A New Highly Efficient Three-Component Domino Heck – Diels – Alder Reaction with Bicyclopropylidene: Rapid Access to Spiro[2.5]oct-4-ene Derivatives[**]

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Abstract: Bicyclopropylidene (**1**) was found to surpass even methyl acrylate (**17a**) in its rate of undergoing carbopalladation with aryl- or alkenylpalladium species, leading to substituted allylidenecyclopropanes **5**, **7** and **10**, mostly in high yields (37 – 78 %). These dienes and cross-conjugated trienes react in a Diels – Alder mode with dienophiles to give spiro[2.5]octenes **18a**-Ph, **18b**-Ph and **18a**-Vin, respectively, in good yields (89, 69 and 65 %). The overall transformation can be achieved as a one-pot three-component reaction with a variety of dienophiles to furnish the domino Heck – Diels – Alder products **18** regioselectively in most cases in good to very high yields (49 – 100 %). The reaction of **1** with iodobenzene (**2**-Ph) and **17a** gave **18a**-Ph in virtually quantitative yield—also on a gram scale—using only 1 mol % of catalyst, and even bromobenzene (**22**) gave **18a**-Ph in 59 % yield. Bicyclopropylidene (**1**), in the presence of palladium acetate/triphenylphosphane underwent rearrangement to allylidenecyclopropane (**5**-H), which in turn dimerized (73 %) in the absence of other reaction partners, or could be trapped by diethyl fumarate (**17c**) to give the Diels – Alder adduct **18c**-H in 45 % yield. The coupling of oligoiodobenzenes with **1** and subsequent cycloaddition could be extended to a multicomponent reaction. In this way, 1,4-diiodobenzene (**37**), **1** and an alkyl acrylate gave the products **38** of a twofold Heck – Diels – Alder reaction in up to 87 % yield, 1,3,5-triiodobenzene (**39**) reacted in up to 72 % yield and ultimately 1,2,4,5-tetraiodobenzene (**41**) gave the fourfold domino Heck – Diels – Alder product **42** in 47 % isolated yield, in a single operation in which 12 new carbon-carbon bonds were formed.

Keywords: bicyclopropylidene · Diels – Alder reactions · domino reactions · Heck reaction · multicomponent reactions

Introduction

Domino processes have stirred a steadily increasing interest in recent years,[1] and multicomponent reactions have definitely found an important place in the tool-box of organic chemists. Several elegant and facile constructions of highly complex structures starting from simple molecules in one synthetic operation make use of these concepts. Especially the need for highly efficient and flexible synthetic approaches to carbo- and heterocyclic systems with a combinatorial potential has led to a dramatic increase in research activities.

In the context of studying various aspects of intramolecular Heck reactions,[2] we also examined domino Heck – Heck-[3a] and Heck – Diels – Alder processes[3b,c] which led to an easy access to bicyclo[4.3.0]nonene systems. Thus we became aware that the Heck – Diels – Alder reaction even proceeds with 2-bromo-1,*m*-dienes containing a highly strained methylenecyclopropane end group or bromomethylenecyclopropane starter to yield α-spirocyclopropane-annelated bicyclo[4.3.0]nonene skeletons.[3c] In this context, the reactions of certain tetrasubstituted alkenes[4] were examined, most of which are generally referred to as being unreactive in the Heck coupling.[2] Several methylenecyclopropanes with two substituents at the methylene terminus, and especially bicyclopropylidene (**1**) were found to be highly reactive alkenes that underwent palladium-catalyzed cocyclizations with acceptor-activated and with strained alkenes[5] as well as Heck-type carbopalladations, the latter even more rapidly than alkyl

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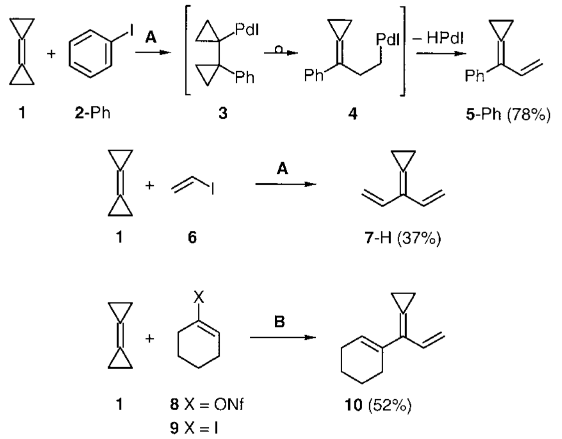
acrylates.[6] Herein we present the full account of the recently developed[6] new three-component domino reaction combining bicyclopropylidene (**1**) with aryl or alkenyl halides and a dienophile. For comparison, some other methylenecycloalkanes with tetrasubstituted double bonds were also tested.

Results and Discussion

The cross-coupling reaction of bicyclopropylidene (**1**), a particularly strained tetrasubstituted alkene, which has recently become easily available,[7] with iodobenzene (**2**-Ph) under typical Heck conditions[8] gave the 1-phenylallylidenecyclopropane (**5**-Ph) as a sensitive oil in 78% yield (Scheme 1).[9] Besides this product, a significant amount of polymeric material containing cyclopropane moieties was observed.[6] The mechanism involves carbopalladation of the double bond in **1** by the initially formed phenylpalladium iodide, cyclopropylmethyl to homoallyl rearrangement and subsequent *β*-hydride elimination to form the diene substructure. The reaction of **1** with iodoethene (**6**) gave the unusual cross-conjugated triene **7**-H in up to 37% yield. This represents a novel access to the so-called dendralenes which are usually prepared by pyrolysis or elimination reactions.[10, 11] Another [3]dendralene, the hydrocarbon **10**, was obtained in 52% yield by the palladium-catalyzed reaction of cyclohexenyl nonaflate (**8**) with **1**. Both new dendralenes **7**-H and **10** are prone to undergo polymerization and thus—to achieve better yields of their cycloadducts—ought to be trapped with a dienophile immediately after formation or in situ.

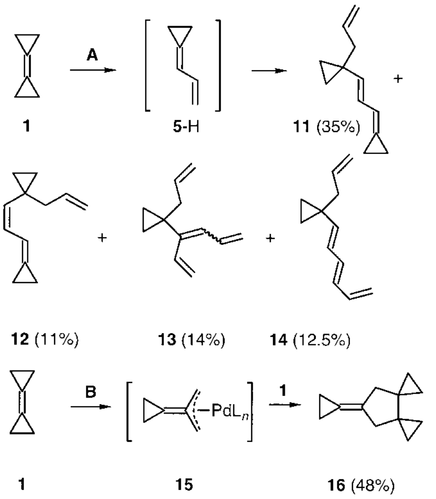


Scheme 1. Heck reaction of bicyclopropylidene (**1**) with aryl (**2**-Ph) and alkenyl halides (**6**, **9**) or alkenyl nonaflates (**8**) and rearrangement to allylidenecyclopropanes. **A**: Pd(OAc)$_2$, PPh$_3$, Et$_3$N, DMF, 80°C; **B**: Pd(PPh$_3$)$_4$, Et$_3$N, MeCN, 80°C.

Upon treatment of bicyclopropylidene (**1**) alone with palladium acetate and triphenylphosphane in benzene at room temperature, it underwent a slow isomerization to allylidenecyclopropane (**5**-H)[12] (Scheme 2), the appearance of which can be monitored by ^{1}H NMR spectroscopy. The formation of the diene **5**-H is presumably initiated by a palladium hydride addition to the double bond in **1**, followed by cyclopropylmethyl to homoallyl rearrangement and terminated by *β*-hydride elimination. The yield of **5**-H increased from 43 to 55% when the reaction was performed in the presence of a mixture of 10% Et$_3$N/HOAc (1:1). This isomerization was not observed in diethyl ether. In dichloromethane the conversion was only 20% after 24 h at ambient temperature.

Although allylidenecyclopropane (**5**-H) had been reported to be unreactive in palladium-catalyzed transformations,[12d] prolonged stirring of the mixture of **1** and the catalyst in benzene at ambient temperature led to slow formation of oligomers of **5**-H. Upon heating at 80°C, a mixture of four bicyclopropylidene dimers **11**–**14** was formed within 2 h, apparently by a Pd-catalyzed subsequent reaction of the initially formed diene **5**-H.

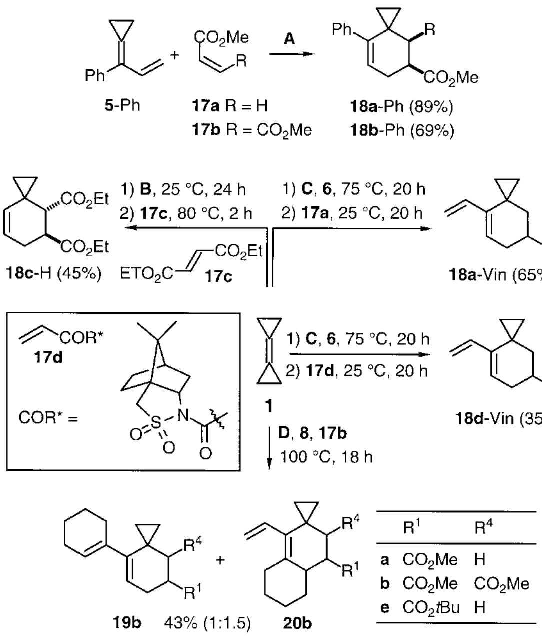
This type of transformation turned out to be highly dependent on the type of catalyst and ligand additive. Thus, bicyclopropylidene (**1**) remained unchanged under similar conditions (heating at 80°C in benzene), but with Pd(dba)$_2$•*i*Pr$_3$P as a catalyst. Yet at 110°C in the absence of any other activated alkene, one molecule of bicyclopropylidene (**1**), after opening of a distal bond, underwent formal [3+2] cycloaddition to a second molecule of **1** to give 8-cyclopropylidenedispiro[2.0.2.3]nonane (**16**).[5]



Scheme 2. Palladium-catalyzed isomerization of bicyclopropylidene (**1**) and further transformations. **A**: Pd(OAc)$_2$•2PPh$_3$, C$_6$D$_6$, 80°C, 2 h; **B**: Pd(dba)$_2$, P(*i*Pr)$_3$, toluene, 110°C, 4 h.

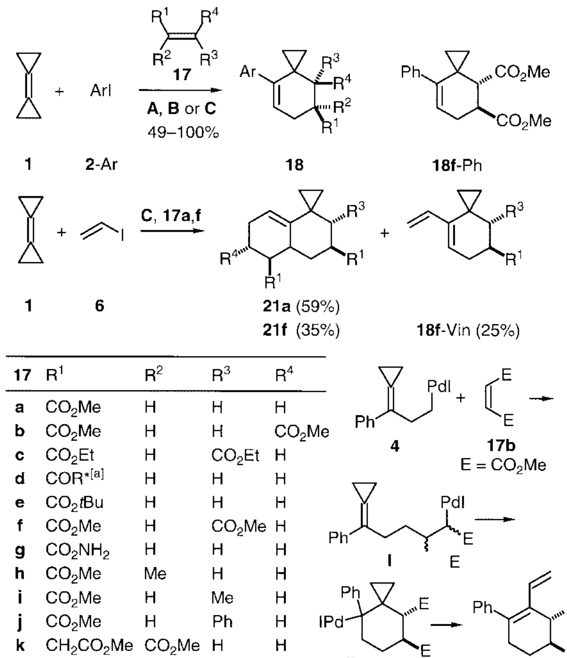
The allylidenecyclopropanes **5**-Ph, **5**-H and **10**,[13, 14] when heated either in isolated form or without isolation after having been formed in the Heck reaction, with a dienophile gave the Diels–Alder products[15] **18a**-Ph, **18c**-H, **18a**-Vin, **18d**-Vin, **19b** and **20b** in moderate to good yields (Scheme 3).

The constitutions of the Diels–Alder products were determined by extensive NMR studies as well as by X-ray crystal structure analysis in several cases (Figure 1), and it turned out that in all reactions with alkyl acrylates only the quasi-*meta* product was formed, in accordance with previously reported observations.[15] Calculations showed that allylidenecyclopropane (**5**-H) has an almost symmetrical highest occupied molecular orbital (HOMO),[16] which is in contrast to other 1-donor-substituted alkenes.[17] The [3]dendralene **10**



	R^1	R^4
a	CO_2Me	H
b	CO_2Me	CO_2Me
e	CO_2tBu	H

Scheme 3. Stepwise Heck–Diels–Alder reactions with bicyclopropylidene (**1**). **A**: $CDCl_3$, Δ, 12 h; **B**: $Pd(OAc)_2$, PPh_3, C_6D_6; **C**: $Pd(OAc)_2$, PPh_3, Et_3N, DMF; **D**: $Pd(PPh_3)_4$, Et_3N, DMF.



17	R^1	R^2	R^3	R^4
a	CO_2Me	H	H	H
b	CO_2Me	H	H	CO_2Me
c	CO_2Et	H	CO_2Et	H
d	COR*[a]	H	H	H
e	CO_2tBu	H	H	H
f	CO_2Me	H	CO_2Me	H
g	CO_2NH_2	H	H	H
h	CO_2Me	Me	H	H
i	CO_2Me	H	Me	H
j	CO_2Me	H	Ph	H
k	CH_2CO_2Me	CO_2Me	H	H

[a] See Scheme 3.

Scheme 4. Three-component reactions with bicyclopropylidene (**1**). For details and conditions see Table 1.

underwent a single Diels–Alder reaction with dimethyl maleate with low regioselectivity to yield both the cyclohexenyl-substituted spiro[2.5]octene **19b** and the spirocyclopropanated octahydronaphthalene derivative **20b** (ratio 1:1.5). Apparently, both 1,3-diene units in the dendralene **10** have about the same reactivity towards the dienophile.

Surprisingly, when the three components bicyclopropylidene (**1**), iodobenzene (**2**-Ph) and methyl acrylate (**17a**), were mixed with the palladium catalyst system [$Pd(OAc)_2$, PPh_3, K_2CO_3/Et_4NCl or Et_3N] in acetonitrile and the mixture heated in a Pyrex bottle, only a trace of methyl cinnamate, the Heck coupling product of **2**-Ph and **17a**, was detected. Best yields of the domino Heck–Diels–Alder products **18** were obtained applying the Jeffery protocol [$Pd(OAc)_2$, PPh_3, K_2CO_3, Et_4NCl, MeCN],[18] and increasing the concentration of all reactants to 4 M finally led to a virtually quantitative formation of **18a**-Ph with 1.0 mol% of precatalyst (Scheme 4). Thus, the tetrasubstituted alkene **1** is more rapidly carbopalladated than even methyl acrylate, which is known to be a particularly good substrate in Heck coupling reactions. This high reactivity of **1** must have to do with its unusual nucleophilicity[19] which facilitates the attack of the electrophilic organopalladium species.

However, only the *trans*-spiro[2.5]oct-4-ene-7,8-dicarboxylate **18f**-Ph was isolated from the one-pot Heck–Diels–Alder reaction of bicyclopropylidene **1** and phenyl iodide (**2**-Ph) with dimethyl *cis*-but-2-ene-1,4-dioate (dimethyl maleate) (**17b**) under Heck as well as under Jeffery conditions (Table 1, entries 3, 4). The identity of the samples of **18f**-Ph prepared with dimethyl maleate (**17b**) (Table 1, entry 3) and with dimethyl fumarate (**17f**) (Table 1, entry 7) was corroborated by their NMR spectral data and was rigorously proved by X-ray crystal structure analyses (Figure 1).[20] Moreover, excessive **17b** isomerized to **17f** (15 to 30%) under the conditions employed.[21] Partial isomerization of excessive dimethyl maleate (**17b**) (10%) was detected even in the Diels–Alder reaction of **17b** with isolated diene **5**-Ph (Scheme 3), yet in this case the major Diels–Alder product was *cis*-configurated *cis*-**18b**-Ph, and the *trans*-diastereomer **18f**-Ph was formed only in trace quantities. No isomerization of dimethyl maleate **17b** was observed upon heating in the absence of **1** and **2**-Ph under Heck or Jeffery conditions for extended times (20–24 h). It is not quite clear at this point whether these findings indicate that the [4+2] cycloaddition (at least in some extent) proceeds stepwise under these conditions and thus partially forms the thermodynamically more stable *trans*-isomer. A conceivable alternative mechanism with addition of the homoallylpalladium intermediate **4** onto **17b**, followed by 6-*endo-trig* ring closure in intermediate **I** is highly unlikely. Just like the cyclopropylcarbinylpalladium intermediate **3**, the cyclization product **II** should rapidly rearrange to the corresponding ring-opened homoallylpalladium species which would undergo β-hydride elimination to yield the diene **III** or its [4+2] cycloaddition product.

The cross-conjugated triene **7**-H formed from bicyclopropylidene (**1**) and iodoethene (**6**) is prone to undergo a so-called transmissive cycloaddition,[22] that is a domino Diels–Alder reaction in which the diene for the second step is formed by the first reaction. The three-component reaction of **1**, **6** and methyl acrylate (**17a**) gave the spirocyclopropanated octahydronaphthalene derivative **21a** in 59% isolated yield. The analogous reaction of **1**, **6** and dimethyl fumarate (**17f**) yielded only 35% of the twofold adduct **21f** along with 25% of the onefold Diels–Alder product **18f**-Vin (Scheme 4).

Scope and limitations of this new three-component reaction were tested with variation of the aryl and alkenyl halide as well as the dienophile (Scheme 4 and Table 1).

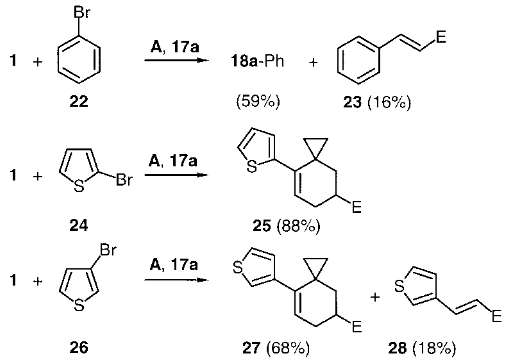
Table 1. Three-component reactions of bicyclopropylidene (**1**), an aryl **2** or alkenyl iodide **9** and a dienophile **17**. See Scheme 4.

Entry	Aryl/ Alkenyl halide	Dienophile	Conditions[a]	Product	Yield [%]
1	PhI (**2**-Ph)	**17a**	**A**	**18a**-Ph	100
2	PhI (**2**-Ph)	**17a**	**B**	**18a**-Ph	99
3	PhI (**2**-Ph)	**17b**	**A**	**18f**-Ph	96
4	PhI (**2**-Ph)	**17b**	**C**	**18f**-Ph	98
5	PhI (**2**-Ph)	**17e**	**A**	**18e**-Ph	87
6	PhI (**2**-Ph)	**17e**	**C**	**18e**-Ph	78
7	PhI (**2**-Ph)	**17f**	**A**	**18f**-Ph	97
8	PhI (**2**-Ph)	**17g**	**A**	**18g**-Ph	49
9	4-TolI (**2**-Tol)	**17a**	**A**	**18a**-Tol	91
10	4-TolI (**2**-Tol)	**17a**	**C**	**18a**-Tol	87
11	4-TolI (**2**-Tol)	**17e**	**A**	**18e**-Tol	83
12	4-TolI (**2**-Tol)	**17f**	**A**	**18f**-Tol	99
13	4-TolI (**2**-Tol)	**17f**	**C**	**18f**-Tol	80
14	3-PyI (**2**-Py)	**17a**	**A**	**18a**-Py	67
15	3-PyI (**2**-Py)	**17e**	**A**	**18e**-Py	81
16	3-PyI (**2**-Py)	**17f**	**A**	**18f**-Py	63
17	PhI (**2**-Ph)	**17h**	**A**	**18h**-Ph	76
18	PhI (**2**-Ph)	**17i**	**A**	**18i**-Ph	0
19	PhI (**2**-Ph)	**17j**	**A**	**18j**-Ph	0
20	**9**	**17a**	**A**	**19a** + **20a** (1:2)	84
21	**9**	**17e**	**A**	**19e** + **20e** (1:3)	83
22	PhI (**2**-Ph)	**17k**	**A**	**18k**-Ph	47

[a] **A**: 5 mol% $Pd(OAc)_2$, 15 mol% PPh_3, K_2CO_3, Et_4NCl, MeCN, 80°C, one step. **B**: as in **A**, 1 mol% $Pd(OAc)_2$, 3 mol% PPh_3. **C**: $Pd(OAc)_2$, PPh_3, Et_3N, DMF, 80°C, one step.

Excellent results were obtained with iodobenzene (**2**-Ph), 4-iodotoluene (**2**-Tol; Table 1, entries 1–7, 9–13) as well as 3-iodopyridine (**2**-Py; Table 1, entries 14–16) with various dienophiles **17**. The reaction with acrylic acid amide (**17g**, entry 8) gave the corresponding spiro[2.5]octene derivative **18g**-Ph in moderate yield (49% isolated). With 1-iodocyclohexene (**9**) instead of cyclohexenyl nonaflate (**8**) and methyl (**17a**) or *tert*-butyl acrylate (**17e**) in highly concentrated solution the products **19** and **20** were also isolated in high yields (Table 1, entries 20, 21). Even aryl bromides such as bromobenzene (**22**) and bromothiophenes (**24**, **26**) underwent coupling with **1**, but in two of these cases significant amounts of the products arising from direct coupling of the bromides and the acrylate, were isolated (Scheme 5).

A special feature of the 8-phenylspiro[2.5]oct-7-ene derivatives **18** prepared, as demonstrated by the X-ray crystal structure analyses of the dimethyl spiro[2.5]octenedicarboxylate **18f**-Ph, **18f**-Tol and and **18k**-Ph (Figure 1), is that the phenyl ring is perpendicular to the plane of the double bond which must be caused by steric interaction between the spirocyclopropane moieties and the *ortho* hydrogens on the aromatic rings.



Scheme 5. Heck–Diels–Alder reactions of bicyclopropylidene (**1**) with bromoarenes and methyl acrylate (**17a**). **A**: $Pd(OAc)_2$, PPh_3, K_2CO_3, Et_4NCl, MeCN, 80°C, 48 h; E = CO_2Me.

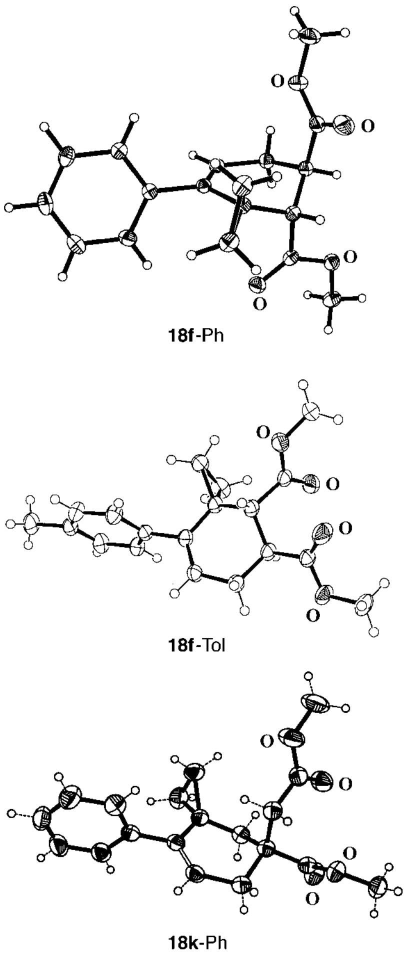
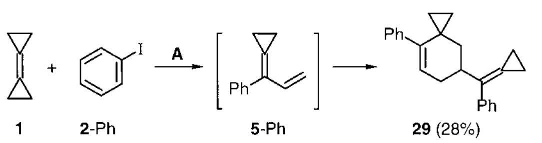


Figure 1. Structures of **18f**-Ph, **18f**-Tol and **18k**-Ph in the crystals.[20]

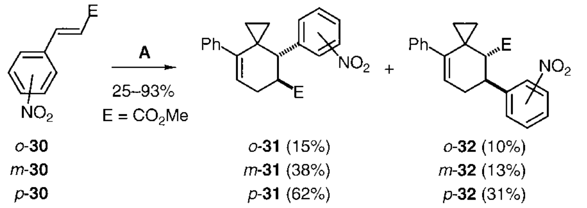
In the absence of any dienophile and under high pressure (10 kbar), the dendralene **5**-Ph itself acted as the dienophile to give the spiro[2.5]octene derivative **29** in 28% yield (Scheme 6).



Scheme 6. Dimerization of the allylidenecyclopropane **5**-Ph. **A**: $Pd(OAc)_2$, PPh_3, Et_3N, DMF, 10 kbar, 80°C, 24 h.

Substituted acrylates were also tested. Whereas methyl α-methylacrylate **17h** gave the corresponding spiro[2.5]octene derivative **18h**-Ph in good yield (76%), no products could be isolated from reactions with the β-substituted **17i** and **17j** (Table 1, entries 18, 19).[13d]

The lack of reactivity of methyl cinnamate (**17j**) as a dienophile in this Heck–Diels–Alder sequence could be overcome by the introduction of a strongly electron-withdrawing substituent. Thus, *o*-, *m*- and *p*-nitrocinnamates **30** all gave the corresponding cross-coupling cycloadducts, but interestingly both possible regioisomers **31** as well as **32** (Scheme 7). The reactions required longer heating (up to 4 d).



Scheme 7. Heck–Diels–Alder reactions of **1** and iodobenzene (**2**-Ph) with nitro-substituted cinnamic acid esters **30**. **A**: **1**, **2**-Ph, Pd(OAc)$_2$, PPh$_3$, K$_2$CO$_3$, Et$_4$NCl, MeCN, 80 °C, 4 d.

In the case of *p*-**30** one third (31 % isolated) of the product mixture was the quasi-*ortho* adduct *p*-**32** as proved by an X-ray crystal structure analysis (Figure 2).

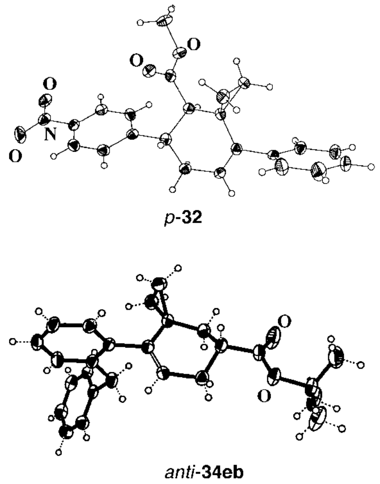
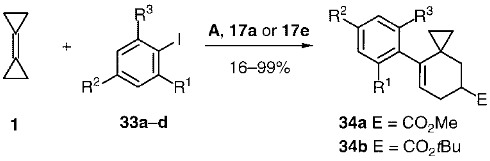


Figure 2. Structures of *p*-**32** and *anti*-**34eb** in the crystals.[20]

The influence of substituents on the aryl iodides was also examined. An *ortho*-methyl group on the iodobenzene does not interfere with the Heck–Diels–Alder reaction with methyl acrylate (**17a**) but does cause a significant decrease in yield in the reaction with the bulkier *tert*-butyl acrylate (**17e**) (Scheme 8 and Table 2). This steric effect is even more pronounced in the reaction with the *ortho*-benzyl substituted iodide **33b**. In all reactions with *ortho*-substituted phenyl iodides, two atropisomeric products *anti*- and *syn*-**34** were formed due to the hindered rotation around the aryl-spirooctene bond, with a predominance of the *anti*-isomer (with respect to the substituent on the aryl group and the alkoxycarbonyl group on the spirooctane moiety) of up to 3:1 (^{1}H NMR), slightly depending on the size of the alkoxycarbonyl group. Based on a coalescence temperature between 50 and 75 °C the rotational barrier is estimated to be in the range of 75–81 kJ mol^{-1}.[23] The structure of crystalline *anti*-**34eb** was proved by X-ray crystal structure analysis (Figure 2). The coupling product of the *o*,*o*′-disubstituted iodoarene **33d** underwent [4+2] cycloaddition only with methyl (**17a**) and not with *tert*-butyl acrylate (**17e**), and a significant amount (39 %) of the unreacted 1-(2′,6′-dimethylphenyl)allylidenecyclopropane was isolated.



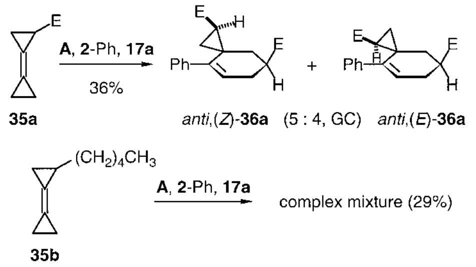
Scheme 8. Heck–Diels–Alder reactions of **1** with substituted iodoarenes **33** and methyl (**17a**) or *tert*-butyl acrylate (**17e**). **A**: Pd(OAc)$_2$, PPh$_3$, K$_2$CO$_3$, Et$_4$NCl, MeCN, 80 °C, 48 h. For details see Table 2.

Table 2. Heck–Diels–Alder reactions of **1** with substituted iodoarenes **33**. See Schemes 4 and 8.

ArI	R^1	R^2	R^3	Dienophile	Product	Yield [%]	Isomer ratio *anti*/*syn*
33a	Me	H	H	**17a**	**34aa**	99	2.0:1
33a	Me	H	H	**17e**	**34ea**	76[a]	3.0:1
33b	Bn	H	H	**17a**	**34ab**	85	2.0:1
33b	Bn	H	H	**17e**	**34eb**	39[a]	3.0:1
33c	Me	Me	H	**17a**	**34ac**	98	2.5:1
33c	Me	Me	H	**17e**	**34ec**	16[a]	2.7:1
33d	Me	H	Me	**17a**	**34ad**	56[b]	–

[a] Along with traces of the corresponding cinnamic acid esters formed by direct coupling of **33** with **17**. [b] Along with 22 % of the corresponding allylidenecyclopropane formed from **1** and **33d**.

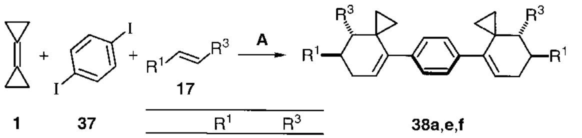
Eventually, substituted bicyclopropylidenes **35** were used in the Heck–Diels–Alder sequence (Scheme 9). In this case, depending on the regio- and stereochemical differentiation in the initial attack of the arylpalladium species on **35**, up to four different regioisomers are possible.[24] With the easily accessible[25] methyl bicyclopropylidenecarboxylate (**35a**), surprisingly, only two diastereomeric products *anti*,(*Z*)-**36a** and *anti*,(*E*)-**36a** (36 %, 5:4 according to GC) stemming from the opening of the unsubstituted cyclopropane ring were isolated, none of the other isomers was detected by NMR spectroscopy in the crude product. NOESY NMR measurements disclosed that in both stereoisomers the ester group on the cyclopropane ring is orientated towards the phenyl substituent. In contrast, the reaction of the alkyl-substituted *n*-pentylbicyclopropylidene (**35b**) led to a complex mixture of isomers and stereoisomers (29 % yield), in this case the NMR spectrum



Scheme 9. Heck–Diels–Alder reaction with substituted bicyclopropylidenes **35**. **A**: Pd(OAc)$_2$, PPh$_3$, K$_2$CO$_3$, Et$_4$NCl, MeCN, 80 °C, 48 h. E = CO$_2$Me.

showed signals indicating that also the substituted ring had been opened in the course of the reaction.

