohexylethylidene)]acetohydrazide (23b):** Na_2SO_4 (1.41 g, 9.93 mmol) and acetohydrazide (**22**) (2.00 g, 27.0 mmol) were added to cyclohexyl methyl ketone (**21b**) (3.51 g, 27.8 mmol) and the suspension was stirred for 13 h at room temperature. DCM (50 mL) was added and the Na_2SO_4 was filtered off and washed several times with DCM. The solvent was removed in vacuo to afford colourless crystals of **23b** (4.49 g, 91%). The corresponding (*Z*) isomer could not be detected. M.p. 92−94 °C. IR (film, NaCl): $\tilde{\nu}$ = 3180, 3107, 2924, 2851, 1728, 1667, 1449, 1427, 1393, 1371, 1108, 1023, 750, 657 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.28 (m, 6 H), 1.77 (m, 8 H), 2.24 (s, 3 H), 8.43 (s, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.2 (q), 20.5 (q), 25.8 (t, 2 C), 25.9 (t), 29.9 (t, 2 C), 46.7 (d), 155.0 (s), 172.8 (s). $C_{10}H_{18}N_2O$ (182.3): calcd. C 65.90, H 9.95, N 15.37; found C 65.62, H 9.76, N 15.40.

***N*′-[(2′*R*,5′*S*)-2′-Isopropyl-5′-methylcyclohexylidene]acetohydrazide (23d):** Na_2SO_4 (1.41 g, 9.93 mmol) and acetohydrazide (**22**) (2.00 g, 27.0 mmol) were added to (−)-L-menthone (4.27 g, 27.7 mmol) and the suspension was stirred for 12 h at room temperature. DCM (50 mL) was added, and Na_2SO_4 was filtered off and washed several times with DCM. The solvent was removed in vacuo. The oily residue was frozen with liquid nitrogen and slowly warmed to +4 °C. The precipitating, colourless crystals were filtered off, washed with cold hexane and dried in vacuo to afford 4.75 g (84%) of an (*E*)/(*Z*) mixture [(*E*)/(*Z*) > 5:1]) of **23d**. The mixture was used in the following reactions without further separation. IR (film, NaCl): $\tilde{\nu}$ = 3193 (N−H), 1713 (C=N), 1668 (C=O) cm^{-1}. $C_{12}H_{22}N_2O$ (210.3): calcd. C 68.53, H 10.54, N 13.32; found C 68.69, H 10.42, N 13.34.

***N*′-[(1*R*)-(+)-Camphan-2-yl]acetohydrazide (23e):** Compound **23e** was prepared according to the literature procedure.[31] ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.74 (s, 3 H), 0.94 (s, 3 H), 1.00 (s, 3 H), 1.11−1.44 (m, 3 H), 1.62−2.06 (m, 3 H), 2.26 (s, 3 H), 2.26−2.35 (m, 1 H), 8.04 (s, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 10.9 (q), 18.5 (q), 19.3 (q), 20.1 (q), 27.1 (t), 32.4 (t), 33.1 (t), 43.8 (q), 47.7 (s), 52.3 (s), 164.8 (s), 173.1 (s).

***N*′-(Adamantylidene)acetohydrazide (23g):** Acetohydrazide (2.47 g, 33.3 mmol) and adamantone (5.00 g, 33.3 mmol) were dissolved in ethanol (20 mL), and Na_2SO_4 (4.00 g, 28.2 mmol) and a catalytic amount of acetic acid (100 μL, 1.75 mmol) were added. The suspension was then heated under reflux for 24 h. The solvent was removed in vacuo and the residue was recrystallized from ethanol to afford **23g** (4.77 g, 69%) as a mixture of its (*E*) and (*Z*) isomers, which was used in the following reaction without further purification. ^1H NMR of the mixture of isomers ($CDCl_3$, 250 MHz): δ = 2.21 (s, 3 H, main isomer), 8.40 (br. s, 1 H, -NH, main isomer), 2.00 (s, 3 H, minor isomer), 8.26 (br. s, 1 H, -NH, minor isomer). MS (70 eV): m/z (%) = 206 (81) [M^+], 60 (100). $C_{12}H_{18}N_2O$ (206.3): calcd. C 69.87, H 8.80, N 13.58; found C 70.05, H 8.73, N 13.57.

