Cyclopropyl Building Blocks for Organic Synthesis, 37[◇]

Syntheses and Diels–Alder Reactions of 2-Substituted 2-Cyclopropylideneacetates in Comparison with Allenecarboxylate and Ordinary Acrylates

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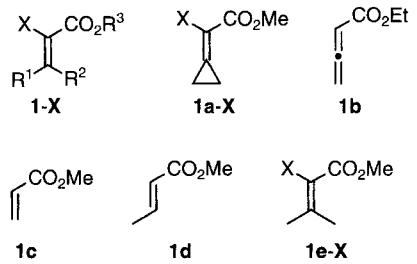
Several new 2-substituted 2-cyclopropylideneacetates **1a**-X (X = F, N_3, SPh, OTBDMS, OTBDPS) have been prepared. Their cycloadditions and those of some previously described compounds of type **1a**-X (X = H, Br, Cl) with furan (**5**) and/or 6,6-dimethylfulvene (**7**) are reported. Several of these peculiar acrylates **1a**-X (X = H, Br, Cl, F, N_3), as well as allenecarboxylate **1b**, regular acrylate **1c**, crotonate **1d**, and 3,3-disubstituted acrylates **1e**-X (X = H, Cl), were reacted with furan (**5**) and 6,6-dimethylfulvene (**7**) in two series of competition experiments at 64 °C. The [2 + 4] cycloaddition of **1a**-Cl and **1a**-Br to furan (**5**) are both about 16 times as fast and to dimethylfulvene (**7**) 230 and 210 times as fast as that of the parent acrylate **1c**, while allenecarboxylate **1b** reacts with **4** only 30 times as fast as **1c**, and the 3-substituted acrylates **1d** and **1a**-X (X = H, Cl) were all too sluggish to react under these conditions. The kinetic data obtained for the cycloadditions of **1a**-X suggest a mechanism involving either diradicals or zwitterions as intermediates.

Since its discovery in 1928 the Diels-Alder reaction has been extended to become one of the most useful synthetic methods of modern organic chemistry[1]. This [4 + 2] cycloaddition is a powerful tool, because it results in the formation of two new C–C bonds and is capable of selectively generating up to four contiguous stereogenic centers in the resultant cyclohexene. Its paramount significance also derives from its immense versatility, which allows a wide range of dienes and dienophiles to be employed. Frequently the Diels-Alder reaction is employed for the construction of polycyclic compounds, which serve as core structures at an early stage of the total syntheses of natural products and are subsequently further elaborated into the more complex targets. The 2-chloro-2-cyclopropylideneacetate **1a**-Cl, which has been made readily available in three simple steps from ethylene and tetrachlorocyclopropene[2], has turned out to be a particularly reactive dienophile[2c,d] and as such can favorably be employed in the construction of core structures containing a spirocyclopropane group like that of the illudins[3] and several structurally related sesquiterpenes[4]. However, in order to get a feeling for the scope and limitations of the applicability of the 2-chloro- and other 2-substituted 2-cyclopropylideneacetates **1a**-X, it was important to determine their reactivities as dienophiles at least in relation to well known cycloaddends like allenecarboxylate **1b**, acrylate **1c**, and crotonate **1d**.



Syntheses of Starting Materials and Their [4 + 2] Cycloadditions

The cyclopropylideneacetates **1a**-H[5], **1a**-Cl[2b], and **1a**-Br[6] were prepared according to published procedures. For the synthesis of the new compounds **1a**-F, **1a**-N_3, and **1a**-OTBDPS, two variants of the method previously developed for the preparation of **1a**-SPh[7] from **1a**-Cl were employed. Both are sequences of a Michael addition, nucleophilic substitution and β-elimination (Scheme 1 and Table 1).

The addition of dimethylamine to **1a**-Cl gave **2a**-Cl in high yield (93%). Nucleophilic substitution of the chlorine in **2a**-Cl with sodium azide in DMF to yield **2a**-N_3 or silver-assisted hydrolysis to yield **2a**-OH proceeded well (73 and 83%, respectively). The hydroxy group could be protected with a triorganylsilyl group to give **2a**-OTBDPS as well as **2a**-OTBDMS (90 and 87%). All of these α-substituted (1′-dimethylaminocyclopropyl)acetates **2a**-X could be converted to the quaternary ammonium salts **4a**-X by treatment with methyl iodide in acetone at room temperature, and these in turn eliminated trimethylamine to give the α-

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Scheme 1. For conditions see Table 1

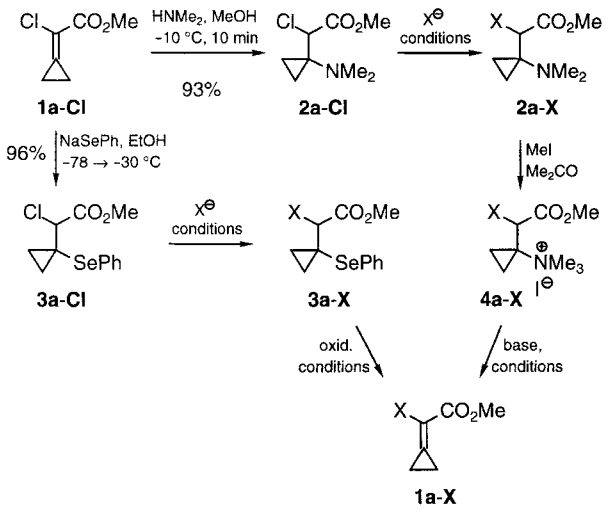


Table 1. Various 2-substituted methyl 2-cyclopropylideneacetates **1a**-X from methyl 2-chloro-2-cyclopropylideneacetate **1a**-Cl

Starting Material	Conditions	Product	Yield (%)
2a-Cl	NaN_3, NaI, DMF, 22 °C, 48 h	**2a-N_3**	73
2a-N_3	MeI, Me_2CO, 22 °C, 48 h	**4a-N_3**	85
4a-N_3	NaOH, $BzlEt_3NCl$, Et_2O/H_2O (1:1), 22 °C, 6 min	**1a-N_3**	83
3a-Cl	NaN_3, $(nBu)_4NCl$, Me_2CO/CH_2Cl_2 (1:1), 22 °C, 28 d	**3a-N_3**	84
3a-N_3	H_2O_2, CH_2Cl_2, 22 °C, 7 min	**1a-N_3**	75
2a-Cl	Ag_2CO_3, THF/H_2O (4:1), 35 °C, 48 h	**2a-OH**	83
2a-OH	TBDPSCl, ImH, DMAP, DMF, 22 °C, 26 h	**2a-OTBDPS**	90
2a-OTBDPS	MeI, Me_2CO, 22 °C, 4 d	**4a-OTBDPS**	98
4a-OTBDPS	NaOH, $BzlEt_3NCl$, Et_2O/H_2O (1:1), 22 °C, 1.5 h	**1a-OTBDPS**	75
2a-OH	TBDMSCl, ImH, DMF, 22 °C, 24 h	**2a-OTBDMS**	87
2a-OTBDMS	MeI, Me_2CO, 22 °C, 48 h	**4a-OTBDMS**	77
4a-OTBDMS	NaOH, $BzlEt_3NCl$, Et_2O/H_2O (1:1), 22 °C, 10 min	**1a-OTBDMS**	80
3a-Cl	Ag_2NO_3, H_2O/Me_2CO (7.5:1), 100 °C, 1 h	**3a-OH**	90
3a-OH	Et_2NSF_3, CH_2Cl_2, 22 °C, 3 h	**3a-F**	87
3a-F	1) O_3, CH_2Cl_2, –78 °C 2) Et_3N, $CHCl_3$, 55 °C, 130 min	**1a-F**	71
3a-Cl	NaSPh, HSPh, DMSO, 22 °C, 10 min	**3a-SPh**	92
3a-SPh	*m*CPBA, $CHCl_3$, 22 °C, 10 min	**1a-SPh**	89

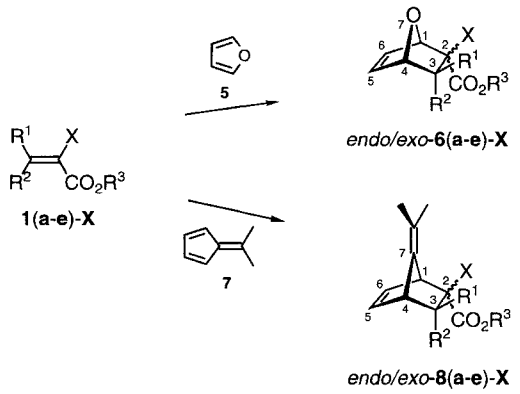
substituted cyclopropylideneacetates **1a**-X (X = N_3, OTBDPS, OTBDMS) in high yields (75–83%), within minutes when treated with 6 M sodium hydroxide in a liquid/liquid two-phase system consisting of diethyl ether and water (1:1) in the presence of triethylbenzylammonium chloride (TEBACl) as a phase-transfer catalyst.

On the other hand, sodium phenylselenide, generated from diphenyldiselenide with sodium borohydride in ethanol, also added to **1a**-Cl extremely rapidly and gave an almost quantitative yield of **3a**-Cl, which underwent nucleophilic substitution with azide or phenylsulfide to give **3a**-N_3 or **3a**-SPh (yields of 84 and 92%) and silver-assisted hydrolysis to the α-hydroxyester **3a**-OH (90%). The latter could be converted to the α-fluoroester **3a**-F by treatment with diethylaminosulfur trifluoride (DAST) in methylene chloride (87%). As documented for β-phenylselenylcarbonyl compounds[8,9], all of these α-substituted (1′-phenylselenocyclopropyl)acetates **3a**-X readily underwent β-elimination after oxidation of the phenylselenyl group with hydrogen peroxide, ozone or *m*-chloroperbenzoic acid to yield the corresponding α,β-unsaturated esters **1a**-X (X = N_3, F, SPh).

The relative reactivities of dienophiles **1a**–**e** were studied by employing furan (**5**) and 6,6-dimethylfulvene (**7**) as independent dienes. As pointed out by Sustmann et al.[10], it is tempting but dangerous to describe the reactions of a particular diene with a series of dienophiles in terms of a single mechanism. However, the cyclic dienes **5** and **7** help one to eliminate competing pathways arising from complicating conformational contributions, thus ensuring a high probability of a common reaction mechanism. Furthermore, furan (**5**) was a logical choice because it is the closest convenient approximation to the diene that should be used in a new synthesis of illudin M[3]. The choice of 6,6-dimethylfulvene (**7**), on the other hand, was based on its known high reactivity and its ready accessibility[11]. Unlike cyclopentadiene, **7** does not tend to react with itself and thereby complicate kinetic measurements.

The 2-substituted 2-cyclopropylideneacetates **1a**-X generally added readily to both dienes to give the respective diastereomeric Diels-Alder adducts in good yields (Table 2). Under thermal conditions, however, decomposition of 2-azido-2-cyclopropylideneacetate (**1a**-N_3) always appeared to dominate over its addition to furan (**5**) and no cycloadducts were obtained. Only when the rate of the cycloaddition reaction was enhanced by applying high pressure (8 kbar) was it possible to isolate the Diels-Alder adducts *endo/exo*-**6a**-N_3 in modest yield (16%).

Scheme 2



	R^1, R^2	R^3	X
1a-H	CH_2–CH_2	Me	H
1a-Br	CH_2–CH_2	Me	Br
1a-Cl	CH_2–CH_2	Me	Cl
1a-F	CH_2–CH_2	Me	F
1a-N_3	CH_2–CH_2	Me	N_3
1a-OTBDPS	CH_2–CH_2	Me	OTBDPS
1b	$=CH_2$	Et	H
1c	H, H	Me	H
1d	Me, H	Me	H
1e-H	Me, Me	Me	H
1e-Cl	Me, Me	Me	Cl

Table 2. Cycloadditions of dienophiles **1a**-X, **1b**, **1c**, **1d** and **1e**-X to furan (**5**) and 6,6-dimethylfulvene (**7**)

Diene	Dienophile	*T* [°C]/ React. time	Product	*endo*/*exo*[a] Ratio	Yield[b] (%)
5	**1a-H**	60/4 d	**6a-H**	4.3:1[c]	60
5	**1a-Br**	60/85 h	**6a-Br**	1.0:1[c]	43
5	**1a-Cl**	45/48h	**6a-Cl**	1.3:1[c]	63[d]
5	**1a-F**	45/12 d	**6a-F**	0.5:1[c]	72
5	**1a-N_3**	22[e]/7.5 h	**6a-N_3**	1.7:1[c]	16
5	**1a-OTBDPS**	22[f]/7 d	**6a-OTBDPS**	0.25:1[c]	47
5	**1b**	60/16 d	**6b**	4.9:1[c]	78
5	**1c**	60/9 d	**6c**	0.8:1[c]	38
5	**1d**	70/4 d	—	—	no rct.
5	**1e-H**	120/5 d	—	—	no rct.
5	**1e-Cl**	80/6 d	—	—	no rct.
7	**1a-H**	64/66 h	**8a-H**	1.8:1[g]	49
7	**1a-Br**	64/12 h	**8a-Br**	1.2:1[g]	86
7	**1a-Cl**	64/21 h	**8a-Cl**	1.3:1[g]	66
7	**1a-F**	45/36 d	**8a-F**	0.5:1[g]	85
7	**1a-N_3**	32/10 d	**8a-N_3**	1.8:1[g]	34
7	**1b**	64/69 h	**8b**	2.1:1[g]	58
7	**1c**	64/12 d	**8c**	1.3:1[g]	69
7	**1d**	120/60 h	—	—	no rct.
7	**1e-H**	120/60 h	—	—	no rct.
7	**1e-Cl**	120/60 h	—	—	no rct.