The extension of this new domino three-component reaction to oligoiodoarenes was also examined. Treatment of 1,4-diiodobenzene (**37**) in the presence of the palladium catalyst system, with bicyclopropylidene (**1**) and a dienophile **17**, gave the products **38** of a twofold Heck–Diels–Alder reaction in good yields (Scheme 10, Table 3). Under high pressure the yield of **38a** could be raised to 87 %. Performing the reaction at lower concentrations (0.2 M) of the starting materials yielded the mono-coupling-cycloaddition products **18**-C_6H_4I predominantly along with only small amounts of **38**. Surprisingly, the product **38a** was formed as a single diastereomer, as proved by an X-ray crystal structure analysis.[26] Even the crude product showed only a single set of signals in the ^{13}C NMR spectrum.



Scheme 10. Twofold Heck–Diels–Alder reaction of bicyclopropylidene (**1**) with 1,4-diiodobenzene (**37**). **A**: $Pd(OAc)_2$, PPh_3, K_2CO_3, Et_4NCl, MeCN, 80 °C. For details see Table 3.

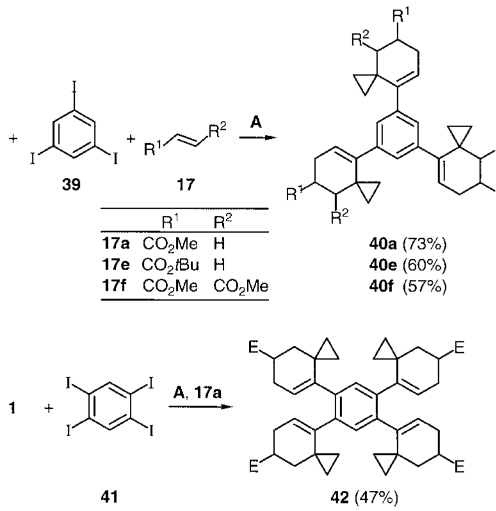
Table 3. Heck–Diels–Alder reaction of bicyclopropylidene (**1**) with 1,4-diiodobenzene (**37**) and alkyl acrylates **17a**, **e**, **f**.

Dienophile	Conditions[a]	Time [h]	Product	Yield [%]
17a	**A**	48	**38a**	64
17a	**B**	24	**38a**	87
17a	**C**	21	**18a**-C_6H_4I	45
			38a	8
17e	**A**	48	**38e**	69
17e	**B**	24	**38e**	60
17e	**C**	72	**18e**-C_6H_4I	50
			38e	6
17f	**A**	48	**38f**	54
17f	**B**	24	**38f**	60

[a] **A**: $Pd(OAc)_2$, PPh_3, K_2CO_3, Et_4NCl, MeCN, 80 °C, one step. **B**: $Pd(OAc)_2$, PPh_3, Et_3N, DMF, 80 °C, 10 kbar, one step. **C**: As in **B**, decreased concentration (0.2 M), 1 bar.

Even the reaction of **1** with 1,3,5-triiodobenzene (**39**) and a dienophile **17** gave excellent results: In these formal seven-component reactions yields of up to 60 % of the nominally C_3-symmetrical products **40** were achieved. Finally, with 1,2,4,5-tetraiodobenzene (**41**) twelve new carbon–carbon bonds were formed in one synthetic operation to give the fourfold cross-coupling cycloadduct **42** in 47 % yield (Scheme 11). This result shows that this unprecedented assembly of nine highly reactive small molecules proceeds smoothly and completely selectively. Nine component all-carbon-carbon bond forming reactions have been, if at all, scarcely ever been observed.

In order to probe the unique features of bicyclopropylidene (**1**), some other tetrasubstituted alkenes with alkylidenecycloalkane units were tested in the palladium-catalyzed coupling with iodobenzene (**2**-Ph) (Scheme 12). Such tetrasubstituted alkenes are readily accessible in good yields by Wittig olefinations of the corresponding ketones with in situ formed cycloalkylidenephosphoranes.[27]

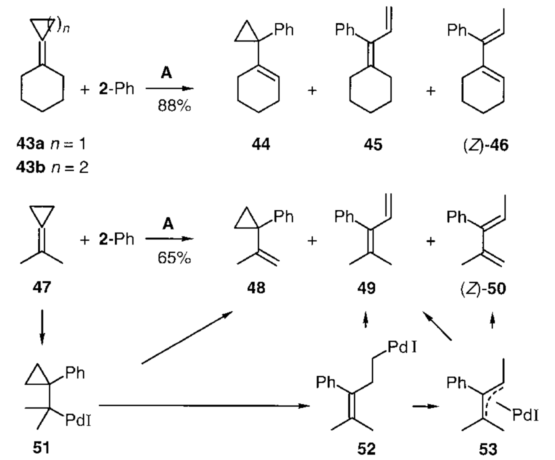


Scheme 11. Multicomponent domino reactions of **1** with 1,3,5-triiodobenzene (**39**) as well as 1,2,4,5-tetraiodobenzene (**41**) and dienophiles **17**. **A**: $Pd(OAc)_2$, PPh_3, K_2CO_3, Et_4NCl, MeCN, 80 °C, 2–3 d; E = CO_2Me.

The reaction of cyclopropylidenecyclohexane (**43a**) with **2**-Ph under Heck conditions [$Pd(OAc)_2$, PPh_3, Et_3N, DMF, 80 °C, 12 h] gave the three isomeric olefins **44**, **45** (isolated as an unseparable 1:1 mixture, 35 % yield) and (*Z*)-**46**[28] (53 %). The reaction of isopropylidenecyclopropane (**47**) with **2**-Ph under the same conditions gave 1-phenyl-1-(2′-propenyl)cyclopropane (**48**) (5 %), 4-methyl-3-phenyl-1,3-pentadiene (**49**)[28] and 2-methyl-3-phenyl-1,3-pentadiene [(*Z*)-**50**] (obtained as an unseparable 1.7:1 mixture, 60 % yield). Cyclobutylidenecyclohexane (**43b**) did not react with **2**-Ph under the applied conditions and could be completely recovered. The alkene **43b** was also left unchanged when it was added to a reacting mixture of **43a** and **2**-Ph.

Apparently, these transformations of **43a** and **47** start with a regioselective carbopalladation of the double bond in such a way that the phenyl group is attached at the less sterically demanding cyclopropane ring. The resulting cyclopropylmethylpalladium iodide of type **51** then rapidly rearranges to the homoallylpalladium iodide of type **52**, which, by β-hydride elimination yields **49**. The dienes (*Z*)-**46** and (*Z*)-**50** must arise by deprotonation of a π-allylpalladium iodide of type **53** (Scheme 12), probably formed by β-dehydropalladation of **52** with rehydridopalladation. Proton abstraction from **53** can also lead to **49**, while **48** is formed by β-dehydropalladation from **51** without rearrangement.[29]

Thus, the domino Heck–Diels–Alder reaction of bicyclopropylidene (**1**) with a variety of aryl as well as alkenyl halides and dienophiles is indeed unique in terms of regioselectivity, achievable yields and versatility. This new three-component reaction holds a high potential for combinatorial applications, since various hetero-dienophiles[30] and acceptor-substituted bicyclopropylidenes can be employed. Its suitability for solid-phase synthesis has already been demonstrated.[25] The resulting spiro[2.5]octene derivatives can be further elaborated, for example the 4-ethenyl derivative **18**-Vin might be used as a precursor to carotenoid analogues[31] in which the



Scheme 12. Heck reactions with tetrasubstituted alkenes other than bicyclopropylidene (**1**). **A**: Pd(OAc)$_2$, PPh$_3$, Et$_3$N, DMF, 75 °C.

spirocyclopropane unit mimics a *gem*-dimethyl group. Spiro[2.5]octene substructures are also present in various natural products such as the cytotoxic illudines, carcinogenic ptaquilosides or the antibiotic leaianafulvene.[32] Therefore, the presented chemistry is set for applications in combinatorial and natural product synthesis.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were recorded with Bruker AW 250 or Inova-500 instruments at 250 or 500 MHz and 62.9 or 125.7 MHz, respectively. Chemical shifts in CDCl$_3$ or [D$_6$]benzene are reported in δ (ppm) relative to tetramethylsilane (TMS), chloroform or benzene as internal reference unless otherwise stated. IR spectra were recorded with a Perkin–Elmer 1720 FTIR or a Bruker IFS 66. Low resolution EI mass spectra were obtained on a Varian MAT 731 with Varian Aerograph 1740 with an ionizing voltage of 70 eV. High resolution MS were obtained with a VG-70-250S. Elemental analyses were performed by the Mikroanalytisches Laboratorium der Universität Göttingen (Germany). Melting points are uncorrected. Solvents for extraction and chromatography were technical grade and distilled before use. Flash chromatography was performed using Merck silica gel 60 (200–400 mesh). Analytical gas chromatography (GC) was performed using a Siemens Sichromat 4 equipped with a 25 m capillary column coated with CP-Sil-55-5B. All reactions were carried out under an atmosphere of anhydrous nitrogen or argon in oven- and/or flame-dried glassware. Acetonitrile was dried over phosphorus pentoxide, DMF and CH$_2$Cl$_2$ were distilled from CaH$_2$. Bicyclopropylidene (**1**) and isopropylidenecyclopropane (**47**) were prepared according to de Meijere et al.[7]

General procedure for the Heck reaction on methylenecyclopropane derivatives and bicyclopropylidene (1) (GP 1): A 50 mL Pyrex-bottle containing anhydrous DMF (10 mL) was charged under argon with palladium(II) acetate (11.2 mg, 49.9 µmol) and triphenylphosphane (39.3 mg, 150 µmol). argon was bubbled through the mixture for 5 min and the mixture was treated with 1.00 mmol of the respective aryl or alkenyl halide, triethylamine (202 mg, 2.00 mmol) and 2.00 mmol of the respective alkene. After the reaction mixture had been stirred for the given time at the stated temperature it was cooled to ambient temperature, extracted with pentane (5 × 20 mL); the combined organic phases were washed with water (15 mL) and dried (MgSO$_4$). After removal of the solvent in a rotatory evaporator the residue was subjected to chromatography on silica gel eluting with pentane.

General procedure for the Heck–Diels–Alder reaction on methylenecyclopropane derivatives and bicyclopropylidene (1), one-pot, two steps (GP 2): A 50 mL Pyrex-bottle containing anhydrous DMF (10 mL) was charged under argon with palladium(II) acetate (11.2 mg, 49.9 µmol) and triphenylphosphane (39.3 mg, 150 µmol), argon was bubbled through the mixture for 5 min and the mixture treated with 1.00 mmol of the respective aryl or alkenyl halide, triethylamine (202 mg, 2.00 mmol) and 2.00 mmol of the respective alkene. After the reaction mixture had been stirred for the given time at the stated temperature, the bottle was cooled to ambient temperature, the corresponding dienophile (2.00 mmol) added, and then the mixture was stirred for additional time at the given temperature. The solution was added to water (10 mL), extracted with diethyl ether (5 × 20 mL), the combined organic phases washed with water (4 × 10 mL) and NaCl solution (10 mL) and dried (MgSO$_4$). After removal of the solvent in a rotatory evaporator the residue was subjected to chromatography on silica gel.

General procedure for the Heck–Diels–Alder reaction on methylenecyclopropane derivatives and bicyclopropylidene (1), one-pot, one step, Heck conditions (GP 3): A 5 mL sealable bottle with anhydrous DMF (1 mL) was charged under argon with palladium(II) acetate (11.2 mg, 49.9 µmol) and triphenylphosphane (39.3 mg, 150 µmol). Argon was bubbled through the mixture for 5 min and the mixture was treated with 1.00 mmol of the respective aryl or alkenyl halide, triethylamine (202 mg, 2.00 mmol), 2.00 mmol of the respective alkene and 2.00 mmol of the respective dienophile. After having stirred the mixture for the given time at the stated temperature the mixture was cooled to ambient temperature, the solution added to water and extracted with diethyl ether (5 × 20 mL). The combined organic phases were washed with water (4 × 10 mL) and NaCl solution (10 mL) and dried (MgSO$_4$). After removal of the solvent in a rotatory evaporator the residue was subjected to chromatography on silica gel.

General procedure for the Heck–Diels–Alder reaction on methylenecyclopropane derivatives and bicyclopropylidene (1), one-pot, two steps, alkenylsulfonates (GP 4): A 50 mL Pyrex-bottle was charged under argon with anhydrous acetonitrile (10 mL) and treated with tetrakis(triphenylphosphano)palladium (57.8 mg, 50.0 µmol). Argon was bubbled through the mixture for 5 min and then it was treated with cyclohexenylnonaflate (**8**-ONf, 380 mg, 1.00 mmol), triethylamine (202 mg, 2.00 mmol) and 2.00 mmol of the respective alkene. After having stirred the mixture for the given time at the stated temperature the bottle was cooled to ambient temperature, the corresponding dienophile (2.00 mmol) added, and then the mixture was stirred for additional time at the given temperature. Water was added and the aqueous phase was extracted with diethyl ether (5 × 20 mL). The combined organic phases were washed with water (4 × 10 mL), NaCl solution (10 mL) and dried (MgSO$_4$). After removal of the solvent in a rotatory evaporator the residue was subjected to chromatography on silica gel.

General procedure for the Heck–Diels–Alder reaction on bicyclopropylidene (1), one-pot, one step, Jeffery conditions (GP 5): A 5 mL sealable bottle was charged with anhydrous acetonitrile (1 mL), K$_2$CO$_3$ (277 mg, 2.00 mmol) and Et$_4$NCl (166 mg, 1.00 mmol). Argon was bubbled through the mixture for 5 min. After the reaction mixture was stirred for another 10 min, palladium(II) acetate (11.2 mg, 49.9 µmol), triphenylphosphane (39.3 mg, 150 µmol), 1.00 mmol of the respective aryl or alkenyl halide, bicyclopropylidene (**1**, 160 mg, 2.00 mmol) and 2.00 mmol of the respective dienophile were added. After the reaction mixture had been stirred for the given time at the stated temperature the bottle was cooled to ambient temperature, diethyl ether (50 mL) was added, the mixture washed with water (5 × 25 mL) and dried (MgSO$_4$). After removal of the solvent in a rotatory evaporator the residue was subjected to chromatography on silica gel.

General procedure for the Heck–Diels–Alder reaction on bicyclopropylidene (1), one-pot, one step, high pressure conditions (GP 6): A sealable Teflon tube with anhydrous DMF (5 mL) was charged under argon with palladium(II) acetate (11.2 mg, 49.9 µmol) and triphenylphosphane (39.3 mg, 150 µmol). Argon was bubbled through the mixture for 5 min and the mixture was treated with 1.00 mmol of the respective aryl halide, triethylamine (202 mg, 2.00 mmol), bicyclopropylidene (**1**, 160 mg, 2.00 mmol) and 2.00 mmol of the respective dienophile. After heating at the given temperature for the given time at 10 kbar, the solution was cooled to ambient temperature, added to water (50 mL) and extracted with diethyl ether (5 × 20 mL). The combined organic phases were washed with water (4 × 10 mL), NaCl solution (10 mL) and being dried (MgSO$_4$). After removal of the solvent in a rotatory evaporator the residue was subjected to chromatography on silica gel.

1-Cyclopropylidene-1-phenylpropene (5-Ph): According to GP 1, bicyclopropylidene (**1**, 160 mg, 2.00 mmol), iodobenzene (**2**-Ph, 204 mg, 1.00 mmol), palladium(II) acetate (11.2 mg, 49.9 μmol), triphenylphosphane (39.3 mg, 150 μmol) and triethylamine (202 mg, 2.00 mmol) were heated in anhydrous DMF (5 mL) for 4 h at 100 °C. Work-up and chromatography on silica gel (column 1 × 20 cm, pentane) yielded **5**-Ph as a colorless oil (122 mg, 78 %), which polymerized upon standing at ambient temperature. $R_f = 0.42$ (pentane); IR (film): $\tilde{\nu} = 3111$, 3047, 3014, 2951, 2913, 2860, 1680 (C=C), 1513, 1368, 1237, 1078, 911, 831, 762, 737, 704, 649 cm^{-1}; ^{1}H NMR (250 MHz, C_6D_6): $\delta = 7.40 - 7.20$ (m, 5H; Ar-H), 6.25 (dd, $^3J = 17.0$, $^3J = 10.6$ Hz, 1H; CH$_2$=C*H*), 4.90 (dd, $^2J_{AB} = 2.3$, $^3J = 17.0$ Hz, 1H; C*H*$_2$=CH), 4.70 (dd, $^2J_{AB} = 2.3$, $^3J = 10.6$ Hz, 1H; C*H*$_2$=CH), 1.00 – 0.80 (m, 4H; *c*Pr-H); ^{13}C NMR (125.7 MHz, CDCl$_3$): $\delta = 139.6$ (C$_{quat}$), 134.6 (+, *C*H=C), 132.8 (C$_{quat}$), 128.8 (+, Ar-C), 127.9 (+, Ar-C), 127.3 (+, Ar-C), 112.4 (C$_{quat}$, C=C), 111.9 (−, CH$_2$), 6.4 (−, CH$_2$), 4.2 (−, CH$_2$); MS (70 eV, EI): *m*/*z* (%): 156 (82) [M^+], 141 (56) [$M^+ - CH_3$], 128 (66) [$M^+ - C_2H_4$], 115 [$M^+ - C_3H_5$]; HRMS: *m*/*z* (%): calcd for $C_{12}H_{12}$: 156.0939; found: 156.0939.

Dimerization of bicyclopropylidene (1)

***trans*-1-(3″-Cyclopropylidenepropen-1″-yl)-1-(propen-3′-yl)cyclopropane (11)**, ***cis*-1-(3″-cyclopropylidenepropen-1′-yl)-1-(propen-3′-yl)cyclopropane (12)**, **3-[1′-(propen-3″-yl)cyclopropyl]-1,3,5-hexatriene (13)**, **and 1-[1′-(propen-3″-yl)cyclopropyl]-1,3,5-hexatriene (14)**: Under argon, a mixture of bicyclopropylidene (**1**, 400 mg, 469 μL, 5.00 mmol), Pd(OAc)$_2$ (56 mg, 0.25 mmol, 5 mol %) and PPh$_3$ (131 mg, 0.500 mmol) was heated under stirring in anhydrous benzene (5 mL) at 80 °C for 2 h, then cooled and concentrated under reduced pressure. Column chromatography (50 g silica gel, 120 × 2 cm column, hexane, $R_f = 0.48$) gave a mixture of $C_{12}H_{16}$ hydrocarbons (290 mg, 72.5 %) which according to GC analysis contained **11** (48.3 %), **12** (15.2 %), **13** (19.3 %), and **14** (17.2 %). This corresponds to yields of 35, 11, 14, and 12.5 %, respectively. The analytical samples were prepared by preparative gas chromatography (20 % SE 30 on Chromosorb W-AW-DMCS, 2000 mm × 8.2 mm column, 135 °C).

Compound **11**: ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 6.35$ (dm, $^3J = 11.3$ Hz, 1H; =CH), 6.14 (dd, $^3J = 16.1$, $^3J = 11.3$ Hz, 1H; =CH), 5.69 – 5.91 (m, 1H; =CH), 5.47 (d, $^3J = 16.1$ Hz, 1H; =CH), 5.07 (dd, $^3J = 15.2$, $^2J = 1.0$ Hz, 1H; =CH$_2$), 5.02 (dd, $^3J = 8.0$, $^2J = 1.0$ Hz, 1H; =CH$_2$), 2.22 (d, $^3J = 8.1$ Hz, 2H; CH$_2$), 1.09 (brs, 4H; *c*Pr-H), 0.65 (brs, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, CDCl$_3$): $\delta = 138.0$ (+, C-3″), 136.2 (+, C-2″), 126.1 (+, C-1″), 123.7 (C$_{quat}$, *c*Pr-C), 118.9 (+, C-2′), 116.2 (−, C-1′), 40.0 (−, C-3′), 21.2 (C$_{quat}$, *c*Pr-C), 14.1 (−, 2 *c*Pr-C), 2.5 (−, *c*Pr-C), 2.2 (−, *c*Pr-C); MS (EI): *m*/*z* (%): 160 (19) [M^+], 145 (10) [$M^+ - H - CH_2$], 132 (9) [$M^+ - C_2H_4$], 131 (21) [$M^+ - H - C_2H_4$], 117 (36) [$M^+ - H - CH_2 - C_2H_4$], 105 (38) [$C_8H_9^+$], 92 (20) [$C_7H_8^+$], 91 (100) [$C_7H_7^+$], 79 (77) [$C_6H_7^+$], 77 (65) [$C_6H_5^+$]; HRMS: *m*/*z* (%): calcd for $C_{12}H_{16}$: 160.1252; found: 160.1252.

Compound **12**: ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 6.35$ (dm, $^3J = 11.3$ Hz, 1H; =CH), 6.13 (dd, $^3J = 10.5$, $^3J = 11.3$ Hz, 1H; =CH), 5.92 – 5.76 (m, 1H; =CH), 5.55 (d, $^3J = 10.5$ Hz, 1H; =CH), 5.05 (dd, $^2J = 1.0$, $^3J = 17.0$ Hz, 1H; =CH$_2$), 5.00 (dd, $^2J = 1.0$, $^3J = 8.0$ Hz, 1H; =CH$_2$), 2.16 (d, $^3J = 7.0$ Hz, 2H; CH$_2$), 1.13 (dm, $^3J = 7.5$ Hz, 4H; *c*Pr-H), 0.60 (brs, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, CDCl$_3$): $\delta = 136.4$ (+, =CH), 132.5 (+, =CH), 129.8 (+, =CH), 126.8 (C$_{quat}$, *c*Pr-C), 115.9 (+, C-2′), 115.6 (−, C-1′), 43.4 (−, C-3′), 19.5 (C$_{quat}$, *c*Pr-C), 12.9 (−, 2 *c*Pr-C), 2.6 (−, *c*Pr-C), 1.8 (−, *c*Pr-C); the mass spectrum is analogous to the previous one; HRMS: *m*/*z* (%): calcd for $C_{12}H_{16}$: 160.1252; found: 160.1252.

Compound **13** (a 6.2:1 mixture of isomers): Major isomer: ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 6.73$ (ddd, $^3J = 17.0$, $^3J = 12.0$, $^3J = 8.6$ Hz, 1H; =CH), 6.05 (d, $^3J = 12.0$, 1H; =CH), 5.88 – 5.72 (m, 1H; =CH), 5.65 (dd, $^3J = 17.1$, $^3J = 9.5$ Hz, 1H; =CH), 5.26 – 4.76 (m, 6H; 3 =CH$_2$), 2.11 (d, $^3J = 7.5$ Hz, 2H; CH$_2$), 0.55 (brs, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, CDCl$_3$): $\delta = 139.0$ (C$_{quat}$, C-3), 136.5 (+, =CH), 134.3 (+, =CH), 132.2 (+, =CH), 131.7 (+, =CH), 117.9 (−, =CH$_2$), 116.0 (−, =CH$_2$), 115.7 (−, =CH$_2$), 41.8 (−, C-3″), 18.8 (C$_{quat}$, *c*Pr-C), 11.6 (−, 2 *c*Pr-C); the signals of the minor isomer are covered by the signals of the major diastereomer or are indistinguishable; HRMS: *m*/*z* (%): calcd for $C_{12}H_{16}$: 160.1252; found: 160.1252.

Compound **14** (a mixture of isomers): Major (*trans*,*trans*-isomer): ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 6.55 - 6.51$ (m, 1H; =CH), 6.37 (dd, $^3J = 16.6$, $^3J = 10.8$ Hz, 1H; =CH), 6.14 (dd, $^3J = 16.6$, $^3J = 8.5$ Hz, 1H; =CH), 5.99 (dd, $^3J = 15.7$, $^3J = 8.5$ Hz, 1H; =CH), 5.86 – 5.68 (m, 1H; =CH), 5.47 (d, $^3J = 15.7$ Hz, 1H; =CH), 5.19 (dd, $^3J = 17.5$, $^3J = 9.5$ Hz, 2H; =CH$_2$), 5.05 (ddd, $^3J = 17.0$, $J = 9.8$, $^4J = 1.7$ Hz, 2H; =CH$_2$), 2.23 (d, $^3J = 6.5$ Hz, 2H; CH$_2$), 0.67 (dm, $^3J = 8.0$ Hz, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, CDCl$_3$): $\delta = 141.4$ (+, =CH), 137.2 (+, =CH), 136.0 (+, =CH), 133.6 (+, =CH), 130.6 (+, =CH), 126.6 (+, =CH), 116.3 (−, =CH$_2$), 116.0 (−, =CH$_2$), 38.7 (−, C-3′), 21.4 (C$_{quat}$, *c*Pr-C), 14.5 (−, *c*Pr-C); the signals of the minor isomers are covered by the signals of the major diastereomer or are indistinguishable; MS (EI): *m*/*z* (%): 160 (48) [M^+], 145 (20) [$M^+ - H - CH_2$], 132 (10) [$M^+ - C_2H_4$], 131 (26) [$M^+ - H - C_2H_4$], 119 (34), 117 (55) [$M^+ - H - CH_2 - C_2H_4$], 105 (20) [$C_8H_9^+$], 92 (18) [$C_7H_8^+$], 91 (100) [$C_7H_7^+$], 79 (19) [$C_6H_7^+$], 77 (35) [$C_6H_5^+$]; HRMS: *m*/*z* (%): calcd for $C_{12}H_{16}$: 160.1252; found: 160.1252.

8-(Cyclopropylidene)dispiro[2.0.2.3]nonane (16): Under argon, a mixture of bicyclopropylidene (**1**, 86 mg, 1.07 mmol), Pd(dba)$_2$ (15 mg, 0.026 mmol, 2.4 mol %) and triisopropylphosphane (4.2 mg, 5 μL, 0.026 mmol) was heated under stirring in anhydrous toluene (1 mL) at 110 °C for 4 h, cooled, concentrated under reduced pressure and purified by column chromatography (50 g silica gel, 20 × 2 cm column, hexane) to give **16** as an oil (41 mg, 48 %). $R_f = 0.62$ (hexane); ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 2.51$ (t, $^5J = 2.2$ Hz, 4H; 2 CH$_2$), 1.00 (p, $^5J = 2.2$ Hz, 4H; *c*Pr-H), 0.35 – 0.14 (m, AA′BB′, 8H; *c*Pr-H); ^{13}C NMR (62.9 MHz, CDCl$_3$): $\delta = 128.9$ (C$_{quat}$, *c*Pr-C), 110.8 (C$_{quat}$, =C), 41.6 (−, 2 CH$_2$), 26.2 (C$_{quat}$, 2 *c*Pr-C), 8.3 (−, 4 *c*Pr-C), 2.2 (−, 2 *c*Pr-C); MS (EI): *m*/*z* (%): 160 (3) [M^+], 159 (6) [$M^+ - H$], 145 (52) [$M^+ - H - CH_2$], 132 (26) [$M^+ - C_2H_4$], 131 (52) [$M^+ - H - C_2H_4$], 117 (85) [$M^+ - H - CH_2 - C_2H_4$], 105 (56) [$C_8H_9^+$], 92 (40) [$C_7H_8^+$], 91 (100) [$C_7H_7^+$]; HRMS: *m*/*z* (%): calcd for $C_{12}H_{16}$: 160.1252; found: 160.1252.

