

Facile Construction of Spirocyclopropanated Bi-, Tri- and Tetracyclic Skeletons by Novel Cascades Involving Intra- and Intermolecular Heck Reactions of 2-Bromo-1,6-enynes and Bicyclopropylidene^[‡]

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Dedicated to Professor Goverdhan Mehta on the occasion of his 60th birthday

Keywords: Cyclopropane / Palladium / Transition metal / Cascade reactions / Electrocyclization

Acyclic 2-bromo-1,6-enynes **5-R**, **9-R** and **11-R** with bulky substituents at the acetylenic terminus were co-cyclized with the highly strained bicyclopropylidene (**12**) under palladium catalysis at 80 °C to give the cross-conjugated tetraenes **13-R**, **18-R** and **19-R** in moderate-to-good yields (34–71%). Only the co-cyclization of **5-Ph** gave rise to an additional product, which was identified as the 11-membered ring **20**. At elevated temperatures (120–140 °C) the initially formed tetraenes underwent 6 π -electrocyclization to give spiro[cyclopropane-1,4'-bicyclo[4.3.0]-1(6),2-dienes] **21-R**, **22-R** and **23-R**. This novel class of spirocyclopropanated oligocycles is also accessible by a one-pot protocol. The highest yields for both

the tetraenes and bicyclo[4.3.0]nonadiene and its heteroanalogues were obtained with bulky substituents at the alkyne terminus of the precursors. Heteroatom-containing precursors **9-R** and **11-R** gave lower yields than their all-carbon analogues **5-R**. The acyclic 2-bromo-1,8-dien-6-ynes **28a,b,c** upon palladium-catalyzed co-cyclization with bicyclopropylidene (**12**) at 110 °C gave spirocyclopropanated tricycles **31a,b** and **32**, respectively, in moderate yields (14, 31 and 32%). These products were formed by two consecutive 6 π -electrocyclizations.

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Introduction

In the last two decades, the palladium-catalyzed cascade cyclization-cycloaddition reactions of 2-bromo-1,*n,m*-enynes and 2-bromo-1,*m,n*-dienynes have evolved as an efficient way to construct oligocarbo- and oligoheterocyclic skeletons.^[1] In particular, the cyclization of 2-bromo-1,6-enynes by intramolecular carbopalladation of the triple bond by the initially formed alkenylpalladium bromide leads to a new alkenylpalladium bromide, that is, a “living” intermediate that can intra- or intermolecularly carbopalladate other double or triple bond moieties. This strategy, therefore, has a lot of scope and can thus lead to a multitude of applications. While alkyne moieties have been employed with good results in several cases, both intra- and intermolecularly,^[2] they have mainly been utilized in all-in-

tramolecular reaction cascades, often followed by further transformations of the initial products by 6 π -electrocyclic rearrangements.^[3] Successful intra-intermolecular cascade co-cyclizations of 2-bromo-1,6-enynes with simple alkenes are scarce,^[4] probably because most alkenes are less reactive than alkynes in carbopalladation reactions. Bicyclopropylidene (**12**),^[5] however, is an alkene that exhibits superior reactivity towards carbopalladation in palladium-catalyzed cross-coupling reactions. As has been shown recently, **12** readily reacts with a wide variety of aryl and alkenyl halides under palladium catalysis in high yields.^[6] Since the initial carbopalladation intermediate swiftly undergoes a cyclopropylmethyl-to-homoallyl rearrangement, the primary coupling products are aryl- and alkenyl-substituted allylidene-cyclopropanes which can be captured in situ by various dienophiles to furnish the corresponding [4+2] cycloadducts which exhibit further increased structural complexity.

We herein report the successful co-cyclization of acyclic 2-bromo-1,6-enynes with bicyclopropylidene (**12**) under palladium catalysis to yield a spectrum of interesting spirocyclopropanated oligocycles.

Results and Discussion

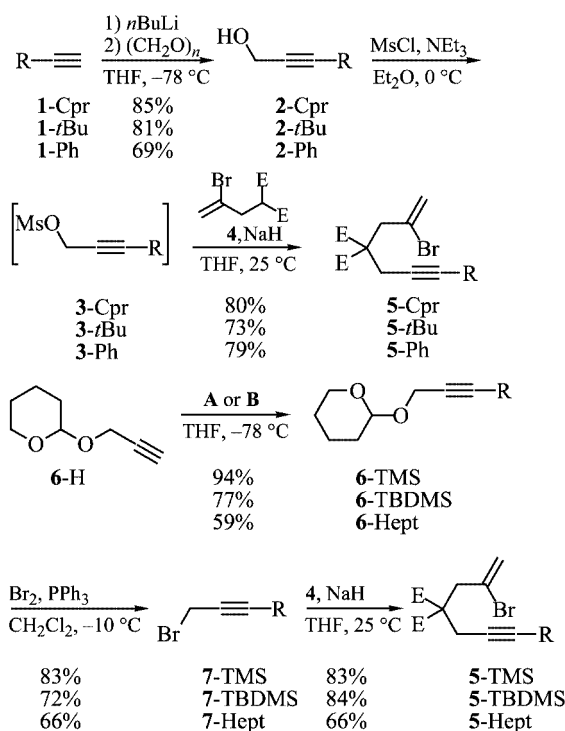
Acyclic 2-bromo-1,6-enynes as cyclization precursors were efficiently synthesized by two major routes. Terminal

[‡] Cyclopropyl Building Blocks for Organic Synthesis, 104. Part 103: A. de Meijere, H. Winsel, B. Stecker, *Org. Synth.* **2004**, *81*, 14–25. Part 102: A. Zanobini, M. Gensini, J. Magull, S. I. Kozhushkov, A. de Meijere, A. Brandi, *Eur. J. Org. Chem.* **2004**, 4158–4166.

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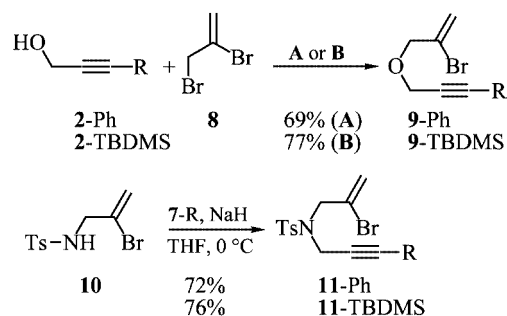
alkynes **1-R** were deprotonated with *n*-butyllithium, and the resulting acetylides trapped with paraformaldehyde to give the corresponding propargyl alcohols **2-R** in good yields (Scheme 1). The alcohols were then transformed into the corresponding mesylates **3-R**, which were treated in situ with the sodium enolate of dimethyl (2'-bromoallyl)malonate (**4**). Alternatively, the THP-protected propargyl alcohol **6-H** was deprotonated in a similar fashion and the acetylide trapped with a trialkylsilyl chloride or 6-heptenyl bromide, respectively. The resulting THP ethers **6-R** were subsequently transformed by treatment with the triphenylphosphane-bromine reagent into the corresponding bromides **7-R**, and the latter used to alkylate the enolate of **4**.



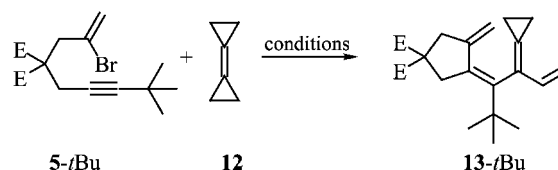
Scheme 1. Preparation of acyclic 2-bromo-1,6-enynes. Reagents and conditions: **A**: *n*BuLi, Me₃SiCl or *t*BuMe₂SiCl, THF, -78 °C; **B**: *n*BuLi, 6-heptenyl bromide, HMPA, THF, -78 °C. E = CO₂Me; R = Cpr (cyclopropyl), *t*Bu, Ph and Hept (6'-heptenyl).

In addition to the all-carbon-chain starting materials, cyclization precursors containing oxygen and tosylated nitrogen atoms were prepared as well. The former were synthesized by alkylation of the substituted propargyl alcohols **2-R** with 2,3-dibromopropene (**8**) under suitable conditions, whilst the latter were accessible by alkylation of 1-(*p*-tosylamino)-2-bromoprop-2-ene (**10**) with the corresponding propargyl bromides **7-R** (Scheme 2).

At first, **5-*t*Bu**, in the presence of 2 equivalents of bicyclopropylidene (**12**), was subjected to several cross-coupling conditions (Scheme 3). It was found that a protocol similar to that originally suggested by Jeffery,^[7] but without a quaternary ammonium salt, as had been found for all-intramolecular cascade reactions,^[3,4] gave the best results with the cross-conjugated tetraene **13-*t*Bu** being obtained in 66% yield.



Scheme 2. Preparation of heteroatom-containing 2-bromo-1,6-enynes. Reagents and conditions: **A**: CETAB (cetyltrimethylammonium bromide), NaOH, CH₂Cl₂, H₂O, 25 °C; **B**: NaH, THF, 0 → 25 °C.



Scheme 3. E = CO₂Me. For reaction details see Table 1.

Table 1. Palladium-catalyzed cyclization-cross-coupling reactions of **5-*t*Bu** with bicyclopropylidene (**12**)

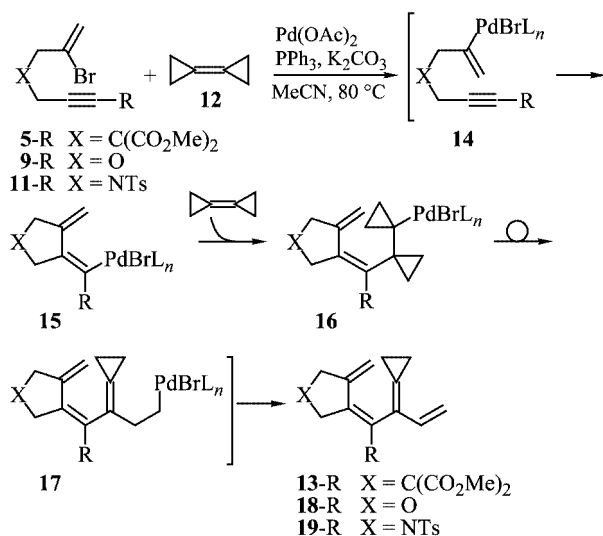
Entry	Conditions	Yield [%]
A	Pd(OAc) ₂ (10 mol %), PPh ₃ (30 mol %), NEt ₃ (2 equiv.), MeCN, 80 °C, 5 h	45
B	Pd(PPh ₃) ₄ (10 mol %), NEt ₃ (2 equiv.), MeCN, 80 °C, 6 h	36
C	Pd(OAc) ₂ (10 mol %), PPh ₃ (30 mol %), Et ₄ NBr (1 equiv.), K ₂ CO ₃ (2 equiv.), MeCN, 80 °C, 5 h	33
D	Pd(OAc) ₂ (10 mol %), PPh ₃ (30 mol %), K ₂ CO ₃ (2 equiv.), MeCN, 80 °C, 5 h	66
E	Pd(OAc) ₂ (10 mol %), PPh ₃ (30 mol %), Ag ₂ CO ₃ (2 equiv.), MeCN, 80 °C, 5 h	41

After this, all the synthesized 2-bromo-1,6-enynes were subjected to these optimized conditions. The domino-cyclization-cross-coupling reactions proceeded reasonably well, and the starting materials were consumed within four to five hours. As in the test case with **5-*t*Bu**, the resulting products were cross-conjugated tetraenes and not the bicyclic systems resulting from a subsequent 6π-electrocyclization. The yield of the *tert*-butyldimethylsilyl-substituted tetraene **13-TBDMS** slightly exceeded that of the model system **13-*t*Bu** (71 vs. 66%) (Table 2, Scheme 4). Only moderate yields were obtained for the phenyl derivative **13-Ph** (see discussion below) and the cyclopropyl-substituted tetraene **13-Cpr**, the latter being accompanied by by-products that could not be separated. This demonstrates a positive correlation between the size of the substituent and the observed yield of the sensitive tetraenes. The precursors with het-

Table 2. Palladium-catalyzed cyclization-cross-coupling reactions of acyclic 2-bromo-1,6-enynes with bicyclopopylidene (**12**) to give cross-conjugated tetraenes.