Compound 23h: Identical to **23b**.

Synthesis of the 2,5-Dihydro-1,3,4-oxadiazoles 24 and Their Side Products 25

***rac*-5,5-Dihexyl-2,5-dihydro-2-methoxy-2-methyl-1,3,4-oxadiazole (24a):** 85% yield; R_f (hexane/ethyl acetate, 10:1) = 0.51. IR (film, NaCl): $\tilde{\nu}$ = 3409, 1715, 1571, 1466, 1376, 1195, 1152, 1058, 908 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.83 (m, 6 H), 1.09−1.89 (m, 23 H), 3.18 (s, 3 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.8 (q, 2 C), 21.8 (q), 22.3 (t, 2 C), 23.2 (t), 23.5 (t), 29.1 (t), 29.3 (t), 31.4 (t, 2 C), 35.3 (t), 35.6 (t), 50.4 (q), 125.0 (s), 131.9 (s). $C_{16}H_{32}N_2O_2$ (284.4): calcd. C 67.56, H 11.34, N 9.85; found C 67.82, H 11.15, N 9.63.

***rac*-2-Acetoxy-5,5-dihexyl-2,5-dihydro-2-methyl-1,3,4-oxadiazole (25a):** 14% yield. R_f (hexane/ethyl acetate, 10:1) = 0.42. IR (film, NaCl): $\tilde{\nu}$ = 2929, 2858, 1759, 1715, 1573, 1462, 1378, 1219, 1110, 1012, 934 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.80 (m, 6 H), 0.88−1.00 (m, 1 H), 1.18 (s, 16 H), 1.57−1.96 (m, 3 H), 1.97 (s, 3 H), 1.98 (s, 3 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.8 (q, 2 C), 21.5 (q), 21.6 (q), 22.3 (t, 2 C), 22.6 (t), 23.4 (t), 28.9 (t), 29.1 (t), 31.4 (t, 2 C), 35.4 (t), 36.5 (t), 129.1 (s), 129.4 (s), 167.8 (s). $C_{17}H_{32}N_2O_3$ (312.5): calcd. C 65.35, H 10.32, N 8.97; found C 65.48, H 10.31, N 8.74.

5-Cyclohexyl-2-methoxy-2,5-dihydro-2,5-dimethyl-1,3,4-oxadiazole (24b): Mixture of diastereomers: 61% yield. R_f (hexane/ethyl acetate, 10:1) = 0.41. IR (film, NaCl): $\tilde{\nu}$ = 1573 (N=N) cm^{-1}. $C_{11}H_{20}N_2O_2$ (212.3): calcd. C 62.24, H 9.50, N 13.20; found C 62.33, H 9.36, N 13.24.

2-Acetoxy-5-cyclohexyl-2,5-dihydro-2,5-dimethyl-1,3,4-oxadiazole (25b): Mixture of diastereomers: 9% yield. R_f (hexane/acetone, 10:1) = 0.26. IR (film, NaCl): $\tilde{\nu}$ = 1759 (C=O), 1573 (N=N) cm^{-1}. $C_{12}H_{20}N_2O_3$ (240.3): calcd. C 59.98, H 8.39, N 11.66; found C 60.24, H 8.40, N 11.39.

(6*R*,9*S*)-6-Isopropyl-3-methoxy-3,9-dimethyl-2-oxa-3,4-diazaspiro-[5.4]dec-4-ene (24d): Mixture of diastereomers: 59% yield. R_f (hexane/ethyl acetate, 10:1) = 0.62. IR (film, NaCl): $\tilde{\nu}$ = 1566 (N=N) cm^{-1}. $C_{13}H_{24}N_2O_2$ (240.3).

(6*R*,9*S*)-3-Acetoxy-6-isopropyl-3,9-dimethyl-2-oxa-3,4-diazaspiro-[5.4]dec-4-ene (25d): Mixture of diastereomers: 6% yield. R_f (hexane/ethyl acetate, 10:1) = 0.55. IR (film, NaCl): $\tilde{\nu}$ =1760 (C=O), 1560 (N=N) cm^{-1}. $C_{14}H_{24}N_2O_3$ (268.4): calcd. C 62.66, H 9.01, N 10.44; found C 62.68, H 8.80, N 10.24.