Methyl 8-phenylspiro[2.5]oct-7-ene-5-carboxylate (18a-Ph): a) According to GP 5, palladium(II) acetate (11.2 mg, 49.9 μmol), triphenylphosphane (39.3 mg, 150 μmol), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K$_2$CO$_3$ (277 mg, 2.00 mmol), Et$_4$NCl (166 mg, 1.00 mmol) and iodobenzene (**2**-Ph, 204 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with methyl acrylate (**17a**, 172 mg, 2.00 mmol) for 48 h at 80 °C. After work-up and being dried over MgSO$_4$ the solvent was removed in a rotatory evaporator. The residue was subjected to chromatography on 50 g silica gel (column 2 × 20 cm, pentane/diethyl ether 10:1) and yielded **18a**-Ph as a yellowish oil (241 mg, 100 %). $R_f = 0.45$ (pentane/diethyl ether 30:1); IR (film): $\tilde{\nu} = 3030$, 2990, 1730 (C=O), 1650 (C=C), 1575, 1510, 1100, 890, 830, 750, 730 cm^{-1}; ^{1}H NMR (250 MHz, C_6D_6): $\delta = 7.30 - 7.00$ (m, 5H; Ar-H), 5.53 (dd, $^3J_{6A\text{-}7} = 6.0$, $^3J_{6B\text{-}7} = 2.8$ Hz, 1H; 7-H), 3.85 (s, 3H; CH$_3$O), 2.86 (dddd, $^3J_{4A\text{-}5} = 2.9$, $^3J_{4B\text{-}5} = 11.6$, $^3J_{5\text{-}6A} = 6.0$, $^3J_{5\text{-}6B} = 9.9$ Hz, 1H; 5-H), 2.58 (ddd, $^2J_{AB} = 17.7$, $^3J_{5\text{-}6B} = 9.9$, $^3J_{6B\text{-}7} = 2.8$ Hz, 1H; 6-H$_B$), 2.42 (ddd, $^2J_{AB} = 17.7$, $^3J_{5\text{-}6A} = 6.0$, $^3J_{6A\text{-}7} = 6.0$ Hz, 1H; 6-H$_A$), 2.24 (ddd, $^2J_{AB} = 12.9$, $^3J_{4B\text{-}5} = 11.6$, $^4J_{4B\text{-}6B} = 1.4$ Hz, 1H; 4-H$_B$), 1.36 (ddd, $^2J_{AB} = 12.9$, $^3J_{4A\text{-}5} = 2.9$, $^4J_{4A\text{-}6} = 1.0$ Hz, 1H; 4-H$_A$), 0.73 (ddd, $^2J_{AB} = 3.9$, $^3J_{1A\text{-}2B} = 9.1$, $^3J_{1B\text{-}2B} = 5.2$ Hz, 1H; 2-H$_B$), 0.56 (ddd, $^2J_{AB} = 3.5$, $^3J_{1B\text{-}2A} = 9.8$, $^3J_{1B\text{-}2B} = 5.2$ Hz, 1H; 1-H$_B$), 0.44 (ddd, $^2J_{AB} = 3.9$, $^3J_{1A\text{-}2A} = 5.5$, $^3J_{1B\text{-}2A} = 9.8$ Hz, 1H; 2-H$_A$), 0.30 (ddd, $^2J_{AB} = 3.5$, $^3J_{1A\text{-}2A} = 5.5$, $^3J_{1A\text{-}2B} = 9.1$ Hz, 1H; 1-H$_A$); ^{13}C NMR (62.9 MHz, C_6D_6, DEPT): $\delta = 174.8$ (C$_{quat}$, CO), 143.0 (C$_{quat}$, C-8*), 140.4 (C$_{quat}$, Ar-C*), 129.2 (+, Ar-C), 128.1 (+, Ar-C), 126.6 (+, Ar-C), 124.0 (+, C-7), 50.8 (+, CH$_3$O), 39.3 (+, C-5), 37.5 (−, C-6), 28.6 (−, C-4), 20.0 (C$_{quat}$, C-3), 12.8 (−, C-2), 11.6 (−, C-1); MS (70 eV, EI): *m*/*z* (%): 242 (25) [M^+], 210 (65) [$M^+ - CH_4O$], 183 (100) [$M^+ - CO_2CH_3$], 91 (49) [$C_7H_7^+$]; HRMS: *m*/*z* (%): calcd for $C_{16}H_{18}O_2$: 242.1307; found: 242.1307.

b) According to GP 5, palladium(II) acetate (11.2 mg, 49.9 μmol), triphenylphosphane (39.3 mg, 150 μmol), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K$_2$CO$_3$ (277 mg, 2.00 mmol), Et$_4$NCl (166 mg, 1.00 mmol) and bromobenzene (**22**, 157 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with methyl acrylate (**17a**, 172 mg, 2.00 mmol) for 48 h at 80 °C. After work-up the residue was subjected to chromatography on 50 g silica gel (column 2 × 20 cm, pentane/diethyl ether 10:1) and yielded **18a**-Ph as a yellowish oil (144 mg, 59 %).

c) According to GP 3, palladium(II) acetate (27.0 mg, 120 μmol, 1 mol %), triphenylphosphane (94.2 mg, 360 μmol, 3 mol %), bicyclopropylidene (**1**, 1.92 g, 24.0 mmol), K$_2$CO$_3$ (1.66 g, 12.0 mmol), Et$_4$NCl (966 mg, 5.8 mmol) and iodobenzene (**2**-Ph, 2.45 g, 12.0 mmol) were stirred in anhydrous acetonitrile (3 mL) with methyl acrylate (**17a**, 2.07 g, 24.0 mmol) for 48 h at 80 °C. After work-up, the crude product was subjected to chromatography on 50 g silica gel (column 2 × 20 cm, pentane/diethyl ether 10:1) and yielded **18a**-Ph as a yellowish oil (2.86 g, 99 %).

d) According to GP 5, palladium(II) acetate (11.2 mg, 49.9 μmol, 5 mol %), triphenylphosphane (39.2 mg, 150 μmol, 15 mol %), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K$_2$CO$_3$ (277 mg, 2.00 mmol), Et$_4$NCl (166 mg, 1.00 mmol) and bromobenzene (**22**, 157 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with methyl acrylate (**17a**, 172 mg, 2.00 mmol) for 48 h at 80 °C. After work-up, chromatography of the crude product on 50 g silica gel (column 2 × 20 cm, pentane/diethyl ether 10:1) gave:

Fraction I: Methyl cinnamate (**23**) as a colorless oil (26 mg, 16 %); $R_f = 0.58$ (pentane/diethyl ether 10:1).

Fraction II: **18a**-Ph as a yellowish oil (144 mg, 59 %); $R_f = 0.50$ (pentane/diethyl ether 10:1).

Methyl 8-ethenylspiro[2.5]oct-7-ene-5-carboxylate (18a-Vin): According to GP 2, iodoethene (**6**, 154 mg, 1.00 mmol), bicyclopropylidene (**1**, 320 mg, 3.99 mmol), palladium(II) acetate (11.2 mg, 49.9 µmol), triphenylphosphane (39.3 mg, 150 µmol) and triethylamine (202 mg, 2.00 mmol) were heated in anhydrous DMF (10 mL) at 75 °C for 20 h. After cooling, methyl acrylate (**17a**, 172 mg, 2.00 mmol) was added and stirred for additional 20 h at ambient temperature. After work-up, chromatography of the crude product on silica gel (column 2 × 20 cm, pentane → pentane/diethyl ether 50:1) gave:

Fraction I: A mixture (100 mg) of polymers and **7**-H, solvents not completely evaporated; $R_f = 0.8-0.5$ (pentane).

Fraction II: **18a**-Vin as a colorless oil (125 mg, 65 %); $R_f = 0.35$ (pentane/diethyl ether 10:1); IR (film): $\tilde{\nu} = 2990$, 1730 (C=O), 1650 (C=C), 1100, 890, 840, 730 cm^{-1}; ^{1}H NMR (250 MHz, C_6D_6): $\delta = 5.81$ (dd, $^3J_{6A\text{-}7} = 5.4$, $^3J_{6B\text{-}7} = 3.0$ Hz, 1H; 7-H), 5.75 (dd, $^3J = 10.6$, $^3J = 17.0$ Hz, 1H; 1′-H), 5.27 (dd, $^2J_{AB} = 2.3$, $^3J = 17.0$ Hz, 1H; 2′-H_B), 4.85 (dd, $^2J_{AB} = 2.3$, $^3J = 10.6$ Hz, 1H; 2′-H_A), 3.85 (s, 3H; OCH_3), 2.71 (dddd, $^3J_{4A\text{-}5} = 2.9$, $^3J_{4B\text{-}5} = 11.6$, $^3J_{5\text{-}6A} = 5.0$, $^3J_{5\text{-}6B} = 10.0$ Hz, 1H; 5-H), 2.52 (ddd, $^2J_{AB} = 17.8$, $^3J_{5\text{-}6B} = 10.0$, $^3J_{6B\text{-}7} = 3.0$ Hz, 1H; 6-H_B), 2.31 (ddd, $^2J_{AB} = 17.8$, $^3J_{5\text{-}6A} = 5.0$, $^3J_{6A\text{-}7} = 5.4$ Hz, 1H; 6-H_A), 2.11 (dd, $^2J_{AB} = 12.9$, $^3J_{4B\text{-}5} = 11.6$ Hz, 1H; 4-H_B), 1.36 (dd, $^2J_{AB} = 12.9$, $^3J_{4A\text{-}5} = 2.9$ Hz, 1H; 4-H_A), 0.90 (ddd, $^2J_{AB} = 4.6$, $^3J_{1A\text{-}2B} = 9.4$, $^3J_{1B\text{-}2B} = 5.9$ Hz, 1H; 2-H_B), 0.65 (ddd, $^2J_{AB} = 4.3$, $^3J_{1B\text{-}2A} = 10.4$, $^3J_{1B\text{-}2B} = 5.9$ Hz, 1H; 1-H_B), 0.40 (ddd, $^2J_{AB} = 4.6$, $^3J_{1A\text{-}2A} = 5.6$, $^3J_{1B\text{-}2A} = 10.4$ Hz, 1H; 2-H_A), 0.25 (ddd, $^2J_{AB} = 4.3$, $^3J_{1A\text{-}2A} = 5.6$, $^3J_{1A\text{-}2B} = 9.4$ Hz, 1H; 1-H_A); ^{13}C NMR (62.9 MHz, C_6D_6, DEPT): $\delta = 174.2$ (C_{quat}, CO), 139.4 (C_{quat}, C-8), 139.4 (C_{quat}, C-8), 134.6 (+, CH=*), 121.6 (+, C-7*), 114.8 (−, CH_2), 51.1 (+, CH_3O), 39.3 (+, C-5), 37.7 (−, C-6), 28.9 (−, C-4), 19.5 (C_{quat}, C-3), 13.5 (−, C-2), 11.3 (−, C-1); MS (70 eV, EI): *m*/*z* (%): 192 (20) [M^+], 160 (65) [$M^+ - CH_4O$], 133 (100) [$M^+ - CO_2CH_3$]; HRMS: *m*/*z* (%): calcd for $C_{12}H_{16}O_2$: 192.1150; found: 192.1150.

Methyl 8-(4′-methylphenyl)spiro[2.5]oct-7-ene-5-carboxylate (18a-Tol): a) According to GP 3, palladium(II) acetate (11.2 mg, 49.9 µmol, 5 mol %), triphenylphosphane (39.2 mg, 150 µmol, 15 mol %), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), *para*-iodotoluene (**2**-Tol, 218 mg, 1.00 mmol) and triethylamine (204 mg, 2.02 mmol) in anhydrous DMF (1 mL) were heated with methyl acrylate (**17a**, 172 mg, 2.00 mmol) for 2 d at 80 °C. After work-up, chromatography of the crude product on 50 g silica gel (column 2 × 20 cm, pentane/diethyl ether 10:1) yielded **18a**-Tol as a yellow oil (223 mg, 87 %). $R_f = 0.50$ (pentane/diethyl ether 10:1); IR (film): $\tilde{\nu} = 2998$, 2949, 1736 (C=O), 1636 (C=C), 1512, 1435, 1259, 1193, 1168, 1022, 820 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.07$ (d, $^3J = 7.9$ Hz, 2H; Ar-H), 6.94 (d, $^3J = 7.9$ Hz, 2H; Ar-H), 5.52 (t, $^3J = 3.8$ Hz, 1H; 7-H), 3.72 (s, 3H; OCH_3), 2.91 (ddt, $^3J = 11.8$, $^3J = 8.0$, $^3J = 3.0$ Hz, 1H; 5-H), 2.48 (dd, $^3J = 8.0$, $^3J = 3.8$ Hz, 2H; 6-H), 2.33 (s, 3H; Ar-CH_3), 2.20 (dd, $^2J = 12.9$, $^3J = 11.8$ Hz, 1H; 4-H), 1.50 (dd, $^2J = 12.9$, $^3J = 3.0$ Hz, 1H; 4-H), 0.69–0.38 (m, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 176.0$ (C_{quat}, CO), 142.8 (C_{quat}, Ar-C*), 137.2 (C_{quat}, Ar-C*), 136.1 (C_{quat}, C-8*), 129.0 (+, Ar-C), 128.1 (+, Ar-C), 123.6 (+, C-7), 51.6 (+, OCH_3), 39.3 (+, C-5), 37.4 (−, C-6), 28.5 (−, C-4), 21.1 (+, Ar-CH_3), 20.0 (C_{quat}, C-3), 12.8 (−, *c*Pr-C), 11.5 (−, *c*Pr-C); MS (70 eV): *m*/*z* (%): 256 (60) [M^+], 225 (14) [$M^+ - OCH_3$], 197 (100) [$M^+ - CO_2Me$], 181 (88) [$M^+ - CH_3 - MeOH - CO$], 169 (40), 155 (35); elemental analysis calcd (%) for $C_{17}H_{20}O_2$ (256.3): C 79.65, H 7.86; found: C 79.37, H 8.05.

b) According to GP 5, palladium(II) acetate (11.2 mg, 49.9 µmol, 5 mol %), triphenylphosphane (39.2 mg, 150 µmol, 15 mol %), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K_2CO_3 (277 mg, 2.00 mmol), Et_4NCl (166 mg, 1.00 mmol) and *para*-iodotoluene (**2**-Tol, 218 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with methyl acrylate (**17a**, 172 mg, 2.00 mmol) for 48 h at 80 °C. After work-up, chromatography of the crude product on 50 g silica gel (column 2 × 20 cm, pentane/diethyl ether 10:1) yielded **18a**-Tol as a yellow oil (233 mg, 91 %). $R_f = 0.63$ (pentane/diethyl ether 10:1).

Methyl 8-(3′-pyridinyl)spiro[2.5]oct-7-ene-5-carboxylate (18a-Py): According to GP 5, palladium(II) acetate (11.2 mg, 49.9 µmol, 5 mol %), triphenylphosphane (39.2 mg, 150 µmol, 15 mol %), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K_2CO_3 (277 mg, 2.00 mmol), Et_4NCl (166 mg, 1.00 mmol) and 3-iodopyridine (**2**-Py, 205 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with methyl acrylate (**17a**, 172 mg, 2.00 mmol) for 24 h at 80 °C. After work-up, chromatography of the crude product on 50 g silica gel (column 2 × 20 cm, diethyl ether) yielded **18a**-Py as a yellowish oil (163 mg, 67 %). $R_f = 0.74$ (diethyl ether); IR (film): $\tilde{\nu} = 3001$, 2950, 2927, 1734 (C=O), 1652 (C=C), 1636, 1436, 1262, 1195, 1173, 1027, 805, 720 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 8.44$ (dd, $^3J = 4.9$, $^4J = 1.9$ Hz, 1H; 4′-H), 8.28 (dd, $^4J = 2.0$, $^5J = 0.6$ Hz, 1H; 2′-H), 7.32 (ddd, $^3J = 7.7$, $^4J = 2.0$, $^4J = 1.9$ Hz, 1H; 6′-H), 7.15 (ddd, $^3J = 7.7$, $^3J = 4.9$, $^5J = 0.6$ Hz, 1H; 5′-H), 5.54 (t, $^3J = 3.9$ Hz, 1H; 7-H), 3.67 (s, 3H; OCH_3), 2.87 (ddt, $^3J = 11.6$, $^3J = 8.6$, $^3J = 3.0$ Hz, 1H; 5-H), 2.47 (dd, $^3J = 8.6$, $^3J = 3.9$ Hz, 2H; 6-H), 2.15 (dd, $^2J = 13.0$, $^3J = 11.6$ Hz, 1H; 4-H), 1.49 (dd, $^2J = 13.0$, $^3J = 3.0$ Hz, 1H; 4-H), 0.57–0.36 (m, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 175.6$ (C_{quat}, CO), 149.7 (+, C-6′*), 148.0 (+, C-2′*), 139.4 (C_{quat}, C-3′**), 136.4 (+, C-7), 135.5 (C_{quat}, C-8**), 125.8 (+, C-4′*), 122.4 (+, C-5′*), 51.6 (+, OCH_3), 39.0 (+, C-5), 37.1 (−, C-6), 28.3 (−, C-4), 20.0 (C_{quat}, C-3), 12.4 (−, *c*Pr-C), 11.1 (−, *c*Pr-C); MS (70 eV): *m*/*z* (%): 243 (28) [M^+], 228 (3) [$M^+ - CH_3$], 212 (9) [$M^+ - OCH_3$], 184 (100) [$M^+ - CO_2CH_3$], 168 (29), 156 (55), 132 (13); elemental analysis calcd (%) for $C_{15}H_{17}NO_2$ (243.3): C 74.05, H 7.04; found: C 74.34, H 7.32.

Dimethyl *cis*-8-phenylspiro[2.5]oct-7-ene-4,5-dicarboxylate (18b-Ph): In an NMR tube, **5**-Ph (50.0 mg, 320 µmol), dimethyl maleate (**17b**, 72.0 mg, 500 µmol) and hydroquinone (2 mg) were heated under nitrogen in $CDCl_3$ (0.5 mL) at 60 °C. In certain intervals the probe was cooled and a ^{1}H NMR spectrum recorded. After 30 min, a conversion of ca. 50 % was determined, while after 12 h complete conversion to **18b**-Ph was detected. The solvent was removed in vacuo and the residue was subjected to chromatography on silica gel (column 1 × 20 cm, hexane/diethyl ether 5:1) to yield **18b**-Ph as a colorless oil (66.5 mg, 69 %). $R_f = 0.13$ (hexane/diethyl ether 5:1); IR (film): $\tilde{\nu} = 3030$, 2990, 1730 (C=O), 1650 (C=C), 1575, 1510, 1100, 890, 830, 750, 730 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.35-7.15$ (m, 3H; Ar-H), 7.08–7.04 (m, 2H; Ar-H), 5.54 (dd, $^3J = 2.7$, $^3J = 4.6$ Hz, 1H; 7-H), 3.75 (s, 3H; OCH_3), 3.73 (s, 3H; OCH_3), 3.14 (ddd, $^3J = 3.6$, $^3J = 6.5$, $^3J = 11.3$ Hz, 1H; 5-H), 2.77 (ddd, $^2J = 18.5$, $^3J = 2.7$, $^3J = 11.3$ Hz, 1H; 6-H), 2.58 (d, $^3J = 3.6$ Hz, 1H; 4-H), 2.56 (ddd, $^2J = 18.5$, $^3J = 4.6$, $^3J = 6.5$ Hz, 1H; 6-H), 1.00–0.87 (m, 2H; *c*Pr-H), 0.60–0.47 (m, 2H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 173.9$ (C_{quat}, CO_2), 172.6 (C_{quat}, CO_2), 141.0 (C_{quat}, Ar-C*), 139.8 (C_{quat}, C-8*), 129.0 (+, 2 Ar-C), 127.5 (+, 2 Ar-C), 126.7 (+, Ar_{para}-C), 124.4 (+, C-7*), 51.9 (+, OCH_3), 51.7 (+, OCH_3), 50.7 (+, C-5*), 40.9 (+, C-4*), 25.4 (−, C-6), 23.0 (C_{quat}, C-3), 13.4 (−, C-2), 13.1 (−, C-1); MS (70 eV, EI): *m*/*z* (%): 300 (7) [M^+], 268 (15) [$M^+ - CH_4O$], 241 (81) [$M^+ - CO_2CH_3$], 209 (63) [$M^+ - CO_2CH_3 - CH_4O$], 181 (100) [$M^+ - 2\,CO_2CH_3 - H$]; HRMS: *m*/*z* (%): calcd for $C_{18}H_{20}O_4$: 300.1362; found: 300.1362.

Diethyl *trans*-spiro[2.5]oct-7-ene-4,5-dicarboxylate (18c-H): Under argon, an NMR tube was charged with bicyclopropylidene (**1**, 86 mg, 1.07 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol, 4.6 mol %), PPh_3 (26 mg, 0.10 mmol), AcOH (6 mg, 5.7 µL, 0.1 mmol) and Et_3N (10.1 mg, 13.9 µL, 0.10 mmol) in C_6D_6 (1 mL) and stirred at ambient temperature. The conversion of starting materials was monitored by ^{1}H NMR spectroscopy to be complete before the work-up. After 24 h, when the allylidenecyclopropane **15** had been formed in 55 % yield, the mixture was filtered through a pad of celite, diethyl fumarate (**17c**, 100 mg, 95 µL, 0.58 mmol) was added to the filtrate, and the obtained solution was heated at 80 °C for 1 h. After cooling and concentration under reduced pressure, the residue was purified by column chromatography (50 g silica gel, 15 × 1.5 cm column, hexane/Et_2O 4:1) to give the diester **18c**-H (66 mg, 45 %). $R_f = 0.20$ (hexane/Et_2O 4:1); b.p. 95 °C (1 Torr); IR (film): $\tilde{\nu} = 2982$, 1734, 1445, 1373, 1307, 1249, 1186, 1097, 1036, 975, 717 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 5.63$ (ddd, $^3J = 9.8$, $^3J = 4.3$, $^3J = 3.2$ Hz, 1H; 7-H), 5.00 (dt, $^3J = 9.8$, $^4J = 2.0$ Hz, 1H; 8-H), 4.17–4.00 (m, 4H; 2 OCH_2), 3.11 (ddd, $^3J = 9.0$, $^3J = 9.0$, $^3J = 5.5$ Hz, 1H; 5-H), 2.97 (d, $^3J = 9.0$ Hz, 1H; 4-H), 2.43 (dddd, $^2J = 17.7$, $^3J = 5.5$, $^3J = 4.3$, $^4J = 2.0$ Hz, 1H; 6-H), 2.28 (dddd, $^2J = 17.7$, $^3J = 9.0$, $^3J = 3.2$, $^4J = 2.0$ Hz, 1H; 6-H), 1.24 (t, $^3J = 7.1$ Hz, 3H; CH_3), 1.23 (t, $^3J = 7.2$ Hz, 3H; CH_3), 0.98–0.79 (m, 1H; *c*Pr-H), 0.72–0.69 (m, 1H; *c*Pr-H), 0.58–0.49 (m, 2H;

*c*Pr-H); ^{13}C NMR (62.9 MHz, CDCl$_3$): $\delta = 174.2$ (C$_{quat}$, CO), 172.3 (C$_{quat}$, CO), 133.8 (+, C-8), 122.6 (+, C-7), 60.33 (–, *C*H$_2$CH$_3$), 60.25 (–, *C*H$_2$CH$_3$), 46.8 (+, C-5), 41.4 (+, C-4), 26.6 (–, C-6), 18.3 (C$_{quat}$, *c*Pr-C), 14.0 (+, 2 CH$_3$), 12.9 (–, *c*Pr-C), 11.9 (–, *c*Pr-C); MS (EI): *m*/*z* (%): 252 (8) [M^+], 207 (20) [$M^+ - \mathrm{OC_2H_5}$], 206 (11) [$M^+ - \mathrm{H} - \mathrm{OC_2H_5}$], 179 (71) [$M^+ - \mathrm{CO_2C_2H_5}$], 151 (19) [$M^+ - \mathrm{C_2H_4} - \mathrm{CO_2C_2H_5}$], 133 (35), 105 (100) [$\mathrm{C_8H_9^+}$], 91 (23) [$\mathrm{C_7H_7^+}$], 79 (20) [$\mathrm{C_6H_7^+}$]; HRMS: *m*/*z* (%): calcd for $\mathrm{C_{14}H_{20}O_4}$: 252.1361; found: 252.1361; elemental analysis calcd (%) for $\mathrm{C_{14}H_{20}O_4}$ (252.3): C 66.64, H 7.99; found: C 66.92, H 8.29.

[3a*S*-[(1*R),3a*α*,6*α*,7a*β*]]-1-[(8-Ethenylspiro[2.5]oct-7-en-5-yl)carbonyl]-8,8-dimethyl-3a,6-methanohexahydro-3*H*-2,1-benzisothiazole-2,2-dioxide (18d-Vin)**: According to GP 2, bicyclopropylidene (**1**, 320 mg, 3.99 mmol), iodoethene (**6**, 154 mg, 1.00 mmol), palladium(II) acetate (11.2 mg, 49.9 μmol), triphenylphosphane (39.3 mg, 150 μmol) and triethylamine (202 mg, 2.00 mmol) were heated in DMF (10 mL) for 4 h at 100 °C, the mixture then stirred with (7′*R*)-1-(10′,10′-dimethyl-3′-thia-4′-azatricyclo[5.2.1.0^{1,5}]dec-4′-yl)prop-2-enon (**17d**, 270 mg, 1.00 mmol) for additional 4.5 h at 75 °C. Chromatography on silica gel (column 2 × 20 cm, pentane → pentane/ethyl acetate 1:1) gave three fractions:

Fraction I: Polymers and **7**-H, which had not completely evaporated; $R_f = 0.8 - 0.5$ (pentane).

Fraction II: **18d**-Vin as a colorless solid (130 mg, 35 %); m.p. 61 °C; $R_f = 0.25$ (petroleum ether/ethyl acetate 10:1); $[\alpha]_D^{20} = -14.9$ ($c = 1.0$ in CHCl$_3$); IR (KBr): $\tilde{\nu} = 2995$, 1715 (C=O), 1650 (C=C), 1175, 1100, 890, 830, 750, 735 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 6.08$ (dd, $^3J = 5.4$, $^3J = 3.0$ Hz, 1 H; CH=C), 5.81 (dd, $^3J = 17.0$, $^3J = 10.6$Hz, 1 H; C*H*=CH$_2$), 5.75 (dd, $^2J_{AB} = 2.3$, $^3J = 17.0$ Hz, 1 H; CH=C*H*$_2$), 5.50 (dd, $^2J_{AB} = 2.3$, $^3J = 10.6$ Hz, 1 H; CH=C*H*$_2$), 3.84 (dd, $^3J = 6.9$, $^3J = 6.9$ Hz, 1 H; C*H*NCH$_2$), 3.60 – 3.75 (m, 1 H; CHCO), 3.50 (d, $^2J_{AB} = 13.9$ Hz, 1 H; CH$_2$SO$_2$), 3.44 (d, $^2J_{AB} = 13.9$ Hz, 1 H; CH$_2$SO$_2$), 2.50 (ddt, $^4J = 1.6$, $^2J_{AB} = 17.0$, $^3J = 5.3$ Hz, 1 H; CH$_2$C=), 2.40 (dd, $^2J_{AB} = 17.0$, $^3J = 2.5$ Hz, 1 H; CH$_2$C=), 2.36 – 2.30 (m, 1 H; CH$_2$), 2.10 – 2.08 (m, 2 H; CH$_2$), 1.90 – 1.84 (m, 3 H; CH$_2$), 1.45 (d, $^3J = 9.0$ Hz, 1 H; CH$_2$), 1.40 – 1.35 (m, 2 H; CH$_2$), 1.20 (s, 3 H; CH$_3$), 0.99 (s, 3 H; CH$_3$), 0.72 – 0.68 (m, 1 H; *c*Pr-H), 0.56 – 0.55 (m, 2 H; *c*Pr-H), 0.48 – 0.44 (m, 1 H; *c*Pr-H); ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): $\delta = 174.9$ (C$_{quat}$, CO), 138.6 (C$_{quat}$, CH=*C*), 135.2 (+, *C*H=C), 120.5 (+, *C*H=C), 116.1 (–, CH$_2$), 64.6 (+, CHN), 53.8 (–, CH$_2$SO$_2$), 48.4 (C$_{quat}$, *C*CH$_2$), 46.4 [C$_{quat}$, *C*(CH$_3$)$_2$], 45.0 (+, CH), 40.8 (+, *C*HCO), 38.6 (–, CH$_2$), 36.4 (–, CH$_2$), 32.5 (–, CH$_2$), 30.3 (–, CH$_2$), 27.0 (–, CH$_2$), 21.6 (+, CH$_3$), 20.9 (+, CH$_3$), 20.6 (C$_{quat}$, *c*Pr-C), 13.2 (–, *c*Pr-C), 11.4 (–, *c*Pr-C); MS (70 eV, EI): *m*/*z* (%): 375 (25) [M^+], 160 (9) [$\mathrm{C_{11}H_{12}O^+}$], 159 (17) [$\mathrm{C_{11}H_{11}O^+}$], 132 (100) [$\mathrm{C_{10}H_{12}^+}$]; HRMS: *m*/*z* (%): calcd for $\mathrm{C_{21}H_{29}NO_3S}$: 375.1868; found: 375.1868.

***tert*-Butyl 8-phenylspiro[2.5]oct-7-ene-5-carboxylate (18e-Ph)**: a) According to GP 3, palladium(II) acetate (11.2 mg, 49.9 μmol), triphenylphosphane (39.3 mg, 150 μmol), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), iodobenzene (**2**-Ph, 204 mg, 1.00 mmol) and triethylamine (202 mg, 2.00 mmol) with *tert*-butyl acrylate (**17e**, 256 mg, 2.00 mmol) in anhydrous DMF (1 mL) were heated at 80 °C for 2 d. After work-up, chromatography of the crude product on 50 g silica gel (column 2 × 20 cm, pentane/diethyl ether 10:1) yielded **18e**-Ph as a yellowish oil (222 mg, 78 %). $R_f = 0.59$ (pentane/diethyl ether 10:1); IR (film): $\tilde{\nu} = 3078$, 2977, 2930, 1727 (C=O), 1642 (C=C), 1600, 1492, 1456, 1442, 1367, 1259, 1151, 1023, 849, 703 cm^{-1}; ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 7.26 - 7.22$ (m, 3 H; Ar-H), 7.05 – 7.01 (m, 2 H; Ar-H), 5.52 (t, $^3J = 3.6$ Hz, 1 H; 7-H), 2.79 (ddt, $^3J = 11.7$, $^3J = 9.7$, $^3J = 2.8$ Hz, 1 H; 5-H), 2.43 (dd, $^3J = 9.7$, $^3J = 3.6$ Hz, 2 H; 6-H), 2.15 (dd, $^2J = 12.8$, $^3J = 11.7$ Hz, 1 H; 4-H), 1.47 (s, 9 H; *t*Bu-H), 1.44 (dd, $^2J = 12.8$, $^3J = 2.8$ Hz, 1 H; 4-H), 0.63 – 0.34 (m, 4 H; *c*Pr-H); ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): $\delta = 175.0$ (C$_{quat}$, CO), 142.9 (C$_{quat}$, Ar-C*), 140.4 (C$_{quat}$, C-8*), 129.2 (+, Ar-C), 127.4 (+, Ar-C), 126.5 (+, Ar-C), 124.0 (+, C-7), 80.0 (C$_{quat}$, *t*Bu-C), 40.4 (+, C-5), 37.4 (–, C-6), 28.7 (–, C-4), 28.1 (+, *t*Bu-C), 20.1 (C$_{quat}$, C-3), 12.8 (–, *c*Pr-C), 11.6 (–, *c*Pr-C); MS (70 eV): *m*/*z* (%): 284 (2) [M^+], 228 (100) [$M^+ - \mathrm{C_4H_8}$], 211 (29), 182 (83) [$M^+ - t\mathrm{BuOH} - \mathrm{CO}$], 167 (37), 155 (46), 141 (39), 57 (48) [$\mathrm{C_4H_9^+}$]; elemental analysis calcd (%) for $\mathrm{C_{19}H_{24}O_2}$ (284.4): C 80.24, H 8.51; found: C 80.07, H 8.48.

b) According to GP 5, palladium(II) acetate (11.2 mg, 49.9 μmol), triphenylphosphane (39.3 mg, 150 μmol), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K$_2$CO$_3$ (277 mg, 2.00 mmol), Et$_4$NCl (166 mg, 1.00 mmol) and iodobenzene (**2**-Ph, 204 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with *tert*-butyl acrylate (**17e**, 256 mg, 2.00 mmol) for 48 h at 80 °C. After work-up, chromatography of the crude product on 50 g silica gel (column 2 × 20 cm, pentane/diethyl ether 10:1) yielded **18e**-Ph as a yellowish oil (248 mg, 87 %). $R_f = 0.66$ (pentane/diethyl ether 10:1).