[a] The configurational assignment relates to the *endo*- or *exo*-position of the methoxycarbonyl group, not the heteroatom. – [b] Yields are based on entered starting material and were not optimized. – [c] After column chromatography. – [d] See ref.[3]. – [e] Under high pressure (8 kbar). – [f] Under high pressure (11.5 kbar). – [g] Ratios were determined by GC analysis of the reaction mixture.

Even under high pressure (9.5 kbar) the 2-(*tert*-butyldimethylsilyloxy)cyclopropylidene **1a**-OTBDMS upon reaction with furan (**5**) gave a complex product mixture, from which one of the two diastereomeric cycloadducts *endo*/*exo*-**6a**-OTBDMS could be isolated in impure form and poor yield (22%). The analogous cyclopropylideneacetate **1a**-OTBDPS with its more stable *tert*-butyldiphenylsilyloxy group, however, gave the [4 + 2] cycloadducts *endo*- and *exo*-**6a**-OTBDPS in yields of 10 and 41% respectively, when reacted under 11.5 kbar for 7 d. Although the configurations of these products were not proved by a decisive method, the major product in this case was most probably the *exo*-diastereomer in view of the steric requirements of the *tert*-butyldiphenylsilyloxy group.

As cyclic dienes both 6,6-dimethylfulvene (**7**) and furan (**5**) provide the 1,3-diene moiety in the fixed synperiplanar conformation which is optimal for Diels-Alder reactions. In contrast to the heterocycle though, 6,6-dimethylfulvene (**7**) is non-aromatic and would therefore be expected to be considerably more reactive. Thus, it came as no surprise that dimethylfulvene **7** succeeded in its reaction with **1a**-N_3 where furan (**5**) failed, and afforded the cycloadducts *endo*/*exo*-**8a**-N_3 in moderate yield (34%) even under thermal conditions. Nevertheless, due to its thermolability, 2-azido-2-cyclopropylideneacetate **1a**-N_3 was clearly excluded as a suitable candidate for any kinetic measurements.

Although methyl acrylate (**1c**) added readily to both dienes, its β-substituted derivatives **1d** and **1e**-X reacted only sluggishly both with furan (**5**) and with dimethylfulvene **7**. However, this unanticipated result confirmed the finding of Oppolzer et al. who reported that a chiral crotonate was rather reluctant to cycloadd to cyclopentadiene as a reasonably reactive diene at room temperature or even in the presence of Lewis acids[12].

Reaction of the allenecarboxylate **1b** with furan (**5**) at 60 °C afforded the two diastereomeric cycloadducts in good yield. However, three side-products could also be isolated, a fact that disqualified the allenecarboxylate from any further consideration in furan additions in the kinetic experiments.

In general, mixtures of *endo*/*exo*-isomers obtained in the additions of dienophiles to 6,6-dimethylfulvene (**7**) could not be separated. These products were therefore characterized by spectroscopic measurements on the corresponding mixtures.

Competition Experiments

The relative Diels-Alder reactivities of dienophiles **1a**–**e** were determined by competition experiments. This procedure, which is based on the competition of two substrates A and B for a reagent C, has been used in the measurement of kinetic isotope effects and also for very fast processes[13,14a,b]. Kinetic experiments were performed at 64 °C in the presence of *n*-dodecane as an internal standard. Consumption of the competing dienophiles, as reflected by a decrease in their concentration, was followed by gas chromatography (GC).

Generally, when 6,6-dimethylfulvene (**7**) served as the diene, the experiments were carried out in diisopropyl ether as solvent, and an excess of the two competing esters was employed. In contrast, furan (**5**) was used as both the reagent and solvent because of its considerably lower reactivity towards dienophiles.

It should be pointed out that the cycloadducts resulting from the addition of methyl acrylate (**1c**) to furan (**5**) are subjected to a retrograde Diels-Alder reaction. In fact, upon heating a mixture of the two cycloadducts in $CDCl_3$ at 64 °C slow formation of the starting materials was observed. While this particular retro-Diels-Alder reaction is likely to profit from the aromaticity of one of its products, namely furan, no such decomposition was observed for the other cycloadducts of **5**. For these cases it can be assumed that the drive towards aromaticity in one of the products of the retrograde process is counterbalanced by the build-up of strain associated with the formation of an allenic ester (**1b**) or a 2-cyclopropylideneacetate **1a**-X. However, it is important to bear in mind that, with respect to the cycloadditions involving furan (**5**), the retrograde reaction formally reduces the reactivity of methyl acrylate (**1c**) in comparison to the other dienophiles. On the other hand, with furan (**5**) serving both as a reagent and solvent, the equilibrium is shifted to strongly favor formation of products so that the impact of the reverse reaction on the rate of formation of the cycloadducts is essentially negligible.

Results and Discussion

The remarkably poor Diels-Alder reactivity of 3,3-dimethylacrylates **1e**-H and even **1e**-Cl towards furan (**5**) and 6,6-dimethylfulvene (**7**) is presumably caused by steric factors. Moreover, the two methyl groups may provide an ad-

ditional deactivating effect apart from their sheer bulk. As electron-releasing substituents they raise the LUMO of dienophiles **1e**-X in energy, thereby diminishing the reactivity of the latter even further. The α-chloro substituent in **1e**-Cl was expected to counteract the electronic influence exerted by the methyl groups, but failed to bring about any noticeable enhancement in Diels-Alder reactivity. This suggests that the electronic deactivation of dienophiles **1e**-X is indeed rather of secondary significance. The paramount influence of steric factors is also underlined by the fact that the Diels-Alder reactivity of simple methyl acrylate (**1c**) is relatively high in comparison with its β-substituted derivatives **1d** and **1e**-X (Table 3).

Table 3. Relative reaction rates of 2-cyclopropylideneacetates **1a**-X, allenecarboxylate **1b**, and acrylates **1c**, **1d**, and **1e**-X for their cycloadditions to furan (**5**) (k_{rel}[furan]) and 6,6-dimethylfulvene (**7**) (k_{rel}[fulvene]) at 64 °C

Dienophile	k_{rel}[furan]	k_{rel}[fulvene]
1a-Br	16	230
1a-Cl	16	210
1b	—	30
1a-H	4	10
1a-F	3	9
1c	1	1
1d	0	0
1e-Cl	0	0
1e-H	0	0

Yet the 2-cyclopropylideneacetates **1a**-X, which in principle are also 3,3-disubstituted acrylates, are amazingly reactive dienophiles, easily surpassing the unsubstituted methyl acrylate (**1c**). This is most likely due to the ring strain inherent in the methylenecyclopropane moiety, which significantly increases the ground state energy of the 2-cyclopropylideneacetates **1a**-X compared with the other acrylates, and as a result reactivity is enhanced. The relatively high Diels-Alder reactivity of the allenecarboxylate **1b** can be understood in similar terms. In addition, **1b** is sterically less demanding than the 2-cyclopropylideneacetates **1a**-X. As a consequence, the corresponding Diels-Alder transition state should be sterically less congested. Hence it is not unexpected that allenecarboxylate **1b** was found to be more reactive than 2-cyclopropylideneacetate **1a**-H. Interestingly, the electronic activation resulting from the electron-withdrawing capacity of the halogen substituents in **1a**-Cl and **1a**-Br is manifested in their being even more reactive than **1b**. Strangely enough, however, the 2-fluoro-2-cyclopropylideneacetate **1a**-F does not fit into the pattern. Of all the halogens, fluorine is the most electronegative and correspondingly should have the greatest negative inductive effect (−I). Amongst the 2-cyclopropylideneacetates **1a**-X the fluoro-substituted **1a**-F should therefore display the highest Diels-Alder reactivity, yet the opposite is observed.

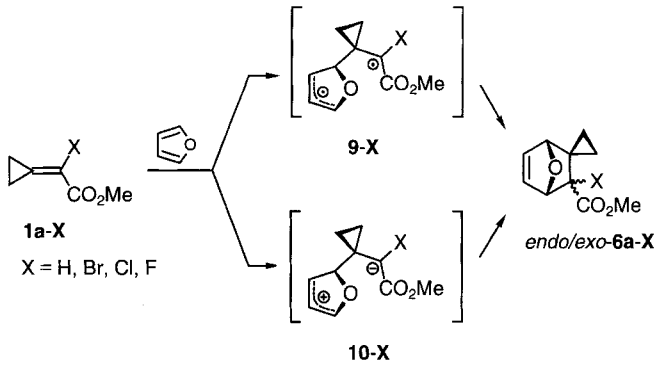
As an explanation for this unexpected result, it was first assumed that the σ-electron-withdrawing effect of fluorine might be overcompensated by its ability to act as a π-electron donor (+M-effect). At first sight this idea may seem absurd, but it is known that a fluorine substituent can either activate or deactivate an aromatic system for electrophilic aromatic substitution. The activation can be understood in terms of donation of charge from occupied *p*-orbitals of fluorine to the π-system. Favorable conditions of orbital overlap – both fluorine and carbon are second-row elements – can probably compensate the unfavorable energy factor created by the great difference of the interacting orbital energies[15,16]. It is also known that the electron-releasing capacity of halogens can be observed, e.g. in haloalkenes, -alkynes and -allenes, by means of ^{13}C-NMR spectroscopy[17,18]. The donation of charge induces a stronger shielding of the β-carbon adjacent to the halogen-substituted one, resulting in a shift of the corresponding signal towards higher field by several ppm. This effect is stronger for fluorine than for any other halogen because fluorine is closest to carbon in size. However, the ^{13}C-NMR spectrum of **1a**-F is not reflective of a distinct donation of charge from fluorine to the π-system, and consequently the comparatively low Diels-Alder reactivity of the 2-fluoro-2-cyclopropylideneacetate **1a**-F cannot be understood on the basis of simple FMO theory. In fact, the same is true for 2-bromo-2-cyclopropylideneacetate **1a**-Br, which proved to be slightly more reactive – at least towards 6,6-dimethylfulvene (**7**) – than **1a**-Cl, although the contrary was to be expected as bromine is sterically more demanding than chlorine and has a smaller −I-effect.

The mechanism of the Diels-Alder reaction has long been a subject of controversy revolving around the question as to whether the [4 + 2] cycloaddition is a concerted or rather a two-step reaction involving a stable zwitterion or diradical intermediate. Furthermore, there was discussion of whether the [4 + 2] cycloaddition as a concerted reaction indeed takes place in a synchronous manner with all bond-breaking and bond-forming processes proceeding in parallel. With regard to the latter question, Dewar clearly favored a nonsynchronous mechanism and introduced the term "two-stage" reaction for concerted reactions that proceed via unsymmetrical transition states similar to diradicals or zwitterions in structure and energy[19,20]. The latest calculations by Houk et al.[21] suggest in contrast to Dewar's postulate, that [4 + 2] cycloadditions of unsubstituted, symmetrical dienes and dienophiles are both concerted *and* synchronous. However, further calculations by the same authors show that substituents definitely have an impact on both the geometry and energy of the transition structures of cycloadditions, to the effect that there are various reaction pathways ranging from synchronous bond formation to a stepwise process via diradicals or zwitterions, either as stable intermediates or in the sense of Dewar's "two-stage" process.

The relative Diels-Alder reactivities found for 2-cyclopropylideneacetates **1a**-X are in accordance with either a concerted or a nonconcerted mechanism involving a diradical species. This is true on the condition that the formation of **9**-X as the first step is rate determining and that the diradical collapses to the product without further activation.

When several substituents are attached to a radical centre, their effects are approximately additive[22]. Fluorine has

Scheme 3



a destabilizing effect on radicals[23]. Everything else being equal, the fluoro-substituted diradical **9**-F should be the least stable in the series of intermediates **9**-X. Hence, the formation of **9**-F ought to be associated with the highest activation barrier and thus proceed more slowly than the formation of **9**-H, while the radical-stabilizing influences of chlorine and bromine account for the enhanced reactivity of **1a**-Cl and **1a**-Br.

The assumption of a reaction mechanism involving diradicals or diradicaloids of type **9**-X is not unproblematic, though, as cyclopropylcarbinyl radicals are known to undergo very rapid rearrangement with ring opening to homoallyl radicals[24]. One therefore expects the formation of at least small quantities of ring-opened products arising from such rearrangement, and the fact that none could be isolated for the reactions of 2-cyclopropylideneacetates **1a**-X with furan (**5**) or 6,6-dimethylfulvene (**7**) may seem a bit suspicious with respect to the assumed mechanism. Yet, this result is no evidence against the proposed reaction pathway via **9**-X, since radicals are subject to so-called capto-dative stabilization[25], and in fact [2 + 2] cycloadditions of **1a**-Cl have exhibited a capto-dative effect in the corresponding intermediates[26]. Indeed, even simple ester groups that are directly attached to the radical centre of a cyclopropylcarbinyl radical can considerably decrease the rate of the ring-opening process[27]. Cyclization of a diradical-like intermediate **9**-X to the corresponding Diels-Alder adduct can, under the given circumstances, be assumed to be more rapid than the potentially competitive ring-opening reaction.