2,5-Dihydro-5-methoxy-1′,5,7′,7′-tetramethylspiro[1,3,4-oxadiazole-2,2′-bicyclo[2.2.1]heptane] (24e): Mixture of diastereomers: 44% yield. R_f (hexane/ethyl acetate, 5:1) = 0.54. ^1H NMR ($CDCl_3$, 250 MHz): δ = Major isomer 2.94 (s, 3 H), second isomer 2.99 (s, 3 H), third isomer 3.26 (s, 3 H), fourth isomer 3.28 (s, 3 H).

2,5-Dihydro-5-methoxy-5-methylspiro[1,3,4-oxadiazole-2,2′-tricyclo-[3.3.1.1^{3,7}]decane] (24g): 28% yield. M.p. 72 °C; R_f (hexane/ethyl acetate, 20:1) = 0.43. IR (film, NaCl): $\tilde{\nu}$ = 2938, 2908, 2855, 1574, 1450, 1375, 1351, 1196, 1152, 1110, 1059, 1023, 913, 859, 800 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.48 (br. s, 1 H), 1.56 (s, 3 H), 1.63−1.95 (m, 8 H), 1.94−2.03 (m, 3 H), 2.41 (bd, 1 H), 2.58 (bd, 1 H), 3.00 (s, 3 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 24.1 (q), 26.4 (d), 27.2 (d), 33.8 (t), 34.2 (t), 34.8 (t), 34.9 (t), 36.3 (d), 37.0 (t), 38.0 (d), 50.0 (q), 125.0 (s), 131.4 (s). $C_{13}H_{20}N_2O_2$ (236.3): calcd. C 66.07, H 8.53, N 11.85; found C 66.20, H 8.68, N 11.85.

5-Acetoxy-2,5-dihydro-5-methylspiro[1,3,4-oxadiazole-2,2′-tricyclo-[3.3.1.1^{3,7}]decane] (25g): 11% yield. R_f (hexane/ethyl acetate, 20:1) = 0.21. IR (film, NaCl): $\tilde{\nu}$ = 2935, 2909, 1763, 1570, 1452, 1370, 1232, 1214, 1106, 1086, 1014, 932, 915, 869 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.53−2.15 (m, 12 H), 1.89 (s, 3 H), 1.96 (s, 3 H), 2.41−2.53 (m, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 21.8 (q), 23.0 (q), 26.3 (d), 27.0 (d), 33.9 (t), 34.2 (t), 34.9 (t), 35.3 (t), 36.7 (d), 36.9 (t), 37.3 (d), 127.9 (s), 128.9 (s), 167.7 (s). $C_{14}H_{20}N_2O_3$ (264.3): calcd. C 63.62, H 7.63, N 10.60; found C 63.55, H 7.82, N 10.74.

Compound 24h: Identical to **24b**.

Synthesis of the Cyclopropenes 1γ and Side Products

Dimethyl 3,3-Dihexyl-1-cyclopropene-1,2-dicarboxylate (1γa): Irradiation of **24a** (1.50 g, 5.27 mmol) and **8a** (2.25 g, 15.8 mmol) for 11 h afforded **1γa** (670 mg, 69%) as a colourless oil. Compound **24a** (650 mg, 2.29 mmol) was reisolated. R_f (hexane/ethyl acetate, 3:1) = 0.55. IR (film, NaCl): $\tilde{\nu}$ = 2955, 2926, 2855, 1830, 1720, 1458, 1435, 1250, 1062, 917 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.85 (m, 6 H), 1.18 (m, 16 H), 1.68 (m, 4 H), 3.85 (s, 6 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.9 (q, 2 C), 22.4 (t, 2 C), 26.9 (t, 2 C), 29.0 (t, 2 C), 31.6 (t, 2 C), 36.3 (t, 2 C), 40.4 (s), 52.4 (q, 2 C), 129.4 (s, 2 C), 160.7 (s, 2 C). $C_{19}H_{32}O_4$ (324.5): calcd. C 70.33, H 9.94; found C 70.16, H 9.95.