***tert*-Butyl 8-(4′-methylphenyl)spiro[2.5]oct-7-ene-5-carboxylate (18e-Tol)**: According to GP 5, palladium(II) acetate (11.2 mg, 49.9 μmol, 5 mol %), triphenylphosphane (39.2 mg, 150 μmol, 15 mol %), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K$_2$CO$_3$ (277 mg, 2.00 mmol), Et$_4$NCl (166 mg, 1.00 mmol) and *para*-iodotoluene (**2**-Tol, 218 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with *tert*-butyl acrylate (**17e**, 256 mg, 2.00 mmol) for 48 h at 80 °C. After work-up, chromatography of the crude product on 50 g silica gel (column 2 × 20 cm, pentane/diethyl ether 20:1) yielded **18e**-Tol as a yellow oil (247 mg, 83 %). $R_f = 0.66$ (pentane/diethyl ether 20:1); IR (film): $\tilde{\nu} = 3080$, 2929, 1727 (C=O), 1635 (C=C), 1456, 1367, 1259, 1151, 1027, 806 cm^{-1}; ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 7.07$ (d, $^3J = 7.8$ Hz, 2 H; Ar-H), 6.93 (d, $^3J = 7.8$ Hz, 2 H; Ar-H), 5.51 (t, $^3J = 3.7$ Hz, 1 H; 7-H), 2.79 (ddt, $^3J = 11.7$, $^3J = 9.7$, $^3J = 2.9$ Hz, 1 H; 5-H), 2.43 (dd, $^3J = 9.7$, $^3J = 3.7$ Hz, 2 H; 6-H), 2.32 (s, 3 H; Ar-CH$_3$), 2.16 (dd, $^2J = 12.8$, $^3J = 11.7$ Hz, 1 H; 4-H), 1.48 (s, 9 H; *t*Bu-H), 1.45 (dd, $^2J = 12.8$, $^3J = 2.9$ Hz, 1 H; 4-H), 0.68 – 0.37 (m, 4 H; *c*Pr-H); ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): $\delta = 175.0$ (C$_{quat}$, CO), 142.9 (C$_{quat}$, Ar-C*), 137.4 (C$_{quat}$, Ar-C*), 136.0 (C$_{quat}$, C-8*), 129.1 (+, Ar-C), 128.1 (+, Ar-C), 123.8 (+, C-7), 80.0 (C$_{quat}$, *t*Bu-C), 40.5 (+, C-5), 37.4 (–, C-6), 28.7 (–, C-4), 28.1 (+, *t*Bu-C), 21.1 (+, Ar-CH$_3$), 20.1 (C$_{quat}$, C-3), 12.8 (–, *c*Pr-C), 11.6 (–, *c*Pr-C); MS (70 eV): *m*/*z* (%): 298 (5) [M^+], 242 (100) [$M^+ - \mathrm{C_4H_8}$], 225 (22) [$M^+ - \mathrm{O}t\mathrm{Bu}$], 197 (37) [$M^+ - \mathrm{CO_2}t\mathrm{Bu}$], 181 (51), 169 (19), 155 (22); elemental analysis calcd (%) for $\mathrm{C_{20}H_{26}O_2}$ (298.4): C 80.50, H 8.78; found: C 80.71, H 8.79.

***tert*-Butyl 8-(3′-pyridinyl)spiro[2.5]oct-7-ene-5-carboxylate (18e-Py)**: According to GP 5, palladium(II) acetate (11.2 mg, 49.9 μmol, 5 mol %), triphenylphosphane (39.2 mg, 150 μmol, 15 mol %), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K$_2$CO$_3$ (277 mg, 2.00 mmol), Et$_4$NCl (166 mg, 1.00 mmol) and 3-iodopyridine (**2**-Py, 205 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with *tert*-butyl acrylate (**17e**, 256 mg, 2.00 mmol) for 24 h at 80 °C. After work-up, chromatography of the crude product on 50 g silica gel (column 2 × 20 cm, diethyl ether) yielded **18e**-Py as a yellowish oil (231 mg, 81 %). $R_f = 0.62$ (diethyl ether); IR (film): $\tilde{\nu} = 3080$, 2977, 2931, 1726 (C=O), 1641 (C=C), 1367, 1263, 1154, 1026, 806, 719 cm^{-1}; ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 8.47$ (dd, $^3J = 4.8$, $^4J = 1.8$ Hz, 1 H; 6′-H*), 8.31 (d, $^4J = 3.9$ Hz, 1 H; 2′-H*), 7.19 (dd, $^3J = 7.8$, $^3J = 4.8$ Hz, 1 H; 5′-H), 5.57 (t, $^3J = 3.6$ Hz, 1 H; 7-H), 2.79 (ddt, $^3J = 11.6$, $^3J = 9.5$, $^3J = 3.5$ Hz, 1 H; 5-H), 2.45 (dd, $^3J = 9.5$, $^3J = 3.6$ Hz, 2 H; 6-H), 2.14 (dd, $^2J = 12.2$, $^3J = 11.6$ Hz, 1 H; 4-H), 1.47 (dd, $^2J = 12.3$, $^3J = 3.5$ Hz, 1 H; 4-H), 1.46 [s, 9 H; C(CH$_3$)$_3$], 0.61 – 0.41 (m, 4 H; *c*Pr-H); ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): $\delta = 174.6$ (C$_{quat}$, CO), 149.8 (+, Ar-C), 148.0 (+, Ar-C), 139.4 (C$_{quat}$, Ar-C**), 136.5 (+, Ar-C), 135.8 (C$_{quat}$, C-8**), 126.1 (+, Ar-C*), 122.4 (+, C-7*), 80.2 (C$_{quat}$, *t*Bu-C), 40.3 (+, C-5), 37.1 (–, C-6), 28.6 (–, C-4), 28.1 (+, *t*Bu-C), 20.0 (C$_{quat}$, C-3), 12.4 (–, *c*Pr-C), 11.3 (–, *c*Pr-C); MS (70 eV): *m*/*z* (%): 285 (1) [M^+], 228 (68) [$M^+ - \mathrm{C_4H_9}$], 212 (17) [$M^+ - \mathrm{C_4H_9O}$], 184 (100) [$M^+ - \mathrm{C_4H_9O} - \mathrm{CO}$], 168 (21), 156 (42), 115 (40), 57 (55) [$\mathrm{C_4H_9^+}$]; elemental analysis calcd (%) for $\mathrm{C_{18}H_{23}NO_2}$ (285.4): C 75.77, H 8.12; found: C 75.67, H 8.15.

Dimethyl (*E*)-8-phenylspiro[2.5]oct-7-ene-4,5-dicarboxylate (18f-Ph): a) According to GP 5, palladium(II) acetate (11.2 mg, 49.9 μmol, 5 mol %), triphenylphosphane (39.2 mg, 150 μmol, 15 mol %), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K$_2$CO$_3$ (277 mg, 2.00 mmol), Et$_4$NCl (166 mg, 1.00 mmol) and iodobenzene (**2**-Ph, 204 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (5 mL) with dimethyl fumarate (**17f**, 288 mg, 2.00 mmol) for 48 h at 80 °C. After work-up, chromatography of the crude product on 50 g silica gel (column 2 × 20 cm, hexane/diethyl ether 5:1) yielded **18f**-Ph as colorless crystals (291 mg, 97 %). $R_f = 0.27$ (hexane/diethyl ether 5:1); m.p. 71 – 73 °C (from hexane); IR (film): $\tilde{\nu} = 3021$, 2951, 1737 (C=O), 1492, 1436, 1259, 1196, 1025, 760, 705 cm^{-1}; ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 7.28 - 7.22$ (m, 3 H; Ar-H), 7.08 – 7.05 (m, 2 H; Ar-H), 5.53 (dd, $^3J = 3.8$, $^3J = 3.8$ Hz, 1 H; 7-H), 3.72 (s, 6 H; 2 OCH$_3$), 3.31 (ddd, $^3J = 6.4$, $^3J = 6.4$, $^3J = 6.4$ Hz, 1 H; 5-H), 2.97 (d, $^3J = 6.4$ Hz, 1 H; 4-H), 2.55 (ddd, $^3J = 3.8$, $^3J = 6.4$, $^3J = 6.4$ Hz, 2 H; 6-H), 0.69 – 0.59 (m, 3 H; *c*Pr-H), 0.49 – 0.43 (m, 1 H; *c*Pr-H); ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): $\delta = 174.5$ (C$_{quat}$, CO$_2$), 173.3 (C$_{quat}$, CO$_2$), 141.8 (C$_{quat}$, Ar-C*), 139.7 (C$_{quat}$, C-8*), 129.2 (+, 2 Ar-C), 127.5 (+, 2 Ar-C), 126.7 (+, Ar$_{para}$-C), 123.4 (+, C-7*), 51.88 (+, OCH$_3$), 51.84 (+, OCH$_3$), 49.3 (+, C-5*), 41.4 (+, C-4*), 26.3 (–, C-6), 20.0 (C$_{quat}$, C-3), 11.0 (–, C-2), 10.2 (–, C-1); MS (70 eV, EI): *m*/*z*

(%): 300 (18) $[M^+]$, 268 (22) $[M^+-\mathrm{CH_4O}]$, 267 (18), 241 (81) $[M^+-\mathrm{CO_2CH_3}]$, 240 (85), 209 (63) $[M^+-\mathrm{CO_2CH_3}-\mathrm{CH_4O}]$, 181 (100) $[M^+-2\,\mathrm{CO_2CH_3}-\mathrm{H}]$; elemental analysis calcd (%) for $\mathrm{C_{18}H_{20}O_4}$ (300.4): C 71.98, H 6.71; found: C 71.76, H 6.68.

b) From the same quantities of reagents, but dimethyl maleate **17b** instead of dimethyl fumarate **17f**, compound **18f**-Ph (288 mg, 96%) was obtained according to GP 5 after column chromatography.

c) According to GP 3, palladium(II) acetate (11.2 mg, 49.9 μmol), triphenylphosphane (39.3 mg, 150 μmol), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), iodobenzene (**2**-Ph, 204 mg, 1.00 mmol) and triethylamine (202 mg, 2.00 mmol) with dimethyl maleate (**17b**, 288 mg, 2.00 mmol) in anhydrous DMF (3 mL) were heated at 80 °C for 20 h. After work-up, chromatography of the crude product on 50 g silica gel (column 2 × 20 cm, pentane/diethyl ether 10:1) yielded **18f**-Ph (294 mg, 98%).

Dimethyl (*E*)-8-(4′-methylphenyl)spiro[2.5]oct-7-ene-4,5-dicarboxylate (18f-Tol): a) According to GP 3, palladium(II) acetate (11.2 mg, 49.9 μmol, 5 mol%), triphenylphosphane (39.2 mg, 150 μmol, 15 mol%), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), *para*-iodotoluene (**2**-Tol, 218 mg, 1.00 mmol) and triethylamine (204 mg, 2.02 mmol) in anhydrous DMF (1 mL) were heated with dimethyl fumarate (**17f**, 288 mg, 2.00 mmol) for 48 h at 80 °C. After work-up, chromatography of the crude product on 50 g silica gel (column 2 × 20 cm, pentane/diethyl ether 5:1) yielded **18f**-Tol as colorless crystals (252 mg, 80%). $R_f=0.33$ (pentane/diethyl ether 5:1); m.p. 48 °C; IR (KBr): $\tilde{\nu}=3008$, 2953, 2929, 1731 (C=O), 1719 (C=O), 1652 (C=C), 1437, 1321, 1179, 1159, 1127, 818 cm^{-1}; ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): $\delta=7.06$ (d, $^3J=7.8$ Hz, 2H; Ar-H), 6.95 (d, $^3J=7.8$ Hz, 2H; Ar-H), 5.50 (t, $^3J=3.8$ Hz, 1H; 7-H), 3.72 (s, 6H; $\mathrm{OCH_3}$), 3.30 (dt, $^3J=6.7$, $^3J=6.5$ Hz, 1H; 5-H), 2.97 (d, $^3J=6.7$ Hz, 1H; 4-H), 2.53 (dd, $^3J=6.5$, $^3J=3.8$ Hz, 2H; 6-H), 2.32 (s, 3H; Ar-$\mathrm{CH_3}$), 0.69–0.59 (m, 3H; *c*Pr-H), 0.50–0.44 (m, 1H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $\mathrm{CDCl_3}$, DEPT): $\delta=174.6$ ($\mathrm{C_{quat}}$, CO), 173.4 ($\mathrm{C_{quat}}$, CO), 141.7 ($\mathrm{C_{quat}}$, Ar-C*), 136.8 ($\mathrm{C_{quat}}$, Ar-C*), 136.3 ($\mathrm{C_{quat}}$, C-8*), 129.1 (+, Ar-C), 128.2 (+, Ar-C), 123.2 (+, C-7), 51.8 (+, $\mathrm{OCH_3}$), 49.2 (+, C-4), 41.5 (+, C-5), 26.4 (−, C-6), 21.1 (+, Ar-$\mathrm{CH_3}$), 20.1 ($\mathrm{C_{quat}}$, C-3), 10.9 (−, *c*Pr-C), 10.2 (−, *c*Pr-C); MS (70 eV): *m*/*z* (%): 314 (21) $[M^+]$, 282 (14) $[M^+-\mathrm{CH_4O}]$, 255 (100) $[M^+-\mathrm{CO_2CH_3}]$, 223 (52) $[M^+-\mathrm{CO_2CH_3}-\mathrm{CH_4O}]$, 195 (86) $[M^+-\mathrm{CO_2CH_3}-\mathrm{CH_4O}-\mathrm{CO}]$, 179 (31), 165 (34); elemental analysis calcd (%) for $\mathrm{C_{19}H_{22}O_4}$ (314.4): C 72.59, H 7.05; found: C 71.94, H 7.30.

b) According to GP 5, palladium(II) acetate (11.2 mg, 49.9 μmol, 5 mol%), triphenylphosphane (39.2 mg, 150 μmol, 15 mol%), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), $\mathrm{K_2CO_3}$ (277 mg, 2.00 mmol), $\mathrm{Et_4NCl}$ (166 mg, 1.00 mmol) and *para*-iodotoluene (**2**-Tol, 218 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with dimethyl fumarate (**17f**, 288 mg, 2.00 mmol) for 48 h at 80 °C. After work-up, chromatography of the crude product on 50 g silica gel (column 2 × 20 cm, pentane/diethyl ether 10:1) yielded **18f**-Tol as a yellow oil (310 mg, 99%). $R_f=0.22$ (pentane/diethyl ether 10:1).

Dimethyl (*E*)-8-(3′-pyridinyl)spiro[2.5]oct-7-ene-4,5-dicarboxylate (18f-Py): According to GP 5, palladium(II) acetate (11.2 mg, 49.9 μmol, 5 mol%), triphenylphosphane (39.2 mg, 150 μmol, 15 mol%), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), $\mathrm{K_2CO_3}$ (277 mg, 2.00 mmol), $\mathrm{Et_4NCl}$ (166 mg, 1.00 mmol) and 3-iodopyridine (**2**-Py, 205 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with dimethyl fumarate (**17f**, 288 mg, 2.00 mmol) for 48 h at 80 °C. After work-up, chromatography of the crude product on 50 g silica gel (column 2 × 20 cm, diethyl ether) yielded **18f**-Py as a yellowish oil (190 mg, 63%). $R_f=0.54$ (diethyl ether); IR (film): $\tilde{\nu}=3005$, 2952, 1734 (C=O), 1646 (C=C), 1436, 1262, 1197, 1172, 1027, 804, 720 cm^{-1}; ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): $\delta=8.47$ (dd, $^3J=4.9$, $^4J=1.6$ Hz, 1H; 2′-H), 8.32 (d, $^4J=2.0$ Hz, 1H; 2′-H*), 7.42 (ddd, $^3J=7.7$, $^4J=2.0$, $^4J=1.8$ Hz, 1H; 4′-H*), 7.19 (dd, $^3J=7.7$, $^3J=4.9$ Hz, 1H; 5′-H), 5.58 (dd, $^3J=3.9$, $^3J=3.8$ Hz, 1H; 7-H), 3.73 (s, 6H; $\mathrm{OCH_3}$), 3.33 (ddd, $^3J=6.4$, $^3J=6.1$, $^3J=5.2$ Hz, 1H; 5-H), 2.92 (d, $^3J=6.1$ Hz, 1H; 4-H), 2.63 (ddd, $^2J=18.3$, $^3J=5.2$, $^3J=3.9$ Hz, 1H; 6-H), 2.51 (ddd, $^2J=18.3$, $^3J=6.4$, $^3J=3.8$ Hz, 1H; 6-H), 0.73–0.59 (m, 3H; *c*Pr-H), 0.44–0.39 (m, 1H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $\mathrm{CDCl_3}$, DEPT): $\delta=174.2$ ($\mathrm{C_{quat}}$, CO), 173.1 ($\mathrm{C_{quat}}$, CO), 149.8 (+, Ar-C), 148.2 (+, Ar-C), 138.3 ($\mathrm{C_{quat}}$, Ar-C*), 136.5 (+, Ar-C*), 135.2 ($\mathrm{C_{quat}}$, C-8*), 125.6 (+, Ar-C*), 122.5 (+, C-7*), 52.0 (+, $\mathrm{OCH_3}$), 51.9 (+, $\mathrm{OCH_3}$), 49.2 (+, C-5), 41.1 (+, C-4), 25.9 (−, C-6), 19.9 ($\mathrm{C_{quat}}$, C-3), 10.9 (−, *c*Pr-C), 10.1 (−, *c*Pr-C); MS (70 eV): *m*/*z* (%): 301 (8) $[M^+]$, 242 (100) $[M^+-\mathrm{CO_2Me}]$, 210 (60) $[M^+-\mathrm{CO_2Me}-\mathrm{MeOH}]$, 182 (76) $[M^+-\mathrm{CO_2Me}-\mathrm{MeOH}-\mathrm{CO}]$, 167 (29), 154 (7), 128 (4), 77 (4), 59 (9); elemental analysis calcd (%) for $\mathrm{C_{17}H_{19}NO_4}$ (301.3): C 67.76, H 6.36; found: C 68.61, H 6.69.

8-Phenylspiro[2.5]oct-7-ene-5-carboxylic amide (18g-Ph): According to GP 5, palladium(II) acetate (11.2 mg, 49.9 μmol), triphenylphosphane (39.3 mg, 150 μmol), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), $\mathrm{K_2CO_3}$ (277 mg, 2.00 mmol), $\mathrm{Et_4NCl}$ (166 mg, 1.00 mmol) and iodobenzene (**2**-Ph, 204 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with acrylic acid amide (**17g**, 142 mg, 2.00 mmol) for 48 h at 80 °C. After work-up, chromatography of the crude product on 50 g silica gel (column 2 × 20 cm, pentane/diethyl ether 5:1 → $\mathrm{Et_2O}$/MeOH 10:1) yielded **18g**-Ph as colorless crystals (112 mg, 49%). $R_f=0.10$ (pentane/diethyl ether 2:1); m.p. 159 °C; IR (film): $\tilde{\nu}=3184$, 3057, 2991, 2927, 1654 (C=O), 1617 (C=C), 1437, 1375, 1178, 1120, 748, 722 cm^{-1}; ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): $\delta=7.70$–7.62 (m, 1H; 4′-H), 7.55–7.43 (m, 2H; 3′-H, 5′-H), 7.04–7.0 (m, 2H; 2′-H, 6′-H), 5.84 (brs, 1H; $\mathrm{NH_2}$), 5.74 (brs, 1H; $\mathrm{NH_2}$), 5.54 (d, $^3J=3.5$ Hz, 1H; 7-H), 2.78 (ddd, $^3J=11.6$, $^3J=8.9$, $^3J=2.7$ Hz, 1H; 5-H), 2.48 (dd, $^3J=8.9$, $^3J=3.5$ Hz, 2H; 6-H), 2.24 (dd, $^2J=13.0$, $^3J=11.6$ Hz, 1H; 4-H), 1.43 (dd, $^2J=13.0$, $^3J=2.7$ Hz, 1H; 4-H), 0.69–0.37 (m, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $\mathrm{CDCl_3}$, DEPT): $\delta=178.1$ ($\mathrm{C_{quat}}$, CO), 143.3 ($\mathrm{C_{quat}}$, Ar-C*), 140.1 ($\mathrm{C_{quat}}$, C-8*), 129.1 (+, Ar-C), 127.5 (+, Ar-C), 126.6 (+, Ar-C), 123.6 (+, C-7), 40.7 (−, C-6), 37.9 (+, C-5), 29.2 (−, C-4), 20.1 ($\mathrm{C_{quat}}$, C-3), 12.9 (−, *c*Pr-C), 11.6 (−, *c*Pr-C); MS (70 eV): *m*/*z* (%): 227 (30) $[M^+]$, 183 (100) $[M^+-\mathrm{CONH_2}]$, 155 (80), 115 (18), 91 (16) $[\mathrm{C_7H_7}^+]$; elemental analysis calcd (%) for $\mathrm{C_{15}H_{17}NO}$ (227.3): C 79.26, H 7.54; found: 79.33, H 7.54.

Methyl 5-methyl-8-phenylspiro[2.5]oct-7-ene-5-carboxylate (18h-Ph): According to GP 5, palladium(II) acetate (11.2 mg, 49.9 μmol, 5 mol%), triphenylphosphane (39.3 mg, 150 μmol, 15 mol%), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), $\mathrm{K_2CO_3}$ (277 mg, 2.00 mmol), $\mathrm{Et_4NCl}$ (166 mg, 1.00 mmol) and iodobenzene (**2**-Ph, 204 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with methyl methylacrylate (**17h**, 200 mg, 2.00 mmol) for 48 h at 80 °C. After work-up, chromatography of the crude product on 25 g silica gel (column 2 × 20 cm, pentane/diethyl ether 10:1) yielded **18h**-Ph as a yellowish oil (195 mg, 76%). $R_f=0.58$ (pentane/diethyl ether 10:1); IR (film): $\tilde{\nu}=3070$, 2998, 2950, 2922, 1736 (C=O), 1645 (C=C), 1600, 1435, 1371, 1189, 1019, 823 cm^{-1}; ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): $\delta=7.25$–7.22 (m, 3H; Ar-H), 7.04–7.01 (m, 2H; Ar-H), 5.50 (dd, $^3J=4.0$, $^3J=3.7$ Hz, 1H; 7-H), 3.71 (s, 3H; $\mathrm{OCH_3}$), 2.73 (dd, $^2J=17.7$, $^3J=3.7$ Hz, 1H; 6-H), 2.13 (dd, $^2J=17.7$, $^3J=4.0$ Hz, 1H; 6-H), 2.04 (d, $^2J=13.2$ Hz, 1H; 4-H), 1.65 (d, $^2J=13.2$ Hz, 1H; 4-H), 1.36 (s, 3H; $\mathrm{CH_3}$), 0.54–0.45 (m, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $\mathrm{CDCl_3}$, DEPT): $\delta=177.9$ ($\mathrm{C_{quat}}$, CO), 141.9 ($\mathrm{C_{quat}}$, Ar-C*), 140.3 ($\mathrm{C_{quat}}$, C-8*), 129.3 (+, Ar-C), 127.4 (+, Ar-C), 126.5 (+, Ar-C), 123.4 (+, C-7), 51.6 (+, $\mathrm{OCH_3}$), 43.1 (−, C-6), 42.1 ($\mathrm{C_{quat}}$, C-5), 35.1 (−, C-4), 24.1 (+, $\mathrm{CH_3}$), 18.5 ($\mathrm{C_{quat}}$, C-3), 11.7 (−, *c*Pr-C), 10.6 (−, *c*Pr-C); MS (70 eV): *m*/*z* (%): 256 (28) $[M^+]$, 241 (4) $[M^+-\mathrm{CH_3}]$, 225 (8) $[M^+-\mathrm{OCH_3}]$, 197 (100) $[M^+-\mathrm{CO_2Me}]$, 196 (96) $[M^+-\mathrm{CO_2Me}-\mathrm{H}]$, 181 (52) $[M^+-\mathrm{HCO_2Me}-\mathrm{CH_3}]$, 169 (68), 141 (40), 115 (16), 91 (7) $[\mathrm{C_7H_7}^+]$.

Methyl 8-phenyl-5-(methoxycarbonylmethyl)spiro[2.5]oct-7-ene-5-carboxylate (18k-Ph): According to GP 5, palladium(II) acetate (11.2 mg, 49.9 μmol, 5 mol%), triphenylphosphane (39.3 mg, 150 μmol, 15 mol%), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), $\mathrm{K_2CO_3}$ (277 mg, 2.00 mmol), $\mathrm{Et_4NCl}$ (166 mg, 1.00 mmol) and iodobenzene (**2**-Ph, 204 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with itaconic dimethyl ester (**17k**, 316 mg, 2.00 mmol) for 72 h at 80 °C. After work-up, chromatography of the crude product on 25 g silica gel (column 2 × 20 cm, pentane/diethyl ether 10:1) yielded **18k**-Ph as a colorless oil (149 mg, 47%). $R_f=0.18$ (pentane/diethyl ether 10:1); IR (film): $\tilde{\nu}=3060$, 2997, 2951, 2923, 1734 (C=O), 1730 (C=O), 1635 (C=C), 1436, 1371, 1190, 1019 cm^{-1}; ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): $\delta=7.23$–7.20 (m, 3H; Ar-H), 7.02–6.08 (m, 2H; Ar-H), 5.48 (dd, $^3J=4.7$, $^3J=3.1$ Hz, 1H; 7-H), 3.71 (s, 3H; $\mathrm{OCH_3}$), 3.66 (s, 3H; $\mathrm{OCH_3}$), 3.01 (d, $^2J=16.5$ Hz, 1H; $C\!H_2\mathrm{CO_2Me}$), 2.80 (d, $^2J=16.5$ Hz, 1H; $C\!H_2\mathrm{CO_2Me}$), 2.77 (dd, $^2J=17.9$, $^3J=3.1$ Hz, 1H; 6-H), 2.27 (dd, $^2J=17.9$, $^3J=4.7$ Hz, 1H; 6-H), 2.19 (d, $^2J=13.4$ Hz, 1H; 4-H), 1.67 (dd, $^2J=13.4$, $^5J=1.3$ Hz, 1H; 4-H), 0.52–0.39 (m, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $\mathrm{CDCl_3}$, DEPT): $\delta=176.2$ ($\mathrm{C_{quat}}$, CO), 172.0 ($\mathrm{C_{quat}}$, CO), 142.0 ($\mathrm{C_{quat}}$, C-8*), 139.8 ($\mathrm{C_{quat}}$, Ar-C*), 129.2 (+, Ar-C), 127.4 (+, Ar-C), 126.6 (+, Ar-C), 122.6 (+, C-7), 51.9 (+, $\mathrm{OCH_3}$), 51.5 (+, $\mathrm{OCH_3}$), 43.8 ($\mathrm{C_{quat}}$, C-5), 40.2 (−, C-6), 39.9 (−, C-4), 33.5 (−, $C\mathrm{H_2CO_2Me}$), 18.0 ($\mathrm{C_{quat}}$, C-3), 12.0 (−, *c*Pr-C), 9.9 (−, *c*Pr-C); MS (70 eV): *m*/*z* (%): 314 (1) $[M^+]$, 283 (4) $[M^+-\mathrm{CH_3}]$, 254 (28) $[M^+-\mathrm{CO_2Me}-\mathrm{H}]$, 241 (100) $[M^+-\mathrm{CH_2CO_2Me}]$, 195 (24) $[M^+-2\,\mathrm{CO_2Me}-\mathrm{H}]$, 181 (58), 165 (24), 141 (12), 91 (12) $[\mathrm{C_7H_7}^+]$.

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Methyl 8-(1-cyclohex-1-enyl)spiro[2.5]oct-7-ene-5-carboxylate (19a) and methyl 2-ethenylspiro[cyclopropane-1′,3-bicyclo[4.4.0]dec-1-ene]-5-carboxylate (20a): According to GP 5, palladium(II) acetate (11.2 mg, 49.9 μmol, 5 mol%), triphenylphosphane (39.3 mg, 150 μmol, 15 mol%), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K_2CO_3 (278 mg, 2.01 mmol), Et_4NCl (166 mg, 1.00 mmol) and 1-iodocyclohexene (**9**, 200 mg, 0.96 mmol) with methyl acrylate (**17a**, 172 mg, 2.00 mmol) were heated in acetonitrile (1 mL) at 80 °C for 2 d. After work-up, chromatography of the crude product on 50 g silica gel (column 2 × 20 cm, pentane/diethyl ether 10:1) yielded a not completely separable mixture of **19a** and **20a** (1:2, ^{1}H NMR) as a clear oil (200 mg, 84%). $R_f = 0.62$ (pentane/diethyl ether 10:1); IR (film): $\tilde{\nu} = 3078$, 2997, 2928, 2854, 1736 (C=O), 1635 (C=C), 1436, 1256, 1194, 1162, 1026, 920 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): **19a**: $\delta = 5.34$ (t, $^3J = 3.7$ Hz, 1H; 7-H), 5.20 (t, $^3J = 3.6$ Hz, 1H; 2′-H), 3.67 (s, 3H; OCH$_3$), 3.01 – 2.92 (m, 1H; 5-H), 2.35 (dd, $^3J = 9.7$, $^3J = 3.7$ Hz, 1H; 6-H), 2.19 (dd, $^2J = 13.2$, $^3J = 11.6$ Hz, 1H; 4-H), 1.97 – 1.14 (m, 10H; CH$_2$), 0.70 – 0.30 (m, 4H; *c*Pr-H); **20a**: $\delta = 5.79$ (dd, $^3J = 17.5$, $^3J = 11.1$ Hz, 1H; 1″-H), 5.15 (dd, $^2J = 2.6$, $^3J = 11.1$ Hz, 1H; 2″-H), 4.89 (dd, $^2J = 2.6$, $^3J = 17.5$ Hz, 1H; 2″-H), 3.68 (s, 3H; OCH$_3$), 2.87 – 2.81 (m, 1H; 5-H), 2.43 – 2.52 (m, 1H; 6-H), 1.97 – 1.14 (m, 10H; CH$_2$), 0.70 – 0.30 (m, 4H; *c*Pr-H); MS (70 eV): *m*/*z* (%): 246 (31) [M^+], 215 (6) [$M^+ - OCH_3$], 187 (100) [$M^+ - OCH_3 - CO$], 145 (67), 91 (27); elemental analysis calcd (%) for $C_{16}H_{22}O_2$ (246.3): C 78.01, H 9.00; found: C 78.19, H 9.11.

1-(1′-Cyclopropylideneprop-2′-enyl)cyclohex-1-ene (10), dimethyl (4*S,5*S**)-8-cyclohex-1′-enylspiro[2.5]oct-7-ene-4,5-dicarboxylate (19b) and dimethyl (3′*α*,4′*α*,4′a*β*)-1′-ethenyl-4′,4′a,5′,6′,7′,8′-hexahydrospiro[cyclopropane-1,2′(3′H)-naphthalene]-3′,4′-dicarboxylate (20b)**: According to GP 4, cyclohexenylnonaflate (**8**, 380 mg, 1.00 mmol), [Pd(PPh$_3$)$_4$] (57.8 mg, 50.0 μmol, 5 mol%), bicyclopropylidene (**1**, 320 mg, 3.99 mmol), triethylamine (810 mg, 8.00 mmol) and dimethyl maleate (**17b**, 288 mg, 2.00 mmol) in anhydrous DMF (10 mL) were heated at 100 °C for 18 h. After work-up, chromatography of the crude product on silica gel (1 × 20 cm, pentane → pentane/ethyl acetate 10:1) gave:

Fraction I: A colorless oil (100 mg), which rapidly polymerizes and according to ^{1}H NMR and ^{13}C NMR contains ca. 10% of **10**; $R_f = 0.8$ (pentane).