In principle, though, an alternative mechanistic pathway via the zwitterion-like intermediate **10**-X can also be contemplated. In this case the order of the −I-effect for the substituents of F > Cl > Br > H suggests a reactivity pattern **1a**-F > **1a**-Cl > **1a**-Br > **1a**-H which is not observed at all. On the other hand this straightforward interpretation is clearly an oversimplification as it ignores the possibility that factors other than mere electronegativity may also affect the stability of carbanions and thus also need to be taken into account. Therefore fluorine, when directly attached to the carbanionic carbon, has either a moderate stabilizing effect compared with hydrogen ($-I_\sigma$), or causes definite destabilization due to a repulsion of adjacent electron pairs ($+I_\pi$)[15]. The resultant inductive effect depends on the geometry of the system as the I_π repulsion is much greater for planar sp^2-hybridized carbanions. The character of the carbanionic centre in **10**-X will have closer to sp^2 than to sp^3 character, due to conjugation with the ester group, so that I_π destabilization can be expected to dominate over stabilization by I_σ. This might account for the fact that **1a**-H is found to be more reactive than **1a**-F.

While both chlorine and bromine have a stabilizing effect on carbanions ($-I_\sigma$), potential I_π destabilization exerted by these halogens should be comparatively small due to their sizes. Yet, a smaller I_π effect, in combination with the increased polarizability of bromine, may account for the finding that the 2-bromo-2-cyclopropylideneacetate **1a**-Br proved to be even slightly more reactive than its analogous chloro derivative **1a**-Cl.

In summary, the kinetic data found for the Diels-Alder reactions of 2-cyclopropylidene acetates **1a**-X with furan (**5**) and 6,6-dimethylfulvene (**7**) are inconsistent with a concerted, synchronous pathway, but can be understood in terms of a mechanism involving either diradical-type intermediates **9**-X or zwitterion-type intermediates **10**-X. Measurement of activation volumes (ΔV^*), which can be obtained from kinetic studies under high pressure, is potentially a way of differentiating between the two proposed mechanisms[28]. Unfortunately, a preliminary attempt to study the addition of 2-chloro-2-cyclopropylideneacetate **1a**-Cl to furan (**5**) at high pressure (1−3 kbar) by means of quantitative on-line IR spectroscopy[29] failed, since the proceeding of the reaction could not be followed under these conditions.

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Experimental

^{1}H NMR: Bruker WH 270 (270 MHz), AW 250 (250 MHz), AM 250 (250 MHz), WM 400 (400 MHz); δ = 0 for tetramethylsilane, 7.16 for [D_5]benzene, 7.26 for chloroform. Signal multiplicities are designated as follows: s = singlet, bs = broad singlet, d = doublet, dd = doublet of doublets, bd = broad doublet, t = triplet, q = quartet, m = multiplet, mc = multiplet centred. − ^{13}C NMR: Bruker WP 80 (20.17 MHz), AW 250 (62.9 MHz), AM 250 (62.9 MHz) and WM 400 (100.63 MHz); δ = 77.0 for [D]chloroform, 128.0 for [D_6]benzene. − MS: Varian 311 A, INCOS 50. − IR: Perkin Elmer 298 and 399. − GC: Siemens Sichromat 3, 25 m capillary column CB-SE 54 and Siemens Sichromat 4, 25 m capillary column CP-Sil-5-CB, carrier gas: hydrogen. − Column chromatography: Purifications were carried out on Merck silica gel 60 (200−400 mesh) according to the procedure by W. C. Still[30] (flash chromatography). − Reactions under high pressure were carried out in sealed teflon tubes employing a high pressure facility manufactured by Andreas Hofer, Mühlheim, Germany. Prior to use, furan (**5**) was freshly distilled from calcium hydride. Solvents were dried and distilled according to literature procedures.

Ethyl 2-Bromo-2-cyclopropylideneacetate: A slightly modified form of a procedure in the lit.[6] was used: A solution of 12.0 g

(117 mmol) of 1-ethoxycyclopropanol and 1.4 g (11 mmol) of benzoic acid in 250 ml of dry benzene was carefully heated, so that benzene slowly distilled off in a slight stream of nitrogen. Maintaining an approximately constant volume of the reaction mixture, a solution of 55.0 g (129 mmol) of 2-bromo-2-ethoxycarbonylmethylenetriphenylphosphorane in 250 ml of dry benzene was added over a period of 6 h. After completion of the addition the reaction mixture was kept at 80°C for 1 h. After the mixture had cooled down to room temp. the main part of the solvent was evaporated in vacuo, and the residue was taken up in 50 ml of ether. Upon slow addition of 400 ml of pentane, triphenylphosphane oxide precipitated and was filtered off. The filtrate was concentrated in vacuo, and the residue was subjected to column chromatography on 200 g of silica gel (pentane/diethyl ether 4:1), furnishing 9.78 g (41%) of ethyl 2-bromo-2-cyclopropylideneacetate, which crystallized at −20°C, m.p. 31°C. − IR (KBr): $\tilde{\nu}$ = 3100 cm^{-1}, 3060, 2930, 1740 (C=O), 1410, 1380, 1270, 1120, 1060, 990, 880, 840, 770. − ^1H NMR (270 MHz, $CDCl_3$): δ = 1.30 (t, ^3J = 7.9 Hz, 3H, CH_2CH_3), 1.39 (mc, 2H, cpr-H), 1.73 (mc, 2H, cpr-H), 4.18 (q, ^3J = 7.9 Hz, 2H, OCH_2CH_3). − MS (70 eV), *m/z* (%): 178/176 (100) [$M^+ - C_2H_4$], 161/159 (9), 149/147 (5), 97 (51), 51 (63), 69 (23), 29 (53). − $C_7H_9BrO_2$ (205.1): calcd. C 41.00, H 4.42, Br 38.97; found C 40.45, H 4.39, Br 38.56; found C 40.50, H 4.34, Br 38.60.

Methyl 2-Bromo-2-cyclopropylideneacetate (**1a**-Br)[6]: Compound **1a**-Br was obtained in 21% yield following the above procedure. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.40 (m, 2H, cpr-H), 1.74 (m, 2H, cpr-H), 3.82 (s, 3H, CO_2CH_3). − ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 7.04 (−), 12.05 (−), 53.18 (+), 103.68 (C_{quat}), 143.55 (C_{quat}), 162.49 (C_{quat}).

Methyl 2-Chloro-2-(1'-dimethylaminocyclopropyl)acetate (**2a**-Cl): Dry dimethylamine (1.89 g, 42 mmol; sampling cylinder, Fluka) was condensed into 20 ml of dry methanol at −20°C, and the resultant mixture was carefully added to a cooled (−10°C) solution of 6.13 g (42 mmol) of 2-chloro-2-cyclopropylideneacetate **1a**-Cl in 50 ml of dry methanol. Upon completion of the addition the reaction mixture was left stirring for 10 min. The solvent was evaporated in vacuo, and the crude product was chromatographed on 50 g of aluminium oxide (basic, activity III, pentane/diethyl ether 5:1) to give 7.49 g (93%) of **2a**-Cl as a colorless oil, R_f = 0.6. − IR (film): $\tilde{\nu}$ = 3100 cm^{-1}, 2950, 2780, 1760 (C=O), 1150. − ^1H NMR (270 MHz, C_6D_6): δ = 0.75 (m, 3H, cpr-H), 1.05 (m, 1H, cpr-H), 2.24 (s, 6H, NCH_3), 3.28 (s, 3H, OCH_3), 4.48 (s, 1H, 2-H). − MS (70 eV), *m/z* (%): 193/191 (15) [M^+], 156 (100) [M^+ − Cl], 132 (42) [$M^+ - CO_2Me$]. − $C_8H_{14}ClNO_2$ (191.7): calcd. C 50.14, H 7.36, Cl 18.50, N 7.31; found C 50.15, H 7.15, Cl 19.50, N 6.83; found C 50.22, H 7.39, Cl 19.52, N 6.95.

Methyl 2-Azido-2-(1'-dimethylaminocyclopropyl)acetate (**2a**-N_3): A suspension of 1.82 g (9.49 mmol) of **2a**-Cl, 1.86 g (28.6 mmol) of NaN_3 and 300 mg (2.0 mmol) of NaI in 20 ml of dry DMF was stirred at room temp. for 48 h whereupon 20 ml of water and 20 ml of ether were added. The phases were separated, and the aqueous phase was extracted with ether (3 × 20 ml). The combined organic phases were dried over $MgSO_4$, and the solvent was removed in vacuo. Chromatography of the residue over 30 g of aluminium oxide (basic, activity III, pentane/diethyl ether 3:1) yielded 1.38 g (73%) of **2a**-N_3 as a colorless oil. − IR (film): $\tilde{\nu}$ = 3080 cm^{-1}, 2940, 2780, 2100 (azide), 1740 (C=O), 1680, 1200, 1030. − ^1H NMR (270 MHz, C_6D_6): δ = 0.38 (m, 1H, cpr-H), 0.58 (m, 1H, cpr-H), 0.70 (m, 1H, cpr-H), 0.91 (m, 1H, cpr-H), 2.21 (s, 6H, NCH_3), 3.19 (s, 3H, OCH_3), 3.48 (s, 1H, 2-H). − MS (70 eV), *m/z* (%): 170 (15) [$M^+ - N_2$], 139 (25), 111 (100) [$C_6H_{11}N_2^+$], 86 (10), 84 (45).

Methyl 2-Azido-2-(1'-iodotrimethylammoniocyclopropyl)acetate (**4a**-N_3): A solution of 1.20 g (6.06 mmol) of **2a**-N_3 and 2.58 g (18.18 mmol) of methyl iodide in 20 ml of dry acetone was stirred at room temp. in the dark. After 48 h, the solvent was evaporated in vacuo, and the residue was recrystallized from pentane/diethyl ether (1:2) yielding 1.75 g (85%) of **4a**-N_3 as a colorless solid, dec. >110°C. − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 3020, 2860, 2100 (azide), 1740 (C=O), 1480, 1430, 1340, 1260, 1220, 1040, 960, 810, 700, 550. − ^1H NMR (270 MHz, [D_6]DMSO): δ = 1.57 (mc, 2H, cpr-H), 2.51 (m, 2H, cpr-H), 3.80 (s, 9H, NCH_3), 4.49 (s, 3H, OCH_3), 6.26 (s, 1H, 2-H).

Methyl 2-Azido-2-cyclopropylideneacetate (**1a**-N_3): To a suspension of 504 mg (1.5 mmol) of ammonium salt **4a**-N_3 and 109 mg of benzyltriethylammonium chloride in 15 ml of diethyl ether/water (1:1) was added at ambient temperature 5 ml of aqueous 6 N NaOH. The resultant mixture was stirred vigorously at room temp. for 30 s, whereupon the phases were separated. Ether (10 ml) was added to the aqueous phase, and the mixture was stirred for 45 s and separated again. This process was repeated eight times. The combined organic phases were dried over Na_2SO_4 and evaporated in vacuo to afford 189 mg (83%) of **1a**-N_3 as a pale yellow solid, m.p. 55°C. − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 3000, 2940, 2100 (azide), 1730 (C=O), 1430, 1260, 1030, 930, 770, 690. − ^1H NMR (270 MHz, C_6D_6): δ = 0.83 (mc, 2H, cpr-H), 0.99 (mc, 2H, cpr-H), 3.35 (s, 3H, OCH_3). − MS (70 eV), *m/z* (%): 138 (15) [$M^+ - CH_3$], 106 (19), 79 (23), 59 (100) [$C_2H_3O_2^+$], 40 (63). − $C_6H_7N_3O_2$ (153.1): calcd. C 47.06, H 4.61, N 27.44; found C 47.22, H 4.72, N 26.20; found C 46.95, H 4.74, N 26.69.

Methyl 2-Chloro-2-(1'-phenylselenocyclopropyl)acetate (**3a**-Cl): To a solution of 10.0 g (32.2 mmol) of diphenyldiselenide in 400 ml of dry ethanol (degassed!), 2.4 g (63.4 mmol) of $NaBH_4$ was added carefully such that the temp. of the reaction mixture did not exceed 25°C. To the resultant colourless solution of NaSePh in ethanol was slowly added a solution of 9.4 g (64.1 mmol) of 2-chloro-2-cyclopropylideneacetate **1a**-Cl in 100 ml of dry ethanol (degassed!) at −78°C. After the addition was complete (45 min), the mixture was stirred for an additional 30 min and subsequently allowed to warm up to −30°C. The reaction was quenched by addition of 1 l of water, and the aqueous phase was extracted with dichloromethane (5 × 100 ml). The combined organic phases were washed with brine (100 ml), dried over Na_2SO_4 and concentrated in vacuo. The residue was subjected to column chromatography on 200 g of silica gel (pentane/diethyl ether 10:1). Fraction I: 48 mg of diphenyldiselenide, R_f = 0.85. − II (R_f = 0.4): 18.7 g (96%) of **3a**-Cl as a pale yellow oil. − IR (film): $\tilde{\nu}$ = 3050 cm^{-1}, 2950, 1740 (C=O), 1590, 1430, 1150, 1020, 730, 680. − ^1H NMR (400 MHz, $CDCl_3$): δ = 1.19, 1.43 (2 m, 4H, cpr-H), 3.69 (s, 3H, CO_2CH_3), 4.51 (s, 1H, 2-H), 7.3, 7.56 (2 m, 5H, aromatic H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 12.0, 13.2, 22.4 (3 C, cpr-C), 51.6 (1 C, CO_2CH_3), 61.6 (1 C, C-2), 127.2, 128.0, 128.5, 133.2 (6 C, aromatic C), 168.0 (1 C, CO_2CH_3). − MS (70 eV), *m/z*: 306 [M^+, 1:2 Se isotope pattern], 269 [M^+ − Cl]. − $C_{12}H_{13}ClO_2Se$ (303.6): calcd. C 47.47, H 4.32, Cl 11.68, Se 26.00; found C 47.49, H 4.35, Cl 11.38, Se 25.73.