Starting material	R	X	Reaction time [h]	Product	Yield [%]
5-<i>t</i>Bu	<i>tert</i> -butyl	C(CO ₂ Me) ₂	5	13-<i>t</i>Bu	66
5-Cpr	cyclopropyl	C(CO ₂ Me) ₂	4.5	13-Cpr	≈ 34
5-Ph	phenyl	C(CO ₂ Me) ₂	4	13-Ph	38 ^[a]
5-TBDMS	<i>Sit</i> BuMe ₂	C(CO ₂ Me) ₂	3.5	13-TBDMS	71
9-Ph	phenyl	O	5	18-Ph	34
9-TBDMS	<i>Sit</i> BuMe ₂	O	4	18-TBDMS	54
11-Ph	phenyl	NTs	4	19-Ph	35
11-TBDMS	<i>Sit</i> BuMe ₂	NTs	4	19-TBDMS	41

^[a] Accompanied by **20** in a ratio of 1:1 (NMR).



Scheme 4. Formation of cross-conjugated tetraenes from 2-bromo-1,6-enynes and bicyclopopylidene (**12**). For reaction details see Table 2.

eroatoms in the chain consistently gave lower yields than their all-carbon analogues, for example, **13-TBDMS** was obtained in 71% yield, the oxygen analogue **18-TBDMS** in 54% yield and the *N*-tosyl derivative **19-TBDMS** in only 41% yield. The results for the phenyl-substituted derivatives **13-Ph**, **18-Ph** and **19-Ph** followed the same trend. This behavior may be due to the fact that not all of these precursors profit from the *gem*-disubstitution (Thorpe–Ingold) effect.^[8] In addition, the heteroatoms in the chain may coordinate to the active metal catalyst and thereby disturb the course or even alter the mode of the reaction.^[9]

Mechanistically, this transformation can be rationalized by the following reaction sequence: initial oxidative addition of the bromo-ene moiety onto a palladium(0) species, intramolecular carbopalladation of the triple bond to yield the “living” vinylpalladium species **15**, carbopalladation of a molecule of bicyclopopylidene (**12**) by **15** to furnish intermediate **16** containing a (cyclopropylcarbynyl)palladium moiety, which rapidly undergoes a cyclopropylmethyl-to-homoallyl rearrangement to give **17** (Scheme 4). Subsequent *syn*-β-hydride elimination eventually yields the cross-conjugated tetraene.

Although cross-conjugated oligoenes – so-called dendralenes – are usually rather sensitive and reactive structures,^[10] the tetraenes **13**, **18** and **19** proved to be reasonably stable. They could be handled at room temperature for short periods of time (work up, further transformations) and also stored in solution at low temperatures (–20 °C) for days without showing pronounced degeneration. However, they were quite sensitive towards oxygen, and mono-oxygenated products could be detected in some mass spectra.

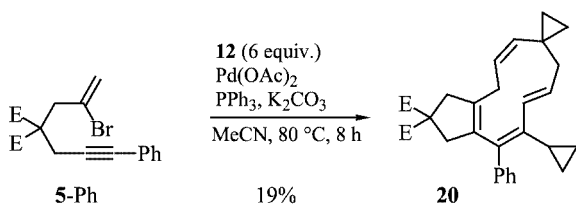
The conformations of the tetraenes **13**, **18** and **19** were proven by 2D-NMR spectroscopy as well as by NOESY experiments, according to which the structural element of a partly twisted 1,3,5-hexatriene is interlinked with a one-sidedly orthogonal [3]dendralene substructure. The UV spectrum of **17-TBDMS** showed a distinct maximum at 240 nm, which corresponds more closely to the absorption of an alkyl-substituted diene than to that of a 1,3,5-hexatriene which usually absorbs around 260 nm. This confirms that the conformation of the tetraene is that of two virtually separate diene units with a torsional angle between the two planes close to 90°, rather than that of a coplanar hexatriene with an out-of-plane vinyl group attached to it. The former conformation is also indicated by simple molecular mechanics (MM2) calculations, by which an almost perpendicular (dihedral angle of 87°) orientation between the two diene moieties is deduced. It is reasonable to assume that this orthogonal arrangement, to a large extent, is responsible for the relative stability of these tetraenes, and a bulky substituent at the C-1' position certainly favors this torsion and therefore increases the stability of the molecule. The yields of these products indeed correlate with the size of the substituent at C-1'.

While all the other precursors **5-R**, **9-R** and **11-R** reacted rather cleanly to yield the cross-conjugated tetraenes, the product **13-Ph** from **5-Ph** was accompanied by a second product in a ratio of 1:1 (NMR) which could not be separated from the mixture. Based on the mass spectrum of the mixture, the latter product appeared to result from a two-fold insertion of bicyclopopylidene (**12**) and this was eventually also concluded from the number of signals in the ¹³C-NMR spectrum. To prove this hypothesis, **5-Ph** was treated with a sixfold amount of **12** under otherwise identical conditions. Although the formation of **13-Ph** was largely suppressed in this case, the 19% isolated yield obtained for the 11-membered ring compound **20** (Scheme 5)

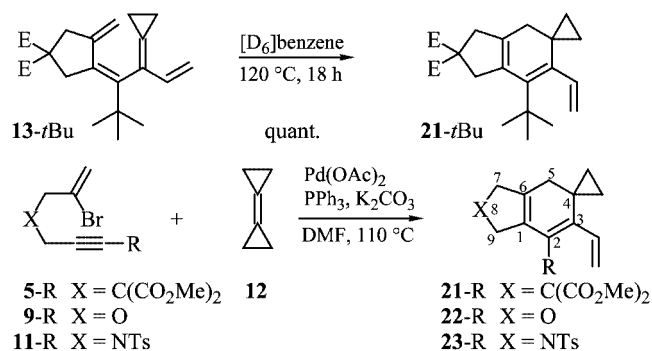
was rather disappointing. However, with an almost pure sample of **20** at hand, its structure could eventually be assigned with the help of an HMBC-2D-NMR spectrum, with the configurations of the double bonds being determined on the basis of their coupling constants in the ^1H -NMR spectrum. Although palladium-catalyzed cascade processes with insertions of more than one bicyclopropylidene molecule have been reported in a different context,^[11] the actual reason and the underlying mechanism for this unusual co-cyclization behaviour of **5-Ph** and **12** can only be speculated about at this stage.

To test whether the obtained tetraenes, in spite of their orthogonal arrangement in the 1,3,5-hexatriene subunit, could undergo 6π -electrocyclization to form spirocyclopropanated bicyclic systems, a sample of **13-*t*Bu** in $[\text{D}_6]\text{benzene}$ in a sealed NMR tube was heated at 120 °C in an oil bath. As monitored by ^1H -NMR spectroscopy, **13-*t*Bu** was cleanly and completely converted into the vinylspiro[cyclopropanebicyclo[4.3.0]nonadiene] derivative **21-*t*Bu** within 18 h (Scheme 6).

According to this observation one ought to be able to perform domino-Heck reactions and subsequent 6π -electrocyclizations in a single operation. To achieve this, **5-*t*Bu** and **12** in DMF were treated with the previously employed catalyst cocktail $[\text{Pd}(\text{OAc})_2, \text{PPh}_3, \text{K}_2\text{CO}_3]$. While at and above 140 °C the transformation proceeded non-uniformly with rapid precipitation of palladium black, it went surprisingly well at lower temperatures, and even at 110 °C came to completion within about 10 h. This suggests that the palladium catalyst assists the electrocyclization, probably by coordination to the methylenecyclopropane moiety of the conjugated 1,3,5-hexatriene.^[12]



Scheme 5. Formation of the 11-membered ring compound **20** from **5-Ph** and **12**. E = CO_2Me .



Scheme 6. Thermal 6π -electrocyclization of **13-*t*Bu** and direct formation of such products from **5-R**, **9-R**, **11-R** and bicyclopropylidene (**12**). E = CO_2Me . For reaction details see Table 3.

Under the same conditions, eight out of ten other acyclic 2-bromo-1,6-enynes, **5-R**, **9-R** and **11-R**, were converted into the corresponding spirocyclopropanated bicycles **21-R**, **22-R** and **23-R** in mostly satisfactory yields (Table 3). In the case of the unsubstituted enyne **5-H** and the trimethylsilyl-substituted **5-TMS**, no product could be isolated. These findings are in line with the observations of previous research in which an unsubstituted enyne could not be co-cyclized with alkenes.^[13] The failure of the trimethylsilyl-substituted precursor **5-TMS** to react, may be attributed to an initial cleavage of the base-sensitive alkynyl–trimethylsilyl bond under the basic conditions used (DMF, K_2CO_3), which gives rise to **5-H**. Similar in situ deprotections are known and may sometimes lead to alternative reaction pathways.^[14]

The highest yields of the spiro[cyclopropane-1,4'-bicyclo[4.3.0]nona-1(6),2-dienes] of type **21** were obtained from precursors with bulky substituents, for example, **5-TBDS**. The phenyl-substituted **5-Ph** furnished the tricycle **21-Ph** in 49% yield with no traces of the previously observed 11-membered ring **20**. Since the yield of the thus formed **21-Ph** is significantly higher than that of the corresponding tetraene precursor **13-Ph** formed at a lower temperature, it appears that the β -hydride elimination leading to **13-Ph** must be slower than in the other cases so that the homoallylpalladium intermediate can carbopalladate a second molecule of **12**. Alkyl-substituted precursors **5-Cpr** and **5-Hept** gave slightly lower yields, the latter without the formation of any side-products from an all-intramolecular reaction. Following the general trend observed in the formation of the tetraenes **13-R**, the heterocyclic compounds gave lower yields than their carbocyclic analogues with the notable exception of **22-Ph** (72%). The reason for this surprisingly high yield of **22-Ph** is not clear at present.

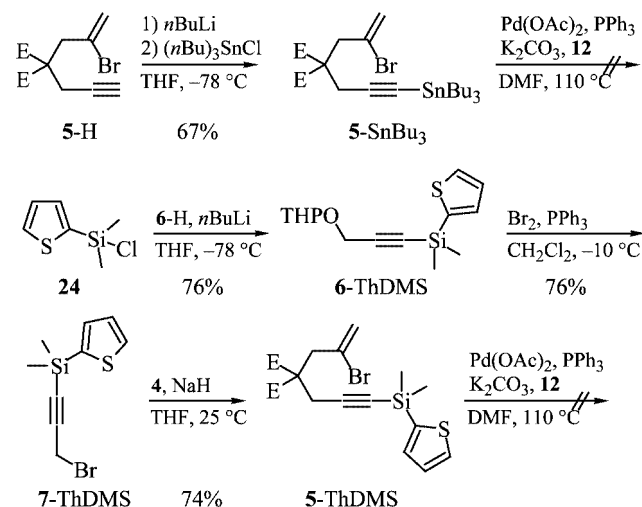
Since the 6π -electrocyclization products contain a newly formed conjugated 1,3-diene system, the possibility of forming an additional ring by a subsequent $[4+2]$ cycloaddition was envisioned. The bulky substituents at C-2, however, rendered this Diels–Alder reaction impossible, as was quickly found out by performing some test runs.

It might also be possible to extend the sequential transformation by attaching another conjugated double bond to the 2-position of the 3-ethynylbicyclo[4.3.0]nona-1(6),2-diene formed from the 2-bromo-1,6-enynes. To achieve this, the latter would have to contain a functional group at the alkyne terminus that would enable it to undergo cross-coupling with an alkenyl halide after the initial domino-Heck reaction. Since this group has to have good transmetalation properties to facilitate the cross-coupling along with a high steric demand to ensure a good yield in the cyclization process, the tributylstannyl group for a subsequent Stille coupling^[15] and alternatively the dimethylthienylsilyl group^[16] for a Hiyama coupling^[17] of the spiro[cyclopropane-1,4'-bicyclo[4.3.0]nona-1(6),2-dienes] were envisioned. The cyclization precursors **5-SnBu₃** and **5-ThDMS** were assembled just like the others described above in 67 and 74% yield, respectively (Scheme 7). However, neither **5-SnBu₃** nor **5-ThDMS** gave the corresponding cyclization-coupling prod-

Table 3. One-pot domino-Heck co-cyclizations of acyclic 2-bromo-1,6-enynes and bicyclopropylidene (**12**) with ensuing 6 π -electrocyclization.