Fraction II: A not completely separable mixture of **19b** and **20b** (130 mg, 43%; 1:1.5 by ^{1}H NMR). **19b**: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 5.3$ (t, $^3J = 4$ Hz, 1H; 2′-H), 3.7 (s, 3H; CH$_3$), 3.6 (s, 3H; CH$_3$), 3.3 (d, $^3J = 7$ Hz, 2H; 3′-H), 2.9 – 2.8 (m, 1H; 4′-H), 2.3 – 1.0 (m, 10H; CH$_2$), 0.8 – 0.5 (m, 4H; *c*Pr-H); **20b**: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 5.85$ (dd, $^3J = 10$, $^3J = 17$ Hz, 1H; CH =), 5.1 (dd, $^2J = 2$, $^3J = 10$ Hz, 1H; CH$_2$ =), 4.9 (dd, $^2J = 2$, $^3J = 17$ Hz, 1H; CH$_2$ =), 3.7 (s, 3H; CH$_3$), 3.6 (s, 3H; CH$_3$), 3.2 (d, $^3J = 7$ Hz, 1H; 3′-H), 3.0 – 2.9 (m, 2H; 4′-H, 5′-H), 2.3 – 1.0 (m, 8H; CH$_2$), 0.8 – 0.5 (m, 4H; *c*Pr-H); **19b** and **20b**: clear oil; $R_f = 0.28$ (pentane/diethyl ether 10:1); IR (film): $\tilde{\nu} = 2990$, 1730 (C=O), 1725 (C=O), 1635 (C=C), 1110, 890, 840, 750, 730 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 304 (8) [M^+], 272 (9) [$M^+ - CH_4O$], 244 (68) [$M^+ - CH_4O - CO$], 213 (40), 185 (100) [$M^+ - CH_4O - CO - CH_3CO_2$]; HRMS: *m*/*z* (%): calcd for $C_{18}H_{24}O_4$: 304.1674; 304.1674.

***tert*-Butyl 8-(1-cyclohex-1-enyl)spiro[2.5]oct-7-ene-5-carboxylate (19e) and *tert*-butyl 2-ethenylspiro[cyclopropane-1′,3-bicyclo[4.4.0]dec-1-ene]-5-carboxylate (20e)**: According to GP 5, palladium(II) acetate (11.2 mg, 49.9 μmol, 5 mol%), triphenylphosphane (39.3 mg, 150 μmol, 15 mol%), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K_2CO_3 (278 mg, 2.01 mmol), Et_4NCl (166 mg, 1.00 mmol) and 1-iodocyclohexene (**9**, 200 mg, 0.96 mmol) with *tert*-butyl acrylate (**17e**, 256 mg, 2.00 mmol) were heated in acetonitrile (1 mL) at 80 °C for 2 d. After work-up, chromatography of the crude product on 50 g silica gel (column 2 × 20 cm, pentane/diethyl ether 10:1) yielded a not completely separable mixture of **19e** and **20e** (1:3, ^{1}H NMR) as a clear oil (231 mg, 83%). $R_f = 0.62$ (pentane/diethyl ether 10:1); IR (film): $\tilde{\nu} = 3079$, 2975, 2929, 1726 (C=O), 1652 (C=C), 1457, 1368, 1257, 1153, 997, 859 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): **19e**: $\delta = 5.33$ (t, $^3J = 4.0$ Hz, 1H; 7-H), 5.21 (t, $^3J = 3.5$ Hz, 1H; 2′-H), 2.58 – 2.74 (m, 1H; 5-H), 2.28 (dd, $^3J = 6.3$, $^3J = 3.2$ Hz, 2H; 6-H), 1.97 (dd, $^2J = 12.7$, $^3J = 11.6$ Hz, 1H; 4-H), 1.43 [s, 9H; C(CH$_3$)$_3$], 1.77 – 0.85 (m, 9H; 4-H, *c*Hex-CH$_2$), 0.68 – 0.33 (m, 4H; *c*Pr-H); **20e**: $\delta = 5.80$ (dd, $^3J = 17.5$, $^3J = 11.1$ Hz, 1H; 1′-H), 5.14 (dd, $^2J = 2.5$, $^3J = 11.1$ Hz, 1H; 2′-H), 4.86 (dd, $^2J = 2.5$, $^3J = 17.5$ Hz, 1H; 2′-H), 2.91 – 2.79 (m, 1H; 5-H), 2.26 – 2.31 (m, 1H; 6-H), 1.43 [s, 9H; C(CH$_3$)$_3$], 1.77 – 0.85 (m, 10H; 4-H, *c*Hex-CH$_2$), 0.70 – 0.30 (m, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): **19e**: $\delta = 175.2$ (C$_\text{quat}$, CO), 144.8 (C$_\text{quat}$, C-8), 137.0 (C$_\text{quat}$, C-1′), 124.1 (–, C-2′), 120.7 (+, C-7), 79.8 [C$_\text{quat}$, *C*(CH$_3$)$_3$], 40.5 (+, C-5), 37.4 (–, C-6), 31.0 (–, *c*Hex-C), 28.4 (–, *c*Hex-C), 28.0 [+, C(*C*H$_3$)$_3$], 25.0 (–, C-4), 22.8 (–, *c*Hex-C), 22.1 (–, *c*Hex-C), 18.8 (C$_\text{quat}$, *c*Pr-C), 13.6 (–, *c*Pr-C), 11.8 (–, *c*Pr-C); **20e**: $\delta = 175.4$ (C$_\text{quat}$, CO), 134.8 (C$_\text{quat}$, C-1), 133.5 (+, C-1′), 129.4 (C$_\text{quat}$, C-2), 118.9 (–, C-2′), 79.9 [C$_\text{quat}$, *C*(CH$_3$)$_3$], 48.5 (+, C-6), 40.9 (+, C-5), 37.3 (–, *c*Hex-C), 34.3 (–, *c*Hex-C), 31.5 (–, *c*Hex-C), 28.2 [+, C(*C*H$_3$)$_3$], 27.8 (–, *c*Hex-C*), 26.2 (–, C-4*), 18.8 (C$_\text{quat}$, *c*Pr-C), 11.7 (–, *c*Pr-C), 10.4 (–, *c*Pr-C); MS (70 eV): *m*/*z* (%): 288 (4) [M^+], 232 (80) [$M^+ - C_4H_8$], 215 (12) [$M^+ - OC_4H_9$], 187 (81) [$M^+ - OC_4H_9 - CO$], 145 (40), 107 (74) [$M^+ - OC_4H_9 - CO - C_6H_8$], 91 (44), 79 (41), 57 (100) [$C_4H_9^+$]; elemental analysis calcd (%) for $C_{19}H_{28}O_2$ (288.4): C 79.12, H 9.78; found: C 78.35, H 9.91.

Dimethyl spiro[cyclopropane-1′,2-bicyclo[4.4.0]dec-10-ene]-4,7-dicarboxylate (21a): According to GP 3, iodoethene (**6**, 154 mg, 1.00 mmol), bicyclopropylidene (**1**, 320 mg, 3.99 mmol), methyl acrylate (**17a**, 344 mg, 4.00 mmol), palladium(II) acetate (11.2 mg, 49.9 μmol), triphenylphosphane (39.3 mg, 150 μmol) and triethylamine (202 mg, 2.00 mmol) in anhydrous DMF (5 mL) were heated at 80 °C for 24 h. After work-up, chromatography of the crude product on silica gel (column 2 × 20 cm, pentane/diethyl ether 10:1) gave:

Fraction I: A mixture of polymers (80 mg); $R_f = 0.9$ (pentane/diethyl ether 10:1).

Fraction II: **21a** as a yellowish oil (164 mg, 59%); $R_f = 0.17$ (pentane/diethyl ether 10:1); IR (film): $\tilde{\nu} = 2980$, 2920, 1734 (C=O), 1653 (C=C), 1456, 1436, 1197, 1032 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 5.25$ (t, $^3J = 9.4$ Hz, 1H; 10-H), 3.68 (s, 3H; OCH$_3$), 3.67 (s, 3H; OCH$_3$), 2.76 – 2.69 (m, 1H; 7-H), 2.67 – 2.52 (m, 1H; 4-H), 2.47 – 2.25 (m, 2H; 8-H), 2.19 – 2.13 (m, 2H; 5-H), 2.06 – 1.97 (m, 2H; 9-H), 1.54 (dt, $^3J = 13.6$, $^3J = 2.3$ Hz, 1H; 6-H), 1.35 – 1.14 (m, 2H; 3-H), 1.02 – 0.76 (m, 1H; *c*Pr-H), 0.59 – 0.32 (m, 2H; *c*Pr-H), 0.29 – 0.21 (m, 1H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 176.4$ (C$_\text{quat}$, CO), 175.5 (C$_\text{quat}$, CO), 142.3 (C$_\text{quat}$, C-1), 114.7 (+, C-10), 51.6 (+, OCH$_3$), 51.4 (+, OCH$_3$), 40.7 (+, C-6*), 39.2 (+, C-7*), 37.3 (–, C-9**), 34.4 (–, C-8**), 33.9 (–, C-5**), 33.2 (+, C-4*), 28.0 (–, C-3), 21.3 (C$_\text{quat}$, C-2), 15.5 (–, *c*Pr-C), 8.0 (–, *c*Pr-C); MS (70 eV): *m*/*z* (%): 278 (18) [M^+], 246 (16) [$M^+ - CH_4O$], 218 (44) [$M^+ - CH_4O - CO$], 187 (26) [$M^+ - CH_4O - CO - OCH_3$], 159 (100) [$M^+ - CH_4O - 2CO - OCH_3$], 133 (44), 117 (41), 91 (42); HRMS: *m*/*z* (%): calcd for $C_{16}H_{22}O_4$: 278.1518; found: 278.1518.

Dimethyl (*E*)-8-ethenylspiro[2.5]oct-7-ene-4,5-dicarboxylate (18f-Vin) and tetramethyl (3*S,4*S**,7*R**,8*R**)-spiro[cyclopropane-1′,2-bicyclo[4.4.0]dec-10-ene]-3,4,7,8-tetracarboxylate (21f)**: According to GP 3, iodoethene (**6**, 154 mg, 1.00 mmol), bicyclopropylidene (**1**, 320 mg, 3.99 mmol), dimethyl fumarate (**17f**, 432 mg, 3.00 mmol), palladium(II) acetate (11.2 mg, 49.9 μmol), triphenylphosphane (39.3 mg, 150 μmol) and triethylamine (202 mg, 2.00 mmol) in anhydrous DMF (10 mL) were heated at 75 °C for 20 h. After work-up, chromatography of the crude product on silica gel (column 2 × 20 cm, pentane → pentane/diethyl ether 2:1) gave:

Fraction I: Polymers and **7**-H; which had not completely evaporated; $R_f = 0.8 – 0.45$ (pentane).

Fraction II: **18f**-Vin as a colorless oil (63.0 mg, 25%); $R_f = 0.35$ (pentane/diethyl ether 10:1); IR (film): $\tilde{\nu} = 2990$, 1730 (C=O), 1725 (C=O), 1650 (C=C), 1110, 890, 840, 750, 730 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 6.04$ (dd, $^3J = 5.4$, $^3J = 3.0$ Hz, 1H; 7-H), 5.89 (dd, $^3J = 17.0$, $^3J = 10.6$ Hz, 1H; C*H*=CH$_2$), 5.43 (dd, $^2J_{AB} = 2.3$, $^3J = 17.0$ Hz, 1H; CH=C*H*$_2$), 4.93 (dd, $^2J_{AB} = 2.3$, $^3J = 10.6$ Hz, 1H; CH=C*H*$_2$), 3.95 (s, 3H; OCH$_3$), 3.85 (s, 3H; OCH$_3$), 3.30 (ddd, $^3J = 6.3$, $^3J = 6.3$, $^3J = 6.4$ Hz, 1H; 5-H), 2.95 (d, $^3J = 6.4$ Hz, 1H; 4-H), 2.55 (dd, $^3J = 6.3$, $^3J = 2.7$ Hz, 2H; 6-H), 0.7 – 0.6 (m, 3H; *c*Pr-H), 0.55 – 0.45 (m, 1H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 174.5$ (C$_\text{quat}$, CO$_2$), 173.1 (C$_\text{quat}$, CO$_2$), 139.1 (C$_\text{quat}$, CH=*C*), 133.9 (+, *C*H=C), 120.4 (+, *C*H=C), 115.8 (–, CH$_2$), 51.8 (+, OCH$_3$), 51.7 (+, OCH$_3$), 48.8 (+, C-5), 41.3 (+, C-4), 26.8 (–, C-6), 19.4 (C$_\text{quat}$, *c*Pr-C), 10.7 (–, *c*Pr-C), 9.9 (–, *c*Pr-C); MS (70 eV, EI): *m*/*z* (%): 250 (12) [M^+], 218 (22) [$M^+ - CH_4O$], 191 (65) [$M^+ - CO_2CH_3$], 159 (41) [$M^+ - CO_2CH_3 - CH_4O$], 131 (100) [$M^+ - CH_4O - CO - CH_3CO_2$].

Fraction III: **21f** as a mixture of three diastereomers (138 mg, 35%); $R_f = 0.11$ (pentane/diethyl ether 10:1); IR (film): $\tilde{\nu} = 2953$, 1734 (C=O), 1649 (C=C), 1436, 1260, 1200, 1172, 1019, 808 cm^{-1}; part of the ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 5.06 – 5.02$ (m, 1H; CH=C, isomer B, rel. intensity 0.40), 4.83 – 4.80 (m, 1H; CH=C, isomer A, rel. intensity 1.0); MS (70 eV): *m*/*z* (%): 394 (7) [M^+], 362 (66) [$M^+ - MeOH$], 334 (21) [$M^+ - MeOH -$

CO], 302 (76), [$M^+ - 2\,\mathrm{MeOH} - \mathrm{CO}$], 274 (74) [$M^+ - 2\,\mathrm{MeOH} - 2\,\mathrm{CO}$], 243 (60) [$M^+ - 2\,\mathrm{MeOH} - 2\,\mathrm{CO} - \mathrm{OCH_3}$], 215 (100) [$M^+ - 2\,\mathrm{MeOH} - 3\,\mathrm{CO} - \mathrm{OCH_3}$], 183 (34) [$M^+ - 3\,\mathrm{MeOH} - 3\,\mathrm{CO} - \mathrm{OCH_3}$], 155 (83) [$M^+ - 3\,\mathrm{MeOH} - 4\,\mathrm{CO} - \mathrm{OCH_3}$]; HRMS: m/z (%): calcd for $C_{20}H_{26}O_8$: 394.1627; found: 394.1627.

Methyl 8-(2-thiophenyl)spiro[2.5]oct-7-ene-5-carboxylate (25): According to GP 5, palladium(II) acetate (11.2 mg, 49.9 µmol, 5 mol %), triphenylphosphane (39.3 mg, 150 µmol, 15 mol %), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K_2CO_3 (277 mg, 2.00 mmol), Et_4NCl (166 mg, 1.00 mmol) and 2-bromothiophene (**24**, 163 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with methyl acrylate (**17a**, 172 mg, 2.00 mmol) for 48 h at 80 °C. After work-up, chromatography of the crude product on 50 g silica gel (column 2 × 20 cm, pentane/diethyl ether 10:1) yielded **25** as a yellowish oil (218 mg, 88 %). $R_f = 0.36$ (pentane/diethyl ether 10:1); IR (film): $\tilde{\nu} =$ 3072, 2998, 2948, 1734 (C=O), 1653 (C=C), 1628, 1436, 1376, 1314, 1260, 1194, 1169, 1023 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.13$ (dd, $^3J = 5.2$, $^4J = 1.2$ Hz, 1 H; 3′-H), 6.90 (dd, $^3J = 5.2$, $^3J = 3.5$ Hz, 1 H; 4′-H), 6.71 (dd, $^3J = 3.4$, $^4J = 1.2$ Hz, 1 H; 5′-H), 5.85 (t, $^3J = 3.8$ Hz, 1 H; 7-H), 3.70 (s, 3 H; OCH_3), 2.87 (ddt, $^3J = 11.7$, $^3J = 8.3$, $^3J = 3.1$ Hz, 1 H; 5-H), 2.49 (dd, $^3J = 8.3$, $^3J = 3.8$ Hz, 2 H; 6-H), 2.17 (dd, $^2J = 13.1$, $^3J = 11.7$ Hz, 1 H; 4-H), 1.49 (dd, $^2J = 13.0$, $^3J = 3.1$ Hz, 1 H; 4-H), 0.96–0.89 (m, 1 H; *c*Pr-H), 0.73–0.47 (m, 3 H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 175.6$ (C_{quat}, CO), 141.0 (C_{quat}, C-2′), 135.6 (C_{quat}, C-8), 127.6 (+, C-3′*), 126.3 (+, C-4′*), 125.3 (+, C-5′*), 124.0 (+, C-7*), 51.6 (+, OCH_3), 38.9 (+, C-5), 37.4 (−, C-6), 28.6 (−, C-4), 20.0 (C_{quat}, C-3), 14.0 (−, *c*Pr-C), 12.2 (−, *c*Pr-C); MS (70 eV): m/z (%): 248 (82) [M^+], 217 (10) [$M^+ - \mathrm{OCH_3}$], 189 (100) [$M^+ - \mathrm{CO_2CH_3}$], 168 (51), 161 (44), 137 (68); elemental analysis calcd (%) for $C_{14}H_{16}O_2S$ (248.3): C 67.71, H 6.49; found: C 67.83, H 6.54.

Methyl 8-(3-thiophenyl)spiro[2.5]oct-7-ene-5-carboxylate (27) and methyl (*E*)-3-thiophen-3-ylacrylate (28): According to GP 5, palladium(II) acetate (11.2 mg, 49.9 µmol), triphenylphosphane (26.3 mg, 100 µmol), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K_2CO_3 (277 mg, 2.00 mmol), Et_4NCl (166 mg, 1.00 mmol) and 3-bromothiophene (**26**, 163 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with methyl acrylate (**17a**, 172 mg, 2.00 mmol) for 72 h at 80 °C. After work-up, chromatography of the crude product on 50 g silica gel (column 2 × 20 cm, pentane/diethyl ether 10:1) gave:

Fraction I: **27** as a yellowish oil (169 mg, 68 %); $R_f = 0.50$ (pentane/diethyl ether 10:1); IR (film): $\tilde{\nu} = 3064$, 2996, 2951, 1736 (C=O), 1635 (C=C), 1435, 1371, 1259, 1196, 1170, 1021, 971 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.18$ (dd, $^3J = 4.9$, $^4J = 3.0$ Hz, 1 H; 5′-H), 6.90 (dd, $^4J = 3.0$, $^4J = 1.2$ Hz, 1 H; 2′-H), 6.83 (dd, $^3J = 4.9$, $^4J = 1.2$ Hz, 1 H; 4′-H), 5.64 (t, $^3J = 3.8$ Hz, 1 H; 7-H), 3.70 (s, 3 H; OCH_3), 2.88 (ddd, $^3J = 11.8$, $^3J = 8.2$, $^3J = 3.0$ Hz, 1 H; 5-H), 2.46 (dd, $^3J = 8.2$, $^3J = 3.8$ Hz, 2 H; 6-H), 2.17 (dd, $^2J = 12.9$, $^3J = 11.8$ Hz, 1 H; 4-H), 1.47 (dd, $^2J = 12.9$, $^3J = 3.0$ Hz, 1 H; 4-H), 0.79–0.67 (m, 1 H; *c*Pr-H), 0.58–0.42 (m, 3 H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 175.8$ (C_{quat}, CO), 140.5 (C_{quat}, C-3′), 138.0 (C_{quat}, C-8), 128.7 (+, C-5′*), 124.7 (+, C-2′*), 124.0 (+, C-4′*), 122.0 (+, C-7), 51.6 (+, OCH_3), 39.1 (+, C-5), 37.4 (−, C-6), 28.5 (−, C-4), 20.0 (C_{quat}, C-3), 13.4 (−, *c*Pr-C), 11.7 (−, *c*Pr-C); MS (70 eV): m/z (%): 248 (66) [M^+], 233 (2) [$M^+ - \mathrm{CH_3}$], 217 (9) [$M^+ - \mathrm{OCH_3}$], 189 (100) [$M^+ - \mathrm{CO_2Me}$], 161 (44) [$M^+ - \mathrm{CO_2Me} - \mathrm{C_2H_4}$], 155 (28); elemental analysis calcd (%) for $C_{14}H_{16}O_2S$ (248.4): C 67.71, H 6.49; found: C 66.80, H 6.47.

Fraction II: **28** (30 mg, 18 %); $R_f = 0.34$ (pentane/diethyl ether 10:1). The spectroscopic data are in accordance with the literature.[33]

7-[Cyclopropylidene(phenyl)methyl]-4-phenylspiro[2.5]oct-4-ene (29): In a sealable Teflon tube palladium(II) acetate (22.4 mg, 100 µmol), triphenylphosphane (78.6 mg, 300 µmol), bicyclopropylidene (**1**, 320 mg, 4.00 mmol), iodobenzene (**2**-Ph, 408 mg, 2.00 mmol) and triethylamine (405 mg, 4.00 mmol) in anhydrous DMF (7.5 mL) were heated for 24 h at 80 °C under a pressure of 10 kbar. After work-up, chromatography of the crude product on 30 g flash silica gel (column 2 × 15 cm, pentane) yielded **29** as a clear oil (89 mg, 28 %). $R_f = 0.33$ (pentane); IR (film): $\tilde{\nu} = 3057$, 2966, 2918, 2849, 1771, 1717, 1675 (C=C), 1598, 1491, 1446, 1260, 1095, 1025, 801 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.40$–7.20 (m, 10 H; Ar-H), 5.59 (t, $^3J = 3.7$ Hz, 1 H; 5-H), 3.36 (ddt, $^3J = 11.9$, $^3J = 8.3$, $^3J = 2.9$ Hz, 1 H; 7-H), 2.49 (dd, $^3J = 8.3$, $^3J = 3.7$ Hz, 2 H; 6-H), 2.34 (dd, $^2J = 12.8$, $^3J = 11.9$ Hz, 1 H; 8-H), 1.35 (dd, $^2J = 12.8$, $^3J = 2.9$ Hz, 1 H; 8-H), 1.40–1.17 (m, 4 H; *c*Pr-H), 0.75 (m, 1 H; 2-H), 0.64–0.60 (m, 1 H; 2-H), 0.52–0.38 (m, 2 H; 1-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 153.0$ (C_{quat}, *c*Pr-C=CPh*), 142.9 (C_{quat}, *c*Pr-C*), 141.5 (C_{quat}, Ar-C*), 140.8 (C_{quat}, Ar-C*), 131.6 (C_{quat}, C-4*), 129.3 (+, Ar-C), 128.1 (+, Ar-C), 127.7 (+, Ar-C), 127.4 (+, Ar-C), 127.3 (+, Ar-C), 126.4 (+, Ar-C), 119.4 (+, C-5), 40.7 (−, C-6), 38.1 (+, C-7), 27.7 (−, C-8), 21.3 (C_{quat}, C-3), 13.1 (−, C-2), 11.3 (−, C-1), 3.3 (−, *c*Pr-C), 1.7 (−, *c*Pr-C); MS (70 eV): m/z (%): 312 (100) [M^+], 284 (61) [$M^+ - \mathrm{C_2H_4}$], 255 (72) [$M^+ - \mathrm{C_2H_5} - \mathrm{C_2H_4}$], 167 (83); HRMS: m/z (%): calcd for $C_{24}H_{24}$ (312.4): 312.1878 (correct HRMS); found: 312.1878.

Methyl 4-(4-nitrophenyl)-8-phenylspiro[2.5]oct-7-ene-5-carboxylate (*p*-31) and methyl 5-(4-nitrophenyl)-8-phenylspiro[2.5]oct-7-ene-4-carboxylate (*p*-32): According to GP 5, palladium(II) acetate (11.2 mg, 49.9 µmol, 5 mol %), triphenylphosphane (39.3 mg, 150 µmol, 15 mol %), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K_2CO_3 (277 mg, 2.00 mmol), Et_4NCl (166 mg, 1.00 mmol) and iodobenzene (**2**-Ph, 204 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with methyl 3-(4-nitrophenyl)acrylate (*p*-**30**, 414 mg, 2.00 mmol) for 96 h at 80 °C. After work-up, chromatography of the crude product on 25 g silica gel (column 2 × 20 cm, pentane/diethyl ether 2:1) gave:

Fraction I: *p*-**32** as a yellowish oil (113 mg, 31 %); $R_f = 0.49$ (pentane/diethyl ether 2:1); IR (film): $\tilde{\nu} = 3040$, 2957, 1732 (C=O), 1645 (C=C), 1532, 1435, 1341, 1261, 1174, 1030, 802 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 8.20$ (d, $^3J = 8.7$ Hz, 2 H; 3″-H, 5″-H), 7.62 (d, $^3J = 8.7$ Hz, 2 H; 2″-H, 6″-H), 7.34–7.28 (m, 3 H; 3′-H, 4′-H, 5′-H), 7.14–7.11 (m, 2 H; 2′-H, 6′-H), 5.66 (dd, $^3J = 4.9$, $^3J = 3.0$ Hz, 1 H; 7-H), 3.72 (s, 3 H; OCH_3), 3.26 (d, $^3J = 4.4$ Hz, 1 H; 4-H), 3.09 (ddd, $^3J = 5.8$, $^3J = 4.9$, $^3J = 4.4$ Hz, 1 H; 5-H), 2.64 (ddd, $^2J = 18.0$, $^3J = 5.8$, $^3J = 3.0$ Hz, 1 H; 6-H), 2.11 (ddd, $^2J = 18.0$, $^3J = 5.8$, $^3J = 3.0$ Hz, 1 H; 6-H), 0.76–0.31 (m, 4 H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 173.8$ (C_{quat}, CO), 150.3 (C_{quat}, C-4″*), 146.6 (C_{quat}, C-8*), 141.6 (C_{quat}, Ar-C*), 139.7 (C_{quat}, Ar-C*), 129.2 (+, Ar-C), 129.2 (+, Ar-C), 127.7 (+, Ar-C), 127.0 (+, C-4′), 124.6 (+, C-7), 123.4 (+, C-3″, C-5″), 51.8 (+, OCH_3), 49.4 (+, C-5), 45.0 (+, C-4), 24.4 (−, C-6), 20.9 (C_{quat}, C-3), 12.9 (−, *c*Pr-C), 9.4 (−, *c*Pr-C); MS (70 eV): m/z (%): 363 (16) [M^+], 332 (2) [$M^+ - \mathrm{OCH_3}$], 303 (16) [$M^+ - \mathrm{MeOH} - \mathrm{CO}$], 207 (63) [$C_{10}H_9NO_4^+$], 176 (100) [$C_{10}H_9NO_4^+ - \mathrm{OCH_3}$], 130 (20), 102 (20); elemental analysis calcd (%) for $C_{22}H_{21}NO_4$ (363.4): C 72.71, H 5.82; found: C 72.82, H 5.96.

Fraction II: *p*-**31** as yellow crystals (225 mg, 62 %); m.p. 115 °C; $R_f = 0.43$; IR (film): $\tilde{\nu} = 3040$, 2962, 2931, 1735 (C=O), 1651 (C=C), 1532, 1437, 1259, 1176, 1074, 1027, 800 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 8.19$ (d, $^3J = 8.8$ Hz, 2 H; 3″-H, 5″-H), 7.53 (d, $^3J = 8.8$ Hz, 2 H; 2″-H, 6″-H), 7.32–7.24 (m, 3 H; 3′-H, 4′-H, 5′-H), 7.12–7.08 (m, 2 H; 2′-H, 6′-H), 5.69 (t, $^3J = 3.7$ Hz, 1 H; 7-H), 3.69 (ddd, $^3J = 7.1$, $^3J = 6.2$, $^3J = 6.2$ Hz, 1 H; 5-H), 3.61 (s, 3 H; OCH_3), 2.85 (d, $^3J = 7.1$ Hz, 1 H; 4-H), 2.71 (ddd, $^2J = 18.5$, $^3J = 6.2$, $^3J = 3.7$ Hz, 1 H; 6-H), 2.48 (ddd, $^2J = 18.5$, $^3J = 6.2$, $^3J = 3.7$ Hz, 1 H; 6-H), 0.68–0.56 (m, 2 H; *c*Pr-H), 0.43–0.34 (m, 1 H; *c*Pr-H), 0.18–0.12 (m, 1 H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 172.92$ (C_{quat}, CO), 152.5 (C_{quat}, C-4″*), 147.7 (C_{quat}, C-8*), 142.9 (C_{quat}, Ar-C*), 139.7 (C_{quat}, Ar-C*), 129.2 (+, Ar-C), 128.4 (+, Ar-C), 126.91 (+, Ar-C), 126.91 (+, C-4′), 123.8 (+, C-7), 123.6 (+, C-3″, C-5″), 53.7 (+, C-5), 51.7 (+, OCH_3), 41.7 (+, C-4), 30.8 (−, C-6), 20.1 (C_{quat}, C-3), 11.4 (−, *c*Pr-C), 9.5 (−, *c*Pr-C); MS (70 eV), m/z (%): 363 (10) [M^+], 304 (15) [$M^+ - \mathrm{CO_2Me}$], 279 (36), 167 (44), 149 (100) [$M^+ - \mathrm{C_6H_5} - \mathrm{C_6H_4NO_2} - \mathrm{CH_3}$], 113 (16); elemental analysis calcd (%) for $C_{22}H_{21}NO_4$ (363.4): C 72.71, H 5.82; found: C 72.50, H 5.64.