Methyl 2-Azido-2-(1'-phenylselenocyclopropyl)acetate (**3a**-N_3): A mixture of 1.0 g (3.3 mmol) of **3a**-Cl, 640 mg, (9.9 mmol) of NaN_3, and 473 mg (1.7 mmol) of tetrabutylammonium chloride in 40 ml of acetone/CH_2Cl_2 (1:1) was stirred at room temp. for 28 d. The phase transfer catalyst was filtered off and the filtrate was concentrated in vacuo. The resultant residue was chromatographed on 70 g of silica gel (PE/diethyl ether 10:1). Fraction I (R_f = 0.57): 706 mg of starting material. − II (R_f = 0.39): 253 mg (84%, referring

to consumed starting material) of **3a**-N_3, colorless oil. – IR (film): $\tilde{\nu}$ = 3100 cm^{-1}, 3000, 2195 (azide), 1780 (CO), 1600, 1505, 1470, 1240, 1055, 770, 720. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.06–1.42 (m, 4H, cpr-H), 3.64 (s, 3H, CO_2CH_3), 3.81 (s, 1H, 2-H), 7.26–7.38 (m, 3H, aromatic H), 7.54–7.66 (m, 2H, aromatic H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 14.1 (–, cpr-C), 14.3 (–, cpr-C), 23.1 (C_{quat}, cpr-C), 52.4 (+, OCH_3), 68.9 (+, C-2), 127.9 (+, aromatic C), 128.8 (C_{quat}, aromatic C), 129.0 (+, 2 C, aromatic C), 134.1 (+, 2 C, aromatic C), 168.6 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 313/311/309/308/307 (9/53/27/9/9) [M^+], 159/157/155/154/153 (18/100/50/19/19) [$ScPh^+$].

Methyl 2-Azido-2-cyclopropylideneacetate (**1a**-N_3): To a cooled (15 °C) solution of 100 mg (0.32 mmol) of **3a**-N_3 in 3 ml of CH_2Cl_2 was added 57 µl (0.64 mmol) of H_2O_2 (35%). The mixture was stirred vigorously for 5 min, whereupon its colour turned to yellow. As TLC monitoring still indicated the presence of unconsumed starting material, a further 10 µl of H_2O_2 (35%) was added. After 2 min, the orange reaction mixture was diluted with 7 ml of dichloromethane and 5 ml of sat. aqueous $NaHCO_3$. The aqueous phase was extracted with dichloromethane (2 × 5 ml), and the combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. Chromatography of the crude product on 4 g of silica gel (PE/diethyl ether 5:1) afforded 37 mg (75%) of **1a**-N_3 as a pale yellow solid.

Methyl 2-(1'-Dimethylaminocyclopropyl)-2-hydroxyacetate (**2a**-OH): A mixture of 7.29 g (38.0 mmol) of 2-chloroacetate **2a**-Cl and 7.86 g (28.5 mmol) of Ag_2CO_3 in 50 ml of THF/water (4:1) was stirred in the dark at 35 °C. After 48 h, the reaction mixture was filtered through celite, and the precipitate was washed with 60 ml of ether. The phases were separated, and the aqueous phase was extracted with ether (2 × 20 ml). The combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on 50 g of basic aluminium oxide (activity III, pentane/diethyl ether 4:1) to furnish 5.48 g (83%) of **2a**-OH as a colorless oil, R_f = 0.49. – IR (film): $\tilde{\nu}$ = 3500 cm^{-1} (OH), 3090, 2940, 2780, 1750 (C=O), 1450, 1150. – ^1H NMR (270 MHz, C_6D_6): δ = 0.52 (m, 1H, cpr-H), 0.72 (m, 2H, cpr-H), 0.89 (m, 1H, cpr-H), 2.31 (s, 6H, NCH_3), 3.43 (s, 3H, OCH_3), 4.13 (s, 1H, 2-H). – MS (70 eV), *m/z* (%): 173 (3) [M^+], 142 (11) [$M^+ - OCH_3$], 125 (43) [$C_7H_{11}NO^+$], 84 (100) [$C_5H_{10}N^+$].

Methyl 2-tert-Butyldiphenylsilyloxy-2-[1'-(N,N-dimethylamino)-cyclopropyl]acetate (**2a**-OTBDPS): A solution of 1.00 g (5.75 mmol) of amino alcohol **2a**-OH, 675 mg (10 mmol) of imidazole, 122 mg (1.0 mmol) of 4-(*N*,*N*-dimethylamino)pyridine, and 1.8 g (1.7 ml, 6.5 mmol) of *tert*-butyldiphenylchlorosilane in 10 ml of dry DMF was stirred at room temp. in the dark for 26 h, whereupon 20 ml of ether and 15 ml of water were added. The phases were separated, and the aqueous phase was extracted with ether (4 × 15 ml). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The crude product was chromatographed on 50 g of silica gel (PE/diethyl ether 4:1) to give 2.15 g (90%) of **2a**-OTBDPS as a colorless oil, R_f = 0.3. – IR (film): $\tilde{\nu}$ = 3060 cm^{-1}, 2920, 2850, 1750 (C=O), 1425, 1020, 820, 700. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.59–0.72 (m, 3H, cpr-H), 0.90 (m, 1H, cpr-H), 1.12 [s, 9H, $C(CH_3)_3$], 2.41 [s, 6H, $N(CH_3)_2$], 3.40 (s, 3H, CO_2CH_3), 4.00 (s, 1H, 2-H), 7.31–7.49 (m, 6H, aromatic H), 7.62–7.73 (m, 4H, aromatic H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 12.7 (–, cpr-C), 13.7 (–, cpr-C), 15.2 [C_{quat}, $C(CH_3)_3$], 27.0 [+, $C(CH_3)_3$], 41.6 [+, $N(CH_3)_2$], 47.8 (C_{quat}, cpr-C), 51.1 (+), 74.4 (+), 127.4 (+, 2 C, aromatic C), 127.5 (+, 2 C, aromatic C), 129.7 (+, aromatic C), 129.8 (+, aromatic C), 133.1 (C_{quat}, aromatic C), 133.3 (C_{quat}, aromatic C), 136.0 (+, 2 C, aromatic C), 136.2 (+, 2 C, aromatic C), 173.1 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 411 (3) [M^+], 354 (26) [$M^+ - C_4H_9$], 84 (95), 57 (46) [$C_4H_9^+$]. – $C_{24}H_{33}NO_3Si$ (411.6): calcd. C 70.03, H 8.08; found C 70.06, H 8.05.

Methyl 2-tert-Butyldiphenylsilyloxy-2-(1'-iodotrimethylammonio-cyclopropyl)acetate (**4a**-OTBDPS): Acetate **2a**-OTBDPS (2.1 g, 5.1 mmol) was reacted with 0.96 ml (2.2 g, 15.3 mmol) of methyl iodide at room temp. in 8 ml of dry acetone. After 4 d in the dark, 60 ml of pentane was added and the product was filtered off and thoroughly washed with more pentane. The resultant white powder was dried in vacuo to afford 2.8 g (98%) of **4a**-OTBDPS, dec. >250 °C. – $C_{25}H_{36}INO_3Si$ (553.6): calcd. C 54.25, H 6.56; found C 54.25, H 6.52.

Methyl 2-tert-Butyldiphenylsilyloxy-2-cyclopropylideneacetate (**1a**-OTBDPS): To a suspension of 2.8 g (5.1 mmol) of ammonium salt **4a**-OTBDPS and 181 mg of benzyltriethylammonium chloride in 120 ml of diethyl ether/water (1:1) was added at room temp. 20 ml of aqueous 6 N NaOH. The resultant mixture was stirred vigorously for 1.5 h. The phases were separated, the aqueous phase was extracted with ether (5 × 25 ml), the combined organic phases were dried over Na_2SO_4, and the solvent was removed in vacuo. Column chromatography of the crude product on 46 g of silica gel (PE/diethyl ether 10:1) afforded 1.38 g (75%) of **1a**-OTBDPS as a colorless oil, R_f = 0.56, which solidified at –20 °C, m.p. 60–62 °C. – IR (film): $\tilde{\nu}$ = 3060 cm^{-1}, 3040, 2940, 2840, 1710 (C=O), 1580, 1465, 1425, 1285, 1210, 1095, 1015, 885, 815. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.47 (mc, 2H, cpr-H), 1.13 [s, 9H, $C(CH_3)_3$], 1.24 (mc, 2H, cpr-H), 3.79 (s, 3H, CO_2CH_3), 7.32–7.48 (m, 6H, aromatic H), 7.70–7.81 (m, 4H, aromatic H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 5.45 (–, cpr-C), 5.48 (–, cpr-C), 19.42 [C_{quat}, $C(CH_3)_3$], 26.45 [+, $C(CH_3)_3$], 51.7 (+, OCH_3), 115.3 (C_{quat}, cpr-C), 127.5 (+, 4 C, aromatic C), 129.7 (+, 2 C, aromatic C), 132.8 (C_{quat}, 2 C, aromatic C), 133.5 (C_{quat}, C-2), 135.4 (+, 4 C, aromatic C), 164.9 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 366 (2) [M^+], 309 (9) [$M^+ - C_4H_9$], 199 (100), 127 (5) [$M^+ - Si(Ph)_2tBu$], 57 (7) [$C_4H_9^+$]. – $C_{22}H_{26}O_3Si$ (366.5): calcd. C 72.09, H 7.15; found C 72.08, H 7.17.

Methyl 2-tert-Butyldimethylsilyloxy-2-[1'-(N,N-dimethylamino)-cyclopropyl]acetate (**2a**-OTBDMS): A solution of 4.45 g (25.7 mmol) of **2a**-OH, 4.10 g (60 mmol) of imidazole, and 4.61 g (30.6 mmol) of *tert*-butyldimethylchlorosilane in 30 ml of dry DMF was stirred at room temp. for 24 h. The reaction mixture was diluted with 40 ml of diethyl ether and 40 ml of water, and the phases were separated. The aqueous phase was extracted with ether (3 × 30 ml) and the combined organic phases were washed with water (2 × 30 ml), and dried over $MgSO_4$. The solvent was evaporated in vacuo, and the resultant residue was chromatographed on 50 g of aluminium oxide (basic, activity III, pentane/diethyl ether 5:1) to furnish 6.43 g (87%) of **2a**-OTBDMS as a colorless oil. – IR (film): $\tilde{\nu}$ = 3090 cm^{-1}, 2960, 2860, 2780, 1760 (C=O), 1460, 1360, 1260, 1030, 1010, 840, 780. – ^1H NMR (270 MHz, C_6D_6): δ = 0.01 (s, 3H, $SiCH_3$), 0.10 (s, 3H, $SiCH_3$), 1.00 (s, 9H, *t*Bu), 2.43 (s, 6H, NCH_3), 3.34 (s, 3H, OCH_3), 4.13 (s, 1H, 2-H). – MS (70 eV), *m/z* (%): 231 (1) [$M^+ - C_4H_8$], 189 (23), 147 (100) [$C_5H_{11}O_3Si^+$], 98 (23), [$C_6H_{12}N^+$]. – $C_{14}H_{29}NO_3Si$ (287.5): calcd. C 58.49, H 10.17, N 4.87; found C 58.55, H 10.09, N 4.83.

Methyl 2-tert-Butyldimethylsilyloxy-2-(1'-iodotrimethylammonio-cyclopropyl)acetate (**4a**-OTBDMS): A solution of 6.23 g (21.7 mmol) of **2a**-OTBDMS and 9.24 g (4 ml, 65 mmol) of methyl iodide in 20 ml of dry acetone was stirred at room temp. for 48 h. The pale yellow reaction product was filtered off and recrystallized from

pentane/diethyl ether (1:2) to give 7.22 g (77%) of **4a**-OTBDMS as a colorless solid, dec. >250°C. – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3010, 2950, 1750 (C=O), 1250, 1130, 840, 780. – ^1H NMR (270 MHz, $CDCl_3$): δ = 0.12 (s, 3H, $SiCH_3$), 0.15 (s, 3H, $SiCH_3$), 0.63 [s, 10H, $C(CH_3)_3$, cpr-H), 1.45 (m, 1H, cpr-H), 1.92 (m, 2H, cpr-H), 3.50 (s, 9H, NCH_3), 3.83 (s, 3H, OCH_3), 3.99 (s, 1H, 2-H). – $C_{15}H_{32}INO_3Si$ (429.4): calcd. C 41.96, H 7.51, I 29.55, N 3.26; found C 42.05, H 7.46, I 29.42, N 3.30; found C 41.77, H 7.50, I 29.56, N 3.29.

Methyl 2-tert-Butyldimethylsilyloxy-2-cyclopropylideneacetate (**1a**-OTBDMS): To a stirred solution of 2.43 g (5.66 mmol) of **4a**-OTBDMS in 30 ml of diethyl ether/water (1:1) were added 100 mg (0.44 mmol) of benzyltriethylammonium chloride and, dropwise, 10 ml of aqueous 6 N NaOH. After 10 min, the phases were separated, and the aqueous phase was extracted with ether (3 × 20 ml). The combined organic phases were dried over $MgSO_4$ and concentrated in vacuo. The crude product was subjected to column chromatography on 70 g of aluminium oxide (basic, activity III, pentane/diethyl ether 4:1) yielding 1.1 g (80%) of **1a**-OTBDMS as a colorless oil. – IR (film): $\tilde{\nu}$ = 2960 cm^{-1}, 2860, 1740 (C=O), 1460, 1250, 1220, 840, 780. – ^1H NMR (270 MHz, $CDCl_3$): δ = 0.13 (s, 6H, $SiCH_3$), 0.96 [s, 9H, $C(CH_3)_3$], 1.28 (m, 2H, cpr-H), 1.51 (m, 2H, cpr-H), 3.78 (s, 3H, OCH_3). – MS (70 eV), *m/z* (%): 242 (0.2) [M^+], 185 (14) [M^+ – *t*Bu], 127 (53) [M^+ – TBDMS], 75 (100) [$C_2H_7OSi^+$]. – $C_{12}H_{22}O_3Si$ (242.4): calcd. C 59.46, H 9.15; found C 59.11, H 9.01; found C 58.85, H 9.18.