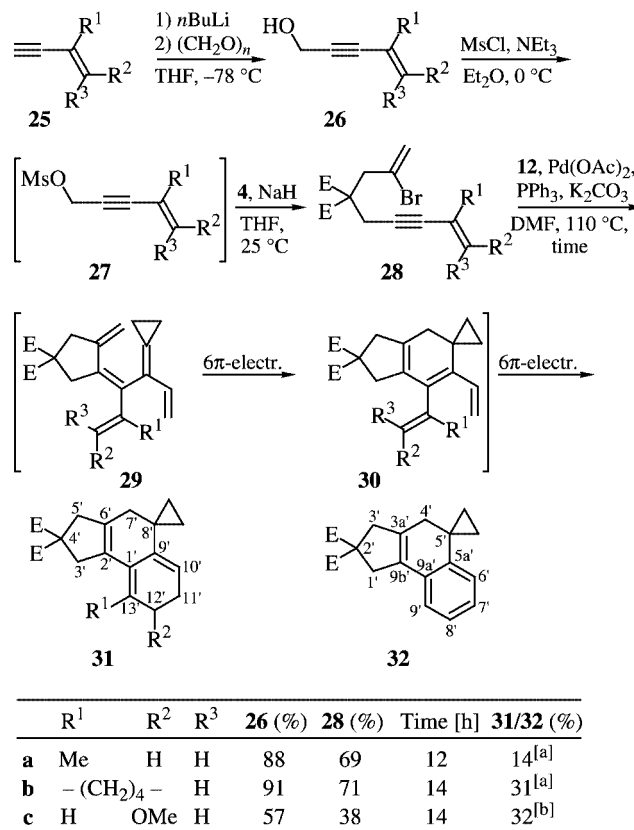
Starting material	R	X	Reaction time [h]	Product	Yield [%]
5-H	hydrogen	C(CO ₂ Me) ₂	12	21-H	—
5-Cpr	cyclopropyl	C(CO ₂ Me) ₂	12	21-Cpr	38
5-<i>t</i>Bu	<i>tert</i> -butyl	C(CO ₂ Me) ₂	10	21-<i>t</i>Bu	56
5-Ph	phenyl	C(CO ₂ Me) ₂	12	21-Ph	49
5-Hept	6-heptenyl	C(CO ₂ Me) ₂	12	21-Hept	48
5-TMS	SiMe ₃	C(CO ₂ Me) ₂	10	21-TMS	—
5-TBDMS	Si <i>t</i> BuMe ₂	C(CO ₂ Me) ₂	11	21-TBDMS	65
9-Ph	phenyl	O	11	22-Ph	72
9-TBDMS	Si <i>t</i> BuMe ₂	O	12	22-TBDMS	41
11-Ph	phenyl	NTs	10	23-Ph	44
11-TBDMS	Si <i>t</i> BuMe ₂	NTs	12	23-TBDMS	32

uct of type **21** when treated with the palladium catalyst in the presence of bicyclopropylidene (**12**). It can only be speculated that, on the one hand, the alkynylstannane might serve as an adequate coupling partner for an intermediate of type **14** in this reaction,^[18] thus leading eventually to oligomeric materials. On the other hand, the dimethylthienylsilyl group – which can be removed more easily than the *tert*-butyldimethylsilyl group – may be cleaved just like the trimethylsilyl group under the basic conditions employed, as described above.

Scheme 7. Syntheses and attempted cyclizations of tributylstannyl- and (dimethylthiophenylsilyl)-substituted 2-bromo-1,6-enynes. E = CO₂Me.

To overcome these difficulties, the required additional alkenyl moiety was directly introduced into the 2-bromo-1,6-enyne. By utilizing the first general route (see above) to the precursors of such compounds, three suitable 2-bromo-dienynes **28a–c** were prepared from commercially available or readily accessible enynes (Scheme 8). They were all isolated as oils, although prone to oxidation, with **28c** being the least stable one.

By applying the established cyclization-cross-coupling-cyclization protocol, **28a** was treated with Pd(OAc)₂/PPh₃/K₂CO₃ in DMF in the presence of **12** to give the cyclopropanated tricycle **31a** in 14% yield. Although the yield was



[^a] Product **31**. [^b] Product **32**.

Scheme 8. Syntheses and domino-Heck co-cyclizations of 2-bromo-1,8-dien-6-ynes and bicyclopropylidene (**12**) by subsequent “transmissive electrocyclizations”. E = CO₂Me.

rather disappointing, the concept of two consecutive 6 π -electrocyclizations proved to be feasible. Note that the second electrocyclization can only take place after the first one has occurred since it is this reaction that actually generates the conjugated π -system with the additional isopropenyl group of the original precursor. By analogy to the known cascades of two consecutive Diels–Alder reactions in which the first cycloaddition is also a prerequisite to generate the 1,3-diene system for the second [4+2] cycloaddition, and which have been termed “transmissive cycloadd-

ditions",^[19] the new type of reaction may be termed a "transmissive electrocyclization".

A better yield was obtained from the co-cyclization of **28b** with bicyclopropylidene (**12**) to give the cyclopropanated tetracycle **31b** probably because of the enhanced stability of the intermediate cross-conjugated pentaene **29b** which contains the sterically demanding cyclohexenyl group. These cross-conjugated pentaene intermediates turned out to be extremely sensitive, and all attempts to isolate intermediates **29**, even at a lower temperature, proved to be futile. The methoxyethenyl-substituted precursor **28c** gave the cyclopropanated tricycle **32** with an aromatic third ring which results from the elimination of methanol from the initially formed **31c**. This elimination reaction may occur during chromatographic purification since the ¹H-NMR spectrum of the crude product showed some distinct signals that indicated the presence of the methoxy-substituted cyclohexadiene moiety of **31c**.

Conclusions

Once again the unique tetrasubstituted alkene bicyclopropylidene (**12**) has proved its suitability as a building block in palladium-catalyzed cascade reactions, in this case by incorporating a 1'-substituted allylidene cyclopropane moiety into a substituted dimethylenecyclopentane to give cross-conjugated tetraenes which undergo 6 π -electrocyclization to yield spiro[cyclopropane-1,4'-bicyclo[4.3.0]nona-1(6),2-dienes]. The cross-conjugated tetraenes of type **13**, **18** and **19** can be isolated and may probably also serve as precursors for other transformations. The concept of domino-Heck reactions with a consecutive thermal ring closure can even be extended to the novel "transmissive electrocyclizations", a sequence of two interdependent electrocyclizations, to furnish a bicyclic framework via a cross-conjugated pentaene.

Experimental Section

General: All reagents were used as purchased from commercial suppliers without further purification. All reactions in nonaqueous solvents were carried out using standard Schlenk techniques under dry nitrogen. Solvents were purified and dried according to conventional methods prior to use; diethyl ether (Et₂O) and tetrahydrofuran (THF) were freshly distilled from sodium/benzophenone. Solvents are abbreviated as follows: DCM = dichloromethane, MeCN = acetonitrile, DMF = dimethylformamide, EtOAc = ethyl acetate, MeOH = methanol, THF = tetrahydrofuran. ¹H and ¹³C NMR spectra were recorded at ambient temperature with Varian Mercury 200, Bruker AM 250 and Varian Unity 300 instruments. Chemical shifts δ are given in ppm relative to solvent resonances (¹H: 7.26 ppm for chloroform; ¹³C: 77.0 ppm for [D]chloroform), coupling constants, *J*, are given in Hertz. Characterization of the multiplicity of signals: s = singlet, br. s = broad singlet, d = doublet, t = triplet, m = multiplet. The multiplicities of signals were determined by the DEPT technique [DEPT: + = primary or tertiary (positive DEPT signal), - = secondary (negative DEPT signal), C_{quat} = quaternary carbon atoms] or the APT technique

[APT: + = primary or tertiary (positive APT signal), - = secondary and quaternary carbon atoms (negative APT signal)]. IR spectra were recorded on a Bruker IFS 66 spectrometer. Mass spectra were acquired with a Finnigan MAT 95 spectrometer. High-resolution mass spectra (HRMS) were obtained by preselected-ion peak matching at *R* $\approx$ 10000 and are within ± 2 ppm of the exact mass. Chromatographic separations were carried out on Merck Silica 60 (0.063–0.200 mm, 70–230 mesh ASTM). The dimensions of the columns are given as "diameter $\times$ height of the silica column". TLC was performed with Macherey–Nagel TLC Alugram® Sil G/UV254 plates; detection was under UV light at 254 nm and development with MOPS reagent (10%, solution in ethanol). Melting points were obtained with a Büchi Dr. Tottoli apparatus; values are uncorrected. Elemental analysis were carried out by the Mikroanalytisches Laboratorium des Instituts für Organische und Biomolekulare Chemie der Universität Göttingen.

General Procedure for the Palladium-Catalyzed Co-Cyclization of 2-Bromo-1,6-enynes with Bicyclopropylidene (GP 1): Palladium acetate (22.4 mg, 100 μ mol, 10 mol %), triphenylphosphane (78.7 mg, 300 μ mol, 30 mol %) and potassium carbonate (276 mg, 2.00 mmol) were suspended in anhydrous acetonitrile (10 mL) in a screw-cap Pyrex bottle. The respective bromoenyne (1.00 mmol) was added and argon was bubbled through the mixture for 5 min after which bicyclopropylidene (160 mg, 2.00 mmol) was added. Then the bottle was tightly closed, and the mixture heated at 80 °C in a preheated oil bath for the given period of time. After cooling to room temperature, the reaction mixture was taken up in diethyl ether (20 mL), the mixture filtered through a pad of Celite (5 cm) and the solvent evaporated in vacuo to leave about 1 mL. The crude product was purified by chromatography on silica gel, eluting with pentane/diethyl ether mixtures.

Dimethyl 3-[(Z)-1'-Cyclopropyl-2'-cyclopropylidene-3'-butenylidene]-4-methylene-1,1-cyclopentenedicarboxylate (13-Cpr): According to GP1, Pd(OAc)₂ (22.4 mg, 100 μ mol, 10 mol %), PPh₃ (78.6 mg, 300 μ mol, 30 mol %), K₂CO₃ (276 mg, 2.00 mmol) and dimethyl 2-(2'-bromoallyl)-2-(3''-cyclopropyl-2''-propynyl)malonate (**5-Cpr**, 329 mg, 999 μ mol) were stirred in acetonitrile (10 mL) with bicyclopropylidene (160 mg, 2.00 mmol) at 80 °C for 4.5 h. Column chromatography on silica gel (100 g, 3 $\times$ 30 cm, pentane/diethyl ether, 10:1, *R*_f = 0.45) yielded 151 mg of a yellow oil, containing approximately 75% (¹H NMR) of **13-Cpr** (34% yield). ¹H NMR (250 MHz, CDCl₃): δ = 0.19–0.42 (m, 2 H, Cpr-H), 0.48–0.69 (m, 2 H, Cpr-H), 0.88–1.18 (m, 5 H, Cpr-H), 2.95 (br. s, 2 H, 5-H), 3.25 (br. s, 2 H, 2-H), 3.71 (s, 6 H, OCH₃), 4.71 (s, 1 H, C=CH₂), 4.87 (s, 1 H, C=CH₂), 4.95 (d, ³*J* = 10.0 Hz, 1 H, 4'-H), 5.09 (d, ³*J* = 17.3 Hz, 1 H, 4'-H), 6.40 (dd, ³*J* = 17.3, ³*J* = 10.0 Hz, 1 H, 3''-H) ppm. ¹³C NMR (62.9 MHz, CDCl₃, DEPT): δ = 2.82 (–, Cpr-C), 2.99 (–, Cpr-C), 5.39 (–, 2 C, Cpr-C), 15.08 (+, Cpr-C), 39.60 (–, C-2), 43.64 (–, C-5), 52.70 (+, OCH₃), 52.86 (+, OCH₃), 57.08 (C_{quat}, C-1), 107.64 (–, C-1'), 113.35 (–, C-4'), 126.42 (C_{quat}, Cpr-C*), 126.71 (C_{quat}, C-3*), 132.3 (C_{quat}, C-4), 133.98 (C_{quat}, C-2'), 134.94 (+, C-3'), 143.57 (C_{quat}, C-1'), 171.96 (C_{quat}, 2 C, C=O) ppm. C₂₀H₂₄O₄ (328.4).