Methyl 4-(3-nitrophenyl)-8-phenylspiro[2.5]oct-7-ene-5-carboxylate (*m*-31) and methyl 5-(3-nitrophenyl)-8-phenylspiro[2.5]oct-7-ene-4-carboxylate (*m*-32): According to GP 5, palladium(II) acetate (11.2 mg, 49.9 µmol, 5 mol %), triphenylphosphane (39.3 mg, 150 µmol, 15 mol %), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K_2CO_3 (277 mg, 2.00 mmol), Et_4NCl (166 mg, 1.00 mmol) and iodobenzene (**2**-Ph, 204 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with methyl 3-(3-nitrophenyl)acrylate (*m*-**30**, 414 mg, 2.00 mmol) for 96 h at 80 °C. After work-up, chromatography of the crude product on 25 g silica gel (column 2 × 20 cm, pentane/diethyl ether 5:1) gave:

Fraction I: *m*-**31** as a yellowish oil (139 mg, 38 %), $R_f = 0.24$ (pentane/diethyl ether 5:1); IR (film): $\tilde{\nu} = 3042$, 2958, 2929, 1734 (C=O), 1650 (C=C), 1530, 1437, 1348, 1261, 1200, 1175, 1074, 1027, 805 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 8.31$ (dd, $^4J = 1.1$, $^4J = 0.9$ Hz, 1 H; 2″-H), 8.09 (ddd, $^3J = 7.7$, $^4J = 1.1$, $^4J = 0.8$ Hz, 1 H; 4″-H), 7.63 (ddd, $^3J = 7.4$, $^4J = 0.9$, $^4J = 0.8$ Hz, 1 H; 6″-H), 7.43 (dd, $^3J = 7.7$, $^3J = 7.4$ Hz, 1 H; 5″-H), 7.32–7.20 (m, 3 H; 3′-H, 4′-H, 5′-H), 7.14–7.08 (m, 2 H; 2′-H, 6′-H), 5.71 (t, $^3J = 3.6$ Hz, 1 H; 7-H), 3.71 (ddd, $^3J = 7.2$, $^3J = 6.3$, $^3J = 6.3$ Hz, 1 H; 5-H), 3.63 (s, 3 H; OCH_3), 2.74 (ddd, $^2J = 18.4$, $^3J = 6.3$, $^3J = 3.6$ Hz, 1 H; 6-H), 2.69 (d,

$^3J = 7.2$ Hz, 1H; 4-H), 2.50 (ddd, $^2J = 18.4$, $^3J = 6.3$, $^3J = 3.6$ Hz, 1H; 6-H), 0.97–0.83 (m, 1H; *c*Pr-H), 0.67–0.58 (m, 2H; *c*Pr-H), 0.40–0.30 (m, 1H; *c*Pr-H); ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): $\delta = 173.8$ ($\mathrm{C_{quat}}$, CO), 166.6 ($\mathrm{C_{quat}}$, C-3″), 148.2 ($\mathrm{C_{quat}}$, C-8), 144.8 ($\mathrm{C_{quat}}$, C-1″), 139.7 ($\mathrm{C_{quat}}$, C-1′), 133.6 ($\mathrm{C_{quat}}$, C-4″), 130.0 (+, C-2″), 129.3 (+, C-2′, C-6′), 127.7 (+, C-3′, C-5′), 124.5 (+, C-6″), 122.4 (+, C-4′), 120.9 (+, C-7), 52.0 (+, OCH$_3$), 44.9 (+, C-4), 39.7 (+, C-5), 23.7 (−, C-6), 20.7 ($\mathrm{C_{quat}}$, C-3), 13.0 (−, *c*Pr-C), 9.6 (−, *c*Pr-C); MS (70 eV): *m*/*z* (%): 363 (15) [M^+], 332 (3) [$M^+ - \mathrm{OCH_3}$], 303 (17) [$M^+ - \mathrm{MeOH} - \mathrm{CO}$], 207 (61) [$\mathrm{C_{10}H_9NO_4^+}$], 176 (100) [$\mathrm{C_{10}H_9NO_4^+} - \mathrm{OCH_3}$], 130 (24); elemental analysis calcd (%) for $\mathrm{C_{22}H_{21}NO_4}$ (363.4): C 72.71, H 5.82, N 3.85; found: C 72.66, H 5.87, N 3.87.

Fraction II: *m*-**32** as a yellowish oil (46 mg, 13%); $R_f = 0.22$ (pentane/diethyl ether 5:1); IR (film): $\tilde{\nu} = 3041$, 2958, 2930, 1735 (C=O), 1651 (C=C), 1529, 1435, 1347, 1260, 1073, 1027, 802 cm^{-1}; ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 8.37$ (dd, $^4J = 1.1$, $^4J = 1.0$ Hz, 1H; 2″-H), 8.11 (ddd, $^3J = 7.5$, $^4J = 1.1$, $^4J = 0.8$ Hz, 1H; 4″-H), 7.80 (ddd, $^3J = 7.3$, $^4J = 1.0$, $^4J = 0.8$ Hz, 1H; 6″-H), 7.51 (dd, $^3J = 7.5$, $^3J = 7.3$ Hz, 1H; 5″-H), 7.34–7.2 (m, 3H; 3′-H, 4′-H, 5′-H), 7.19–7.15 (m, 2H; 2′-H, 6′-H), 5.65 (dd, $^3J = 4.3$, $^3J = 2.8$ Hz, 1H; 7-H), 3.74 (s, 3H; OCH$_3$), 3.22 (d, $^3J = 4.4$ Hz, 1H; 4-H), 3.10 (ddd, $^3J = 5.5$, $^3J = 4.3$, $^3J = 3.4$ Hz, 1H; 5-H), 2.63 (ddd, $^2J = 18.2$, $^3J = 4.3$, $^3J = 3.4$ Hz, 1H; 6-H), 2.04 (ddd, $^2J = 18.2$, $^3J = 5.5$, $^3J = 2.8$ Hz, 1H; 6-H), 0.87–0.29 (m, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): $\delta = 10.9$ (−, *c*Pr-C), 14.1 (−, *c*Pr-C), 20.7 ($\mathrm{C_{quat}}$, C-3), 23.0 (−, C-6), 38.7 (+, C-5), 49.1 (+, C-4), 51.8 (+, OCH$_3$), 173.8 ($\mathrm{C_{quat}}$, CO), 167.8 ($\mathrm{C_{quat}}$, C-3″), 148.6 ($\mathrm{C_{quat}}$, C-8), 141.4 ($\mathrm{C_{quat}}$, C-1″), 136.1 ($\mathrm{C_{quat}}$, C-1′), 134.4 (+, C-4″), 129.2 (+, C-2′, C-6′), 128.8 (+, C-2″), 126.9 (+, C-3′, C-5′), 124.8 (+, C-6″), 123.2 (+, C-4′), 121.6 (+, C-7); MS (70 eV): *m*/*z* (%): 363 (9) [M^+], 304 (17) [$M^+ - \mathrm{CO_2Me}$], 149 (100) [$M^+ - \mathrm{C_6H_5} - \mathrm{C_6H_4NO_2} - \mathrm{CH_3}$], 113 (19); elemental analysis calcd (%) for $\mathrm{C_{22}H_{21}NO_4}$ (363.4): C 72.71, H 5.82, N 3.85; found: C 72.82, H 5.95, N 3.91.

Methyl 4-(2-nitrophenyl)-8-phenylspiro[2.5]oct-7-ene-5-carboxylate (*o*-31) and methyl 5-(2-nitrophenyl)-8-phenylspiro[2.5]oct-7-ene-4-carboxylate (*o*-32): According to GP 5, palladium(II) acetate (11.2 mg, 49.9 µmol, 5 mol%), triphenylphosphane (39.3 mg, 150 µmol, 15 mol%), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K$_2$CO$_3$ (277 mg, 2.00 mmol), Et$_4$NCl (166 mg, 1.00 mmol) and iodobenzene (**2**-Ph, 204 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with methyl 3-(2-nitrophenyl)acrylate (*o*-**30**, 414 mg, 2.00 mmol) for 96 h at 80 °C. After work-up, chromatography of the crude product on 25 g silica gel (column 2 × 20 cm, pentane/diethyl ether 10:1) gave:

Fraction I: **29** as a yellowish oil (83 mg, 27%); $R_f = 0.86$ (pentane/diethyl ether 10:1).

Fraction II: An unseparable mixture of *o*-**31** and *o*-**32** (3:2, ^{1}H NMR) as a yellowish oil (92 mg, 25%). $R_f = 0.31$ (pentane/diethyl ether 10:1); *o*-**32**: ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 7.75$ (d, $^3J = 8.1$ Hz, 1H; 3″-H), 7.65–7.52 (m, 2H; 4″-H, 5″-H), 7.41 (d, $^3J = 8.0$ Hz, 1H; 6″-H), 7.32–7.21 (m, 3H; 3′-H, 4′-H, 5′-H), 7.14–7.10 (m, 2H; 2′-H, 6′-H), 5.69 (dd, $^3J = 4.2$, $^3J = 3.4$ Hz, 1H; 7-H), 4.01 (ddd, $^3J = 7.9$, $^3J = 7.1$, $^3J = 5.8$ Hz, 1H; 5-H), 3.06 (d, $^3J = 7.9$ Hz, 1H; 4-H), 3.51 (s, 3H; OCH$_3$), 2.87 (ddd, $^2J = 18.3$, $^3J = 5.8$, $^3J = 4.2$ Hz, 1H; 6-H), 2.43 (ddd, $^2J = 18.3$, $^3J = 7.1$, $^3J = 3.4$ Hz, 1H; 6-H), 0.75–0.27 (m, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): $\delta = 172.6$ ($\mathrm{C_{quat}}$, CO), 142.6 ($\mathrm{C_{quat}}$, C-2″), 139.7 ($\mathrm{C_{quat}}$, Ar-C*), 138.9 ($\mathrm{C_{quat}}$, C-8*), 136.9 ($\mathrm{C_{quat}}$, Ar-C*), 132.4 (+, Ar-C), 129.2 (+, Ar-C), 128.8 (+, Ar-C), 127.5 (+, Ar-C), 127.2 (+, Ar-C), 126.8 (+, Ar-C), 124.4 (+, C-4′), 123.9 (+, C-7), 52.8 (+, C-5), 51.6 (+, OCH$_3$), 36.3 (+, C-4), 31.7 (−, C-6), 20.6 ($\mathrm{C_{quat}}$, C-3), 11.0 (−, *c*Pr-C), 9.5 (−, *c*Pr-C); *o*-**31**: ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 7.95$ (d, $^3J = 7.9$ Hz, 1H; 3″-H), 7.80 (d, $^3J = 8.1$ Hz, 1H; 6″-H), 7.65–7.52 (m, 2H; 4″-H, 5″-H), 7.32–7.21 (m, 3H; 3′-H, 4′-H, 5′-H), 7.14–7.11 (m, 2H; 2′-H, 6′-H), 5.69 (dd, $^3J = 4.2$, $^3J = 3.4$ Hz, 1H; 7-H), 3.71 (s, 3H; OCH$_3$), 3.70 (d, $^3J = 9.3$ Hz, 1H; 4-H), 3.16 (ddd, $^3J = 9.3$, $^3J = 5.6$, $^3J = 4.6$ Hz, 1H; 5-H), 2.68 (ddd, $^2J = 18.0$, $^3J = 4.6$, $^3J = 4.2$ Hz, 1H; 6-H), 2.16 (ddd, $^2J = 18.0$, $^3J = 5.6$, $^3J = 3.4$ Hz, 1H; 6-H), 0.75–0.27 (m, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): $\delta = 173.6$ ($\mathrm{C_{quat}}$, CO), 150.1 ($\mathrm{C_{quat}}$, C-2″), 142.6 ($\mathrm{C_{quat}}$, Ar-C*), 139.7 ($\mathrm{C_{quat}}$, Ar-C*), 136.9 ($\mathrm{C_{quat}}$, C-8*), 132.4 (+, Ar-C), 130.0 (+, Ar-C), 129.2 (+, Ar-C), 127.6 (+, Ar-C), 127.5 (+, Ar-C), 126.9 (+, Ar-C), 124.8 (+, C-4′), 124.2 (+, C-7), 51.7 (+, OCH$_3$), 44.3 (+, C-5), 43.8 (+, C-4), 24.3 (−, C-6), 21.7 ($\mathrm{C_{quat}}$, C-3), 14.5 (−, *c*Pr-C), 9.8 (−, *c*Pr-C); *o*-**31** and *o*-**32**: IR (film): $\tilde{\nu} = 3039$, 2956, 2930, 1735 (C=O), 1648 (C=C), 1531, 1435, 1347, 1260, 1201, 1173, 1075, 1028, 801 cm^{-1}; MS (70 eV): *m*/*z* (%): 363 (1) [M^+], 348 (2) [$M^+ - \mathrm{CH_3}$], 332 (5) [$M^+ - \mathrm{OCH_3}$], 328 (84), 286 (82) [$M^+ - \mathrm{OCH_3} - \mathrm{NO_2}$], 268 (100), 254 (42), 115 (42), 91 (32) [$\mathrm{C_7H_7^+}$].

Methyl *syn*-8-(2-methylphenyl)spiro[2.5]oct-7-ene-5-carboxylate (*syn*-34aa) and methyl *anti*-8-(2-methylphenyl)spiro[2.5]oct-7-ene-5-carboxylate (*anti*-34aa): According to GP 5, palladium(II) acetate (11.2 mg, 49.9 µmol, 5 mol%), triphenylphosphane (39.3 mg, 150 µmol, 15 mol%), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K$_2$CO$_3$ (277 mg, 2.00 mmol), Et$_4$NCl (166 mg, 1.00 mmol) and *ortho*-iodotoluene (**33a**, 218 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with methyl acrylate (**17a**, 172 mg, 2.00 mmol) for 48 h at 80 °C. After work-up, chromatography of the crude product on 25 g silica gel (column 2 × 20 cm, pentane/diethyl ether 10:1) yielded a mixture of two rotamers *syn*-**34aa** and *anti*-**34aa** (1:2.0, ^{1}H NMR) as a yellowish oil (254 mg, 99%). $R_f = 0.54$ (pentane/diethyl ether 10:1); *syn*-**34aa**: ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 7.29$–7.19 (m, 3H; 3′-H, 4′-H, 5′-H), 7.06 (d, $^3J = 6.5$ Hz, 1H; 6′-H), 5.62 (t, $^3J = 3.6$ Hz, 1H; 7-H), 3.85 (s, 3H; OCH$_3$), 3.11–3.01 (m, 1H; 5-H), 2.64 (dd, $^3J = 8.1$, $^3J = 3.6$ Hz, 2H; 6-H), 2.35 (s, 3H; Ar-CH$_3$), 2.30 (dd, $^2J = 13.2$, $^3J = 11.1$ Hz, 1H; 4-H), 1.82 (dd, $^2J = 13.2$, $^3J = 3.1$ Hz, 1H; 4-H), 0.70–0.50 (m, 3H; *c*Pr-H), 0.42–0.23 (m, 1H; *c*Pr-H); ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): $\delta = 175.9$ ($\mathrm{C_{quat}}$, CO), 141.1 ($\mathrm{C_{quat}}$, Ar-C*), 139.2 ($\mathrm{C_{quat}}$, Ar-C*), 136.9 ($\mathrm{C_{quat}}$, C-8*), 130.2 (+, Ar-C), 129.5 (+, Ar-C), 126.7 (+, Ar-C), 124.6 (+, Ar-C), 123.6 (+, C-7), 51.7 (+, OCH$_3$), 39.3 (+, C-5), 37.2 (−, C-6), 28.2 (−, C-4), 19.9 ($\mathrm{C_{quat}}$, C-3), 19.6 (+, Ar-CH$_3$), 12.4 (−, *c*Pr-C), 11.5 (−, *c*Pr-C); *anti*-**34aa**: ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 7.29$–7.19 (m, 3H; 3′-H, 4′-H, 5′-H), 6.99 (d, $^3J = 7.2$ Hz, 1H; 6′-H), 5.60 (t, $^3J = 3.6$ Hz, 1H; 7-H), 3.85 (s, 3H; OCH$_3$), 3.11–3.01 (m, 1H; 5-H), 2.64 (dd, $^3J = 8.1$, $^3J = 3.6$ Hz, 2H; 6-H), 2.38 (dd, $^2J = 12.8$, $^3J = 12.0$ Hz, 1H; 4-H), 2.34 (s, 3H; Ar-CH$_3$), 1.60 (dd, $^2J = 12.8$, $^3J = 2.9$ Hz, 1H; 4-H), 0.70–0.50 (m, 3H; *c*Pr-H), 0.42–0.23 (m, 1H; *c*Pr-H); ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): $\delta = 176.1$ ($\mathrm{C_{quat}}$, CO), 142.3 ($\mathrm{C_{quat}}$, Ar-C*), 139.3 ($\mathrm{C_{quat}}$, Ar-C*), 136.9 ($\mathrm{C_{quat}}$, C-8*), 129.4 (+, Ar-C), 129.3 (+, Ar-C), 126.9 (+, Ar-C), 124.8 (+, Ar-C), 123.0 (+, C-7), 51.7 (+, OCH$_3$), 39.4 (+, C-5), 37.0 (−, C-6), 28.4 (−, C-4), 20.0 ($\mathrm{C_{quat}}$, C-3), 19.6 (+, Ar-CH$_3$), 12.7 (−, *c*Pr-C), 11.5 (−, *c*Pr-C); *syn*-**34aa** and *anti*-**34aa**: IR (film): $\tilde{\nu} = 3081$, 2997, 2949, 2850, 1736 (C=O), 1645 (C=C), 1489, 1436, 1378, 1259, 1193, 1170, 1025, 760, 731 cm^{-1}; MS (70 eV): *m*/*z* (%): 256 (40) [M^+], 225 (8) [$M^+ - \mathrm{OCH_3}$], 197 (80) [$M^+ - \mathrm{CO_2Me}$], 181 (100) [$M^+ - \mathrm{CH_3} - \mathrm{CH_4O} - \mathrm{CO}$], 169 (40), 155 (24), 91 (8) [$\mathrm{C_7H_7^+}$]; elemental analysis calcd (%) for $\mathrm{C_{17}H_{20}O_2}$ (256.3): C 79.65, H 7.86; found: C 79.84, H 7.75.

***tert*-Butyl *syn*-8-(2-methylphenyl)spiro[2.5]oct-7-ene-5-carboxylate (*syn*-34ea) and *tert*-butyl *anti*-8-(2-methylphenyl)spiro[2.5]oct-7-ene-5-carboxylate (*syn*-34ea)**: According to GP 5, palladium(II) acetate (11.2 mg, 49.9 µmol, 5 mol%), triphenylphosphane (39.3 mg, 150 µmol, 15 mol%), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K$_2$CO$_3$ (277 mg, 2.00 mmol), Et$_4$NCl (166 mg, 1.00 mmol) and *ortho*-iodotoluene (**33a**, 218 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with *tert*-butyl acrylate (**17e**, 256 mg, 2.00 mmol) for 48 h at 80 °C. After work-up, chromatography of the crude product on 25 g silica gel (column 2 × 20 cm, pentane/diethyl ether 20:1) yielded a mixture of two rotamers *syn*-**34ea** and *anti*-**34ea** (1:3.0, ^{1}H NMR) as a yellowish oil (227 mg, 76%). $R_f = 0.54$ (pentane/diethyl ether 20:1). *syn*-**34ea**: ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 7.12$–7.07 (m, 3H; 3′-H, 4′-H, 5′-H), 6.92 (d, $^3J = 7.1$ Hz, 1H; 6′-H), 5.48 (t, $^3J = 3.7$ Hz, 1H; 7-H), 2.89–2.77 (m, 1H; 5-H), 2.46 (dd, $^3J = 7.6$, $^3J = 3.7$ Hz, 2H; 6-H), 2.22 (s, 3H; Ar-CH$_3$), 2.12 (dd, $^2J = 13.1$, $^3J = 10.9$ Hz, 1H; 4-H), 1.64 (dd, $^2J = 13.1$, $^3J = 3.0$ Hz, 1H; 4-H), 1.49 [s, 9H; C(CH$_3$)$_3$], 0.55–0.37 (m, 3H; *c*Pr-H), 0.26–0.20 (m, 1H; *c*Pr-H); ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): $\delta = 174.9$ ($\mathrm{C_{quat}}$, CO), 141.1 ($\mathrm{C_{quat}}$, Ar-C*), 139.4 ($\mathrm{C_{quat}}$, Ar-C*), 136.9 ($\mathrm{C_{quat}}$, C-8*), 130.2 (+, Ar-C), 129.5 (+, Ar-C), 126.6 (+, Ar-C), 124.5 (+, Ar-C), 123.8 (+, C-7), 79.9 [$\mathrm{C_{quat}}$, *C*(CH$_3$)$_3$], 40.4 (+, C-5), 37.2 (−, C-6), 28.3 (−, C-4), 28.1 [+, C(*C*H$_3$)$_3$], 19.9 ($\mathrm{C_{quat}}$, C-3), 19.5 (+, Ar-CH$_3$), 12.4 (−, *c*Pr-C), 11.7 (−, *c*Pr-C); *anti*-**34ea**: ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 7.12$–7.07 (m, 3H; 3′-H, 4′-H, 5′-H), 6.86 (d, $^3J = 7.1$ Hz, 1H; 6′-H), 5.47 (t, $^3J = 3.7$ Hz, 1H; 7-H), 2.89–2.77 (m, 1H; 5-H), 2.46 (dd, $^3J = 7.6$, $^3J = 3.7$ Hz, 2H; 6-H), 2.23 (dd, $^2J = 13.0$, $^3J = 12.0$ Hz, 1H; 4-H), 2.21 (s, 3H; Ar-CH$_3$), 1.48 [s, 9H; C(CH$_3$)$_3$], 1.43 (dd, $^2J = 13.0$, $^3J = 2.8$ Hz, 1H; 4-H), 0.55–0.37 (m, 3H; *c*Pr-H), 0.26–0.20 (m, 1H; *c*Pr-H); ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): $\delta = 175.0$ ($\mathrm{C_{quat}}$, CO), 142.2 ($\mathrm{C_{quat}}$, Ar-C*), 139.4 ($\mathrm{C_{quat}}$, Ar-C*), 136.9 ($\mathrm{C_{quat}}$, C-8*), 129.4 (+, Ar-C), 129.2 (+, Ar-C), 126.8 (+, Ar-C), 124.8 (+, Ar-C), 123.2 (+, C-7), 79.9 [$\mathrm{C_{quat}}$, *C*(CH$_3$)$_3$], 40.5 (+, C-5), 36.9 (−, C-6), 28.6 (−, C-4), 28.0 [+, C(*C*H$_3$)$_3$], 20.0 ($\mathrm{C_{quat}}$, C-3), 19.6 (+, Ar-CH$_3$), 12.6 (−, *c*Pr-C), 11.5 (−, *c*Pr-C); *syn*-**34ea** and *anti*-**34ea**: IR (film): $\tilde{\nu} = 3081$, 2977, 2929, 1727 (C=O), 1652 (C=C), 1486, 1456, 1366, 1258, 1152, 1023, 761, 730 cm^{-1}; MS (70 eV);

m/*z* (%): 298 (3) [M^+], 242 (100) [$M^+ - C_4H_8$], 225 (17) [$M^+ -$ O*t*Bu], 197 (39) [$M^+ - CO_2$*t*Bu], 181 (80), 169 (20), 145 (24); elemental analysis calcd (%) for $C_{20}H_{26}O_2$ (298.4): C 80.50, H 8.78; found: C 80.26, H 8.54.

Methyl *syn*-8-(2-benzylphenyl)spiro[2.5]oct-7-ene-5-carboxylate (*syn*-34ab) and methyl *anti*-8-(2-benzylphenyl)spiro[2.5]oct-7-ene-5-carboxylate (*anti*-34ab): According to GP 5, palladium(II) acetate (11.2 mg, 49.9 µmol, 5 mol%), triphenylphosphane (39.3 mg, 150 µmol, 15 mol%), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K_2CO_3 (277 mg, 2.00 mmol), Et_4NCl (166 mg, 1.00 mmol) and *ortho*-benzyliodobenzene (**33b**, 294 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with methyl acrylate (**17a**, 172 mg, 2.00 mmol) for 48 h at 80 °C. After work-up, chromatography of the crude product on 25 g silica gel (column 2 × 20 cm, pentane/diethyl), ether 10:1) gave:

Fraction I: A mixture of polymers and **18a**-H (53 mg). $R_f = 0.57$ (pentane/diethyl), ether 10:1).

Fraction II: A mixture of two rotamers *syn*-**34ab** and *anti*-**34ab** (1:2.0, ^{1}H NMR) as a yellowish oil (282 mg, 85%); $R_f = 0.43$ (pentane/diethyl ether 10:1); *syn*-**34ab**: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.32-7.07$ (m, 8H; Ar-H), 7.00 (dd, $^3J = 6.9$, $^4J = 1.9$ Hz, 1H; 6′-H), 5.42 (t, $^3J = 3.7$ Hz, 1H; 7-H), 4.05–3.88 (AB system: $\delta_A = 4.01$, $\delta_B = 3.91$, $^2J = 15.3$ Hz, 2H; benzyl-CH_2), 3.73 (s, 3H; OCH_3), 3.02–2.90 (m, 1H; 5-H), 2.50–2.43 (m, 2H; 6-H), 2.15 (dd, $^2J = 12.9$, $^3J = 10.1$ Hz, 1H; 4-H), 1.75 (dd, $^2J = 12.9$, $^3J = 2.4$ Hz, 1H; 4-H), 0.63–0.31 (m, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 175.6$ (C_{quat}, CO), 141.6 (C_{quat}, Ar-C*), 140.2 (C_{quat}, Ar-C*), 139.2 (C_{quat}, Ar-C*), 138.7 (C_{quat}, C-8*), 130.4 (+, Ar-C), 129.2 (+, Ar-C), 129.0 (+, Ar-C), 128.9 (+, Ar-C), 128.1 (+, Ar-C), 126.9 (+, Ar-C), 125.1 (+, Ar-C), 124.7 (+, C-7), 51.5 (+, OCH_3), 39.1 (+, C-5), 38.8 (−, benzyl-CH_2), 37.2 (−, C-6), 28.0 (−, C-4), 19.9 (C_{quat}, C-3), 12.1 (−, *c*Pr-C), 11.4 (−, *c*Pr-C); *anti*-**34ab**: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.32-7.07$ (m, 8H; Ar-H), 6.92 (dd, $^3J = 6.9$, $^4J = 1.7$ Hz, 1H; 6′-H), 5.41 (t, $^3J = 3.6$ Hz, 1H; 7-H), 4.02–3.85 (AB system: $\delta_A = 3.98$, $\delta_B = 3.89$, $^2J = 15.3$ Hz, 2H; benzyl-CH_2), 3.72 (s, 3H; OCH_3), 3.02–2.90 (m, 1H; 5-H), 2.50–2.43 (m, 2H; 6-H), 2.29 (dd, $^2J = 12.9$, $^3J = 12.0$ Hz, 1H; 4-H), 1.50 (dd, $^2J = 12.9$, $^3J = 2.4$ Hz, 1H; 4-H), 0.63–0.31 (m, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 175.9$ (C_{quat}, CO), 141.3 (C_{quat}, Ar-C*), 141.2 (C_{quat}, Ar-C*), 139.8 (C_{quat}, Ar-C*), 138.7 (C_{quat}, C-8*), 129.6 (+, Ar-C), 129.0 (+, Ar-C), 128.2 (+, Ar-C), 128.1 (+, Ar-C), 127.1 (+, Ar-C), 125.7 (+, Ar-C), 125.3 (+, Ar-C), 124.3 (+, C-7), 51.6 (+, OCH_3), 39.3 (+, C-5), 39.1 (−, benzyl-CH_2), 37.0 (−, C-6), 28.3 (−, C-4), 20.3 (C_{quat}, C-3), 12.6 (− *c*Pr-C), 11.3 (−, *c*Pr-C); *syn*-**34ab** and *anti*-**34ab**: IR (film): $\tilde{\nu} = 3061$, 3024, 3004, 2948, 2928, 2842, 1735 (C=O), 1610 (C=C), 1495, 1436, 1377, 1259, 1172, 1029, 762, 699 cm^{-1}; MS (70 eV): *m*/*z* (%): 332 (27) [M^+], 304 (8) [$M^+ - C_2H_4$], 301 (2) [$M^+ - OCH_3$], 272 (11) [$M^+ -$ MeOH − CO], 205 (38), 181 (100) [$M^+ -$ MeOH − CO − C_7H_7], 165 (43) [$M^+ - C_7H_7 - C_6H_4$], 129 (26), 91 (70) [$C_7H_7^+$]; elemental analysis calcd (%) for $C_{23}H_{24}O_2$ (332.4): C 83.10, H 7.28; found: C 82.90, H 7.56.

***tert*-Butyl *syn*-8-(2-benzylphenyl)spiro[2.5]oct-7-ene-5-carboxylate (*syn*-34eb) and *tert*-butyl *anti*-8-(2-benzylphenyl)spiro[2.5]oct-7-ene-5-carboxylate (*anti*-34eb)**: According to GP 5, palladium(II) acetate (11.2 mg, 49.9 µmol, 5 mol%), triphenylphosphane (39.3 mg, 150 µmol, 15 mol%), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K_2CO_3 (277 mg, 2.00 mmol), Et_4NCl (166 mg, 1.00 mmol) and *ortho*-benzyliodobenzene (**32b**, 294 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with *tert*-butyl acrylate (**17e**, 256 mg, 2.00 mmol) for 48 h at 80 °C. After work-up, chromatography of the crude product on 25 g silica gel (column 2 × 20 cm, pentane/diethyl ether 20:1) yielded a mixture of two rotamers *syn*-**34eb** and *anti*-**34eb** (1:3.0, ^{1}H NMR) as a yellowish oil (146 mg, 39%). $R_f = 0.48$ (pentane/diethyl ether 20:1); *syn*-**34eb**: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.31-7.06$ (m, 8H; Ar-H), 6.99 (dd, $^3J = 6.4$, $^4J = 2.6$ Hz, 1H; 6′-H), 5.44–5.39 (m, 1H; 7-H), 4.04–3.86 (AB system: $\delta_A = 4.01$, $\delta_B = 3.90$, $^2J = 15.4$ Hz, 2H; benzyl-CH_2), 2.82–2.77 (m, 1H; 5-H), 2.45–2.35 (m, 2H; 6-H), 2.24 (dd, $^2J = 12.8$, $^3J = 12.1$ Hz, 1H; 4-H), 1.68 (dd, $^2J = 12.8$, $^3J = 3.1$ Hz, 1H; 4-H), 1.50 [s, 9H; $C(CH_3)_3$], 0.62–0.31 (m, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 174.7$ (C_{quat}, CO), 141.7 (C_{quat}, Ar-C*), 140.2 (C_{quat}, Ar-C*), 139.3 (C_{quat}, Ar-C*), 138.9 (C_{quat}, C-8*), 130.5 (+, Ar-C), 129.5 (+, Ar-C), 129.2 (+, Ar-C), 129.0 (+, Ar-C), 128.2 (+, Ar-C), 126.9 (+, Ar-C), 125.1 (+, Ar-C), 124.9 (+, C-7), 80.0 [C_{quat}, $\mathit{C}(CH_3)_3$], 40.3 (+, C-5), 38.8 (−, benzyl-CH_2), 37.3 (−, C-6), 28.3 (−, C-4), 28.1 [+, $C(\mathit{CH}_3)_3$], 20.1 (C_{quat}, C-3), 12.2 (−, *c*Pr-C), 11.7 (−, *c*Pr-C); *anti*-**34eb**: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.31-7.07$ (m, 8H; Ar-H), 6.90 (dd, $^3J = 7.0$, $^4J = 1.7$ Hz, 1H; 6′-H), 5.44–5.39 (m, 1H; 7-H), 4.01–3.84 (AB system: $\delta_A = 3.98$, $\delta_B = 3.88$, $^2J = 15.3$ Hz, 2H; benzyl-CH_2), 2.82–2.77 (m, 1H; 5-H), 2.45–2.35 (m, 2H; 6-H), 2.24 (dd, $^2J = 12.6$, $^3J = 12.1$ Hz, 1H; 4-H), 1.49 [s, 9H; $C(CH_3)_3$], 1.42 (dd, $^2J = 12.6$, $^3J = 2.2$ Hz, 1H; 4-H), 0.62–0.31 (m, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 175.0$ (C_{quat}, CO), 141.4 (C_{quat}, Ar-C*), 141.3 (C_{quat}, Ar-C*), 139.9 (C_{quat}, Ar-C*), 139.2 (C_{quat}, C-8*), 129.7 (+, Ar-C), 129.2 (+, Ar-C), 129.1 (+, Ar-C), 128.2 (+, Ar-C), 127.1 (+, Ar-C), 125.8 (+, Ar-C), 125.3 (+, Ar-C), 124.6 (+, C-7), 80.0 [C_{quat}, $\mathit{C}(CH_3)_3$], 40.4 (+, C-5), 39.1 (−, benzyl-CH_2), 37.0 (−, C-6), 28.6 (−, C-4), 28.1 [+, $C(\mathit{CH}_3)_3$], 20.4 (C_{quat}, C-3), 12.7 (−, *c*Pr-C), 11.4 (−, *c*Pr-C); *syn*-**34eb** and *anti*-**34eb**: IR (film): $\tilde{\nu} = 3062$, 3025, 3001, 2976, 2929, 1727 (C=O), 1636 (C=C), 1453, 1367, 1258, 1153, 738 cm^{-1}; MS (70 eV): *m*/*z* (%): 374 (1) [M^+], 318 (42) [$M^+ - C_4H_8$], 301 (4) [$M^+ - OC_4H_9$], 289 (16), 257 (18), 181 (100) [$M^+ - HOC_4H_9 - CO - C_7H_7$], 165 (43), 91 (70) [$C_7H_7^+$]; elemental analysis calcd (%) for $C_{26}H_{30}O_2$ (374.5): C 83.38, H 8.07; found: C 83.65, H 8.27.