Dimethyl 3-Cyclohexyl-3-methyl-1-cyclopropene-1,2-dicarboxylate (1γb): Irradiation of **24b** (1.00 g, 4.71 mmol) and **8a** (2.01 g, 14.1 mmol) for 11 h and further purification of the crude product by HPLC afforded **1γb** (550 mg, 64%) as a colourless oil. Compound **24b** (281 mg, 1.32 mmol) was reisolated. R_f (hexane/ethyl acetate, 3:1) = 0.53. IR (film, NaCl): $\tilde{\nu}$ = 2926, 2853, 1831, 1719, 1435, 1246, 1071, 736 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.76−1.33 (m, 5 H), 1.34 (s, 3 H), 1.52−1.76 (m, 6 H), 3.85 (s, 6 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.1 (q), 26.0 (t), 26.2 (t, 2 C), 30.9 (t, 2 C), 40.0 (s), 44.1 (d), 52.5 (s, 2 C), 129.7 (s, 2 C), 160.6 (s, 2 C). $C_{14}H_{20}O_4$ (252.3): calcd. C 66.65, H 7.99; found C 66.74, H 7.97.

Dimethyl 3-*tert*-Butyl-3-methyl-1-cyclopropene-1,2-dicarboxylate (1γc): Irradiation of **24c** (750 mg, 4.03 mmol) and **8a** (710 mg, 5.00 mmol) for 6 h and further purification of the crude product by HPLC afforded **1γc** (370 mg, 54%) as a colourless oil. Compound **24c** (184 mg, 988 μmol) was reisolated. R_f (hexane/ethyl acetate, 3:1) = 0.51. IR (film, NaCl): $\tilde{\nu}$ = 2963, 2871, 1828, 1715, 1436, 1248, 1118, 1079, 1048 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.94 (s, 9 H), 1.35 (s, 3 H), 3.86 (s, 6 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.8 (q), 28.4 (q, 3 C), 35.4 (s), 43.3 (s), 52.5 (q, 2 C), 130.3 (s, 2 C), 160.5 (s, 2 C). $C_{12}H_{18}O_4$ (226.3): calcd. C 63.70, H 8.02; found C 63.79, H 8.06.

Dimethyl (4*R*,7*S*)-4-Isopropyl-7-methylspiro[4.2]oct-2-ene-2,3-dicarboxylate (1γd): Irradiation of **24d** (2.00 g, 8.32 mmol) and **8a** (3.54 g, 24.9 mmol) for 11 h, column chromatography of the reaction mixture and further purification of the crude product by HPLC afforded **1γd** (386 mg, 40%) as a colourless oil. Compound **24d** (1.17 g, 4.87 mmol) was reisolated. R_f (hexane/ethyl acetate, 3:1) = 0.60. IR (film, NaCl): $\tilde{\nu}$ = 2951, 2925, 1825, 1718, 1436, 1252, 1063 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.58 (d, J = 6.7 Hz, 3 H), 0.83 (d, J = 6.8 Hz, 3 H), 0.87 (d, J = 6.1 Hz, 3 H), 1.03 (m, 1 H), 1.27 (m, 3 H), 1.73 (m, 5 H), 3.86 (s, 3 H), 3.87 (s, 3 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 17.0 (q), 22.0 (q), 22.1 (q), 26.6 (t), 28.4 (d), 32.7 (d), 35.4 (t), 42.3 (s), 46.4 (d), 47.0 (t), 52.5 (q), 52.6 (q), 129.5 (s), 130.3 (s), 160.5 (s), 160.6 (s). $C_{16}H_{24}O_4$ (280.4): calcd. C 68.55, H 8.63; found C 68.77, H 8.59. $[\alpha]_D^{20}$ = +56.7 (c = 3.33 g/l $CHCl_3$).