Dimethyl 3-[(Z)-1'-(*tert*-Butyl)-2'-cyclopropylidene-3'-butenylidene]-4-methylene-1,1-cyclopentenedicarboxylate (13-*t*Bu): According to GP1, Pd(OAc)₂ (22.4 mg, 100 μ mol, 10 mol %), PPh₃ (78.6 mg, 300 μ mol, 30 mol %), K₂CO₃ (276 mg, 2.00 mmol) and dimethyl 2-(2'-bromoallyl)-2-(4'',4''-dimethyl-2''-pentynyl)malonate (**5-*t*Bu**, 345 mg, 999 μ mol) were stirred in acetonitrile (10 mL) with bicyclopropylidene (160 mg, 2.00 mmol) at 80 °C for 5 h. Column chromatography on silica gel (100 g, 3 $\times$ 30 cm, pentane/diethyl ether, 10:1, *R*_f = 0.35) yielded **13-*t*Bu** (227 mg, 66%) as a colorless oil. IR

(film): $\tilde{\nu}$ = 3053, 2930, 2855, 1737, 1720, 1599, 1504, 1473, 1462, 1434, 1390, 1259, 1207, 1164, 1118, 1072, 937, 826, 811, 757, 699 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ = 0.94–1.22 (m, 4 H, Cpr-H), 1.15 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.87 (s, 1 H, 5-H), 2.90 (s, 1 H, 5-H), 3.27 (s, 1 H, 2-H), 3.28 (s, 1 H, 2-H), 3.70 (s, 3 H, OCH_3), 3.71 (s, 3 H, OCH_3), 4.77 (s, 1 H, $\text{C}=\text{CH}_2$), 4.97 (d, 3J = 10.5 Hz, 1 H, 4'-H), 5.06 (d, 3J = 17.6 Hz, 1 H, 4'-H), 5.10 (s, 1 H, $\text{C}=\text{CH}_2$), 6.48 (dd, 3J = 17.6, 3J = 10.5 Hz, 1 H, 3'-H) ppm. ^{13}C NMR (62.9 MHz, CDCl_3 , DEPT): δ = 2.92 (–, Cpr-C), 3.08 (–, Cpr-C), 29.87 [+ , 3 C, $\text{C}(\text{CH}_3)_3$], 36.35 [C_{quat} , $\text{C}(\text{CH}_3)_3$], 40.99 (–, C-2), 42.15 (–, C-5), 52.57 (+, OCH_3), 52.64 (+, OCH_3), 57.28 (C_{quat} , C-1), 109.43 (–, C-1'), 113.16 (–, C-4'), 124.34 (C_{quat} , Cpr-C), 131.51 (C_{quat} , C-4), 132.08 (C_{quat} , C-2'), 136.86 (+, C-3'), 143.42 (C_{quat} , C-1'), 144.57 (C_{quat} , C-3), 171.65 (C_{quat} , C=O), 171.84 (C_{quat} , C=O) ppm. MS (EI, 70 eV): m/z (%) = 344 (19) [M^+], 316 (19) [M^+ – C_2H_4], 287 (79) [M^+ – C_4H_9], 269 (33), 241 (37), 227 (100), 169 (59), 167 (49), 84 (85), 57 (42). $\text{C}_{21}\text{H}_{28}\text{O}_4$ (344.4): calcd. C 73.23, H 8.19; found C 73.50, H 7.89.

Dimethyl 3-[(*E*)-2'-Cyclopropylidene-1'-phenyl-3'-butenylidene]-4-methylene-1,1-cyclopentenedicarboxylate (13-Ph): According to GP1, $\text{Pd}(\text{OAc})_2$ (11.2 mg, 49.9 μmol , 10 mol %), PPh_3 (39.3 mg, 150 μmol , 30 mol %), K_2CO_3 (138 mg, 999 μmol) and dimethyl 2-(2'-bromoallyl)-2-(3''-phenyl-2''-propynyl)malonate (5-Ph, 183 mg, 501 μmol) were stirred in acetonitrile (5 mL) with bicyclopropylidene (80.0 mg, 998 μmol) at 80 °C for 4 h. Column chromatography on silica gel (60 g, 2×25 cm, pentane/diethyl ether, 10:1, R_f = 0.40) yielded 154 mg of a pale yellow oil which consisted of an inseparable mixture of 13-Ph (38%) and 20 in a 1:1 ratio (^1H NMR). ^1H NMR (250 MHz, CDCl_3): δ = 0.99–1.26 (m, 4 H, Cpr-H), 3.05 (br. s, 2 H, 5-H), 3.11 (br. s, 2 H, 2-H), 3.69 (s, 6 H, OCH_3), 4.77 (s, 1 H, $\text{C}=\text{CH}_2$), 4.98 (d, 3J = 10.0 Hz, 1 H, 4'-H), 5.22–5.25 (m, 2 H, 4'-H, $\text{C}=\text{CH}_2$), 6.51 (dd, 3J = 17.0, 3J = 10.0 Hz, 1 H, 3'-H), 7.11–7.40 (m, 5 H, aryl-H) ppm. ^{13}C NMR (62.9 MHz, CDCl_3 , DEPT, only representative data for 13-Ph): δ = 2.71 (–, Cpr-C), 3.03 (–, Cpr-C), 41.28 (–, C-2), 41.73 (–, C-5), 52.59 (+, 2 C, OCH_3), 57.33 (C_{quat} , C-1), 110.23 (–, C-2'), 113.79 (–, C-4'), 171.55 (C_{quat} , 2 C, C=O) ppm. MS (EI, 70 eV, only representative data for 13-Ph): m/z (%) = 364 (86) [M^+], 362 (87), 304 (100) [M^+ – HCO_2CH_3]. $\text{C}_{23}\text{H}_{24}\text{O}_4$ (364.4).

Dimethyl (4'*E*,8'*Z*)-Spiro[cyclopropane-1,7'-(3'-cyclopropyl-2'-phenylbicyclo[9.3.0]tetradeca-1'(11'),2',4',8'-tetraene-13',13'-dicarboxylate)] (20): According to GP1, $\text{Pd}(\text{OAc})_2$ (11.2 mg, 49.9 μmol , 10 mol %), PPh_3 (39.3 mg, 150 μmol , 30 mol %), K_2CO_3 (138 mg, 999 μmol) and dimethyl 2-(2'-bromoallyl)-2-(3''-phenyl-2''-propynyl)malonate (5-Ph, 183 mg, 501 μmol) were stirred in acetonitrile (5 mL) with bicyclopropylidene (240 mg, 3.00 mmol) at 80 °C for 8 h. Column chromatography on silica gel (60 g, 3×30 cm, pentane/diethyl ether, 10:1, R_f = 0.40) yielded 20 (42 mg, 19%) as a yellowish oil that contained only trace amounts of 13-Ph. IR (film): $\tilde{\nu}$ = 3079, 3003, 2953, 2842, 1736, 1600, 1489, 1434, 1259, 1199, 1164, 1108, 1073, 1049, 1022, 965, 912, 733, 704, 649 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ = 0.20–0.37 (m, 6 H, Cpr-H), 0.68–0.79 (m, 2 H, Cpr-H), 1.16–1.38 (m, 1 H, Cpr-H), 2.08 (d, 3J = 7.3 Hz, 2 H, 6'-H), 2.40 (d, 3J = 6.7 Hz, 2 H, 10'-H), 2.74 (br. s, 2 H, 12'-H), 3.20 (br. s, 2 H, 14'-H), 3.66 (s, 6 H, OCH_3), 4.88 (m, 1 H, 4'-H), 5.35 (m, 1 H, 5'-H), 5.48 (dt, 3J = 9.9, 3J = 6.7 Hz, 1 H, 9'-H), 6.14 (d, 3J = 9.9 Hz, 1 H, 8'-H), 7.11–7.39 (m, 5 H, aryl-H) ppm. ^{13}C NMR (62.9 MHz, CDCl_3 , DEPT): δ = 6.33 (–, 2 C, Cpr-C), 13.22 (–, 2 C, Cpr-C), 13.39 (+, Cpr-C), 24.73 (–, C-10'), 27.42 (C_{quat} , Cpr-C), 42.37 (–, C-6'), 42.45 (–, C-12'), 44.08 (–, C-14'), 52.69 (+, OCH_3), 52.75 (+, OCH_3), 58.43 (C_{quat} , C-13'), 122.23 (+, C-9'), 124.92 (+, C-5'), 126.29 (+, aryl-

C), 127.49 (+, 2 C, aryl-C), 129.34 (+, 2 C, aryl-C), 131.55 (+, C-8'), 131.79 (C_{quat} , C-4'), 132.04 (C_{quat} , C-3'), 135.53 (C_{quat} , aryl-C*), 140.19 (C_{quat} , C-11'), 140.96 (C_{quat} , C-1'), 142.17 (C_{quat} , C-2'), 172.35 (C_{quat} , 2 C, C=O) ppm. MS (200 eV, DCI, NH_3): m/z (%) = 906 (6) [$2\text{M} + \text{NH}_4^+$], 462 (100) [$\text{M} + \text{NH}_4^+$], 445 (26) [$\text{M} + \text{H}^+$]. $\text{C}_{29}\text{H}_{32}\text{O}_4$ (444.6).

Dimethyl 3-[(*E*)-1'-*tert*-Butyl(dimethyl)silyl]-2'-cyclopropylidene-3'-butenylidene]-4-methylene-1,1-cyclopentenedicarboxylate (13-TDBMS): According to GP1, $\text{Pd}(\text{OAc})_2$ (22.4 mg, 100 μmol , 10 mol %), PPh_3 (78.6 mg, 300 μmol , 30 mol %), K_2CO_3 (276 mg, 2.00 mmol) and dimethyl 2-(2'-bromoallyl)-2-[3''-*tert*-butyl-(dimethyl)silyl]-2'-propynylmalonate (5-TDBMS, 404 mg, 1.00 mmol) were stirred in acetonitrile (10 mL) with bicyclopropylidene (160 mg, 2.00 mmol) at 80 °C for 3.5 h. Column chromatography on silica gel (100 g, 3×30 cm, pentane/diethyl ether, 10:1, R_f = 0.45) yielded 13-TDBMS (286 mg, 71%) as a colorless oil. IR (film): $\tilde{\nu}$ = 3086, 2954, 2930, 2897, 2856, 1739, 1626, 1604, 1435, 1361, 1251, 1203, 1164, 1072, 991, 899, 833, 772, 734, 673 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ = –0.01 [s, 3 H, $\text{Si}(\text{CH}_3)_3$], 0.16 [s, 3 H, $\text{Si}(\text{CH}_3)_3$], 0.85–1.27 (m, 4 H, Cpr-H), 0.93 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.94 (s, 2 H, 5-H), 3.12 and 3.27 (br. AB, 2J = 15.7 Hz, 2 H, 2-H), 3.72 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3), 4.89 (s, 1 H, $\text{C}=\text{CH}_2$), 4.96 (d, 3J = 10.4 Hz, 1 H, 4'-H), 5.05 (d, 3J = 17.3 Hz, 1 H, 4'-H), 5.20 (s, 1 H, $\text{C}=\text{CH}_2$), 6.45 (dd, 3J = 17.3, 3J = 10.4 Hz, 1 H, 3'-H) ppm. ^{13}C NMR (62.9 MHz, CDCl_3 , DEPT): δ = –3.53 [+ , $\text{Si}(\text{CH}_3)_3$], –3.16 [+ , $\text{Si}(\text{CH}_3)_3$], 2.35 (–, Cpr-C), 3.71 (–, Cpr-C), 18.79 [C_{quat} , $\text{C}(\text{CH}_3)_3$], 28.03 [+ , 3 C, $\text{C}(\text{CH}_3)_3$], 42.05 (–, C-2), 43.47 (–, C-5), 52.69 (+, 2 C, OCH_3), 57.16 (C_{quat} , C-1), 111.76 (–, C-1'), 113.01 (–, C-4'), 122.83 (C_{quat} , Cpr-C), 132.27 (C_{quat} , C-2'), 135.27 (C_{quat} , C-4), 136.51 (+, C-3'), 144.14 (C_{quat} , C-1'), 146.45 (C_{quat} , C-3), 171.66 (C_{quat} , 2 C, C=O) ppm. MS (EI, 70 eV): m/z (%) = 402 (3) [M^+], 345 (7) [M^+ – C_4H_9], 317 (5) [M^+ – C_4H_9 – C_2H_4], 285 (12) [M^+ – TDBMS – H_2], 257 (5), 227 (18), 169 (32), 89 (63), 73 (100). $\text{C}_{23}\text{H}_{34}\text{O}_4\text{Si}$ (402.6): calcd. C 68.62, H 8.51; found C 68.52, H 8.24.