Methyl *syn*-8-(2,4-dimethylphenyl)spiro[2.5]oct-7-ene-5-carboxylate (*syn*-34ac) and methyl *anti*-8-(2,4-dimethylphenyl)spiro[2.5]oct-7-ene-5-carboxylate (*anti*-34ac): According to GP 5, palladium(II) acetate (11.2 mg, 49.9 µmol, 5 mol%), triphenylphosphane (39.3 mg, 150 µmol, 15 mol%), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K_2CO_3 (277 mg, 2.00 mmol), Et_4NCl (166 mg, 1.00 mmol) and 2,4-dimethyliodobenzene (**33c**, 232 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with methyl acrylate (**17a**, 172 mg, 2.00 mmol) for 48 h at 80 °C. After work-up, chromatography of the crude product on 25 g silica gel (column 2 × 20 cm, pentane/diethyl ether 10:1) gave a mixture of two rotamers *syn*-**34ac** and *anti*-**34ac** (1:2.5, ^{1}H NMR) as a yellowish oil (265 mg, 98%). $R_f = 0.48$ (pentane/diethyl ether 10:1); *syn*-**34ac**: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 6.98$ (s, 1H; 3′-H), 6.92–6.77 (m, 2H; 5′-H, 6′-H), 5.49 (t, $^3J = 3.7$ Hz, 1H; 7-H), 3.74 (s, 3H; OCH_3), 3.01–2.89 (m, 1H; 5-H), 2.53 (dd, $^3J = 8.3$, $^3J = 3.7$ Hz, 2H; 6-H), 2.32 (s, 3H; 4′-CH_3), 2.22 (s, 3H; 2′-CH_3), 2.32–2.18 (m, 1H; 4-H), 1.82 (dd, $^2J = 13.0$, $^3J = 3.2$ Hz, 1H; 4-H), 0.60–0.30 (m, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 175.5$ (C_{quat}, CO), 140.9 (C_{quat}, Ar-C*), 136.4 (C_{quat}, Ar-C*), 136.1 (C_{quat}, Ar-C*), 135.8 (C_{quat}, C-8*), 130.1 (+, Ar-C), 129.1 (+, Ar-C), 125.2 (+, Ar-C), 123.4 (+, C-7), 51.3 (+, OCH_3), 39.1 (+, C-5), 37.1 (−, C-6), 28.0 (−, C-4), 20.8 (+, 4′-CH_3), 19.7 (C_{quat}, C-3), 19.3 (+, 2′-CH_3), 12.3 (−, *c*Pr-C), 11.4 (−, *c*Pr-C); *anti*-**34ac**: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 6.98$ (s, 1H; 3′-H), 6.92–6.77 (m, 2H; 5′-H, 6′-H), 5.49 (t, $^3J = 3.7$ Hz, 1H; 7-H), 3.74 (s, 3H; OCH_3), 3.01–2.89 (m, 1H; 5-H), 2.53 (dd, $^3J = 8.3$, $^3J = 3.7$ Hz, 2H; 6-H), 2.32 (s, 3H; 4′-H), 2.21 (s, 3H; 2′-CH_3), 2.32–2.18 (m, 1H; 4-H), 1.52 (dd, $^2J = 12.8$, $^3J = 2.9$ Hz, 1H; 4-H), 0.60–0.30 (m, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 175.7$ (C_{quat}, CO), 142.1 (C_{quat}, Ar-C*), 136.4 (C_{quat}, Ar-C*), 136.1 (C_{quat}, Ar-C*), 135.9 (C_{quat}, C-8*), 129.9 (+, Ar-C), 129.1 (+, Ar-C), 125.3 (+, Ar-C), 122.9 (+, C-7), 51.3 (+, OCH_3), 39.3 (+, C-5), 36.9 (−, C-6), 28.3 (−, C-4), 20.8 (+, 4′-CH_3), 19.9 (C_{quat}, C-3), 19.3 (+, 2′-CH_3), 12.5 (−, *c*Pr-C), 11.4 (−, *c*Pr-C); *syn*-**34ac** and *anti*-**34ac**: IR (film): $\tilde{\nu} = 3078$, 2997, 2949, 2920, 2852, 1737 (C=O), 1646 (C=C), 1613, 1435, 1377, 1316, 1259, 1193, 1170, 1025, 820 cm^{-1}; MS (70 eV): *m*/*z* (%): 270 (35) [M^+], 239 (5) [$M^+ - OCH_3$], 211 (36) [$M^+ - OCH_3 - CO$], 195 (100) [$M^+ - HOCH_3 - CO - CH_3$], 165 (15) [$M^+ - C_8H_9$], 91 (8) [$C_7H_7^+$]; elemental analysis calcd (%) for $C_{18}H_{22}O_2$ (270.4): C 79.96, H 8.20; found: C 79.76, H 8.14.

***tert*-Butyl *syn*-8-(2,4-dimethylphenyl)spiro[2.5]oct-7-ene-5-carboxylate (*syn*-34ec) and *tert*-butyl *anti*-8-(2,4-dimethylphenyl)spiro[2.5]oct-7-ene-5-carboxylate (*anti*-34ec)**: According to GP 5, palladium(II) acetate (11.2 mg, 49.9 µmol, 5 mol%), triphenylphosphane (39.3 mg, 150 µmol, 15 mol%), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K_2CO_3 (277 mg, 2.00 mmol), Et_4NCl (166 mg, 1.00 mmol) and 2,4-dimethyliodobenzene (**33c**, 232 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with *tert*-butyl acrylate (**17e**, 256 mg, 2.00 mmol) for 48 h at 80 °C. After work-up, chromatography of the crude product on 25 g silica gel (column 2 × 20 cm, pentane/diethyl ether 20:1) yielded a mixture of two rotamers *syn*-**34ec** and *anti*-**34ec** (1:2.7, ^{1}H NMR) as a yellowish oil (51 mg, 16%). $R_f = 0.62$ (pentane/diethyl ether 20:1); *syn*-**34ec**: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.12-7.06$ (m, 2H; 3′-H, 5′-H), 6.93 (d, $^3J = 7.1$ Hz, 1H; 6′-H), 5.48 (t, $^3J = 3.6$ Hz, 1H; 7-H), 2.87–2.79 (m, 1H; 5-H), 2.45 (dd, $^3J = 7.7$, $^3J = 3.6$ Hz, 2H; 6-H), 2.22 (br s, 3H; 2′-CH_3), 2.16 (br s, 3H; 4′-CH_3), 2.11 (dd, $^2J = 13.0$, $^3J = 10.9$ Hz, 1H; 4-H), 1.64 (dd, $^2J = 13.0$, $^3J = 3.0$ Hz, 1H; 4-H), 1.44 [br s, 9H; $C(CH_3)_3$], 0.57–0.37 (m, 3H; *c*Pr-H), 0.26–0.20 (m, 1H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 174.9$ (C_{quat}, CO), 142.0 (C_{quat}, Ar-C*), 136.4 (C_{quat}, Ar-C*), 136.2 (C_{quat}, C-8*), 131.5 (C_{quat}, Ar-C), 130.2 (+, Ar-C), 129.2 (+, Ar-C), 125.2 (+, Ar-C), 123.8 (+, C-7), 79.9 [C_{quat}, *C*(CH$_3$)$_3$], 40.4 (+, C-5), 37.2 (−, C-6), 28.4 (−, C-4), 28.1 [+, C(*C*H$_3$)$_3$], 20.9 (+, 4′-CH$_3$), 19.9 (C_{quat}, C-3), 19.4 (+, 2′-CH$_3$), 12.5 (−, *c*Pr-C), 11.5 (−, *c*Pr-C); *anti*-**34ec**: ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 7.12-7.06$ (m, 2H; 3′-H, 5′-H), 6.86 (d, $^3J = 7.1$ Hz, 1H; 6′-H), 5.47 (t, $^3J = 3.7$ Hz, 1H; 7-H), 2.87–2.79 (m, 1H; 5-H), 2.46 (dd, $^3J = 7.6$, $^3J = 3.7$ Hz, 2H; 6-H), 2.23 (dd, $^2J = 13.0$, $^3J = 12.0$ Hz, 1H; 4-H), 2.21 (brs, 3H; 2′-CH$_3$), 2.17 (brs, 3H; 4′-CH$_3$), 1.48 [brs, 9H; C(CH$_3$)$_3$], 1.43 (dd, $^2J = 13.0$, $^3J = 2.9$ Hz, 1H; 4-H), 0.57–0.37 (m, 3H; *c*Pr-H), 0.26–0.20 (m, 1H; *c*Pr-H); ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): $\delta = 175.0$ (C_{quat}, CO), 142.1 (C_{quat}, Ar-C*), 136.4 (C_{quat}, Ar-C*), 136.2 (C_{quat}, C-8*), 131.5 (C_{quat}, Ar-C), 130.0 (+, Ar-C), 129.2 (+, Ar-C), 125.3 (+, Ar-C), 123.2 (+, C-7), 79.9 [C_{quat}, *C*(CH$_3$)$_3$], 40.4 (+, C-5), 36.9 (−, C-6), 28.6 (−, C-4), 28.0 [+, C(*C*H$_3$)$_3$], 20.9 (+, 4′-CH$_3$), 19.9 (C_{quat}, C-3), 19.4 (+, 2′-CH$_3$), 12.6 (−, *c*Pr-C), 11.5 (−, *c*Pr-C); *syn*-**34ec** and *anti*-**34ec**: IR (film): $\tilde{\nu} = 3079$, 2976, 2924, 1729 (C=O), 1635 (C=C), 1456, 1366, 1260, 1151, 1023, 820, 736 cm^{-1}; MS (70 eV): *m*/*z* (%): 312 (1) [M^+], 255 (100) [$M^+ - C_4H_9$], 239 (18) [$M^+ - OC_4H_9$], 211 (29) [$M^+ - OC_4H_9 - CO$], 195 (86) [$M^+ - HOC_4H_9 - CO - CH_3$], 169 (19), 91 (9) [$C_7H_7^+$].

Methyl 8-(2,6-dimethylphenyl)spiro[2.5]oct-7-ene-5-carboxylate (34ad) and 1-cyclopropylidene-1-(2,6-dimethylphenyl)-2-propene (5-2,6-Me$_2$Ph): According to GP 5, palladium(II) acetate (22.4 mg, 100 µmol, 5 mol%), triphenylphosphane (78.7 mg, 300 µmol, 15 mol%), bicyclopropylidene (**1**, 320 mg, 4.00 mmol), K$_2$CO$_3$ (553 mg, 4.00 mmol), Et$_4$NCl (331 mg, 2.00 mmol) and 2,6-dimethyliodobenzene (**33d**, 464 mg, 2.00 mmol) were stirred in anhydrous acetonitrile (2 mL) with methyl acrylate (**17a**, 344 mg, 4.00 mmol) for 48 h at 80 °C. After work-up, chromatography of the crude product on 25 g silica gel (column 2 × 20 cm, pentane/diethyl ether 10:1) gave:

Fraction I: **5**-2,6-Me$_2$Ph as a clear oil (81 mg, 22%); $R_f = 0.91$ (pentane/diethyl ether 10:1); IR (film): $\tilde{\nu} = 3060$, 2959, 2930, 1680, 1640 (C=C), 1455, 1379, 1035 cm^{-1}; ^{1}H NMR (250 MHz, C$_6$D$_6$): $\delta = 7.13-7.05$ (m, 3H; Ar-H), 6.77 (dd, $^3J = 16.9$, $^3J = 10.3$ Hz, 1H; 2-H), 5.08 (d, $^3J = 10.3$ Hz, 1H; 3-H), 4.65 (d, $^3J = 16.9$ Hz, 1H; 3-H), 2.12 (s, 6H; Ar-CH$_3$), 1.36–1.02 (m, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, C$_6$D$_6$, DEPT): $\delta = 138.1$ (C_{quat}, C-1), 136.9 (+, C-2), 136.7 (C_{quat}, C-2′, C-6′), 129.1 (C_{quat}, *c*Pr-C), 126.8 (C_{quat}, C-1′), 126.7 (+, C-3′, C-5′), 126.7 (+, C-4′), 113.1 (−, C-3), 19.7 (+, 2 Ar-CH$_3$), 2.9 (−, *c*Pr-C), 2.7 (−, *c*Pr-C); MS (70 eV): *m*/*z* (%): 184 (4) [M^+], 169 (56) [$M^+ - CH_3$], 154 (100) [$M^+ - 2CH_3$], 143 (68), 128 (48), 91 (3) [$C_7H_7^+$].

Fraction II: **34ad** as a yellowish oil (305 mg, 56%); $R_f = 0.56$ (pentane/diethyl ether 10:1); IR (film): $\tilde{\nu} = 3063$, 2997, 2949, 2933, 2852, 1734 (C=O), 1640 (C=C), 1577, 1435, 1376, 1310, 1258, 1170, 1025, 905, 771 cm^{-1}; ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 7.09-6.91$ (m, 3H; Ar-H), 5.48 (t, $^3J = 3.9$ Hz, 1H; 7-H), 3.74 (s, 3H; OCH$_3$), 2.97 (ddd, $^3J = 11.5$, $^3J = 8.1$, $^3J = 3.1$ Hz, 1H; 5-H), 2.53 (dd, $^3J = 8.1$, $^3J = 3.9$ Hz, 2H; 6-H), 2.22 (s, 3H; Ar-CH$_3$), 2.19 (s, 3H; Ar-CH$_3$), 2.22 (dd, $^2J = 13.0$, $^3J = 11.5$ Hz, 1H; 4-H), 1.61 (dd, $^2J = 13.0$, $^3J = 3.1$ Hz, 1H; 4-H), 0.60–0.35 (m, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): $\delta = 175.8$ (C_{quat}, CO), 140.2 (C_{quat}, Ar-C*), 138.2 (C_{quat}, Ar-C*), 137.1 (C_{quat}, Ar-C*), 136.1 (C_{quat}, C-8*), 126.9 (+, Ar-C), 126.8 (+, Ar-C), 126.5 (+, Ar-C), 123.8 (+, C-7), 51.5 (+, OCH$_3$), 39.4 (+, C-5), 37.3 (−, C-6), 28.4 (−, C-4), 20.01 (+, Ar-CH$_3$), 19.98 (C_{quat}, C-3), 19.9 (+, Ar-CH$_3$), 13.3 (−, *c*Pr-C), 12.3 (−, *c*Pr-C); MS (70 eV): *m*/*z* (%): 270 (47) [M^+], 255 (5) [$M^+ - CH_3$], 239 (3) [$M^+ - OCH_3$], 211 (42) [$M^+ - CO_2Me$], 195 (100) [$M^+ - MeOH - CO - CH_3$], 165 (20) [$M^+ - C_8H_9$]; elemental analysis calcd (%) for C$_{18}$H$_{22}$O$_2$ (270.4): C 79.96, H 8.20; found: C 79.66, H 8.28.

Dimethyl 8-phenylspiro[2.5]oct-7-ene-1,5-dicarboxylate (36a): According to GP 5, palladium(II) acetate (22.4 mg, 100 µmol, 5 mol%), triphenylphosphane (52.4 mg, 200 µmol, 10 mol%), methyl bicyclopropylidenecarboxylate (**35a**, 345 mg, 2.50 mmol), K$_2$CO$_3$ (415 mg, 3.00 mmol), Et$_4$NCl (331 mg, 2.00 mmol) and iodobenzene (**2**-Ph, 408 mg, 2.00 mmol) were stirred in anhydrous acetonitrile (1 mL) with methyl acrylate (**17a**, 258 mg, 3.00 mmol) for 24 h at 80 °C. After work-up, chromatography of the crude product on 25 g silica gel (column 2 × 20 cm, pentane/diethyl ether 2:1) gave:

Fraction I: A mixture of polymers (40 mg), $R_f = 0.82$ (pentane/diethyl ether 2:1).

Fraction II: **36a** as a mixture of two isomers (5:4, ^{1}H NMR); yellowish oil (216 mg, 36%); $R_f = 0.46$ (pentane/diethyl ether 2:1); isomer 1: ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): $\delta = 175.1$ (C_{quat}, CO), 170.5 (C_{quat}, CO), 141.3 (C_{quat}, C-8*), 141.1 (C_{quat}, Ar-C*), 129.3 (+, Ar-C), 127.7 (+, Ar-C), 127.4 (+, Ar-C*), 126.4 (+, C-7*), 51.8 (+, OCH$_3$), 51.1 (+, OCH$_3$), 38.4 (+, C-5), 37.3 (−, C-6), 29.3 (+, C-1), 28.8 (C_{quat}, C-3), 27.1 (−, C-4), 17.9 (−, *c*Pr-C); isomer 2: ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): $\delta = 175.2$ (C_{quat}, CO), 170.5 (C_{quat}, CO), 140.6 (C_{quat}, C-8*), 139.0 (C_{quat}, Ar-C*), 129.6 (+, Ar-C), 127.9 (+, Ar-C), 127.3 (+, Ar-C*), 126.3 (+, C-7*), 51.6 (+, OCH$_3$), 51.2 (+, OCH$_3$), 39.2 (+, C-5), 38.7 (−, C-6), 30.4 (+, C-1), 30.1 (C_{quat}, C-3), 28.6 (−, C-4), 19.7 (−, *c*Pr-C); isomer 1 and 2: ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 7.30-7.06$ (m, 5H; Ar-H), 5.87 (dd, $^3J = 4.9$, $^3J = 4.0$ Hz, 1H; 7-H, isomer 1), 5.76 (dd, $^3J = 3.8$, $^3J = 3.7$ Hz, 1H; 7-H, isomer 2), 3.34 (s, 3H; OCH$_3$), 3.33 (s, 3H; OCH$_3$), 3.10–3.06 (m, 1H; 5-H, isomer 2), 2.88–2.80 (m, 1H; 1-H, isomer 1), 2.70–2.43 (m, 2H; 6-H), 2.32–2.16 (m, 1H; *c*Pr-H), 1.91–1.74 (m, 1H; 4-H), 1.68–1.60 (m, 1H; *c*Pr-H), 1.44–1.14 (m, 2H; 4-H; *c*Pr-H); MS (70 eV): *m*/*z* (%): 300 (14) [M^+], 268 (13) [$M^+ - MeOH$], 240 (55) [$M^+ - MeOH - CO$], 225 (1) [$M^+ - MeOH - CH_3 - CO$], 209 (19) [$M^+ - CO_2Me - MeOH$], 181 (100) [$M^+ - CO_2Me - MeOH - CO$], 167 (36), 91 (6) [$C_7H_7^+$], 59 (5) [CO_2Me^+].

Methyl 8-(4′-iodophenyl)spiro[2.5]oct-7-ene-5-carboxylate (18a-C$_6$H$_4$I) and 1,4-bis[5′-methoxycarbonylspiro[2.5]oct-7′-ene-8′-yl]benzene (38a): a) In a 25 mL Pyrex bottle, palladium(II) acetate (22.4 mg, 100 µmol, 5 mol%), triphenylphosphane (78.6 mg, 300 µmol, 15 mol%), bicyclopropylidene (**1**, 640 mg, 8.00 mmol), 1,4-diiodobenzene (**37**, 660 mg, 2.00 mmol) and triethylamine (810 mg, 8.00 mmol) in anhydrous DMF (10 mL) were heated with methyl acrylate (**17a**, 689 mg, 8.00 mmol) for 21 h at 80 °C. After work-up, chromatography of the crude product on silica gel (50 g, column 2 × 20 cm, pentane/diethyl ether 5:1 → diethyl ether) gave:

Fraction I: **18a**-C$_6$H$_4$I as a colorless oil (330 mg, 45%); $R_f = 0.45$ (pentane/diethyl ether 10:1); IR (film): $\tilde{\nu} = 3079$, 2949, 1734 (C=O), 1653 (C=C), 1635 (C=C), 1478, 1434, 1169, 1007, 824 cm^{-1}; ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 7.56$ [d, $^3J = 8.2$ Hz, 2H; 3′(5′)-H], 6.77 [d, $^3J = 8.2$ Hz, 2H; 2′(6′)-H], 5.50 (t, $^3J = 3.8$ Hz, 1H; 7-H), 3.69 (s, 3H; OCH$_3$), 2.87 (ddt, $^3J = 12.0$, $^3J = 8.0$, $^3J = 3.0$ Hz, 1H; 5-H), 2.45 (dd, $^3J = 8.0$, $^3J = 3.8$ Hz, 2H; 6-H), 2.15 (dd, $^2J = 12.9$, $^3J = 12.0$ Hz, 1H; 4-H), 1.49 (dd, $^2J = 12.9$, $^3J = 3.0$ Hz, 1H; 4-H), 0.61–0.38 (m, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): $\delta = 175.6$ (C_{quat}, CO), 141.8 (C_{quat}, C-1′*), 139.6 (C_{quat}, C-8*), 136.5 [+, C-2′(6′)], 131.1 [+, C-3′(5′)], 124.3 (+, C-7), 92.3 (C_{quat}, C-4′), 51.6 (+, OCH$_3$), 39.1 (+, C-5), 37.2 (−, C-6), 28.3 (−, C-4), 19.9 (C_{quat}, C-3), 12.7 (−, *c*Pr-C), 11.4 (−, *c*Pr-C); MS (70 eV): *m*/*z* (%): 368 (40) [M^+], 308 (21) [$M^+ - MeOH - CO$], 181 (100) [$M^+ - MeOH - CO - I$], 165 (19) [$M^+ - C_6H_4I$], 154 (11), 141 (7), 128 (7), 115 (7); elemental analysis calcd (%) for C$_{16}$H$_{17}$IO$_2$ (368.2): C 52.19, H 4.65; found: C 52.31, H 4.83.

Fraction II: **38a** as a yellowish oil (64 mg, 8%); $R_f = 0.32$ (diethyl ether); IR (film): $\tilde{\nu} = 2927$, 1734 (C=O), 1653 (C=C), 1435, 1169, 1095, 745, 694, 526 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 7.08$ (s, 4H; Ar-H), 5.80 (t, $^3J = 4.0$ Hz, 2H; 7′-H), 3.98 (s, 6H; OCH$_3$), 3.18 (ddd, $^3J = 11.0$, $^3J = 9.0$, $^3J = 3.5$ Hz, 2H; 5′-H), 2.76 (dd, $^3J = 9.0$, $^3J = 4.0$ Hz, 4H; 6′-H), 2.47 (dd, $^2J = 13.0$, $^3J = 11.0$ Hz, 2H; 4′-H), 1.77 (dd, $^2J = 13.0$, $^3J = 3.5$ Hz, 2H; 4′-H), 0.90 (m, 2H; *c*Pr-H), 0.81 (m, 2H; *c*Pr-H), 0.75 (m, 2H; *c*Pr-H), 0.72–0.68 (m, 2H; *c*Pr-H); ^{13}C NMR (125.7 MHz, CDCl$_3$, APT): $\delta = 176.0$ (−, CO), 142.7 (−, Ar-C*), 138.5 (−, C-8′*), 128.3 (+, Ar-C), 123.8 (+, C-7′), 51.6 (+, OCH$_3$), 39.4 (+, C-5′), 37.5 (−, C-6′), 28.5 (−, C-4′), 20.1 (−, C-3′), 12.9 (−, *c*Pr-C), 11.6 (−, *c*Pr-C); MS (70 eV): *m*/*z* (%): 406 (31) [M^+], 183 (100) [$C_{14}H_{15}^+$], 152 (6), 108 (14), 84 (14), 77 (6); elemental analysis calcd (%) for C$_{26}$H$_{30}$O$_4$ (406.5): C 76.82, H 7.44; found: C 76.65, H 7.43.

b) According to GP 5, palladium(II) acetate (11.2 mg, 49.9 µmol, 5 mol%), triphenylphosphane (39.3 mg, 150 µmol, 15 mol%), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K$_2$CO$_3$ (277 mg, 2.00 mmol), Et$_4$NCl (166 mg, 1.00 mmol) and 1,4-diiodobenzene (**37**, 166 mg, 0.500 mmol) were stirred in anhydrous acetonitrile (1 mL) with methyl acrylate (**17a**, 172 mg, 2.00 mmol) for 48 h at 80 °C. After work-up, chromatography of the crude product on 50 g silica gel (column 2 × 20 cm, pentane/diethyl ether 2:1) yielded **38a** as colorless crystals (130 mg, 64%).

c) According to GP 6, 1,4-diiodobenzene (**37**, 330 mg, 1.00 mmol), bicyclopropylidene (**1**, 320 mg, 4.00 mmol), methyl acrylate (**17a**, 344 mg, 4.00 mmol), palladium(II) acetate (11.2 mg, 49.9 µmol), triphenylphosphane (39.3 mg, 150 µmol) and triethylamine (404 mg, 2.00 mmol) were heated in anhydrous DMF (5 mL) at 80 °C for 24 h under a pressure of 10 kbar. After work-up, chromatography of the crude product on silica gel (column 2 × 20 cm, pentane/diethyl ether 2:1) gave **38a** as colorless crystals (354 mg, 87%). $R_f = 0.72$ (pentane/diethyl ether 2:1); m.p. 124 °C.

***tert*-Butyl 8-(4′-iodophenyl)spiro[2.5]oct-7-ene-5-carboxylate (18e-C_6H_4I) and 1,4-bis[5′-*tert*-butoxycarbonylspiro[2.5]oct-7′-ene-8′-yl]benzene (38e)**: a) In a 25 mL Pyrex-bottle, palladium(II) acetate (22.4 mg, 100 µmol, 5 mol%), triphenylphosphane (78.6 mg, 300 µmol, 15 mol%), bicyclopropylidene (**1**, 640 mg, 8.00 mmol), 1,4-diiodobenzene (**37**, 660 mg, 2.00 mmol) and triethylamine (810 mg, 8.00 mmol) in anhydrous DMF (10 mL) were heated with *tert*-butyl acrylate (**17e**, 1.03 g, 8.04 mmol) for 3 d at 80 °C. After work-up, chromatography of the crude product on 50 g silica gel (column 2 × 20 cm, pentane/diethyl ether 10:1 → 2:1) gave:

Fraction I: **18e**-C_6H_4I as a yellowish oil (410 mg, 50%); $R_f = 0.62$ (pentane/diethyl ether 2:1); IR (film): $\tilde{\nu} = 3020, 2976, 2930, 1726$ (C=O), 1653 (C=C), 1583, 1478, 1367, 1258, 1152, 1007, 824 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.57$ (d, $^3J = 8.3$ Hz, 2H; Ar-H), 6.77 (d, $^3J = 8.3$ Hz, 2H; Ar-H), 5.50 (t, $^3J = 3.7$ Hz, 1H; 7-H), 2.76 (ddt, $^3J = 11.7$, $^3J = 9.8$, $^3J = 3.0$ Hz, 1H; 5-H), 2.41 (dd, $^3J = 9.8$, $^3J = 3.0$ Hz, 2H; 6-H), 2.11 (dd, $^2J = 12.7$, $^3J = 11.7$ Hz, 1H; 4-H), 1.46 (s, 9H; *t*Bu-H), 1.44 (dd, $^2J = 12.7$, $^3J = 3.0$ Hz, 1H; 4-H), 0.60–0.50 (m, 2H; *c*Pr-H), 0.46–0.37 (m, 2H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 174.8$ (C_{quat}, CO), 141.9 (C_{quat}, C-1′*), 139.9 (C_{quat}, C-8*), 136.6 (+, Ar-C), 131.2 (+, Ar-C), 124.6 (+, C-7), 92.2 (C_{quat}, C-4′), 80.1 (C_{quat}, *t*Bu-C), 40.3 (+, C-5), 37.3 (–, C-6), 28.6 (–, C-4), 28.1 (+, *t*Bu-C), 19.9 (C_{quat}, C-3), 12.7 (–, *c*Pr-C), 11.6 (–, *c*Pr-C); MS (70 eV): *m/z* (%): 410 (2) [M^+], 354 (64) [$M^+ - C_4H_8$], 309 (12) [$M^+ - CO_2t$Bu], 181 (100) [$M^+ - CO_2t$Bu – HI], 57 (25); elemental analysis calcd (%) for $C_{19}H_{23}IO_2$ (410.3): C 55.62; H 5.65; found: C 55.65, H 5.39.