Methyl 2-Hydroxy-2-(1'-phenylselenocyclopropyl)acetate (**3a**-OH): To a solution of 807 mg (2.66 mmol) of **3a**-Cl in 26 ml of acetone was added a solution of 542 mg (3.19 mmol) of silver nitrate in 195 ml of water, and the mixture was heated at 100°C for 1 h. After the usual work-up, the crude product was purified by column chromatography on 50 g of silica gel (column 35 × 3 cm, pentane/diethyl ether 1:1) to give fraction I (R_f = 0.85): 23 mg (0.07 mmol) of diphenyldiselenide. – II (R_f = 0.38): 680 mg (90%) of **3a**-OH. – IR (film): $\tilde{\nu}$ = 3500 cm^{-1} (OH), 1730 (C=O), 1590, 1430, 1270, 1210, 1080, 730, 690. – ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.12, 1.30 (AA'BB' system, 4H, cpr-H), 3.15 (bs, 1H, OH), 3.50 (s, 3H, CH_3O), 3.57 (s, 1H, 2-H), 7.25–7.57 (2 m, 5H, aromatic H). – MS (70 eV), *m/z*: 286/285 [M^+], 268 [M^+ – H_2O], 227 [M^+ – CO_2Me], 129 [M^+ – SePh]. – $C_{12}H_{14}O_3Se$ (285.2): calcd. C 50.53, H 4.94, Se 27.69; found C 50.34, H 5.00, Se 27.69.

Methyl 2-Fluoro-2-(1'-phenylselenocyclopropyl)acetate (**3a-F**): To a cooled (–78°C) solution of 359 mg (1.26 mmol) of **3a**-OH in 10 ml of dry CH_2Cl_2 was added 336 µl (2.56 mmol) of diethylaminosulfur trifluoride (DAST). The reaction mixture was left stirring under argon for 3 h, and was then allowed to warm up to room temperature. After 3 h, the mixture was diluted with 30 ml of brine. The aqueous phase was extracted with dichloromethane (3 × 30 ml), and the combined organic phases were dried over $MgSO_4$. The solvent was evaporated in vacuo, and the residue was subjected to column chromatography on 50 g of silica gel (PE/diethyl ether 5:1) to give 315 mg (87%) of **3a**-F as a colorless oil, R_f = 0.45. – IR (film): $\tilde{\nu}$ = 3045 cm^{-1}, 3004, 2950, 2840, 2640, 2595, 1745 (C=O), 1578, 1476, 1447, 1343, 1275, 1215, 1073, 1020, 995, 880, 739, 690. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.15 (m, 2H, cpr-H), 1.25 (m, 2H, cpr-H), 3.61 (s, 3H, CO_2CH_3), 4.32–4.57 (bd, $^2J_{HF}$ = 50 Hz, 1H, 2-H), 7.21 (m, 3H, aromatic H), 7.51 (m, 2H, aromatic H).

Methyl 2-Fluoro-2-cyclopropylideneacetate (**1a**-F): Ozone was passed through a cooled (–78°C) solution of 1120 mg (3.90 mmol) of **3a**-F in 30 ml of dry CH_2Cl_2 until the reaction mixture turned pale blue. The mixture was then purged of excess ozone by applying a steady stream of oxygen for 2 h. The solution was dried over Na_2SO_4 and concentrated in vacuo to give 1182 mg of selenoxides as a pale yellow oil. A solution of 913 mg (3.01 mmol) of the selenoxides in 8.5 ml of $CHCl_3$ was added to 15 ml of dry Et_3N at 55°C. The reaction mixture was stirred for 130 min at 55°C and then allowed to cool down to room temp. The mixture was diluted with 60 ml of ether and washed with cold (0°C) aqueous HCl (10%, 3 × 15 ml) and then sat. aqueous $NaHCO_3$ (1 × 10 ml). The organic phase was dried over Na_2SO_4, and the solvent was carefully removed in vacuo (p > 200 mbar, 35°C). The crude product was distilled (50–75°C, p = 0.8 mbar, Kugelrohr), affording 280 mg (71%) of **1a**-F as a colorless oil which solidified at –20°C. – IR (film): $\tilde{\nu}$ = 2998 cm^{-1}, 2958, 1784, 1738 (C=O), 1542, 1440, 1308, 1182, 1110, 970, 770. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.46 (m, 2H, cpr-H), 1.61 (m, 2H, cpr-H), 3.84 (s, 3H, CO_2CH_3). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 4.13 (–, d, $^3J_{CF}$ = 2.8 Hz, cpr-C), 5.11 (–, d, $^3J_{CF}$ = 6.0 Hz, cpr-C), 52.2 (+, OCH_3), 114.14 (C_{quat}, d, $^2J_{CF}$ = 23.0 Hz, cpr-C), 140.2 (C_{quat}, d, $^1J_{CF}$ = 250.4 Hz, C-2), 161.3 (C_{quat}, d, $^2J_{CF}$ = 39.8 Hz, C=O). – MS (70 eV), *m/z* (%): 130 (50) [M^+], 115 (33) [M^+ – CH_3], 99 (28) [M^+ – CH_3O], 87 (27) [M^+ – CH_3 – CO], 71 (35), 59 (60), 51 (100), 45 (47). – $C_6H_7FO_2$ (130.1): calcd. C 55.39, H 5.42, F 14.6; found C 55.57, H 5.47, F 14.4.

Methyl 2-(1'-Phenylselenocyclopropyl)-2-phenylthioacetate (**3a**-SPh): To a suspension of 396 mg (3.00 mmol) of sodium thiophenolate and 2.2 g (20 mmol) of thiophenol in 20 ml of freshly distilled dimethylsulfoxide was added dropwise at room temp. a solution of 608 mg (2.00 mmol) of **3a**-Cl in 10 ml of dimethylsulfoxide. After the addition was complete (3 min), the reaction mixture was left stirring for 10 min, whereupon TLC indicated complete consumption of starting material. The reaction was quenched by addition of 200 ml of ice-water at 0°C, and 20 g of NaCl was added to the mixture. Extraction of the mixture with dichloromethane (3 × 40 ml) and subsequent column chromatography of the crude product on 80 g of silica gel (pentane/diethyl ether 10:1) furnished 694 mg (92%) of **3a**-SPh as an oil, R_f = 0.83. – IR (film): $\tilde{\nu}$ = 1720 cm^{-1} (C=O), 1575, 1465, 1420, 1225, 1140, 1005, 725, 680. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.15 (m, 2H, cpr-H), 1.19, 1.44 (AB system, 2H, cpr-H), 3.68 (s, 3H, CH_3O), 4.13 (s, 1H, 2-H), 7.19–7.56 (3 m, 10H, aromatic H). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 12.4, 12.7 (C-2', C-3'), 22.8 (C-1'), 52.0 (C-2), 58.4 (CH_3O), 127.2–134.8 (aromatic C), 170.8 (C-1). – MS (70 eV), *m/z*: 378/376 [M^+], 319 [M^+ – CO_2Me], 269 [M^+ – SPh], 221 [M^+ – SePh].

Methyl 2-Phenylthio-2-cyclopropylideneacetate (**1a**-SPh): To a cooled (–10°C) solution of 378 mg (1.00 mmol) of **3a**-SPh in 20 ml of dry chloroform was added dropwise over 3 min a solution of 190 mg (1.00 mmol) of *m*-chloroperbenzoic acid (90%) in 20 ml of dry chloroform. After 10 min the reaction was quenched by addition of 10 ml of sat. aqueous Na_2CO_3. The aqueous phase was extracted with dichloromethane, and the combined organic phases were briefly dried over $MgSO_4$ and 5 g of dry Na_2CO_3. The solvent was removed in vacuo, and the crude product was prepurified by condensation (oil pump, 20°C) and subsequently subjected to column chromatography on 60 g of degassed silica gel (N_2 atmosphere, pentane/diethyl ether 10:1). Fraction I: 154 mg of diphenyldiselenide, R_f = 0.85. – II (R_f = 0.32): 195 mg (89%) of **1a**-SPh, oil, m.p. –18°C (the compound has to be stored below –22°C under N_2). – IR (film): $\tilde{\nu}$ = 1700 cm^{-1} (C=O), 1575, 1460, 1420, 1240 (C–O), 1045, 735, 680. – ^1H NMR (270 MHz, $CDCl_3$): δ = 1.04, 1.50 (AA'BB' system, 4H, cpr-H), 3.77 (s, 3H, OCH_3), 7.24 (2 m, 5H, aromatic H). – ^{13}C NMR (20.17 MHz, $CDCl_3$): δ = 4.66 (C-2'), 7.30 (C-3'), 52.34 (CH_3O), 117.59 (C-1'), 127.08, 128.70, 131.50, 134.09 (aromatic C), 144.99 (C-2), 165.03 (C-1). – MS (70 eV),

m/z: 220 [M^+], 205 [$M^+ - CH_3$], 189 [$M^+ - OCH_3$], 161 [$M^+ - CO_2Me$], 111 [$M^+ - SPh$]. – $C_{12}H_{12}O_2S$ (220.3): calcd. C 65.43, H 5.49, S 14.55; found C 65.17, H 5.62, S 14.32.

Cycloadditions to Furan (**5**)

Methyl endo/exo-Spiro(cyclopropane-1,3'-[7']oxabicyclo[2.2.1]-hept-5'-ene)-2'-carboxylate (**6a**-H): A mixture of 600 mg (5.35 mmol) of methyl 2-cyclopropylideneacetate **1a**-H and 1.20 g (17.6 mmol) of furan (**5**) was heated with stirring at 60°C in a sealed tube. After 4 d, the mixture was concentrated in vacuo, and the residual oil was chromatographed on 45 g of silica gel (diethylether/pentane 1:8). Fraction I (R_f = 0.53): starting material **1a**-H. – II (R_f = 0.28): 470 mg (49%) of *endo*-**6a**H, colourless oil. – IR (film): $\tilde{\nu}$ = 2999 cm^{-1}, 1738 (C=O), 1437, 1310, 1173, 1025, 890, 807, 716. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.41 (m, 1H, cpr-H), 0.79 (m, 3H, cpr-H), 3.13 (d, ^3J = 5.9 Hz, 1H, 2'-H), 3.59 (s, 3H, CO_2CH_3), 4.22 (s, 1H, 4'-H), 5.15 (d, *J* = 5.9 Hz, 1H, 1'-H), 6.54 [s, 2H, 5'(6')-H]. – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 4.86 (–, cpr-C), 10.59 (–, cpr-C), 28.08 (C_{quat}, C-3'), 50.31 (+, CO_2CH_3), 51.37 (+, C-2'), 80.66 (+, C-4'), 85.55 (+, C-1'), 135.01 (+, C-5'), 136.55 (+, C-6'), 171.81 (C_{quat}, CO_2CH_3).

III (R_f = 0.1): 110 mg (11%) of *exo*-**6a**-H, colourless oil. – IR (film): $\tilde{\nu}$ = 2999 cm^{-1}, 1744 (C=O), 1436, 1166, 1009, 890, 806, 709. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.58 (m, 2H, cpr-H), 0.76 (m, 2H, cpr-H), 2.34 (s, 1H, 2'-H), 3.72 (s, 3H, CO_2CH_3), 4.27 (bs, 1H, 4'-H), 5.21 (bs, 1H, 1'-H), 6.47 (dd, ^3J = 6, ^3J = 1 Hz, 1H, 5'-H), 6.54 (dd, ^3J = 6, ^3J = 1 Hz, 1H, 6'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 6.53 (–, cpr-C), 8.79 (–, cpr-C), 27.61 (C_{quat}, C-3'), 50.00 (+, CO_2CH_3), 51.84 (+, C-2'), 81.64 (+, C-1'), 84.02 (+, C-4'), 135.11 (+, C-5'), 137.02 (+, C-6'), 173.41 (C_{quat}, CO_2CH_3). – $C_{11}H_{14}O_3$ (194.2): calcd. C 68.02, H 7.27; found C 67.51, H 7.15. The elemental analysis was carried out for the ethyl rather than the methyl ester.

Methyl endo/exo-2'-Bromospiro(cyclopropane-1,3'-[7']oxabicyclo[2.2.1]hept-5'-ene)-2'-carboxylate (**6a**-Br): A mixture of 155 mg (0.81 mmol) of methyl 2-bromo-2-cyclopropylideneacetate (**1a**-Br) and 1.20 g (17.6 mmol) of furan (**5**) was heated with stirring at 60°C in a sealed tube for 85 h. The mixture was concentrated in vacuo, and the residue was subjected to column chromatography on 14 g of silica gel (diethyl ether/pentane 1:6) to afford fraction I (R_f = 0.24): 45 mg (21%) of *exo*-**6a**-Br as a colourless oil. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.59 (m, 1H, cpr-H), 1.16 (m, 2H, cpr-H), 1.48 (m, 1H, cpr-H), 3.70 (s, 3H, CO_2CH_3), 4.30 (bs, 1H, 4'-H), 5.33 (bs, 1H, 1'-H), 6.50 (dd, ^3J = 5.8, ^3J = 1.7 Hz, 1H, 5'-H), 6.67 (dd, ^3J = 5.8, ^3J = 1.7 Hz, 1H, 6'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 10.49 (–, cpr-C), 15.85 (–, cpr-C), 35.35 (C_{quat}, C-3'), 52.60 (+, CO_2CH_3), 74.07 (C_{quat}, C-2'), 85.67 (+, C-4'), 88.47 (+, C-1'), 134.05 (+, C-5'), 140.04 (+, C-6'), 168.75 (C_{quat}, CO_2CH_3).