3-[(*E*)-2'-Cyclopropylidene-1'-phenyl-3'-butenylidene]-4-methylene-tetrahydrofuran (18-Ph): According to GP1, $\text{Pd}(\text{OAc})_2$ (11.2 mg, 49.9 μmol , 10 mol %), PPh_3 (39.3 mg, 150 μmol , 30 mol %), K_2CO_3 (138 mg, 998 μmol) and [3'-(2'-bromoallyloxy)-1'-propynyl]benzene (9-Ph, 126 mg, 502 μmol) were stirred in acetonitrile (5 mL) with bicyclopropylidene (80.0 mg, 999 μmol) at 80 °C for 5 h. Column chromatography on silica gel [60 g, 2×25 cm, pentane/diethyl ether, 20:1, R_f = 0.80 (pentane/diethyl ether, 10:1)] yielded 18-Ph (43 mg, 34%) as an unstable yellow oil. IR (film): $\tilde{\nu}$ = 3055, 2977, 2930, 2854, 1734, 1598, 1490, 1442, 1424, 1340, 1261, 1069, 910, 733, 703, 648 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ = 1.09 (m, 4 H, Cpr-H), 4.46 (t, 4J = 2.3 Hz, 2 H, 5-H), 4.59 (s, 2 H, 2-H), 4.95 (s, 1 H, $\text{C}=\text{CH}_2$), 5.04 (d, 3J = 10.5 Hz, 1 H, 4'-H), 5.22 (d, 3J = 17.0 Hz, 1 H, 4'-H), 5.26 (t, 4J = 2.3 Hz, 1 H, $\text{C}=\text{CH}_2$), 6.57 (dd, 3J = 17.0, 3J = 10.5 Hz, 1 H, 3'-H), 7.18–7.33 (m, 5 H, aryl-H) ppm. ^{13}C NMR (62.9 MHz, CDCl_3 , DEPT): δ = 3.08 (–, 2 C, Cpr-C), 72.99 (–, C-2*), 73.32 (–, C-5*), 106.79 (–, C-1'), 114.02 (–, C-4'), 127.30 (C_{quat} , Cpr-C), 127.64 (+, aryl-C), 128.03 (+, 2 C, aryl-C), 128.12 (+, 2 C, aryl-C), 129.10 (C_{quat} , aryl-C), 133.32 (C_{quat} , C-3), 134.72 (C_{quat} , C-2'), 135.21 (+, C-3'), 143.30 (C_{quat} , C-1'), 143.94 (C_{quat} , C-4) ppm. MS (200 eV, DCI, NH_3): m/z (%) = 268 (11) [$\text{M} + \text{NH}_4^+$], 251 (40) [$\text{M} + \text{H}^+$], 238 (17), 134 (100). $\text{C}_{18}\text{H}_{18}\text{O}$ (250.3).

***tert*-Butyl[2-cyclopropylidene-1-(4'-methylenetetrahydro-3'-furanylidene)-3-butenyl]dimethylsilane (18-TBDMS):** According to GP1, $\text{Pd}(\text{OAc})_2$ (11.2 mg, 49.9 μmol , 10 mol %), PPh_3 (39.3 mg, 150 μmol , 30 mol %), K_2CO_3 (138 mg, 999 μmol) and 3-(2'-bromo-

allyloxy)-1-propynyl(*tert*-butyl)dimethylsilane (**9-TBDMS**, 145 mg, 501 μmol) were stirred in acetonitrile (5 mL) with bicyclopopylidene (80.0 mg, 998 μmol) at 80 °C for 4 h. Column chromatography on silica gel [60 g, 2 $\times$ 25 cm, pentane/diethyl ether, 20:1, R_f = 0.75 (pentane/diethyl ether, 10:1)] yielded **18-TBDMS** (78 mg, 54%) as a pale yellow oil. IR (film): $\tilde{\nu}$ = 2954, 2931, 2885, 2857, 2253, 1728, 1472, 1464, 1411, 1390, 1360, 1254, 1171, 1051, 1007, 910, 835, 734, 679, 649 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ = 0.02 [s, 3 H, Si(CH₃)₃], 0.06 [s, 3 H, Si(CH₃)₃], 0.83–1.25 (m, 4 H, Cpr-H), 0.92 [s, 9 H, C(CH₃)₃], 4.35 (t, 4J = 2.2 Hz, 2 H, 5'-H), 4.57 (s, 2 H, 2'-H), 4.86 (s, 1 H, C=CH₂), 5.00 (d, 3J = 10.1 Hz, 1 H, 4-H), 5.12 (d, 3J = 17.5 Hz, 1 H, 4-H), 5.20 (t, 4J = 2.2 Hz, 1 H, C=CH₂), 6.50 (dd, 3J = 17.5, 3J = 10.1 Hz, 1 H, 3-H) ppm. ^{13}C NMR (62.9 MHz, CDCl_3 , DEPT): δ = -3.84 [+], Si(CH₃)₃], -3.38 [+], Si(CH₃)₃], 2.40 (-, Cpr-C), 3.79 (-, Cpr-C), 18.75 [C_{quat}, C(CH₃)₃], 27.74 [+], 3 C, C(CH₃)₃], 73.55 (-, C-2'*), 74.09 (-, C-5'*), 108.23 (-, C-1''), 113.09 (-, C-4), 123.09 (C_{quat}, Cpr-C), 131.44 (C_{quat}, C-3'), 133.52 (C_{quat}, C-2), 136.25 (+, C-3), 143.88 (C_{quat}, C-1), 146.37 (C_{quat}, C-4') ppm. MS (EI, 70 eV): m/z (%) = 288 (1) [M⁺], 260 (1) [M⁺ - C₂H₄], 233 (21), 231 (25) [M⁺ - C₄H₉], 203 (24), 177 (42), 139 (43), 137 (39), 75 (76), 73 (100). HRMS: calcd. for C₁₈H₂₈OSi: 288.1909 (correct mass).

3-[(*E*)-2'-Cyclopropylidene-1'-phenyl-3'-butenylidene]-4-methylene-1-(4'-methylphenylsulfonyl)pyrrolidine (19-Ph): According to **GP1**, Pd(OAc)₂ (11.2 mg, 49.9 μmol , 10 mol %), PPh₃ (39.3 mg, 150 μmol , 30 mol %), K₂CO₃ (138 mg, 999 μmol) and *N*-(2'-bromoallyl)-*N*-(3'-phenyl-2'-propynyl)-4-methylbenzenesulfonamide (**11-Ph**, 202 mg, 500 μmol) were stirred in acetonitrile (5 mL) with bicyclopopylidene (80.0 mg, 998 μmol) at 80 °C for 4 h. Column chromatography on silica gel (60 g, 2 $\times$ 25 cm, pentane/diethyl ether, 10:1, R_f = 0.35) yielded **19-Ph** (71 mg, 35%) as a yellowish oil. IR (film): $\tilde{\nu}$ = 3056, 2925, 2865, 1724, 1594, 1493, 1443, 1399, 1346, 1266, 1163, 1094, 1065, 814, 736, 704, 666 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ = 0.90–1.12 (m, 4 H, Cpr-H), 2.39 (s, 3 H, Ar-CH₃), 3.93–3.95 (m, 2 H, 5-H), 4.05 (br. s, 2 H, 2-H), 4.94 (br. s, 1 H, C=CH₂), 4.97 (br. s, 1 H, 4'-H), 4.99 (br. s, 1 H, 4'-H), 5.22 (t, 4J = 2.0 Hz, 1 H, C=CH₂), 6.44 (dd, 3J = 18.0, 3J = 10.0 Hz, 1 H, 3'-H), 6.83 (d, 3J = 8.0 Hz, 2 H, aryl-H), 7.10–7.35 (m, 5 H, aryl-H), 7.64 (d, 3J = 8.0 Hz, 2 H, aryl-H) ppm. ^{13}C NMR (75.5 MHz, CDCl_3): δ = 3.01 (Cpr-C), 3.11 (Cpr-C), 21.56 (Ar-CH₃), 53.31 (C-2*), 53.47 (C-5*), 109.94 (C-1''), 114.01 (C-4'), 123.25 (Cpr-C), 127.55 (aryl-C), 127.88 (2 C, aryl-C), 128.12 (aryl-C), 128.24 (2 C, aryl-C), 129.72 (2 C, aryl-C), 131.47 (C-3), 132.74 (C-2'), 135.04 (C-3'), 135.57 (aryl-C), 140.80 (aryl-C), 141.02 (C-1'), 143.67 (C-4) ppm. MS (EI, 70 eV): m/z (%) = 403 (3) [M⁺], 364 (<1), 326 (<1) [M⁺ - C₆H₅], 248 (5) [M⁺ - tos], 219 (3), 156 (3) [tosH⁺], 91 (100) [C₇H₇⁺]. HRMS: calcd. for C₂₅H₂₅NO₂S: 403.1606 (correct mass).

***tert*-Butyl[2-cyclopropylidene-1-[4'-methylene-1'-(4'-methylphenylsulfonyl)-3'-pyrrolidinylidene]-3-butenyl]dimethylsilane (19-TBDMS):** According to **GP1**, Pd(OAc)₂ (11.2 mg, 49.9 μmol , 10 mol %), PPh₃ (39.3 mg, 150 μmol , 30 mol %), K₂CO₃ (138 mg, 999 μmol) and *N*-(2'-bromoallyl)-*N*-(3'-[*tert*-butyl(dimethyl)silyl]-2'-propynyl)-4-methylbenzenesulfonamide (**11-TBDMS**, 221 mg, 499 μmol) were stirred in acetonitrile (5 mL) with bicyclopopylidene (80.0 mg, 998 μmol) at 80 °C for 4 h. Column chromatography on silica gel (60 g, 2 $\times$ 25 cm, pentane/diethyl ether, 10:1, R_f = 0.35) yielded **19-TBDMS** (90 mg, 41%) as a yellow oil, which solidified to give an amorphous solid in the freezer. IR (film): $\tilde{\nu}$ = 2955, 2929, 2885, 2857, 1727, 1597, 1494, 1471, 1350, 1306, 1253, 1164, 1093, 1066, 902, 813, 777, 738, 704, 666 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ = 0.00 [s, 3 H, Si(CH₃)₃], 0.13 [s, 3 H, Si(CH₃)₃], 0.82–1.06 (m,

4 H, Cpr-H), 0.90 [s, 9 H, C(CH₃)₃], 2.43 (s, 3 H, Ar-CH₃), 3.80–3.85 (m, 2 H, 5'-H), 3.99–4.06 (m, 2 H, 2'-H), 4.85 (br. s, 1 H, C=CH₂), 4.87–4.99 (m, 2 H, 4-H), 5.18 (t, 4J = 2.1 Hz, 1 H, C=CH₂), 6.42 (dd, 3J = 18.2, 3J = 10.2 Hz, 1 H, 3-H), 6.76 (d, 3J = 8.1 Hz, 2 H, aryl-H), 7.85 (d, 3J = 8.1 Hz, 2 H, aryl-H) ppm. ^{13}C NMR (62.9 MHz, CDCl_3 , DEPT): δ = -3.77 [+], Si(CH₃)₃], -3.29 [+], Si(CH₃)₃], 2.37 (-, Cpr-C), 3.74 (-, Cpr-C), 18.74 [C_{quat}, C(CH₃)₃], 22.27 (+, Ar-CH₃), 27.76 [+], 3 C, C(CH₃)₃], 53.62 (-, C-2'*), 54.64 (-, C-5'*), 111.25 (-, C-1''), 113.16 (-, C-4), 123.25 (C_{quat}, Cpr-C), 127.55 (C_{quat}, aryl-C), 128.00 (+, 2 C, aryl-C), 129.63 (+, 2 C, aryl-C), 131.24 (C_{quat}, C-3'), 132.26 (C_{quat}, C-2), 136.14 (+, C-3), 140.80 (C_{quat}, aryl-C), 142.86 (C_{quat}, C-1), 143.73 (C_{quat}, C-4') ppm. MS (200 eV, DCI, NH₃): m/z (%) = 476 (8) [M + NH₄⁺ + NH₃], 459 (100) [M + NH₄⁺], 288 (42) [M - Tos + H⁺]. C₂₅H₃₅NO₂SSi (441.7).