Efforts to Prepare 1γe: A solution of **24e** (230 mg, 965 μmol) and **8a** (411 mg, 2.89 mmol) in diethyl ether (55 mL) was irradiated with a medium-pressure mercury lamp at room temperature for 8 h. After the volatiles had been removed in vacuo, column chromatography (silica gel, hexane/ethyl acetate, 10:1) provided dimethyl (1*R*,8*R*)-1,11,11-trimethyl-2,3-diazatricyclo[6.2.1.0^{2,6}]undeca-3,5-diene-4,5-dicarboxylate (**26**, 210 mg, 71%) as colourless crystals. Single crystals were obtained by slow concentration of a solution in pentane/dichloromethane at 0 °C. M.p. 109 °C; R_f (hexane/ethyl acetate, 5:1) = 0.18. IR (film, NaCl): $\tilde{\nu}$ = 2952, 1741, 1718, 1544, 1478, 1458, 1438, 1309, 1212, 1177, 1106, 1067, 787 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.79 (s, 3 H), 1.03 (s, 3 H), 1.31−1.44 (m, 1 H), 1.65 (s, 3 H), 1.82−2.12 (m, 4 H), 2.82 (dd, *J* = 18.2, 1.6 Hz, 1 H), 3.00−3.10 (m, 1 H), 3.75 (s, 3 H), 3.86 (s, 3 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 14.7 (q), 17.7 (q), 23.9 (q), 27.4 (t), 30.4 (t), 39.4 (t), 42.0 (d), 44.6 (s), 51.3 (q), 52.3 (q), 72.7 (s), 111.2 (s), 142.5 (s), 142.6 (s), 163.1 (s), 163.2 (s). $C_{16}H_{22}N_2O_4$ (306.4): calcd. C 62.73, H 7.24, N 9.14; found C 62.81, H 7.30, N 9.09.