II (R_f = 0.17): 47 mg (22%) of *endo*-**6a**-Br, colourless oil. – IR (film): $\tilde{\nu}$ = 3005 cm^{-1}, 2954, 1737 (C=O), 1436, 1054, 944. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.72 (m, 1H, cpr-H), 0.94 (m, 2H, cpr-H), 1.46 (m, 1H, cpr-H), 3.78 (s, 3H, CO_2CH_3), 4.29 (bs, 1H, 4'-H), 5.59 (bs, 1H, 1'-H), 6.55 (dd, ^3J = 5.7, ^3J = 1.6 Hz, 1H, 5'-H), 6.59 (dd, ^3J = 5.7, ^3J = 1.6 Hz, 1H, 6'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 11.07 (–, cpr-C), 12.64 (–, cpr-C), 33.72 (C_{quat}, C-3'), 53.14 (+, CO_2CH_3), 63.83 (C_{quat}, C-2'), 85.04 (+, C-1'), 85.25 (+, C-4'), 135.79 (+, C-6'), 136.71 (+, C-5'), 169.48 (C_{quat}, CO_2CH_3). – $C_{10}H_{11}BrO_3$: calcd. 257.9891, found 257.9891 (HRMS).

Methyl endo/exo-2'-Chlorospiro(cyclopropane-1,3'-[7']oxabicyclo[2.2.1]hept-5'-ene)-2'-carboxylate (**6a**-Cl): See ref.[3].

Methyl endo/exo-2'-Fluorospiro(cyclopropane-1,3'-[7']oxabicyclo[2.2.1]hept-5'-ene)-2'-carboxylate (**6a**-F): A solution of 89 mg (0.68 mmol) of methyl 2-fluoro-2-cyclopropylideneacetate (**1a**-F) in 5 ml of furan (**5**) was stirred in a sealed tube at 45°C for 12 d. The excess furan was removed in vacuo, and the resultant residue was chromatographed on 21 g of silica gel (PE/diethyl ether 4:1) to afford fraction I (R_f = 0.23): 34 mg (25%) of *endo*-**6a**-F as a colourless oil. – IR (film): $\tilde{\nu}$ = 3075 cm^{-1}, 3000, 2950, 1740 (C=O), 1435, 1295, 1195, 1120, 1075, 1000, 885. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.50 (m, 1H, cpr-H), 0.68 (m, 1H, cpr-H), 0.94 (m, 1H, cpr-H), 1.10 (m, 1H, cpr-H), 3.74 (s, 3H, OCH_3), 4.36 (s, 1H, 4'-H), 5.12 (d, $^3J_{HF}$ = 6.6 Hz, 1H, 1'-H), 6.52 (d, ^3J = 5.8 Hz, 1H, 5'-H), 6.68 (d, ^3J = 5.8 Hz, 1H, 6'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 8.04 (–, d, $^3J_{CF}$ = 3.6 Hz, cpr-C), 8.19 (–, d, $^3J_{CF}$ = 11.6 Hz, cpr-C), 35.00 (C_{quat}, d, $^2J_{CF}$ = 22.6 Hz, C-3'), 52.40 (+, CO_2CH_3), 84.32 (+, d, $^3J_{CF}$ = 0.9 Hz, C-4'), 85.40 (+, d, $^2J_{CF}$ = 22.8 Hz, C-1'), 100.00 (C_{quat}, d, $^1J_{CF}$ = 205.2 Hz, C-2'), 133.34 (+, d, $^3J_{CF}$ = 4.9 Hz, C-6'), 139.27 (+, d, $^4J_{CF}$ = 3.5 Hz, C-5'), 168.10 (C_{quat}, d, $^2J_{CF}$ = 29.8 Hz, CO_2CH_3). – MS (70 eV), *m/z* (%): 198 (6) [M^+], 183 (10) [$M^+ - CH_3$], 167 (24) [$M^+ - CH_3O$], 166 (43), 139 (22) [$M^+ - CH_3CO_2$], 109 (32), 68 (100).

II (R_f = 0.13): 64 mg (47%) of *exo*-**6a**-F, colourless oil. – IR (film): $\tilde{\nu}$ = 3080 cm^{-1}, 3000, 2965, 1740 (C=O), 1435, 1305, 1265, 1100, 1005, 910, 885, 805, 730. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.54 (m, 1H, cpr-H), 0.70–0.98 (m, 3H, cpr-H), 3.82 (s, 3H, OCH_3), 4.37 (s, 1H, 4'-H), 5.25 (d, $^3J_{HF}$ = 1.0 Hz, 1H, 1'-H), 6.49 (d, ^3J = 5.8 Hz, 1H, 5'-H), 6.75 (d, ^3J = 5.8 Hz, 1H, 6'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 5.10 (–, d, $^3J_{CF}$ = 7.0 Hz, cpr-C), 10.98 (–, d, $^3J_{CF}$ = 2.1 Hz, cpr-C), 34.30 (C_{quat}, d, $^2J_{CF}$ = 23.1 Hz, C-3'), 52.61 (+, d, $^4J_{CF}$ = 0.8 Hz, CO_2CH_3), 82.50 (+, d, $^2J_{CF}$ = 26.5 Hz, C-1'), 84.74 (+, d, $^3J_{CF}$ = 2.1 Hz, C-4'), 97.70 (C_{quat}, d, $^1J_{CF}$ = 203.8 Hz, C-2'), 133.38 (+, d, $^4J_{CF}$ = 1.0 Hz, C-5'), 139.50 (+, d, $^3J_{CF}$ = 3.9 Hz, C-6'), 169.70 (C_{quat}, d, $^2J_{CF}$ = 32.7 Hz, CO_2CH_3). – MS (70 eV), *m/z* (%): 198 (3) [M^+], 183 (8), 167 (15), 166 (21), 139 (14), 109 (37), 91 (21), 68 (100).

Methyl endo/exo-2'-Azidospiro(cyclopropane-1,3'-[7']oxabicyclo[2.2.1]hept-5'-ene)-2'-carboxylate (**6a**-N_3): A solution of 66 mg (0.43 mmol) of methyl 2-azido-2-cyclopropylideneacetate (**1a**-N_3) in 4 ml of furan/dichloromethane (1:1) was exposed to high pressure (8 kbar) for 7.5 h. After the solvent had been evaporated in vacuo, column chromatography on 25 g of silica gel (PE/diethyl ether 6:1) furnished fraction I (R_f = 0.41, PE/diethyl ether 3:1): 6 mg (6%) of *exo*-**6a**-N_3 as a colourless oil. – IR (film): $\tilde{\nu}$ = 3080 cm^{-1}, 3000, 2950, 2110 (azide), 1740 (C=O), 1435, 1190, 1110, 1030. – ^1H NMR (250 MHz, C_6D_6): δ = –0.06 (m, 1H, cpr-H), 0.64 (m, 1H, cpr-H), 0.86 (m, 1H, cpr-H), 1.07 (m, 1H, cpr-H), 3.07 (s, 3H, OCH_3), 3.74 (bs, 1H, 4'-H), 5.05 (m, 1H, 1'-H), 6.10 (dd, ^3J = 5.8, ^3J = 1.6 Hz, 1H, 5'-H), 6.35 (dd, ^3J = 5.8, ^3J = 1.5 Hz, 1H, 6'-H). – ^{13}C NMR (62.9 MHz, C_6D_6, DEPT): δ = 7.07 (–, cpr-C), 9.19 (–, cpr-C), 35.03 (C_{quat}, C-3'), 51.58 (+, CO_2CH_3), 73.70 (C_{quat}, C-2'), 84.82 (+, C-1'), 87.60 (+, C-4'), 134.78 (+, C-5'), 139.25 (+, C-6'), 168.12 (C_{quat}, CO_2CH_3).

II (R_f = 0.18, PE/diethyl ether 3:1): 10 mg (10%) of *endo*-**6a**-N_3, colourless oil. – IR (film): $\tilde{\nu}$ = 3080 cm^{-1}, 3000, 2950, 2110 (N_3), 1725 (C=O), 1430, 1250, 1070, 1030, 955. – ^1H NMR (250 MHz, C_6D_6): δ = 0.06 (m, 1H, cpr-H), 0.40 (m, 1H, cpr-H), 0.85 (m, 2H, cpr-H), 3.29 (s, 3H, OCH_3), 3.71 (s, 1H, 4'-H), 5.12 (s, 1H, 1'-H), 6.16 [s, 2H, 5'(6')-H]. – ^{13}C NMR (62.9 MHz, C_6D_6, DEPT): δ = 5.20 (–, cpr-C), 10.62 (–, cpr-C), 35.22 (C_{quat}, C-3'), 52.10 (+, CO_2CH_3), 71.86 (C_{quat}, C-2'), 84.25 (+, C-4'), 85.46 (+, C-1'), 134.37 (+, C-6'), 138.65 (+, C-5'), 170.04 (C_{quat}, CO_2CH_3).

Methyl endo/exo-2'-tert-Butyldiphenylsilyloxyspiro(cyclopropane-1,3'-[7']oxabicyclo[2.2.1]hept-5'-ene)-2'-carboxylate (**6a**-OTBDPS):

A solution of 203 mg (0.55 mmol) of cyclopropylideneacetate **1a**-OTBDPS in 5 ml of a mixture of dichloromethane and freshly distilled furan (1:1) was exposed to high pressure (11.5 kbar) for 7 d at room temp. The solvent was removed in vacuo, and the residue was subjected to column chromatography on 25 g of silica gel (PE/diethyl ether 9:1). Fraction I: 16 mg (8%) of recovered starting material. – II (R_f = 0.28): 23 mg (9%, 10% based on consumed **1a**-OTBDPS) of *endo*-**6a**-OTBDPS, colourless solid, m.p. 71°C. – IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2920, 2840, 1725 (C=O), 1420, 1380, 1350, 1260, 1185, 1120, 1100, 1060, 995, 900, 880, 735, 700. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.27–0.39 (m, 1H, cpr-H), 0.63–0.75 (m, 1H, cpr-H), 0.76–0.87 (m, 1H, cpr-H), 1.12 [s, 9H, $C(CH_3)_3$], 1.16–1.29 (m, 1H, cpr-H), 3.17 (s, 3H, OCH_3), 4.24 (bs, 1H, 4′-H), 4.84 (bs, 1H, 1′-H), 6.36 (dd, ^3J = 5.7, ^3J = 1.6 Hz, 1H, olefin-H), 6.48 (dd, ^3J = 5.7, ^3J = 1.6 Hz, 1H, olefin-H), 7.29–7.48 (m, 6H, aromatic H), 7.60–7.69 (m, 2H, aromatic H), 7.71–7.82 (m, 2H, aromatic H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 8.11 (–, cpr-C), 8.65 (–, cpr-C), 19.71 [C_{quat}, $C(CH_3)_3$], 27.01 [+, $C(CH_3)_3$], 37.04 (C_{quat}, C-3′), 50.81 (+, OCH_3), 84.47 (+, C-4′), 84.62 (C_{quat}, C-2′), 86.37 (+, C-1′), 127.29 (+, 2 C, aromatic C), 127.38 (+, 2 C, aromatic C), 127.71 (+, aromatic C), 129.65 (+, aromatic C), 129.70 (+, aromatic C), 133.73 (C_{quat}, aromatic C), 134.50 (C_{quat}, aromatic C), 134.81 (+, aromatic C), 135.17 (+, olefin-C), 136.24 (+, 2 C, aromatic C), 137.64 (+, olefin-C), 170.45 (C_{quat}, C=O).

III (R_f = 0.08): 91 mg (38%, 41% based on consumed **1a**-OTBDPS) of *exo*-**6a**-OTBDPS, oil. – IR (film): $\tilde{\nu}$ = 3060 cm^{-1}, 2980, 2940, 2850, 1730 (C=O), 1580, 1465, 1420, 1305, 1250, 1140, 1000, 885. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.43–0.52 (m, 1H, cpr-H), 0.73–0.82 (m, 1H, cpr-H), 0.87–0.94 (m, 2H, cpr-H), 1.02 [s, 9H, $C(CH_3)_3$], 3.48 (s, 3H, OCH_3), 4.24 (bs, 1H, 4′-H), 4.67 (bs, 1H, 1′-H), 6.25 (dd, ^3J = 5.8, ^3J = 1.6 Hz, 1H, olefin-H), 6.63 (dd, ^3J = 5.8, ^3J = 1.6 Hz, 1H, olefin-H), 7.31–7.48 (m, 6H, aromatic H), 7.55–7.68 (m, 4H, aromatic H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 5.31 (–, cpr-C), 10.71 (–, cpr-C), 19.92 [C_{quat}, $C(CH_3)_3$], 27.22 [+, $C(CH_3)_3$], 35.67 (C_{quat}, C-3′), 51.39 (+, OCH_3), 82.52 (C_{quat}, C-2′), 83.90 (+, C-4′), 84.80 (+, C-1′), 127.27 (+, 2 C, aromatic C), 127.32 (+ 2 C, aromatic C), 129.65 (+, aromatic C), 129.74 (+, aromatic C), 133.61 (C_{quat}, aromatic C), 133.98 (C_{quat}, aromatic C), 135.06 (+, olefin-C), 136.06 (+, 2 C, aromatic C), 136.15 (+, 2 C, aromatic C), 138.18 (+, olefin-C), 172.1 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 377 (3) [$M^+ - C_4H_9$], 309 (34), 199 (14), 135 (10), 86 (61).