Fraction II: **38e** as colorless crystals (55 mg, 6%); m.p. 121 °C; $R_f = 0.43$ (pentane/diethyl ether 2:1); IR (KBr): $\tilde{\nu} = 3085, 2925, 1716$ (C=O), 1641 (C=C), 1452, 1365, 1257, 1160, 999, 971, 835 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 6.89$ (s, 4H; Ar-H), 5.50 (t, $^3J = 3.6$ Hz, 2H; 7′-H), 2.77 (ddt, $^3J = 11.9$, $^3J = 9.7$, $^3J = 2.7$ Hz, 2H; 5′-H), 2.41 (dd, $^3J = 9.7$, $^3J = 3.6$ Hz, 4H; 6′-H), 2.13 (dd, $^2J = 12.6$, $^3J = 11.9$ Hz, 2H; 4′-H), 1.46 (s, 18H; *t*Bu-H), 1.42 (dd, $^2J = 12.6$, $^3J = 2.7$ Hz, 2H; 4′-H), 0.60–0.40 (m, 8H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 174.9$ (C_{quat}, CO), 142.7 (C_{quat}, Ar-C*), 138.5 (C_{quat}, C-8′*), 128.2 (+, Ar-C), 124.0 (+, C-7′), 80.0 (C_{quat}, *t*Bu-C), 40.4 (+, C-5′), 37.4 (–, C-6′), 28.6 (–, C-4′), 28.1 (+, *t*Bu-C), 20.1 (C_{quat}, C-3′), 12.8 (–, *c*Pr-C), 11.6 (–, *c*Pr-C); MS (70 eV): *m/z* (%): 490 (13) [M^+], 433 (7) [$M^+ - C_4H_9$], 417 (22) [$M^+ - C_4H_9O$], 378 (100) [$M^+ - 2\,C_4H_8$], 331 (27), 57 (52) [$C_4H_9^+$]; elemental analysis calcd (%) for $C_{32}H_{42}O_4$ (490.7): C 78.33, H 8.63; found: C 78.09, H 8.49.

b) According to GP 5, palladium(II) acetate (11.2 mg, 49.9 µmol, 5 mol%), triphenylphosphane (39.3 mg, 150 µmol, 15 mol%), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K_2CO_3 (277 mg, 2.00 mmol), Et_4NCl (166 mg, 1.00 mmol) and 1,4-diiodobenzene (**37**, 166 mg, 0.500 mmol) were stirred in anhydrous acetonitrile (1 mL) with *tert*-butyl acrylate (**17e**, 256 mg, 2.00 mmol) for 48 h at 80 °C. After work-up, chromatography of the crude product on 50 g silica gel (column 2 × 20 cm, pentane/diethyl ether 4:1) yielded **38e** as colorless crystals (169 mg, 69%).

c) According to GP 6, 1,4-diiodobenzene (**37**, 330 mg, 1.00 mmol), bicyclopropylidene (**1**, 320 mg, 4.00 mmol), *tert*-butyl acrylate (**17e**, 512 mg, 4.00 mmol), palladium(II) acetate (11.2 mg, 49.9 µmol), triphenylphosphane (39.3 mg, 150 µmol) and triethylamine (404 mg, 4.00 mmol) were heated in anhydrous DMF (5 mL) at 80 °C for 24 h under a pressure of 10 kbar. After work-up, chromatography of the crude product on silica gel (column 2 × 20 cm, pentane/diethyl ether 4:1) gave **38e** as colorless crystals (294 mg, 60%); $R_f = 0.82$ (pentane/diethyl ether 4:1); m.p. 121 °C.

1,4-Bis(4′,5′-dimethoxycarbonylspiro[2.5]oct-7′-ene-8′-yl)benzene (38f): a) According to GP 5, palladium(II) acetate (11.2 mg, 49.9 µmol, 5 mol%), triphenylphosphane (39.3 mg, 150 µmol, 15 mol%), bicyclopropylidene (**1**, 160 mg, 2.00 mmol), K_2CO_3 (277 mg, 2.00 mmol), Et_4NCl (166 mg, 1.00 mmol) and 1,4-diiodobenzene (**37**, 166 mg, 0.500 mmol) were stirred in anhydrous acetonitrile (1 mL) with dimethyl fumarate (**17f**, 288 mg, 2.00 mmol) for 48 h at 80 °C. After work-up, chromatography of the crude product on silica gel (column 2 × 20 cm, pentane/diethyl ether 1:1) gave **38f** as colorless crystals (141 mg, 54%). $R_f = 0.42$ (pentane/diethyl ether 1:1); m.p. 139 °C; IR (KBr): $\tilde{\nu} = 3005, 2950, 1734$ (C=O), 1653 (C=C), 1432, 1374, 1324, 1259, 1157, 1023, 998, 851 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 6.95$ (s, 4H; Ar-H), 5.50 (dd, $^3J = 3.8$, $^3J = 3.7$ Hz, 2H; 7′-H), 3.71 (s, 12H; OCH_3), 3.29 (ddd, $^3J = 12.8$, $^3J = 6.6$, $^3J = 6.3$ Hz, 2H; 5′-H), 2.94 (d, $^3J = 6.6$ Hz, 2H; 4′-H), 2.57 (ddd, $^2J = 18.2$, $^3J = 12.8$, $^3J = 3.8$ Hz, 2H; 6′-H), 2.49 (ddd, $^2J = 18.2$, $^3J = 6.3$, $^3J = 3.7$ Hz, 2H; 6′-H), 0.66–0.59 (m, 6H; *c*Pr-H), 0.47–0.43 (m, 2H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 174.5$ (C_{quat}, CO), 173.3 (C_{quat}, CO), 141.6 (C_{quat}, Ar-C*), 138.1 (C_{quat}, C-8′*), 128.3 (+, Ar-C), 123.5 (+, C-7′), 51.9 (+, OCH_3), 51.8 (+, OCH_3), 49.3 (+, C-5′), 41.4 (+, C-4′), 26.3 (–, C-6′), 20.0 (C_{quat}, C-3′), 11.0 (–, *c*Pr-C), 10.3 (–, *c*Pr-C); MS (70 eV): *m/z* (%): 522 (46) [M^+], 491 (24) [$M^+ - OCH_3$], 463 (50) [$M^+ - CO_2CH_3$], 431 (43) [$M^+ - CO_2CH_3$ – MeOH], 403 (100) [$M^+ - CO_2CH_3$ – MeOH – CO], 371 (20), 343 (63) [$M^+ - CO_2CH_3$ – 2MeOH – 2CO], 283 (38); elemental analysis calcd (%) for $C_{30}H_{34}O_8$ (522.6): C 68.95, H 6.56; found: C 69.10, H 6.64.

b) According to GP 6, 1,4-diiodobenzene (**37**, 330 mg, 1.00 mmol), bicyclopropylidene (**1**, 320 mg, 4.00 mmol), dimethyl fumarate (**17f**, 576 mg, 4.00 mmol), palladium(II) acetate (11.2 mg, 49.9 µmol), triphenylphosphane (39.3 mg, 150 µmol) and triethylamine (404 mg, 4.00 mmol) were heated in anhydrous DMF (5 mL) at 80 °C for 24 h under a pressure of 10 kbar. After work-up, chromatography of the crude product on silica gel (column 2 × 20 cm, pentane/diethyl ether 1:1) gave **38f** as colorless crystals (314 mg, 60%). $R_f = 0.44$ (pentane/diethyl ether 1:1); m.p. 137 °C.

1,3,5-Tris(5′-methoxycarbonylspiro[2.5]oct-7′-en-8′-yl)benzene (40a): According to GP 5, palladium(II) acetate (33.7 mg, 150 µmol, 30 mol%), triphenylphosphane (78.7 mg, 300 µmol, 60 mol%), bicyclopropylidene (**1**, 480 mg, 6.00 mmol), K_2CO_3 (829 mg, 6.00 mmol), Et_4NCl (497 g, 3.00 mmol) and 1,3,5-triiodobenzene (**39**, 228 mg, 0.50 mmol) were stirred in anhydrous acetonitrile (1 mL) with methyl acrylate (**17a**, 517 mg, 6.00 mmol) for 48 h at 80 °C. After work-up, chromatography of the crude product on 25 g silica gel (column 2 × 20 cm, pentane/diethyl ether 2:1) gave:

Fraction I: Polymeric material as a yellowish oil (177 mg). $R_f = 0.82$ (pentane/diethyl ether 2:1).

Fraction II: **40a** as a yellowish oil (207 mg, 72%); $R_f = 0.41$ (pentane/diethyl ether 2:1); IR (film): $\tilde{\nu} = 3079, 2998, 2949, 2851, 1736$ (C=O), 1646 (C=C), 1436, 1375, 1258, 1193, 1170, 1019, 904, 885, 812, 729 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 6.58$ (s, 3H; Ar-H), 5.47 (t, $^3J = 3.8$ Hz, 3H; 7′-H), 3.69 (s, 9H; OCH_3), 2.82 (ddd, $^3J = 11.8$, $^3J = 8.1$, $^3J = 2.7$ Hz, 3H; 5′-H), 2.44 (dd, $^3J = 8.1$, $^3J = 3.8$ Hz, 6H; 6′-H), 2.11 (dd, $^2J = 12.8$, $^3J = 11.8$ Hz, 3H; 4′-H), 1.46 (dd, $^2J = 12.8$, $^3J = 2.7$ Hz, 3H; 4′-H), 0.57–0.38 (m, 12H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 175.9$ (C_{quat}, CO), 142.5 (C_{quat}, C-8′*), 138.5 (C_{quat}, Ar-C*), 128.3 (+, Ar-C), 123.7 (+, C-7′), 51.6 (+, OCH_3), 39.3 (+, C-5′), 37.4 (–, C-6′), 28.4 (–, C-4′), 20.1 (C_{quat}, C-3′), 12.8 (–, *c*Pr-C), 11.6 (–, *c*Pr-C); MS (70 eV): *m/z* (%): 570 (100) [M^+], 555 (5) [$M^+ - CH_3$], 539 (25) [$M^+ - OCH_3$], 511 (21) [$M^+ - CO_2$Me], 490 (62), 481 (41), 430 (29), 421 (25), 401 (29), 371 (51), 345 (39), 343 (35), 311 (30), 285 (26), 283 (35), 255 (27).

1,3,5-Tris(5′-*tert*-butoxycarbonylspiro[2.5]oct-7′-en-8′-yl)benzene (40e): According to GP 5, palladium(II) acetate (33.7 mg, 150 µmol, 30 mol%), triphenylphosphane (78.7 mg, 300 µmol, 60 mol%), bicyclopropylidene (**1**, 480 mg, 6.00 mmol), K_2CO_3 (829 mg, 6.00 mmol), Et_4NCl (497 g, 3.00 mmol) and 1,3,5-triiodobenzene (**39**, 228 mg, 0.500 mmol) were stirred in anhydrous acetonitrile (1 mL) with *tert*-butyl acrylate (**17e**, 769 mg, 6.00 mmol) for 72 h at 80 °C. After work-up, chromatography of the crude product on 25 g silica gel (column 2 × 20 cm, pentane/diethyl ether 5:1) gave:

Fraction I: Polymeric material as a clear oil (292 mg); $R_f = 0.88$ (pentane/diethyl ether 5:1).

Fraction II: **40e** as a yellowish oil (208 mg, 60%); $R_f = 0.53$ (pentane/diethyl ether 5:1); IR (film): $\tilde{\nu} = 3042, 2977, 2930, 1727$ (C=O), 1653 (C=C), 1457, 1367, 1257, 1153, 843 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 6.54$ (s, 3H; Ar-H), 5.46 (t, $^3J = 3.7$ Hz, 3H; 7′-H), 2.73 (ddd, $^3J = 12.1$, $^3J = 9.8$, $^3J = 3.0$ Hz, 3H; 5′-H), 2.38 (dd, $^3J = 9.8$, $^3J = 3.7$ Hz, 6H; 6′-H), 2.08 (dd, $^2J = 12.4$, $^3J = 12.1$ Hz, 3H; 4′-H), 1.44 [s, 27H; $C(CH_3)_3$], 1.42 (dd, $^2J = 12.4$, $^3J = 3.0$ Hz, 3H; 4′-H), 0.57–0.38 (m, 12H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 174.9$ (C_{quat}, CO), 142.5 (C_{quat}, C-8′), 138.6 (C_{quat}, Ar-C), 128.3 (+, Ar-C), 123.9 (+, C-7′), 80.0 [C_{quat}, $C(CH_3)_3$], 40.4 (+, C-5′), 37.4 (–, C-6′), 28.6 (–, C-4′), 28.1 [+, $C(CH_3)_3$], 20.1 (C_{quat}, C-3′), 12.9 (–, *c*Pr-C), 11.6 (–, *c*Pr-C); MS (70 eV): *m/z* (%): 697/696 (6/12) [M^+], 640/639 (4/8) [$M^+ - C_4H_9$], 623 (15) [$M^+ - OC_4H_9$], 528 (98) [$M^+ - 3\,C_4H_8$], 481 (21) [$M^+ - 2\,C_4H_9 - CO_2C_4H_9$], 57 (100) [$C_4H_9^+$]; elemental analysis calcd (%) for $C_{45}H_{60}O_6$ (697.0): C 77.55, H 8.68; found: C 77.66, H 8.74.

1,3,5-Tris(4′,5′-dimethoxycarbonylspiro[2.5]oct-7′-en-8′-yl)benzene (40f): According to GP 5, palladium(II) acetate (33.7 mg, 150 µmol, 30 mol%), triphenylphosphane (78.7 mg, 300 µmol, 60 mol%), bicyclopropylidene (**1**, 480 mg, 6.00 mmol), K_2CO_3 (829 mg, 6.00 mmol), Et_4NCl (497 g, 3.00 mmol) and 1,3,5-triiodobenzene (**39**, 228 mg, 0.500 mmol) were stirred in anhydrous acetonitrile (1 mL) with dimethyl fumarate (**17f**, 865 mg, 6.00 mmol) for 72 h at 80 °C. After work-up, chromatography of the crude product on 25 g silica gel (column 2 × 20 cm, pentane/diethyl ether 2:1 → diethyl ether) gave:

Fraction I: Polymeric material and **17f** (260 mg overall); $R_f = 0.77$ (pentane/diethyl ether 2:1).

Fraction II: **40f** as a yellowish oil (211 mg, 57 %); $R_f = 0.11$ (pentane/diethyl ether 2:1); IR (film): $\tilde{\nu} = 3005, 2952, 1734$ (C=O), 1653 (C=C), 1436, 1374, 1265, 1199, 1171, 1024 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 6.62$ (s, 3H; Ar-H), 5.46 (t, $^3J = 3.9$ Hz, 3H; 7′-H), 3.70 (s, 9H; OCH_3), 3.69 (s, 9H; OCH_3), 3.25 (dd, $^3J = 7.0$, $^3J = 6.3$ Hz, 3H; 5′-H), 2.93 (d, $^3J = 7.0$ Hz, 3H; 4′-H), 2.49 (dd, $^3J = 6.3$, $^3J = 3.9$ Hz, 6H; 6′-H), 0.61–0.37 (m, 12H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 174.5$ (C_{quat}, CO), 173.2 (C_{quat}, CO), 141.3 (C_{quat}, Ar-C*), 138.2 (C_{quat}, C-8′*), 128.4 (+, Ar-C), 123.5 (+, C-7′), 51.8 (+, OCH_3), 49.0 (+, C-5′), 41.4 (+, C-4′), 26.3 (−, C-6′), 19.6 (C_{quat}, C-3′), 10.9 (−, *c*Pr-C), 10.1 (−, *c*Pr-C); MS (70 eV): *m*/*z* (%): 744 (100) [M^+], 684 (72) [$M^+ - MeOH - CO$], 624 (44) [$M^+ - 2MeOH - 2CO$], 565 (32) [$M^+ - CO_2Me - 2MeOH - 2CO$], 505 (24) [$M^+ - CO_2Me - 3MeOH - 3CO$], 59 (62) [$CO_2Me^+$].

1,2,4,5-Tetrakis(5′-methoxycarbonylspiro[2.5]oct-7′-en-8′-yl)benzene (42): According to GP 5, palladium(II) acetate (44.8 mg, 200 µmol, 20 mol %), triphenylphosphane (105 mg, 400 µmol, 40 mol %), bicyclopropylidene (**1**, 641 mg, 8.00 mmol), K_2CO_3 (664 mg, 4.80 mmol), Et_4NCl (1.11 g, 6.70 mmol) and 1,2,4,5-tetraiodobenzene (**41**, 582 mg, 1.00 mmol) were stirred in anhydrous acetonitrile (2 mL) with methyl acrylate (**17a**, 689 mg, 8.00 mmol) for 48 h at 80 °C. After work-up, chromatography of the crude product on 25 g silica gel (column 2 × 20 cm, pentane/diethyl ether 1:1) gave:

Fraction I: Polymeric material (65 mg); $R_f = 0.71$ (pentane/diethyl ether 1:1).

Fraction II: **42** as a grey, semi-solid substance (348 mg, 47 %); $R_f = 0.46$ (pentane/diethyl ether 1:1); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 6.34$ (brs, 2H; Ar-H), 5.52–5.41 (m, 4H; 7′-H), 3.70 (brs, 12H; OCH_3), 2.96–2.80 (m, 4H; 5′-H), 2.49–2.39 (m, 8H; 6′-H), 2.11–1.93 (m, 4H; 4′-H), 1.38–1.22 (m, 4H; 4′-H), 0.58–0.36 (m, 16H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 175.9$ (C_{quat}, CO), 140.5 (C_{quat}, Ar-C*), 136.7 (C_{quat}, C-8′*), 126.0 (+, Ar-C), 123.7 (+, C-7′), 51.6 (+, OCH_3), 39.4 (+, C-5′), 37.3 (−, C-4′), 28.3 (−, C-6′), 21.3 (C_{quat}, C-3′), 12.6 (−, *c*Pr-C), 12.4 (−, *c*Pr-C); MS (70 eV): *m*/*z* (%): 734 (86) [M^+], 703 (10) [$M^+ - OCH_3$], 676 (6), 569 (9) [$M^+ - C_{10}H_{13}O_2$], 311 (80), 206 (78), 183 (88), 105 (100).

1-Cyclohex-1′-enyl-1-phenylcyclopropane (44), 1′-phenylprop-2′-enylidenecyclohexane (45) and (*Z*)-(1′-phenylprop-1′-enyl)cyclohex-1-ene [(*Z*)-46]: According to GP 1, iodobenzene (**2**-Ph, 204 mg, 1.00 mmol), cyclopropylidenecyclohexane (**43a**, 490 mg, 4.01 mmol), palladium(II) acetate (11.2 mg, 49.9 µmol), triphenylphosphane (39.3 mg, 150 µmol) and triethylamine (202 mg, 2.00 mmol) in anhydrous DMF (10 mL) were heated at 75 °C for 20 h. After work-up, chromatography of the crude product on silica gel (column 2 × 20 cm, pentane) gave:

Fraction I: (*Z*)-**46** as a colorless oil (105 mg, 53 %); $R_f = 0.8$ (pentane); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.45$–7.25 (m, 3H; Ar-H), 7.2–7.1 (m, 2H; Ar-H), 5.78 (q, $^3J = 7.0$ Hz, 1H; 2′-H), 5.25 (brs, 1H; 2-H), 2.30 (brs, 2H; CH_2), 2.05 (brs, 2H; CH_2), 1.80–1.50 (m, 7H; CH_2, CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 144.4$ (C_{quat}), 140.2 (C_{quat}), 127.9 (+, Ar-C), 127.8 (+, Ar-C), 127.1 (+, Ar-C*), 126.2 (+, C-2′*), 119.3 (+, C-2), 25.9 (−, C-3, C-6), 23.0 (−, C-5*), 22.4 (−, C-4*), 15.1 (+, C-3′); MS (70 eV, EI): *m*/*z* (%): 198 (100) [M^+], 183 (41) [$M^+ - CH_3$], 169 (47) [$M^+ - C_2H_5$], 155 (42) [$M^+ - C_3H_7$], 141 (46) [$M^+ - C_4H_9$], 115 (31) [$M^+ - C_6H_{11} \equiv$ 2-indenyl], 91 (23) [$C_7H_7^+$]; HRMS: *m*/*z* (%): calcd for $C_{15}H_{18}$: 198.1408; found: 198.1408.

Fraction II: A mixture of at least three different $C_{15}H_{18}$ isomers (70 mg, 35 %), among them **44** and **45** (NMR, MS); $R_f = 0.65$ (pentane); MS (EI, 70 eV): *m*/*z* (%): 198 (100) [M^+], 183 (53) [$M^+ - CH_3$], 169 (19) [$M^+ - C_2H_5$], 141 (60), 91 (65) [$C_7H_7^+$].

Fraction III: Biphenyl (6 mg, 8 %); $R_f = 0.63$ (pentane).

1-Phenyl-1-(propen-2′-yl)cyclopropane (48), 4-methyl-3phenyl-1,3-pentadiene (49) and 2-methyl-3-phenyl-1,3-pentadiene [(*Z*)-50]: According to GP 1, iodobenzene (**2**-Ph, 204 mg, 1.00 mmol), isopropylidenecyclopropane (**47**, 329 mg, 4.00 mmol), palladium(II) acetate (11.2 mg, 49.9 µmol), triphenylphosphane (39.3 mg, 150 µmol) and triethylamine (202 mg, 2.00 mmol) were heated in anhydrous DMF (10 mL) at 75 °C for 20 h. After work-up, chromatography of the crude product on silica gel (column 2 × 20 cm, pentane) gave:

Fraction I: **2**-Ph, not completely evaporated; $R_f = 0.85$ (pentane).

Fraction II: A mixture of (*Z*)-**50** and **49** (1.7:1) as a colorless oil (95 mg, 60 %), which could not be separated completely. (*Z*)-**50**: ^{1}H NMR (250 MHz, C_6D_6): $\delta = 7.30$–7.00 (m, 5H; Ar-H), 5.83 (q, $^3J = 7.0$ Hz, 1H; 4-H), 5.01 (q, $^4J = 0.5$ Hz, 1H; 1-H), 4.77 (q, $^4J = 0.5$ Hz, 1H; 1-H), 1.97 (dd, $^4J = 0.5$, $^4J = 0.5$ Hz, 3H; CH_3), 1.54 (d, $^3J = 7.0$ Hz, 3H; CH_3); ^{13}C NMR (62.9 MHz, C_6D_6, DEPT): $\delta = 144.7$ (C_{quat}), 136.0 (C_{quat}), 132.4 (C_{quat}), 130.0 (+, CH), 128.4 (+, CH), 126.8 (+, CH), 123.3 (+, CH), 115.5 (−, C-1), 20.5 (+, CH_3), 15.1 (+, CH_3); **49**: ^{1}H NMR (250 MHz, C_6D_6): $\delta = 7.30$–7.00 (m, 5H; Ar-H), 7.02 (dd, $^3J = 17$, $^3J = 10$ Hz, 1H; 2-H), 5.10 (d, $^3J = 10$ Hz, 1H; 1-H), 4.83 (d, $^3J = 17$ Hz, 1H; 1-H), 1.97 (s, 3H; CH_3), 1.51 (s, 3H; CH_3); ^{13}C NMR (62.9 MHz, C_6D_6, DEPT): $\delta = 144.5$ (C_{quat}), 140.1 (C_{quat}), 134.3 (C_{quat}), 130.4 (+, CH), 130.2 (+, CH), 126.6 (+, CH), 124.7 (+, CH), 115.3 (−, C-1), 22.7 (+, CH_3), 19.4 (+, CH_3).

Fraction III: **48** as a colorless oil (7.3 mg, 5 %); ^{1}H NMR (250 MHz, C_6D_6): $\delta = 7.23$–7.15 (m, 5H; Ar-H), 5.29 (s, 1H; 1′-H), 5.20 (d, $^4J = 0.5$ Hz, 1H; 1′-H), 1.90 (d, $^4J = 0.5$ Hz, 3H; CH_3), 1.0–1.5 (m, 4H; *c*Pr-H).

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[18] a) T. Jeffery, *J. Chem. Soc. Chem. Commun.* **1984**, 1287 – 1289; b) T. Jeffery, *Tetrahedron Lett.* **1985**, *26*, 2667 – 2670; c) T. Jeffery, *Synthesis* **1987**, 70 – 71; d) T. Jeffery, M. David, *Tetrahedron Lett.* **1998**, *39*, 5751 – 5754. However, acetonitrile is not completely inert towards intermediate **4**, and the Ritter-type product, *N*-[(2-cyclopropylidene-1-methyl-2-phenyl)propyl]acetamide, was isolated in 5% yield in the reaction of **1** with PhI and **17b** under these conditions. ^1H NMR (250 MHz, $CDCl_3$): $\delta = 7.58$ (dd, $^3J = 7.2$, $^3J = 1.5$ Hz, 2H; Ar-H), 7.38 – 7.21 (m, 3H; Ar-H), 6.06 (q, $^3J = 7.0$ Hz, 1H; CH), 2.05 (s, 3H; CH_3), 1.50 (d, $^3J = 7.0$ Hz, 3H; CH_3), 1.33 – 1.27 (m, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 170.3$ (C_{quat}, CO), 138.5 (C_{quat}, Ar-C), 128.1 (+, 2CH, Ar-C), 126.8 (+, CH, Ar-C), 126.6 (+, 2CH, Ar-C), 124.2 (C_{quat}), 72.1 (+, CH), 21.2 (+, CH_3), 19.4 (+, CH_3), 2.7 (–, 2*c*Pr-C); MS (70 eV): m/z (%): 215 (20) $[M^+]$, 174 (52) $[M^+ - C_3H_5]$, 159 (38) $[M^+ - C_4H_9]$, 141 (100) $[C_{11}H_9^+]$.

[19] Compare: A. de Meijere, S. I. Kozhushkov, A. F. Khlebnikov, *Top. Curr. Chem.* **2000**, *207*, 89 – 147, and references therein.

[20] Crystals of the compounds were grown by slow evaporation of a solution in a hexane/Et_2O mixture (**18f**-Ph-1, prepared from **17b**) or by slow cooling of their saturated solutions in Et_2O (**18f**-Ph-2, prepared from **17f**), hexane (**18f**-Ph, *p*-**32**) or a hexane/Et_2O mixture (**18f**-Tol) and measured on a SMART Bruker CCD 1 K (**18f**-Ph-1) or an STOE AED2 (other compounds) diffractometer using graphite monochromated $Mo_{K\alpha}$ radiation. The structure solutions and refinements on F^2 were performed with the SHELX program suite (Version 5.10). The hydrogen atoms were located in a difference Fourier map and refined as riding groups with the 1.2-fold isotropic displacement parameter of the corresponding C atom. **18f**-Ph-1: $C_{18}H_{20}O_4$ (300.34), crystal size $0.30 \times 0.18 \times 0.14$ mm^3, monoclinic, $a = 11.7145(4)$, $b = 6.5412(2)$, $c = 20.2856(7)$ Å, $\beta = 101.63(1)°$, $V = 1522.54(9)$ Å^3, $Z = 4$, space group $P2_1/c$, $T = 100.0(2)$ K, $\rho = 1.310$ g cm^{-3}, intensities measured: 13422 ($2\theta_{max} = 61.06$), independent: 4658 ($R_{int} = 0.0276$), 279 parameters refined, $R1 = 0.0559$, $wR2$ (all data) = 0.1156, Gof = 1.018, maximum and minimum residual

electron density 0.390 and −0.202 e Å^{-3}. **18f**-Ph-2: $C_{18}H_{20}O_4$ (300.34), crystal size 0.70 × 0.25 × 0.20 mm^3, monoclinic, $a = 11.714(2)$, $b = 6.5394(13)$, $c = 20.309(4)$ Å, $\beta = 101.47(3)^\circ$, $V = 1524.7(5)$ Å^3, $Z = 4$, space group $P2_1/c$, $T = 133(2)$ K, $\rho = 1.308$ g cm^{-3}, intensities measured: 12368 ($2\theta_{max} = 46.5$), independent: 2188 ($R_{int} = 0.0410$), 206 parameters refined, $R1 = 0.0559$, $wR2$ (all data) = 0.1081, Gof = 1.100, maximum and minimum residual electron density 0.172 and −0.195 e Å^{-3}. **18f**-Tol: $C_{19}H_{22}O_4$ (314.37), crystal size 0.80 × 0.60 × 0.50 mm^3, monoclinic, $a = 14.543(2)$, $b = 5.7066(5)$, $c = 20.334(2)$ Å, $\beta = 92.303(11)^\circ$, $V = 1686.2(3)$ Å^3, $Z = 4$, space group $P2_1/c$, $T = 150(2)$ K, $\rho = 1.238$ g cm^{-3}, intensities measured: 5415 ($2\theta_{max} = 50.16$), independent: 2988 ($R_{int} = 0.0197$), 211 parameters refined, $R1 = 0.0533$, $wR2$ (all data) = 0.1403, Gof = 1.063, maximum and minimum residual electron density 0.296 and −0.221 e Å^{-3}. **18k**-Ph: $C_{19}H_{22}O_4$ (314.37), crystal size 0.80 × 0.70 × 0.40 mm^3, monoclinic, $a = 18.146(4)$, $b = 7.0505(10)$, $c = 13.313(4)$ Å, $\beta = 99.540(14)^\circ$, $V = 1679.7(6)$ Å^3, $Z = 4$, space group $P2_1/c$, $T = 200(2)$ K, $\rho = 1.243$ g cm^{-3}, intensities measured: 4894 ($2\theta_{max} = 50.04$), independent: 2220 ($R_{int} = 0.0418$), 208 parameters refined, $R1 = 0.0694$, $wR2$ (all data) = 0.1397, Gof = 1.048, maximum and minimum residual electron density 0.296 and −0.221 e Å^{-3}. *p*-**32**: $C_{22}H_{21}NO_4$ (363.40), crystal size 0.70 × 0.60 × 0.50 mm^3, triclinic, $a = 7.8064(7)$, $b = 11.4141(10)$, $c = 11.4902(10)$ Å, $\alpha = 111.678(5)$, $\beta = 108.215(5)$, $\gamma = 91.304(5)^\circ$, $V = 892.58$ Å^3, $Z = 2$, space group $P\bar{1}$, $T = 133(2)$ K, $\rho = 1.352$ g cm^{-3}, intensities measured: 10902 ($2\theta_{max} = 49.16$), independent: 2944 ($R_{int} = 0.0594$), 245 parameters refined, $R1 = 0.0935$, $wR2$ (all data) = 0.1432, Gof = 1.271, maximum and minimum residual electron density 0.218 and −0.217 e Å^{-3}. *anti*-**34eb**: $C_{26}H_{30}O_2$ (374.50), crystal size 1.00 × 1.00 × 1.00 mm^3, monoclinic, $a = 12.855(13)$, $b = 7.578(8)$, $c = 22.310(2)$ Å, $\beta = 97.420(10)^\circ$, $V = 2155.0(4)$ Å^3, $Z = 4$, space group $P2_1/c$, $T = 200(2)$ K, $\rho = 1.154$ g cm^{-3}, intensities measured: 4692 ($2\theta_{max} = 50.16$), independent: 3739 ($R_{int} = 0.0918$), 257 parameters refined, $R1 = 0.1461$, $wR2$ (all data) = 0.4298, Gof = 1.137, maximum and minimum residual electron density 0.296 and −0.221 e Å^{-3}. CCDC-176378 (**18f**-Ph-1), -163615 (**18f**-Ph-2), -176661 (**18f**-Tol), -176526 (**18k**-Ph), -133154 (*p*-**32**), -176525 (*anti*-**34eb**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; (fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

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