Dimethyl 3-Adamantyl-3-methylcyclopropene-1,2-dicarboxylate (1γf): Irradiation of **24f** (933 g, 3.53 mmol) and **8a** (1.61 g, 11.3 mmol) for 11 h and further purification of the crude product by HPLC afforded **1γf** (43 mg, 4%) as colourless crystals. In addition, dimethyl *rac*-(2*R*,3*R*)-1-adamantyl-1-methylcylopropane-2,3-dicarboxylate (**27**, 22 mg, 2%), dimethyl *rac*-(1*R*,4*S*,5*S*)-2-methyltetracyclo[6.3.1.1^{6,10}.0^{1,5}]tridec-2-ene-3,4-dicarboxylate (**28**, 311 mg, 29%), dimethyl *rac*-(1*R*,4*R*,5*S*)-2-methyltetracyclo[6.3.1.1^{6,10}.0^{1,5}]tridec-2-ene-3,4-dicarboxylate (**29**, 107 mg, 10%), and dimethyl *rac*-3-adamantyl-1-methoxybuta-1,2-diene-1-carboxylate (**30**, 69 mg 7%) could be isolated as colourless crystals. Compound **1γf**: M.p. 45 °C; R_f (hexane/ethyl acetate, 5:1) = 0.25. IR (film, NaCl): $\tilde{\nu}$ = 2905, 2850, 1830, 1718, 1435, 1380, 1345, 1236, 1076, 1046, 915, 808, 740 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.23 (s, 3 H), 1.43−1.72 (m, 12 H), 1.91 (m, 3 H), 3.80 (s, 6 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 18.5 (q), 28.5 (d, 3 C), 36.6 (t, 3 C), 40.7 (t, 3 C), 43.6 (s), 52.5 (q, 2 C), 129.5 (s, 2 C), 160.7 (s, 2 C), 1 s hidden by signal overlap. $C_{18}H_{24}O_4$ (304.4): calcd. C 71.03, H 7.95; found C 70.79 H 7.88. Compound **27**: M.p. 111 °C; R_f (hexane/ethyl acetate, 5:1) = 0.33. IR (film, NaCl): $\tilde{\nu}$ = 2905, 2850, 1729, 1448, 1436, 1344, 1314, 1254, 1215, 1182, 1167, 1074, 1030, 895, 849, 778 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.11 (s, 3 H), 1.48−1.58 (m, 12 H), 1.90 (m, 3 H), 2.04 (d, J = 7.0 Hz, 1 H), 2.50 (d, J = 7.0 Hz, 1 H), 3.62 (s, 3 H), 3.63 (s, 3 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.3 (q), 26.6 (d), 28.4 (d, 3 C), 33.9 (d), 35.7 (s), 36.6 (t, 3 C), 38.9 (t, 3 C), 42.0 (s), 51.7 (q), 51.8 (q), 170.8 (s), 171.6 (s). MS (80 eV): *m*/*z* (%) = 306 (7) [M$^+$], 274 (40), 247 (100), 233 (22), 215 (7), 135 (65). HRMS (80 eV): *m*/*z* calcd. for $C_{18}H_{26}O_4$ 306.18311, found 306.18317. Compound **28**: M.p. 124 °C; R_f (hexane/ethyl acetate, 5:1) = 0.25. IR (film, NaCl): $\tilde{\nu}$ = 2908, 2856, 1736, 1717, 1628, 1435, 1373, 1345, 1298, 1248, 1227, 1191, 1168, 1146, 1105, 1075, 1057, 1007, 814, 787 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.36−1.41 (m, 1 H), 1.54−1.93 (m, 10 H), 2.04−2.16 (m, 1 H), 2.09 (s, 3 H), 2.28−2.33 (m, 2 H), 3.67−3.70 (m, 1 H), 3.68 (s, 3 H), 3.70 (s, 3 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 11.8 (q), 26.7 (d), 28.8 (d), 29.1 (d), 31.1 (t), 36.8 (t), 37.1 (t), 40.0 (t), 40.3 (t), 49.4 (s), 50.5 (d), 50.9 (q), 51.5 (q), 51.8 (d), 124.4 (s), 166.3 (s), 167.7 (s), 174.1 (s). $C_{18}H_{24}O_4$ (304.4): calcd. C 71.03, H 7.95; found C 70.83, H 7.99. Compound **29**: M.p. 110 °C; R_f (hexane/ethyl acetate, 5:1) = 0.23. IR (film, NaCl): $\tilde{\nu}$ = 2908, 2852, 1739, 1716, 1626, 1452, 1435, 1377, 1332, 1296, 1237, 1210, 1194, 1171, 1125, 1105, 1075, 1048, 1028, 965, 794, 710 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.27−1.32 (m, 1 H), 1.58−2.10 (m, 16 H), 3.62−3.71 (m, 7 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 11.7 (q), 27.0 (d), 28.4 (d, 2 C), 31.1 (t), 36.8 (t), 37.0 (t), 38.4 (t), 39.0 (t), 48.2 (s), 50.9 (q, 2C), 51.6 (d), 55.3 (d), 125.4 (s), 166.3 (s), 166.4 (s), 175.2 (s). $C_{18}H_{24}O_4$ (304.4): calcd. C 71.03, H 7.95; found C 71.14, H 7.98. Compound **30**: M.p. 69 °C; R_f (hexane/ethyl acetate, 5:1) = 0.33. IR (film, NaCl): $\tilde{\nu}$ = 2904, 2849, 1943, 1735, 1437, 1380, 1277, 1192, 1144, 1056, 1004, 937, 875, 800, 771, 721 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.56−1.72 (m, 12 H), 1.82 (s, 3 H), 1.98−2.00 (m, 3 H), 3.40 (s, 3 H), 3.74 (s, 3 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 15.2 (q), 28.4 (d, 3 C), 36.5 (t, 3 C), 37.2 (s), 40.8 (t, 3 C), 52.1 (q), 55.8 (q), 125.0 (s), 128.2 (s), 165.0 (s), 191.4 (s). MS (80 eV): *m*/*z* (%) = 276 (11) [M$^+$], 217 (7), 135 (100). HRMS (80 eV): *m*/*z* calcd. for $C_{17}H_{24}O_3$ 276.172550, found 276.172350.