Ethyl endo/exo-3-Methylene-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylate (**6b**): A solution of 289 mg (2.58 mmol) of ethyl allenecarboxylate (**1b**) in 5 ml of furan (**5**) was stirred in a sealed tube at 60°C. After 16 d, the reaction mixture was concentrated in vacuo and the resultant residue was subjected to column chromatography on 26 g of silica gel (PE/diethyl ether 6:1) to give five products, the last three of which were not identified.

Fraction I (R_f = 0.67, PE/diethyl ether 2:1): 303 mg (65%) of *endo*-**6b**, slightly yellow oil. – IR (film): $\tilde{\nu}$ = 2970 cm^{-1}, 1720 (C=O), 1365, 1295, 1175, 1015, 885, 730. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.29 (t, ^3J = 7.3 Hz, 3H, CH_3CH_2O), 3.57 (m, 1H, 2-H), 4.22 (q, ^3J = 7.3 Hz, 2H, CH_3CH_2O), 5.05 (s, 1H, 1-H), 5.16–5.22 (m, 3H, 4-H and exocyclic $=CH_2$), 6.46 [s, 2H, 5(6)-H]. – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 14.10 (+, CH_3CH_2O), 48.73 (+, C-2), 60.71 (–, CH_3CH_2O), 79.62 (+, C-1), 82.96 (+, C-4), 106.82 (–, CH_2=), 134.77 (+, C-6), 134.90 (+, C-5), 142.94 (C_{quat}, C-3), 170.35 (C_{quat}, $CO_2C_2H_5$). – MS (70 eV), *m/z* (%): 151 (84) [$M^+ - C_2H_5$], 135 (44) [$M^+ - C_2H_5O$], 79 (45), 68 (100).

II (R_f = 0.47, PE/diethyl ether 2:1): 62 mg (13%) of *exo*-**6b**, slightly yellow oil. – IR (film): $\tilde{\nu}$ = 2960 cm^{-1}, 1720 (C=O), 1360, 1250, 1170, 1085, 1010, 895. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.29 (t, ^3J = 7.3 Hz, 3H, CH_3CH_2O), 2.93 (s, 1H, 2-H), 4.21 (m, 2H, CH_3CH_2O), 5.07 (s, 1H, 1-H), 5.28 (m, 3H, 4-H and exocyclic $=H_2$), 6.39 (d, ^3J = 5 Hz, 1H, 6-H), 6.47 (d, ^3J = 5 Hz, 1H, 5-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 14.16 (+, CH_3CH_2O), 47.94 (+, C-2), 61.06 (–, CH_3CH_2O), 81.04 (+, C-1), 81.70 (+, C-4), 107.71 (–, CH_2=), 135.08 (+, C-5), 136.09 (+, C-6), 142.67 (C_{quat}, C-3), 171.25 (C_{quat}, $CO_2C_2H_5$). – MS (70 eV), *m/z* (%): 180 (1) [M^+], 151 (15) [$M^+ - C_2H_5$], 135 (37) [$M^+ - C_2H_5O$], 68 (100).

Methyl endo/exo-7-Oxabicyclo[2.2.1]hept-5-ene-2-carboxylate (**6c**): A mixture of 500 mg (5.81 mmol) of methyl acrylate (**1c**) and 2.0 g (29.4 mmol) of furan (**5**) was heated at 60°C for 9 d in a sealed tube. The excess furan was removed in vacuo, and the residue was chromatographed on 24 g of silica gel (diethyl ether/pentane 1:7). Two fractions and 80 mg (9%) of a mixture of the two desired cycloadducts were obtained. Fraction I (R_f = 0.12): 120 mg (13%) of *endo*-**6c**, colourless oil. – IR (film): $\tilde{\nu}$ = 3009 cm^{-1}, 2955, 1740 (C=O), 1571, 1202, 851. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.59 (dd, ^3J = 4.8, ^2J = 11.4 Hz, 1H, 3-H_{endo}), 2.10 (m, 1H, 3-H_{exo}), 3.11 (m, 1H, 2-H), 3.66 (s, 3H, CO_2CH_3), 5.01 (dd, ^3J = 4.2, ^3J = 1.6 Hz, 1H, 4-H), 5.16 (dd, ^3J = 4.4, ^3J = 1.6 Hz, 1H, 1-H), 6.23 (dd, ^3J = 5.6, ^3J = 1.6 Hz, 1H, olefin-H), 6.44 (dd, ^3J = 5.6, ^3J = 1.6 Hz, 1H, olefin-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 28.56 (–, C-3), 42.72 (+, C-2), 51.76 (+, CO_2CH_3), 78.67 (+, C-4), 79.04 (+, C-1), 132.61 (+, C-5), 137.09 (+, C-6), 172.67 (C_{quat}, CO_2CH_3).

II (R_f = 0.07): 140 mg (16%) of *exo*-**6c**, colourless oil. – IR (film): $\tilde{\nu}$ = 3082 cm^{-1}, 2955, 1737, 1572, 1170, 869. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.56 (dd, ^3J = 8.6, ^2J = 11.6 Hz, 1H, 3-H_{endo}), 2.16 (ddd, ^3J = 8.6, ^3J = 4.3, ^2J = 11.6 Hz, 1H, 3-H_{exo}), 2.44 (dd, ^3J = 4.3, ^3J = 8.6 Hz, 1H, 2-H), 3.72 (s, 3H, CO_2CH_3), 5.07 (d, ^3J = 4.3 Hz, 1H, 4-H), 5.19 (bs, 1H, 1-H), 6.35 (dd, ^3J = 6.0, ^3J = 1.5 Hz, 1H, olefin-H), 6.40 (dd, ^3J = 6.0, ^3J = 1.5 Hz, 1H, olefin-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 29.11 (–, C-3), 42.77 (+, C-2), 52.14 (+, CO_2CH_3), 78.01 (+, C-4), 80.93 (+, C-1), 134.69 (+, C-5), 137.08 (+, C-6), 174.22 (C_{quat}, CO_2CH_3).

Cycloaddition to 6,6-Dimethylfulvene (**7**)

Methyl endo/exo-7′-Isopropylidenespiro(cyclopropane-1,3′-bicyclo[2.2.1]hept-5′-ene)-2′-carboxylate (**8a**-H): A solution of 72 mg (0.64 mmol) of methyl 2-cyclopropylideneacetate (**1a**-H) and 70 mg (0.66 mmol) of fulvene **7** in 0.45 ml of diisopropyl ether was stirred at 64°C in a sealed tube for 66 h. The reaction mixture was concentrated in vacuo, and the resultant residue was chromatographed on 8 g of silica gel (diethyl ether/pentane 1:25). Fraction I (R_f = 0.86): recovered fulvene **7**. – II (R_f = 0.39): 68 mg (49%) of *endo/exo*-**8a**-H (*endo/exo* = 1.8:1 according to GC), oil. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.45 (m, 4H, cpr-H), 0.6 (m, 4H, cpr-H), 1.58, 1.68 [m, s, 12H, $C=C(CH_3)_2$], 2.23 (s, 2H), 2.51 (s, 2H), 2.90 (d, ^3J = 3.4 Hz, 1H, *endo*, 2′-H), 3.54 (s, 1H, *exo*, 2′-H), 3.57 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3), 6.40 [m, 4H, 5′(6′)-H]. – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 7.70 (–, cpr-C), 9.24 (–, cpr-C), 9.71 (–, cpr-C), 11.17 (–, cpr-C), 19.33, 19.63, 19.75, and 19.95 [+, $C=C(CH_3)_2$], 27.84 (C_{quat}, C-3′), 29.31 (C_{quat}, C-3′), 46.77 (+), 47.02 (+), 50.51 (+), 51.00 (+), 51.17 (+), 51.28 (+), 51.46 (+), 51.64 (+), 108.53 [C_{quat}, $C=C(CH_3)_2$], 109.95 [C_{quat}, $C=C(CH_3)_2$], 135.43, 136.46, 136.70, and 137.60 [+, C-5′(6′)], 146.49 [C_{quat}, $C=C(CH_3)_2$], 146.55 [C_{quat}, $C=C(CH_3)_2$], 173.37 (C_{quat}, CO_2CH_3), 174.49 (C_{quat}, CO_2CH_3). – $C_{15}H_{20}O_2$

(232.3): calcd. C 77.55, H 8.68; found C 77.63, H 8.65. The elemental analysis was carried out for the ethyl rather than the methyl ester.

III (R_f = 0.23): recovered ester **1a**-H, liquid.

Methyl endo/exo-2'-Bromo-7'-isopropylidenespiro(cyclopropane-1,3'-bicyclo[2.2.1]hept-5'-ene)-2'-carboxylate (**8a**-Br): A solution of 150 mg (0.79 mmol) of methyl 2-bromo-2-cyclopropylideneacetate (**1a**-Br) and 100 mg (0.94 mmol) of fulvene **7** in 1 ml of diisopropyl ether was stirred at 64°C. After 12 h, the solvent was evaporated in vacuo, and chromatography of the resultant residue on 28 g of silica gel (PE/diethyl ether 80:1) afforded 201 mg (86%) of the diastereomeric cycloadducts *endo/exo*-**8a**-Br (*endo/exo* = 1.2:1 according to GC) as a colourless oil, R_f = 0.33. – IR (film): $\tilde{\nu}$ = 3000 cm^{-1}, 2920, 1730, 1435, 1370, 1310, 1270, 1230, 1045, 840. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.59–0.99 (m, 5H, cpr-H), 1.10 (m, 1H, cpr-H), 1.39–1.51 (m, 2H, cpr-H), 1.56 (s, 3H, C=CCH$_3$), 1.63 (s, 3H, C=CCH$_3$), 1.67 (s, 3H, C=CCH$_3$), 1.69 (s, 3H, C=CCH$_3$), 2.57 (m, 2H), 3.69 (s, 3H, OCH$_3$), 3.73 (s, 3H, OCH$_3$), 4.02 (m, 1H, *exo*), 4.16 (m, 1H, *endo*), 6.26–6.38 (m, 2H, olefin-H), 6.50–6.59 (m, 2H, olefin-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 13.14 (–, cpr-C), 13.41 (–, cpr-C), 14.27 (–, cpr-C), 16.88 (–, cpr-C), 19.54 (+, C=C*C*H$_3$), 19.61 (+, C=C*C*H$_3$), 19.76 (+, 2 C, C=C*C*H$_3$), 34.26 (C$_{quat}$, C-3'), 36.50 (C$_{quat}$, C-3'), 51.56, 51.72, 52.29, and 52.52 [+, C-1'(4')], 54.45 (+, OCH$_3$), 56.94 (+, OCH$_3$), 71.44 (C$_{quat}$, C-2'), 72.43 (C$_{quat}$, C-2'), 112.42 [C$_{quat}$, *C*=C(CH$_3$)$_2$], 112.71 [C$_{quat}$, *C*=(CH$_3$)$_2$], 134.66 (+, C-5'), 137.04 (+, C-5'), 137.57 (+, C-6'), 140.99 (+, C-6'), 143.97 [C$_{quat}$, C=*C*(CH$_3$)$_2$], 144.01 [C$_{quat}$, C=*C*(CH$_3$)$_2$], 169.58 (C$_{quat}$, *C*O$_2$CH$_3$), 170.06 (C$_{quat}$, *C*O$_2$CH$_3$). – $C_{14}H_{17}BrO_2$: calcd. 296.04119, found 296.0412 (HRMS).

Methyl endo/exo-2'-Chloro-7'-isopropylidenespiro(cyclopropane-1,3'-bicyclo[2.2.1]hept-5'-ene)-2'-carboxylate (**8a**-Cl): A solution of 76 mg (0.52 mmol) of methyl 2-chloro-2-cyclopropylideneacetate (**1a**-Cl) and 55 mg (0.52 mmol) of fulvene **7** in 0.4 ml of diisopropyl ether was stirred at 64°C in a sealed tube for 21 h. The solvent was evaporated, and the resulting residue was subjected to column chromatography on 10 g of silica gel (diethyl ether/pentane 1:10), yielding 86 mg (66%) of *endo/exo*-**8a**-Cl (*endo/exo* = 1.3:1 according to GC), colourless oil, R_f = 0.6. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.54, 0.65, 0.77, 0.88, 1.05, 1.16, 1.26 (7 m, 8H, cpr-H), 1.56 (s, 3H, C=CCH$_3$), 1.62 (s, 3H, C=CCH$_3$), 1.68 (s, 6H, C=CCH$_3$), 2.56 (m, 2H), 3.70 (s, 3H, OCH$_3$), 3.73 (s, 3H, OCH$_3$), 3.88 (s, 1H, *exo*), 4.06 (s, 1H, *endo*), 6.56 (3 m, 4H, olefin-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 11.04 (–, cpr-C), 12.29 (–, cpr-C), 12.96 (–, cpr-C), 13.38 (–, cpr-C), 19.65 (+, C=C*C*H$_3$), 19.75 (+, 2 C, C=C*C*H$_3$), 19.80 (+, C=C*C*H$_3$), 35.69 (C$_{quat}$, C-3'), 36.99 (C$_{quat}$, C-3'), 51.43, 51.64, 52.23, and 52.58 [+, C-1'(4')], 54.22 (+, OCH$_3$), 56.47 (+, OCH$_3$), 76.75 (C$_{quat}$, C-2'), 77.22 (C$_{quat}$, C-2'), 112.40 [C$_{quat}$, *C*=C(CH$_3$)$_2$], 112.79 [C$_{quat}$, *C*=C(CH$_3$)$_2$], 134.76, 135.83, 138.22, and 140.63 [+, C-5'(6')], 144.09 [C$_{quat}$, C=*C*(CH$_3$)$_2$], 144.32 [C$_{quat}$, C=*C*(CH$_3$)$_2$], 169.43 (C$_{quat}$, *C*O$_2$CH$_3$), 170.27 (C$_{quat}$, *C*O$_2$CH$_3$).