General Procedure for the Palladium-Catalyzed Co-cyclization of 2-Bromo-1,6-enynes and Bicyclopopylidene with Subsequent 6 π -Electrocyclization(s) (GP 2): Palladium acetate (11.2 mg, 49.9 μmol , 10 mol %), triphenylphosphane (39.3 mg, 150 μmol , 30 mol %) and potassium carbonate (138 mg, 999 μmol) were suspended in anhydrous DMF (5 mL) in a screw-cap Pyrex bottle. The respective bromoenyne or bromodienyne (500 μmol) was added, and argon was bubbled through the reaction mixture for 5 min, after which bicyclopopylidene (80.0 mg, 998 μmol) was added. The bottle was tightly closed, and the mixture heated at 110 °C in a preheated oil bath for a given period of time. After cooling to room temperature, the reaction mixture was directly added onto a prepacked column of silica gel and purified by chromatography, eluting with pentane/diethyl ether mixtures.

Dimethyl Spiro{cyclopropane-1,4'-[2'-cyclopropyl-3'-vinylbicyclo-[4.3.0]nona-1'(6'),2'-diene-8',8'-dicarboxylate} (21-Cpr): According to **GP2**, Pd(OAc)₂ (11.2 mg, 49.9 μmol , 10 mol %), PPh₃ (39.3 mg, 150 μmol , 30 mol %), K₂CO₃ (138 mg, 999 μmol) and dimethyl 2-(2'-bromoallyl)-2-(3'-cyclopropyl-2'-propynyl)malonate (**5-Cpr**, 165 mg, 501 μmol) were stirred in DMF (5 mL) with bicyclopopylidene (80.0 mg, 998 μmol) at 110 °C for 12 h. Column chromatography on silica gel (100 g, 3 $\times$ 30 cm, pentane/diethyl ether, 10:1, R_f = 0.45) yielded **21-Cpr** (63 mg, 38%) as a yellow oil. IR (film): $\tilde{\nu}$ = 3080, 3003, 2954, 1735, 1632, 1435, 1258, 1202, 1170, 1073, 912, 734, 649 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ = 0.21–0.44 (m, 4 H, Cpr-H), 0.66–0.81 (m, 4 H, Cpr-H), 0.96–1.05 (m, 1 H, Cpr-H), 1.96 (br. s, 2 H, 5'-H), 3.00 (br. s, 2 H, 7'-H), 3.30 (br. s, 2 H, 9'-H), 3.73 (s, 6 H, OCH₃), 5.09 (d, 3J = 17.5 Hz, 1 H, C=CH₂), 5.19 (dd, 3J = 11.2, 2J = 2.4 Hz, 1 H, C=CH₂), 5.97 (dd, 3J = 17.5, 3J = 11.2 Hz, 1 H, H=C=CH₂) ppm. ^{13}C NMR (62.9 MHz, CDCl_3 , DEPT): δ = 9.00 (-, 2 C, Cpr-C), 12.03 (+, Cpr-C), 13.30 (-, 2 C, Cpr-C), 18.77 (C_{quat}, Cpr-C), 35.61 (-, C-5'), 43.14 (-, C-9'), 46.03 (-, C-7'), 52.77 (+, 2 C, OCH₃), 58.42 (C_{quat}, C-8'), 118.95 (-, C=CH₂), 129.99 (C_{quat}, C-6'), 131.84 (C_{quat}, C-3'), 132.49 (+, C=CH₂), 133.86 (C_{quat}, C-2'), 136.60 (C_{quat}, C-1'), 172.77 (C_{quat}, 2 C, C=O) ppm. C₂₀H₂₄O₄ (328.4): calcd. C 72.70, H 7.93; found C 72.47, H 8.15.

Dimethyl Spiro{cyclopropane-1,4'-[2'-(*tert*-butyl)-3'-vinylbicyclo-[4.3.0]nona-1'(6'),2'-diene-8',8'-dicarboxylate} (21-*t*Bu): According to **GP2**, Pd(OAc)₂ (11.2 mg, 49.9 μmol , 10 mol %), PPh₃ (39.3 mg, 150 μmol , 30 mol %), K₂CO₃ (138 mg, 999 μmol) and dimethyl 2-(2'-bromoallyl)-2-(4',4'-dimethyl-2'-pentynyl)malonate (**5-*t*Bu**, 173 mg, 501 μmol) were stirred in DMF (5 mL) with bicyclopopylidene (80.0 mg, 998 μmol) at 110 °C for 10 h. Column chromatography on silica gel (100 g, 3 $\times$ 30 cm, pentane/diethyl ether, 10:1, R_f = 0.50) yielded **21-*t*Bu** (97 mg, 56%) as a yellow oil. IR (film): $\tilde{\nu}$ = 2955, 1736, 1626, 1436, 1397, 1364, 1266, 1206, 1073, 970, 896,

853, 803, 738, 703 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ = 0.29 (m_c , 2 H, Cpr-H), 0.57 (m_c , 2 H, Cpr-H), 1.18 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.83 (br. s, 2 H, 5'-H), 3.02 (br. s, 2 H, 7'-H), 3.27 (m_c , 2 H, 9'-H), 3.74 (s, 6 H, OCH_3), 4.64 (dd, 3J = 17.7, 2J = 2.6 Hz, 1 H, $\text{C}=\text{CH}_2$), 4.94 (dd, 3J = 11.0, 2J = 2.6 Hz, 1 H, $\text{C}=\text{CH}_2$), 6.22 (dd, 3J = 17.7, 3J = 11.0 Hz, 1 H, $\text{HC}=\text{CH}_2$) ppm. ^{13}C NMR (62.9 MHz, CDCl_3 , DEPT): δ = 10.14 (–, 2 C, Cpr-C), 19.71 (C_{quat} , Cpr-C), 32.38 [+ , 3 C, $\text{C}(\text{CH}_3)_3$], 34.29 (–, C-5'), 36.26 (C_{quat} , $\text{C}(\text{CH}_3)_3$), 42.57 (–, C-9'), 44.15 (–, C-7'), 52.76 (+, 2 C, OCH_3), 58.99 (C_{quat} , C-8'), 116.37 (–, $\text{C}=\text{CH}_2$), 131.21 (C_{quat} , C-6'*), 133.05 (C_{quat} , C-3'*), 136.45 (C_{quat} , C-2'), 136.67 (+, $\text{C}=\text{CH}_2$), 139.57 (C_{quat} , C-1'), 172.68 (C_{quat} , 2 C, $\text{C}=\text{O}$) ppm. MS (200 eV, DCl, NH_3): m/z (%) = 706 (3) [$2\text{M} + \text{NH}_4^+$], 362 (100) [$\text{M} + \text{NH}_4^+$], 345 (48) [$\text{M} + \text{H}^+$]. $\text{C}_{21}\text{H}_{28}\text{O}_4$ (344.4): calcd. C 73.23, H 8.19; found C 73.08, H 7.98.

Dimethyl Spiro{cyclopropane-1,4'-[2'-phenyl-3'-vinylbicyclo[4.3.0]nona-1'(6'),2'-diene-8',8'-dicarboxylate]} (21-Ph): According to **GP2**, $\text{Pd}(\text{OAc})_2$ (11.2 mg, 49.9 μmol , 10 mol %), PPh_3 (39.3 mg, 150 μmol , 30 mol %), K_2CO_3 (138 mg, 999 μmol) and 2-(2'-bromoallyl)-2-(3''-phenyl-2''-propynyl)malonate (**5-Ph**, 183 mg, 501 μmol) were stirred in DMF (5 mL) with bicyclopopylidene (80.0 mg, 998 μmol) at 110 °C for 12 h. Column chromatography on silica gel (100 g, 3 $\times$ 30 cm, pentane/diethyl ether, 10:1, R_f = 0.50) yielded **21-Ph** (89 mg, 49%) as a yellowish oil, which solidified in the freezer to give an amorphous solid. IR (film): $\tilde{\nu}$ = 3080, 3001, 2953, 2844, 1735, 1601, 1491, 1435, 1258, 1199, 1170, 1072, 912, 733, 702, 649 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ = 0.56 (m_c , 2 H, Cpr-H), 0.93 (m_c , 2 H, Cpr-H), 2.18 (br. s, 2 H, 5'-H), 2.85 (m_c , 2 H, 7'-H), 3.10 (br. s, 2 H, 9'-H), 3.70 (s, 6 H, OCH_3), 4.77 (dd, 3J = 17.8, 2J = 2.0 Hz, 1 H, $\text{C}=\text{CH}_2$), 4.89 (dd, 3J = 11.6, 2J = 2.0 Hz, 1 H, $\text{C}=\text{CH}_2$), 5.82 (dd, 3J = 17.8, 3J = 11.6 Hz, 1 H, $\text{HC}=\text{CH}_2$), 7.06–7.46 (m, 5 H, aryl-H) ppm. ^{13}C NMR (62.9 MHz, CDCl_3 , DEPT): δ = 14.27 (–, 2 C, Cpr-C), 18.55 (C_{quat} , Cpr-C), 36.16 (–, C-5'), 41.45 (–, C-9'), 43.58 (–, C-7'), 52.80 (+, 2 C, OCH_3), 58.12 (C_{quat} , C-8'), 118.75 (–, $\text{C}=\text{CH}_2$), 126.27 (+, aryl-C), 127.83 (+, 2 C, aryl-C), 129.47 (+, 2 C, aryl-C), 130.902 (C_{quat} , C-6'), 132.05 (C_{quat} , C-3'), 132.79 (+, $\text{C}=\text{CH}_2$), 133.87 (C_{quat} , aryl-C), 135.56 (C_{quat} , C-2'), 139.94 (C_{quat} , C-1'), 172.62 (C_{quat} , 2 C, $\text{C}=\text{O}$) ppm. MS (200 eV, DCl, NH_3): m/z (%) = 746 (7) [$2\text{M} + \text{NH}_4^+$], 382 (75) [$\text{M} + \text{NH}_4^+$], 365 (100) [$\text{M} + \text{H}^+$]. $\text{C}_{23}\text{H}_{24}\text{O}_4$ (364.4): calcd. C 75.80, H 6.64; found C 76.13, H 6.33.

Dimethyl Spiro{cyclopropane-1,4'-[2'-(tert-butylidimethylsilyl)-3'-vinylbicyclo[4.3.0]nona-1'(6'),2'-diene-8',8'-dicarboxylate]} (21-TBDMS): According to **GP2**, $\text{Pd}(\text{OAc})_2$ (11.2 mg, 49.9 μmol , 10 mol %), PPh_3 (39.3 mg, 150 μmol , 30 mol %), K_2CO_3 (138 mg, 999 μmol) and dimethyl 2-(2'-bromoallyl)-2-[3''-tert-butyl(dimethyl)silyl-2''-propynyl]malonate (**5-TBDMS**, 202 mg, 501 μmol) were stirred in DMF (5 mL) with bicyclopopylidene (80.0 mg, 998 μmol) at 110 °C for 11 h. Column chromatography on silica gel (100 g, 3 $\times$ 30 cm, pentane/diethyl ether, 10:1, R_f = 0.40) yielded **21-TBDMS** (131 mg, 65%) as a pale yellow oil. IR (film): $\tilde{\nu}$ = 2955, 2932, 2887, 2858, 1737, 1436, 1362, 1265, 1202, 1171, 1069, 837, 776, 737, 703, 677 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ = 0.17 [s, 6 H, $\text{Si}(\text{CH}_3)_2$], 0.44 (m_c , 2 H, Cpr-H), 0.73 (m_c , 2 H, Cpr-H), 0.88 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.96 (br. s, 2 H, 5'-H), 2.99 (br. s, 2 H, 7'-H), 3.22 (m_c , 2 H, 9'-H), 3.73 (s, 6 H, OCH_3), 4.91 (dd, 3J = 17.4, 2J = 2.4 Hz, 1 H, $\text{C}=\text{CH}_2$), 5.10 (dd, 3J = 10.9, 2J = 2.4 Hz, 1 H, $\text{C}=\text{CH}_2$), 6.23 (dd, 3J = 17.4, 3J = 10.9 Hz, 1 H, $\text{HC}=\text{CH}_2$) ppm. ^{13}C NMR (62.9 MHz, CDCl_3 , DEPT): δ = 0.47 [+ , 2 C, $\text{Si}(\text{CH}_3)_2$], 13.08 (–, 2 C, Cpr-C), 18.41 [C_{quat} , $\text{C}(\text{CH}_3)_3$], 19.35 (C_{quat} , Cpr-C), 27.56 [+ , 3 C, $\text{C}(\text{CH}_3)_3$], 34.88 (–, C-5'), 42.79 (–, C-9'), 43.90 (–, C-7'), 52.73 (+, 2 C, OCH_3), 58.64

(C_{quat} , C-8'), 118.77 (–, $\text{C}=\text{CH}_2$), 128.29 (C_{quat} , C-6'*), 129.74 (C_{quat} , C-3'*), 132.15 (C_{quat} , C-2'), 134.18 (C_{quat} , C-1'), 136.37 (+, $\text{C}=\text{CH}_2$), 172.76 (C_{quat} , 2 C, $\text{C}=\text{O}$) ppm. MS (EI, 70 eV): m/z (%) = 402 (12) [M^+], 359 (100) [$\text{M}^+ - \text{C}_2\text{H}_4 - \text{CH}_3$], 345 (47) [$\text{M}^+ - \text{C}_4\text{H}_9$], 317 (30) [$\text{M}^+ - \text{C}_4\text{H}_6 - \text{C}_2\text{H}_4$], 285 (27) [$\text{M}^+ - \text{TBDMS} - \text{H}_2$], 227 (18), 167 (31), 89 (61), 73 (62). $\text{C}_{23}\text{H}_{34}\text{O}_4\text{Si}$ (402.6): calcd. C 68.62, H 8.51; found C 68.84, H 8.32.