Efforts to Prepare 1γg: Irradiation of **24g** (1.00 g, 4.23 mmol) and **8a** (1.50 g, 10.6 mmol) for 10 h and subsequent column chromatography of the crude product on silica gel (hexane/ethyl acetate, 30:1) afforded dimethyl dispiro{tricyclo[3.3.1.1^{3,7}]decane-1,2′-bicyclo[1.1.0]butane-4′,1"-tricyclo[3.3.1.1^{3,7}]decane}-1′,3′-dicarboxylate (**31**, 180 mg, 21%) and dimethyl bis(tricyclo[3.3.1.1^{3,7}]decylidene)ethane-1,2-dicarboxylate (**32**, 296 mg, 34%) as colourless crystals. Compound **31**: M.p. 145 °C; R_f (hexane/ethyl acetate, 3:1) = 0.56. IR (KBr): $\tilde{\nu}$ = 3049, 3007, 2906, 2643, 1735, 1718, 1458, 1388, 1362, 1352, 1330, 1228, 1090, 999, 958, 914, 892, 816, 795, 739 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.55−1.95 (m, 24 H), 2.07 (br. s, 2 H), 2.24 (br. s, 2 H), 3.67 (s, 6 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 27.1 (d, 4 C), 33.4 (d, 2 C), 34.4 (d, 2 C), 36.3 (t, 4 C), 36.9 (t, 4 C), 36.9 (t, 2 C), 41.4 (s, 2 C), 51.7 (q, 2 C), 70.4 (s, 2 C), 168.4 (s, 2 C). $C_{26}H_{34}O_4$ (410.6): calcd. C 76.06, H 8.35; found C 76.08, H 8.35. Compound **32**: M.p. 93 °C; R_f (hexane/ethyl acetate, 3:1) = 0.51. IR (film): $\tilde{\nu}$ = 2909 cm^{-1}, 2850, 1712, 1611, 1449, 1432, 1296, 1232, 1201, 1142, 1100, 1041, 1020, 954, 919, 799, 732. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.67−1.94 (m, 24 H), 2.68 (br. s, 2 H), 3.60 (s, 6 H), 3.65 (br. s, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 27.5 (d, 4 C), 34.4 (d, 2 C), 36.0 (d, 2 C), 37.1 (t, 4 C), 39.3 (t, 4 C), 39.6 (t, 2 C), 51.2 (q, 2 C), 117.8 (s, 2 C), 163.1 (s, 2 C), 168.3 (s, 2 C).

Bis(1-ethoxycarbonylethyl) (*S*,*S*)-3-Cyclohexyl-3-methylcycloprop-1-ene-1,2-dicarboxylate (1γh): Irradiation of **24b** (846 mg, 3.99 mmol) and (*S*,*S*)-**8o** (1.50 g, 4.78 mmol) in diethyl ether (5 mL) for 10 h afforded (*S*,*S*)-**1γh** (350 mg, 48%) as a colourless oil. Compound **24b** (480 mg, 2.26 mmol) was reisolated. R_f (hexane/ethyl acetate, 3:1) = 0.42. IR (film, NaCl): $\tilde{\nu}$ = 2927, 2854, 1835, 1756, 1722, 1450, 1380, 1348, 1308, 1245, 1204, 1133, 1096, 1048, 1021, 859 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.87−1.75 (br. m, 11 H), 1.28 (t, *J* = 7.1 Hz, 6 H), 1.39 (s, 3 H), 1.57 (2 d, *J* = 7.1 Hz, 6 H), 4.22 (q, *J* = 7.1 Hz, 4 H), 5.20 (q, *J* = 7.1 Hz, 1 H), 5.21 (q, *J* = 7.1 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.9 (q, 2 C), (q, 2 C), 22.1 (q), 26.0 (t), 26.2 (t, 2 C), 30.8 (t, 2 C), 40.6 (s), 44.1 (d), 61.3 (t, 2 C), 69.6 (d, 2 C), 130.0 (s), 130.6(s), 159.2 (s), 159.3 (s), 169.8 (s, 2 C). $C_{22}H_{32}O_8$ (424.5): calcd. C 62.25, H 7.60; found C 62.02 H 7.53. $[\alpha]_D^{20}$ = +2.22 (*c* = 5.40 g/l $CHCl_3$).

Dimethyl Spiro[(1*S*,2*R*,3*S*)-cyclopropane-1,1′-[1*H*]indene]-2,3-dicarboxylate (36): Palladium on charcoal (5% Pd, 5 mg) was suspended in a solution of **33** (200 mg, 780 μmol) in acetone (15 mL) under argon. The mixture was stirred, hydrogen was added in portions (3 mL) at atmospheric pressure and the reaction was monitored by NMR. When nearly 50% of **33** had reacted, the palladium on charcoal was filtered off and washed several times with acetone. The solvent was removed under vacuum and the residue was worked up by column chromatography to afford **36** (32 mg, 31% based on recovered **33**), a colourless oil, as the only isolable product. Compound **33** (101 mg, 0.39 mmol) could be reisolated. The