Methyl endo/exo-2'-Fluoro-7'-isopropylidenespiro(cyclopropane-1,3'-bicyclo[2.2.1]hept-5'-ene)-2'-carboxylate (**8a**-F): A solution of 82 mg (0.63 mmol) of methyl 2-fluoro-2-cyclopropylideneacetate (**1a**-F) and 134 mg (1.26 mmol) of 6,6-dimethylfulvene (**7**) in 2.5 ml of diisopropyl ether was stirred at 45°C for 36 d under exclusion of light. The mixture was concentrated in vacuo, and the residue was subjected to column chromatography on 20 g of silica gel (diethyl ether/petroleum ether 1:25) yielding 127 mg (85%) of the diastereomeric mixture *endo/exo*-**8a**-F (*endo/exo* = 0.5:1 according to GC) as an oil, R_f = 0.25. – IR (film): $\tilde{\nu}$ = 3050 cm^{-1}, 2980, 2900, 2840, 1735, 1430, 1365, 1245, 1160, 1100, 1000, 935, 830. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.46–0.78 (m, 5H, cpr-H), 0.79–0.86 (m, 2H, cpr-H), 0.94–1.05 (m, 1H, cpr-H), 1.61 (s, 3H, C=CCH$_3$, *exo*), 1.65 (s, 3H, C=CCH$_3$, *endo*), 1.66 (s, 3H, C=CCH$_3$, *endo*), 1.68 (s, 3H, C=CCH$_3$, *exo*), 2.61 (m, 1H, 4'-H, *endo*), 2.65 (m, 1H, 4'-H, *exo*), 3.70 (s, 3H, OCH$_3$, *endo*), 3.73 (s, 3H, OCH$_3$, *exo*), 3.85 (s, 1H, 1'-H, *endo*), 3.90 (s, 1H, 1'-H, *exo*), 6.33 (m, 2H, olefin-H), 6.58 (m, 1H, olefin-H, *endo*), 6.67 (m, 1H, olefin-H, *exo*). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 6.79 (–, d, $^3J_{CF}$ = 9.9 Hz, cpr-C), 8.73 (–, d, $^3J_{CF}$ = 12.3 Hz, cpr-C), 10.61 (–, d, $^3J_{CF}$ = 3.9 Hz, cpr-C), 11.58 (–, cpr-C), 19.52 (+, C=C*C*H$_3$), 19.61 (+, C=C*C*H$_3$), 19.76 (+, C=C*C*H$_3$), 19.86 (+, C=C*C*H$_3$), 35.37 (C$_{quat}$, d, $^2J_{CF}$ = 24.9 Hz, C-3'), 36.30 (C$_{quat}$, d, $^2J_{CF}$ = 21.8 Hz, C-3'), 49.91 (+, C-4'), 50.59 (+, C-4'), 52.02 (+, OCH$_3$), 52.10 (+, $^2J_{CF}$ = 24.6 Hz, C-1'), 52.18 (+, OCH$_3$), 53.10 (+, d, $^2J_{CF}$ = 25.8 Hz, C-1'), 101.04 (C$_{quat}$, d, $^1J_{CF}$ = 205.2 Hz, C-2'), 101.92 (C$_{quat}$, d, $^1J_{CF}$ = 203.3 Hz, C-2'), 112.38 [C$_{quat}$, d, $^3J_{CF}$ = 3.0 Hz, *C*=C(CH$_3$)$_2$], 112.54 [C$_{quat}$, d, $^3J_{CF}$ = 4.0 Hz, *C*=C(CH$_3$)$_2$], 133.45 (+, 2 C, olefin-C), 133.49 (+, olefin-C), 133.59 (+, olefin-C), 144.78 [C$_{quat}$, C=*C*(CH$_3$)$_2$], 145.23 [C$_{quat}$, C=*C*(CH$_3$)$_2$], 169.60 (C$_{quat}$, d, $^2J_{CF}$ = 31.8 Hz, *C*O$_2$CH$_3$), 170.80 (C$_{quat}$, d, $^2J_{CF}$ = 33.3 Hz, *C*O$_2$CH$_3$). – MS (70 eV), *m/z* (%): 236 (24) [M$^+$], 221 (53) [M$^+$ – CH$_3$], 216 (31), 157 (61), 106 (100), 91 (90).

Methyl endo/exo-2'-Azido-7'-isopropylidenespiro(cyclopropane-1,3'-bicyclo[2.2.1]hept-5'-ene)-2'-carboxylate (**8a**-N$_3$): A solution of 40 mg (0.26 mmol) of methyl 2-azido-2-cyclopropylideneacetate (**1a**-N$_3$) and 40 mg (0.38 mmol) of 6,6-dimethylfulvene (**7**) in 4 ml of diisopropyl ether was stirred at 32°C for 10 d under exclusion of light. The solvent was evaporated in vacuo, and the residue was chromatographed on 20 g of silica gel (PE/diethyl ether 25:1) to give 23 mg (34%) of *endo/exo*-**8a**-N$_3$ (*endo/exo* = 1.8:1 according to GC) as a colourless oil, R_f = 0.45 (PE/diethyl ether 20:1). – IR (film): $\tilde{\nu}$ = 2970 cm^{-1}, 2900, 2080, 1720, 1430, 1230, 1045, 740. – ^{1}H NMR (250 MHz, C_6D_6): δ = 0.28 (m, 1H, cpr-H), 0.40 (m, 2H, cpr-H), 0.55 (m, 1H, cpr-H), 0.85 (m, 1H, cpr-H), 0.99 (m, 1H, cpr-H), 1.09 (m, 2H, cpr-H), 1.43 (s, 3H, C=CCH$_3$), 1.48 (s, 3H, C=CCH$_3$), 1.61 (s, 6H, C=CCH$_3$), 2.19 (bs, 2H, 4'-H), 3.16 (s, 3H, OCH$_3$), 3.20 (s, 3H, OCH$_3$), 3.80 (s, 1H, 1'-H), 3.85 (s, 1H, 1'-H), 6.26–6.41 [m, 4H, 5'(6')]. – ^{13}C NMR (62.9 MHz, C_6D_6, DEPT): δ = 7.90 (–, cpr-C), 10.00 (–, 2 C, cpr-C), 11.40 (–, cpr-C), 19.66 (+, C=C*C*H$_3$), 19.72 (+, C=C*C*H$_3$), 19.80 (+, C=C*C*H$_3$), 19.90 (+, C=C*C*H$_3$), 35.30 (C$_{quat}$, C-3'), 35.70 (C$_{quat}$, C-3'), 51.45, 51.52, 51.80, and 51.90 [+, C-1'(4')], 53.10 (+, OCH$_3$), 53.80 (+, OCH$_3$), 74.80 (C$_{quat}$, 2 C, C-2'), 111.40 [C$_{quat}$, *C*=C(CH$_3$)$_2$], 113.15 [C$_{quat}$, *C*=C(CH$_3$)$_2$], 134.20, 135.00, 139.50, and 139.80 [+, C-5'(6')], 144.60 [C$_{quat}$, C=*C*(CH$_3$)$_2$], 145.20 [C$_{quat}$, C=*C*(CH$_3$)$_2$], 169.40 (C$_{quat}$, *C*O$_2$CH$_3$), 170.80 (C$_{quat}$, *C*O$_2$CH$_3$). – MS (70 eV), *m/z* (%): 231 (31) [M$^+$ – N$_2$], 216 (58), 184 (32), 172 (37), 156 (46), 91 (91).

Ethyl endo/exo-3-Methylene-7-isopropylidenebicyclo[2.2.1]hept-5-ene-2-carboxylate (**8b**): A solution of 101 mg (0.90 mmol) of ethyl allenecarboxylate (**1b**) and 102 mg (0.96 mmol) of fulvene **7** in 0.55 ml of diisopropyl ether was stirred at 64°C in a sealed tube. After 69 h, the mixture was concentrated in vacuo. Chromatography on 10 g of silica gel (diethyl ether/pentane 1:25) furnished 57 mg of a mixture of the desired cycloadducts and starting ester **1b** and 114 mg (58%) of pure *endo/exo*-**8b** (*endo/exo* = 2.1:1 according to GC), colourless oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.25 (t, ^3J = 7.0 Hz, 6H, CH$_2$C*H*$_3$), 1.57, 1.59, 1.63 [3 s, 12H, C=C(CH$_3$)$_2$], 2.88 (m, 1H, *endo*), 3.41 (m, 1H, *exo*), 3.67 (m, 4H), 4.12 (m, 4H, OCH$_2$), 4.96 (d, ^2J = 1.8 Hz, 2H, =CH$_2$), 5.08 (d, ^2J = 1.8 Hz, 2H, =CH$_2$), 6.33 [m, 4H, 5(6)-H]. – ^{13}C NMR (62.9 MHz,

$CDCl_3$, DEPT): δ = 14.26 (+, 2 C, CH_2CH_3), 19.43, 19.59, 19.79, and 19.81 [+, C=C(CH_3)$_2$], 45.93 (+, 2 C), 50.42 (+), 50.51 (+), 51.03 (+), 51.89 (+), 60.48 (−, 2 C, OCH_2CH_3), 105.46 (−, C=CH_2), 105.68 (−, C=CH_2), 110.48 [C_{quat}, C=C(CH_3)$_2$], 112.04 [C_{quat}, C=C(CH_3)$_2$], 135.54, 135.60, 136.68, and 137.25 [+, C-5(6)], 145.43 (C_{quat}), 145.51 (C_{quat}), 146.67 (C_{quat}), 147.09 (C_{quat}), 171.93 (C_{quat}, $CO_2C_2H_5$), 172.61 (C_{quat}, $CO_2C_2H_5$).

Methyl endo/exo-7-Isopropylidenebicyclo[2.2.1]-hept-5-ene-2-carboxylate (**8c**): A solution of 62 mg (0.72 mmol) of methyl acrylate (**1c**) and 62 mg (0.58 mmol) of fulvene **7** in 0.4 ml of diisopropyl ether was stirred at 64 °C in a sealed tube. After 12 d, the solvent was removed in vacuo, and the residue was subjected to column chromatography on 10 g of silica gel (diethyl ether/pentane 1:25) to afford 77 mg (69%) of *endo/exo*-**8c** (*endo/exo* = 1.3:1 according to GC) as a colourless liquid. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.47 (m, 2H, 3-H), 1.55 [m, 12H, C=C(CH_3)$_2$], 1.92 (m, 3H), 2.30 (m, 1H), 2.90 (td, ^3J = 4, ^2J = 9.4 Hz, 1H, 3-H), 3.30 (s, 2H), 3.55 (m, 1H), 3.64 (s, 3H, OCH_3, *exo*), 3.67 (s, 3H, OCH_3, *endo*), 6.09 (dd, ^3J = 6, ^3J = 2.9 Hz, 1H, olefin-H), 6.27, 6.33 (2 m, 3H, olefin-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 19.44, 19.50, 19.59, and 19.62 [+, C=C(CH_3)$_2$], 29.81 (−, C-3), 30.28 (−, C-3), 41.49 (+), 42.27 (+), 42.56 (+), 43.32 (+), 45.24 (+, C-2), 45.72 (+, C-2), 51.51 (+, OCH_3), 51.59 (+, OCH_3), 108.39 [C_{quat}, C=C(CH_3)$_2$], 110.23 [C_{quat}, C=C(CH_3)$_2$], 132.85, 135.85, 138.15, and 138.37 [+, C-5(6)], 145.45 [C_{quat}, C=C(CH_3)$_2$], 147.30 [C_{quat}, C=C(CH_3)$_2$], 174.37 (C_{quat}, CO_2CH_3), 175.44 (C_{quat}, CO_2CH_3).

Kinetic Measurements: Relative rate constants for the cycloadditions of dienophiles **1a**-X, **1b**, and **1c** to dienes **5** and **7** were measured at 64 ± 0.1 °C. In each case two competing dienophiles A and B were reacted with furan (**5**) or 6,6-dimethylfulvene (**7**) in the presence of *n*-dodecane as an internal standard. Kinetic experiments with 6,6-dimethylfulvene were carried out in diisopropyl ether employing an excess of the two dienophiles, while furan was used as both the reagent and the solvent. Samples of a given mixture were taken before heating to 64 °C and the kinetic experiment being started. Subsequent analysis of the samples was performed by gas chromatography. Each analysis was repeated at least three times. Concentrations of both dienophiles, thus determined, served to calculate the corresponding relative reaction rates $r = r_A/r_B$[13]. Two to three samples were taken during the course of each competition experiment, and the competition constants were found to be constant throughout a reaction within ±5% of each average value. A number of cross checks were carried out to ensure accuracy and correspondence of the values obtained for *r*.

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