Dimethyl Spiro{cyclopropane-1,4'-[2'-(6''-heptenyl)-3'-vinylbicyclo[4.3.0]nona-1'(6'),2'-diene-8',8'-dicarboxylate]} (21-Hept): According to **GP2**, $\text{Pd}(\text{OAc})_2$ (22.4 mg, 100 μmol , 10 mol %), PPh_3 (78.6 mg, 300 μmol , 30 mol %), K_2CO_3 (276 mg, 2.00 mmol) and dimethyl 2-bromotetradeca-1,13-dien-6-yne-4,4-dicarboxylate (**5-Hept**, 385 mg, 999 μmol) were stirred in DMF (10 mL) with bicyclopopylidene (160 mg, 2.00 mmol) at 110 °C for 12 h. Column chromatography on silica gel (120 g, 4 $\times$ 25 cm, pentane/diethyl ether, 10:1, R_f = 0.45) yielded **21-Hept** (185 mg, 48%) as a pale yellow oil. IR (film): $\tilde{\nu}$ = 3076, 2997, 2928, 2856, 1737, 1640, 1435, 1252, 1199, 1164, 1072, 994, 912, 819, 734, 646 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ = 0.38 (m_c , 2 H, Cpr-H), 0.72 (m_c , 2 H, Cpr-H), 1.23–1.49 (m, 6 H, 2''-H, 3''-H, 4''-H), 1.97–2.20 (m, 4 H, 1''-H, 5''-H), 2.02 (br. s, 2 H, 5'-H), 3.02 (br. s, 2 H, 7'-H), 3.16 (br. s, 2 H, 9'-H), 3.73 (s, 6 H, OCH_3), 4.84–5.04 (m, 3 H, 7''-H, $\text{C}=\text{CHH}_{\text{vinyl}}$), 5.14 (dd, 3J = 11.4, 2J = 2.4 Hz, 1 H, $\text{C}=\text{CHH}_{\text{vinyl}}$), 5.69–5.87 (m, 1 H, 6''-H), 5.94 (dd, 3J = 17.6, 3J = 11.4 Hz, 1 H, $\text{HC}=\text{CHH}_{\text{vinyl}}$) ppm. ^{13}C NMR (62.9 MHz, CDCl_3 , DEPT): δ = 13.41 (–, 2 C, Cpr-C), 18.22 (C_{quat} , Cpr-C), 28.65 (–, C-3''), 29.07 (–, C-2''), 30.34 (–, C-4''), 30.51 (–, C-1''), 33.69 (–, C-5''), 34.29 (–, C-5'), 40.35 (–, C-9'), 43.26 (–, C-7'), 52.75 (+, 2 C, OCH_3), 58.39 (C_{quat} , C-8'), 114.14 (–, C-7''), 116.37 (–, $\text{C}=\text{CH}_2$), 130.79 (C_{quat} , C-6'), 131.23 (C_{quat} , C-2'), 132.92 (C_{quat} , C-3'), 132.92 (+, $\text{C}=\text{CH}_2$), 134.22 (C_{quat} , C-1'), 139.00 (+, C-6''), 172.61 (C_{quat} , 2 C, $\text{C}=\text{O}$) ppm. MS (EI, 70 eV): m/z (%) = 384 (60) [M^+], 369 (33) [$\text{M}^+ - \text{CH}_3$], 324 (61) [$\text{M}^+ - \text{HCO}_2\text{CH}_3$], 265 (50), 241 (51), 227 (100), 183 (77), 167 (74), 153 (61). $\text{C}_{24}\text{H}_{32}\text{O}_4$ (384.5): calcd. C 74.97, H 8.39; found C 74.73, H 8.11.

Spiro{cyclopropane-1,5'-(7'-phenyl-6'-vinyl-1',3',4',5'-tetrahydroisobenzofuran)} (22-Ph): According to **GP2**, $\text{Pd}(\text{OAc})_2$ (11.2 mg, 49.9 μmol , 10 mol %), PPh_3 (39.3 mg, 150 μmol , 30 mol %), K_2CO_3 (138 mg, 999 μmol) and [3'-(2''-bromoallyloxy)-1'-propynyl]benzene (**9-Ph**, 126 mg, 502 μmol) were stirred in DMF (5 mL) with bicyclopopylidene (80.0 mg, 998 μmol) at 110 °C for 11 h. Column chromatography on silica gel [100 g, 3 $\times$ 30 cm, pentane/diethyl ether, 20:1, R_f = 0.80 (pentane/diethyl ether, 10:1)] yielded **22-Ph** (90 mg, 72%) as a yellow oil. IR (film): $\tilde{\nu}$ = 3060, 2934, 2869, 1728, 1600, 1493, 1443, 1045, 910, 734, 648 cm^{-1} . ^1H NMR (250 MHz, CDCl_3): δ = 0.61 (m_c , 2 H, Cpr-H), 0.98 (m_c , 2 H, Cpr-H), 2.22 (br. s, 2 H, 4'-H), 4.41–4.49 (m, 2 H, 3'-H), 4.63–4.76 (m, 4 H, 1'-H), 4.81 (dd, 3J = 17.4, 2J = 2.0 Hz, 1 H, $\text{C}=\text{CH}_2$), 4.96 (dd, 3J = 11.3, 2J = 2.0 Hz, 1 H, $\text{C}=\text{CH}_2$), 5.89 (dd, 3J = 17.4, 3J = 11.3 Hz, 1 H, $\text{HC}=\text{CH}_2$), 7.03–7.09 (m, 2 H, aryl-H), 7.11–7.31 (m, 3 H, aryl-H) ppm. ^{13}C NMR (62.9 MHz, CDCl_3 , DEPT): δ = 14.25 (–, 2 C, Cpr-C), 18.63 (C_{quat} , Cpr-C), 33.01 (–, C-4'), 75.36 (–, C-1'), 76.52 (–, C-3'), 119.53 (–, $\text{C}=\text{CH}_2$), 126.54 (+, aryl-C), 127.54 (+, 2 C, aryl-C), 128.91 (+, 2 C, aryl-C), 129.82 (C_{quat} , C-6'*), 131.61 (C_{quat} , C-3'*), 132.36 (+, $\text{HC}=\text{CH}_2$), 136.29 (C_{quat} , C-7a'), 139.46 (C_{quat} , aryl-C) ppm. Signal of C-7' not detected. MS (EI, 70 eV): m/z (%) = 250 (38) [M^+], 220 (100) [$\text{M}^+ - \text{C}_2\text{H}_6$], 205 (34), 192 (90), 178 (87), 165 (60), 115 (24). HRMS: calcd. for $\text{C}_{18}\text{H}_{18}\text{O}$: 250.1358 (correct mass).

Spiro{cyclopropane-1,5'-(7'-(tert-butylidimethylsilyl)-6'-vinyl-1',3',4',5'-tetrahydroisobenzofuran)} (22-TBDMS): According to **GP2**, $\text{Pd}(\text{OAc})_2$ (11.2 mg, 49.9 μmol , 10 mol %), PPh_3 (39.3 mg,

150 μmol , 30 mol %), K_2CO_3 (138 mg, 999 μmol) and [3-(2'-bromoallyloxy)-1-propynyl](*tert*-butyl)dimethylsilane (**9-TBDMS**, 145 mg, 501 μmol) were stirred in DMF (5 mL) with bicyclopopylidene (80.0 mg, 998 μmol) at 110 $^\circ\text{C}$ for 12 h. Column chromatography on silica gel [100 g, 3×30 cm, pentane/diethyl ether, 20:1, $R_f = 0.75$ (pentane/diethyl ether, 10:1)] yielded **22-TBDMS** (59 mg, 41%) as a yellow oil. IR (film): $\tilde{\nu} = 3075, 2954, 2930, 2857, 1745, 1463, 1360, 1252, 1050, 911, 835, 734, 677, 648$ cm^{-1} . ^1H NMR (200 MHz, CDCl_3): $\delta = 0.13$ [s, 6 H, $\text{Si}(\text{CH}_3)_2$], 0.51 (m_c , 2 H, Cpr-H), 0.83 (m_c , 2 H, Cpr-H), 0.87 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.02 (br. s, 2 H, 4'-H), 4.54–4.64 (m, 2 H, 3'-H), 4.71–4.80 (m, 2 H, 1'-H), 4.95 (dd, $^3J = 17.6$, $^2J = 2.2$ Hz, 1 H, $\text{C}=\text{CHH}$), 5.15 (dd, $^3J = 11.4$, $^2J = 2.2$ Hz, 1 H, $\text{C}=\text{CHH}$), 6.23 (dd, $^3J = 17.6$, $^3J = 11.4$ Hz, 1 H, $\text{HC}=\text{CHH}$) ppm. ^{13}C NMR (62.9 MHz, CDCl_3 , DEPT): $\delta = -0.17$ [+ , 2 C, $\text{Si}(\text{CH}_3)_2$], 13.44 (–, 2 C, Cpr-C), 18.56 [C_{quat} , $\text{C}(\text{CH}_3)_3$], 19.26 (C_{quat} , Cpr-C), 27.29 [+ , 3 C, $\text{C}(\text{CH}_3)_3$], 31.76 (–, C-4'), 73.04 (–, C-1'), 76.21 (–, C-3'), 118.65 (–, $\text{C}=\text{CH}_2$), 128.13 (C_{quat} , C-3'), 128.28 (C_{quat} , C-6'), 128.58 (C_{quat} , C-7'), 134.22 (+, $\text{C}=\text{CH}_2$), 135.85 (C_{quat} , C-7a') ppm. MS (EI, 70 eV): m/z (%) = 288 (3) [M^+], 247 (6) [$\text{M}^+ - \text{C}_3\text{H}_5$], 231 (29) [$\text{M}^+ - \text{C}_4\text{H}_9$], 229 (11) [$\text{M}^+ - \text{C}_4\text{H}_9 - \text{H}_2$], 191 (12), 149 (10), 99 (22), 83 (100) 79 (23), 43 (100). $\text{C}_{18}\text{H}_{28}\text{OSi}$ (288.5): calcd. C 74.94, H 9.78; found C 75.09, H 9.62.