relative configuration of **36** was determined by ROESY. R_f (hexane/ethyl acetate, 3:1) = 0.31. IR (film, NaCl): $\tilde{\nu}$ = 2951, 1736, 1458, 1438, 1365, 1274, 1216, 1165, 1027, 950, 852, 832, 772, 753 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.94 (s, 2 H), 3.64 (s, 6 H), 5.81 (d, J = 5.5 Hz, 1 H), 6.83 (d, *J* = 5.5 Hz, 1 H), 7.07−7.32 (m, 3 H), 7.46 (m, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 29.9 (d, 2 C), 35.2 (s), 52.0 (q, 2 C), 121.5 (d), 124.1 (d), 125.4 (d), 127.0 (d), 131.2 (d), 137.9 (s), 138.0 (d), 145.0 (s), 167.2 (s, 2 C). $C_{15}H_{14}O_4$ (258.3): calcd. C 69.76, H 5.46; found C 69.49, H 5.71.

Dimethyl 2-(Indan-1-yl)succinate (37): Palladium on charcoal (5% Pd, 5 mg) was suspended in a solution of **33** (308 mg, 1.20 mmol) in acetone (10 mL) and this was stirred under hydrogen until TLC showed all of **33** had reacted. The palladium on charcoal was filtered off and washed several times with acetone. The solvent was removed under vacuum and the residue was worked up by HPLC to afford **37a** (169 mg, 54%) and **37b** (130 mg, 41%) as colourless oils. Compound **37a**: R_f (hexane/ethyl acetate, 4:1) = 0.27. IR (film, NaCl): $\tilde{\nu}$ = 3021, 2952, 2849, 1738, 1437, 1348, 1167, 1012, 895, 845, 758 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.77 (m, 1 H), 2.03 (m, 2 H), 2.65 (dd, *J* = 16.9, 11.3 Hz, 1 H), 2.81 (m, 2 H), 3.32 (m, 1 H), 3.54 (s, 3 H), 3.62−3.67 (m, 4 H), 7.08−7.16 (m, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 27.0 (t), 31.0 (t), 31.3 (t), 44.2 (d), 45.8 (d), 51.6 (q), 51.8 (q), 123.6 (d), 124.6 (d), 126.4 (d), 127.0 (d), 143.0 (s), 144.0 (s), 172.8 (s), 174.4 (s). $C_{15}H_{18}O_4$ (262.3): calcd. C 68.69, H 6.92; found C 68.50, H 7.16. Compound **37b**: R_f (hexane/ethyl acetate, 4:1) = 0.27. IR (film, NaCl): $\tilde{\nu}$ = 3022, 2952, 2849, 1738, 1436, 1349, 1256, 1227, 1194, 1165, 1007, 759 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.90 (m, 1 H), 2.21 (m, 1 H), 2.44 (dd, *J* = 16.9, 6.1 Hz, 1 H), 2.67−2.95 (m, 3 H), 3.10 (m, 1 H), 3.49 (m, 1 H), 3.65 (s, 3 H), 3.67 (s, 3 H), 7.03−7.17 (m, 4 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 29.4 (t), 30.9 (t), 33.5 (t), 44.2 (d), 46.3 (d), 51.6 (q), 51.7 (q), 124.5 (d), 124.6 (d), 125.9 (d), 127.0 (d), 142.9 (s), 144.1 (s), 172.5 (s), 174.3 (s). $C_{15}H_{18}O_4$ (262.3): calcd. C 68.69, H 6.92; found C 68.36, H 7.13.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (Ha 1932/2-1 and Ha 1932/4-1), the Fonds der Chemischen Industrie and the Dr. Otto Röhm Gedächnisstiftung. Palladium salts were generously donated by the Degussa AG.

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[10] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-154584 (**1αa**), -154609 (**1γf**), -154585 (**5j**), -154586 (**5k**), -154587 (**5m**), -154590 (**8h**), -154591 (**8n**·$ZnBr_2$), -154589 (**8o**), -154592 (**9f**), -154588 (**12e**), -154593 (**12f**), -154594 (**13k**), -154595 (**16**), -154605 (**17**),-154596 (**18b**), -154597 (**23b**), -154604 (**23d**), -154606 (**23e**), -154607 (**23g**), -154598 (**24g**), -154599 (**27**), -154608 (**28**), -154610 (**29**), -154600 (**30**), -154601 (**33**), -154602 (**35**), -154603 (**34**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1233/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Received January 30, 2001
[O01042]