Spiro[cyclopropane-1,5'-[2'-(4'-methylphenylsulfonyl)-7'-phenyl-6'-vinyl-2',3',4',5'-tetrahydro-1*H*-isoindole]] (23-Ph): According to **GP2**, $\text{Pd}(\text{OAc})_2$ (11.2 mg, 49.9 μmol , 10 mol %), PPh_3 (39.3 mg, 150 μmol , 30 mol %), K_2CO_3 (138 mg, 999 μmol) and *N*-(2'-bromoallyl)-*N*-[3'-phenyl-2'-propynyl]-4-methylbenzenesulfonamide (**11-Ph**, 202 mg, 500 μmol) were stirred in DMF (5 mL) with bicyclopopylidene (80.0 mg, 998 μmol) at 110 $^\circ\text{C}$ for 10 h. Column chromatography on silica gel (100 g, 3×30 cm, pentane/diethyl ether, 10:1, $R_f = 0.50$) yielded **23-Ph** (89 mg, 44%) as a colorless oil. IR (film): $\tilde{\nu} = 3059, 2925, 2873, 1724, 1598, 1494, 1443, 1345, 1164, 1096, 1062, 911, 814, 733, 704, 669$ cm^{-1} . ^1H NMR (250 MHz, CDCl_3): $\delta = 0.54$ (m_c , 2 H, Cpr-H), 0.92 (m_c , 2 H, Cpr-H), 2.13 (br. s, 2 H, 4'-H), 2.43 (s, 3 H, Ar-CH₃), 3.89 (br. s, 2 H, 3'-H), 4.14 (br. s, 2 H, 1'-H), 4.77 (dd, $^3J = 17.7$, $^2J = 1.8$ Hz, 1 H, $\text{C}=\text{CHH}$), 4.92 (dd, $^3J = 11.5$, $^2J = 1.8$ Hz, 1 H, $\text{C}=\text{CHH}$), 5.78 (dd, $^3J = 17.7$, $^3J = 11.5$ Hz, 1 H, $\text{HC}=\text{CHH}$), 7.00 (d, $^3J = 7.9$ Hz, 2 H, aryl-H), 7.17–7.38 (m, 5 H, aryl-H), 7.67 (d, $^3J = 7.9$ Hz, 2 H, aryl-H) ppm. ^{13}C NMR (75.5 MHz, CDCl_3 , APT): $\delta = 14.34$ (–, 2 C, Cpr-C), 18.24 (–, Cpr-C), 21.53 (+, Ar-CH₃), 33.83 (–, C-4'), 54.92 (–, C-1'), 56.75 (–, C-3'), 119.79 (–, $\text{C}=\text{CH}_2$), 126.79 (+, aryl-C), 127.38 (+, 2 C, aryl-C), 127.65 (–, aryl-C), 128.13 (+, 2 C, aryl-C), 128.99 (+, 2 C, aryl-C), 129.71 (+, 2 C, aryl-C), 130.84 (–, C-7a'), 131.41 (–, C-6'), 132.08 (+, $\text{C}=\text{CH}_2$), 134.49 (–, C-7'), 137.02 (–, aryl-C), 138.82 (–, C-3a'), 143.29 (–, aryl-C) ppm. MS (EI, 70 eV): m/z (%) = 404 (3) [$\text{M}^+ + \text{H}$], 403 (1) [M^+], 367 (<1), 314 (<1), 248 (5) [$\text{M}^+ - \text{Tos}$], 246 (10) [$\text{M}^+ - \text{Tos} - \text{H}_2$], 165 (3), 156 (7) [TosH^+], 124 (21), 91 (100) [C_7H_7^+]. $\text{C}_{25}\text{H}_{25}\text{NO}_2\text{S}$ (403.5): calcd. C 74.41, H 6.24; found C 74.68, H 5.94.

23-TBDMS (see Scheme 6): According to **GP2**, $\text{Pd}(\text{OAc})_2$ (11.2 mg, 49.9 μmol , 10 mol %), PPh_3 (39.3 mg, 150 μmol , 30 mol %), K_2CO_3 (138 mg, 999 μmol) and *N*-(2'-bromoallyl)-*N*-[3'-[*tert*-butyl(dimethyl)silyl]-2'-propynyl]-4-methylbenzenesulfonamide (**11-TBDMS**, 221 mg, 499 μmol) were stirred in DMF (5 mL) with bicyclopopylidene (80.0 mg, 998 μmol) at 110 $^\circ\text{C}$ for 12 h. Column chromatography on silica gel (100 g, 3×30 cm, pentane/diethyl ether, 10:1, $R_f = 0.50$) yielded **23-TBDMS** (71 mg, 32%) as a yellowish oil. IR (film): $\tilde{\nu} = 2928, 2856, 1598, 1462, 1347, 1259, 1164, 1095, 1063, 813, 771, 707, 668$ cm^{-1} . ^1H NMR (250 MHz, C_6D_6): $\delta = 0.20$ [s, 6 H, $\text{Si}(\text{CH}_3)_2$], 0.29 (m_c , 2 H, Cpr-H), 0.74 (m_c , 2 H,

Cpr-H), 0.93 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.96 (br. s, 2 H, 4'-H), 1.58 (s, 3 H, Ar-CH₃), 4.20 (br. s, 2 H, 3'-H), 4.57–4.66 (m, 2 H, 1'-H), 4.83 (dd, $^3J = 17.7$, $^2J = 2.1$ Hz, 1 H, $\text{C}=\text{CHH}$), 4.95 (dd, $^3J = 11.3$, $^2J = 2.1$ Hz, 1 H, $\text{C}=\text{CHH}$), 6.23 (dd, $^3J = 17.7$, $^3J = 11.3$ Hz, 1 H, $\text{HC}=\text{CHH}$), 6.88 (d, $^3J = 8.2$ Hz, 2 H, aryl-H), 7.96 (d, $^3J = 8.2$ Hz, 2 H, aryl-H) ppm. ^{13}C NMR (75.5 MHz, C_6D_6 , APT): $\delta = 0.30$ [+ , 2 C, $\text{Si}(\text{CH}_3)_2$], 13.32 (–, 2 C, Cpr-C), 18.66 [–, $\text{C}(\text{CH}_3)_3$], 19.17 (–, Cpr-C), 21.04 (+, Ar-CH₃), 27.44 [+ , 3 C, $\text{C}(\text{CH}_3)_3$], 32.32 (–, C-4'), 56.46 (–, C-1'), 57.60 (–, C-3'), 118.77 (–, $\text{C}=\text{CH}_2$), 126.16 (–, aryl-C*), 127.28 (–, C-3a'), 127.91 (+, 2 C, aryl-C), 129.75 (+, 2 C, aryl-C), 133.13 (–, C-6'), 135.48 (–, C-7'), 135.99 (+, $\text{C}=\text{CH}_2$), 142.87 (–, aryl-C), 154.38 (–, C-7a') ppm. MS (200 eV, DCI, NH_3): m/z (%) = 476 (3) [$\text{M} + \text{NH}_4^+ + \text{NH}_3$], 459 (7) [$\text{M} + \text{NH}_4^+$], 288 (100), 189 (19) [$\text{TosNH}_2 + \text{NH}_4^+$], $\text{C}_{25}\text{H}_{35}\text{NO}_2\text{SSi}$ (441.7): calcd. C 67.98; H 7.99; found C 68.21, H 8.24.

Dimethyl Spiro[cyclopropane-1,8'-{13'-methyltricyclo[7.4.0.0^{2,6}]trideca-1'(13'),2'(6'),9'-triene-4',4'-dicarboxylate]} (31a): According to **GP2**, $\text{Pd}(\text{OAc})_2$ (11.2 mg, 49.9 μmol , 10 mol %), PPh_3 (39.3 mg, 150 μmol , 30 mol %), K_2CO_3 (138 mg, 999 μmol) and dimethyl 2-(2'-bromoallyl)-2-(4'-methyl-4'-penten-2'-ynyl)malonate (**28a**, 165 mg, 501 μmol) were stirred in DMF (7 mL) with bicyclopopylidene (**12**) (80.0 mg, 998 μmol) at 110 $^\circ\text{C}$ for 12 h. Column chromatography on silica gel (100 g, 3×30 cm, pentane/diethyl ether, 10:1, $R_f = 0.45$) yielded **31a** (23 mg, 14%) as a colorless oil. IR (film): $\tilde{\nu} = 3000, 2953, 1734, 1436, 1373, 1259, 1203, 1171, 1074, 1022, 954, 911, 735, 703$ cm^{-1} . ^1H NMR (250 MHz, CDCl_3): $\delta = 0.39$ (m_c , 2 H, Cpr-H), 0.63 (m_c , 2 H, Cpr-H), 1.93–2.01 (m, 6 H, 7'-H, 11'-H, 12'-H), 2.05 (s, 3 H, CH₃), 2.96 (br. s, 2 H, 5'-H), 3.53 (br. s, 2 H, 3'-H), 3.73 (s, 3 H, OCH₃), 3.74 (s, 3 H, OCH₃), 5.40 (t, $^3J = 3.8$ Hz, 1 H, 10'-H) ppm. ^{13}C NMR (62.9 MHz, CDCl_3 , DEPT): $\delta = 13.10$ (–, 2 C, Cpr-C), 20.73 (+, CH₃), 21.53 (–, C-12'), 22.18 (C_{quat} , Cpr-C), 32.56 (–, C-11'), 36.53 (–, C-7'), 43.29 (–, C-5'), 44.20 (–, C-3'), 52.75 (+, OCH₃), 58.30 (C_{quat} , C-4'), 114.74 (+, C-10'), 125.90 (C_{quat} , C-6'), 129.35 (C_{quat} , C-1'), 129.86 (C_{quat} , C-9'), 135.47 (C_{quat} , C-2'), 138.95 (C_{quat} , C-13'), 172.61 (C_{quat} , $\text{C}=\text{O}$) ppm. MS (EI, 70 eV): m/z (%) = 328 (50) [M^+], 268 (30) [$\text{M}^+ - \text{C}_2\text{H}_4 - \text{CH}_3\text{O}$], 238 (36) [$\text{M}^+ - \text{CO}_2\text{CH}_3 - \text{CH}_3\text{OH}$], 209 (100) [$\text{M}^+ - \text{CO}_2\text{CH}_3 - \text{HCO}_2\text{CH}_3$], 179 (27), 165 (29), 83 (92). $\text{C}_{20}\text{H}_{24}\text{O}_4$ (328.4): calcd. C 73.15, H 7.37; found C 73.35, H 7.08.

31b (see Scheme 8): According to **GP2**, $\text{Pd}(\text{OAc})_2$ (11.2 mg, 49.9 μmol , 10 mol %), PPh_3 (39.3 mg, 150 μmol , 30 mol %), K_2CO_3 (138 mg, 999 μmol) and dimethyl 2-(2'-bromoallyl)-2-[3'-(1'-cyclohexenyl)-2'-propynyl]malonate (**28b**, 184 mg, 498 μmol) were stirred in DMF (7 mL) with bicyclopopylidene (80.0 mg, 998 μmol) at 110 $^\circ\text{C}$ for 14 h. Column chromatography on silica gel (100 g, 3×30 cm, pentane/diethyl ether, 10:1, $R_f = 0.45$) yielded **31b** (57 mg, 31%) as a colorless oil. IR (film): $\tilde{\nu} = 3000, 2935, 2859, 1735, 1435, 1267, 1203, 1170, 1072, 969, 913, 736, 703$ cm^{-1} . ^1H NMR (250 MHz, CDCl_3): $\delta = 0.34$ – 0.46 (m, 2 H, Cpr-H), 0.49–0.58 (m, 1 H, Cpr-H), 0.69–0.77 (m, 1 H, Cpr-H), 1.33–1.91 (m, 8 H, 3'-H, 4'-H, 5'-H, 6'-H), 1.33–1.91 (m, 4 H, 7'-H, 8'-H_A, 12'-H), 2.94 (br. s, 2 H, 14'-H), 2.99–3.18 (m, 1 H, 8'-H_B), 3.41 and 3.53 (br. AB, $^2J = 16.0$ Hz, 2 H, 16'-H), 3.75 (s, 6 H, OCH₃), 5.30 (t, $^3J = 4.0$ Hz, 1 H, 9'-H) ppm. ^{13}C NMR (75.5 MHz, CDCl_3 , APT): $\delta = 12.47$ (–, Cpr-C), 14.39 (–, Cpr-C), 20.81 (–, Cpr-C), 25.32 (–, C-4'), 27.30 (–, C-5'), 29.94 (–, C-6'), 30.77 (–, C-8'), 34.39 (–, C-3'), 36.53 (–, C-12'), 38.26 (+, C-7'), 43.25 (–, C-14'), 44.45 (–, C-16'), 52.65 (+, 2 C, OCH₃), 58.45 (–, C-15'), 113.03 (+, C-9'), 124.19 (–, C-13'), 129.80 (–, C-1'), 136.80 (–, C-17'), 137.33 (–, C-10'), 137.60 (–, C-2'),

172.59 (–, C=O), 172.63 (–, C=O) ppm. MS (200 eV, DCI, NH₃): *m/z* (%) = 750 (<1) {2 [M – H₂] + NH₄⁺}, 384 (100) {[M – H₂] + NH₄⁺}, 367 (37) {[M – H₂] + H⁺}. C₂₃H₂₈O₄ (368.5): calcd. C 74.97, H 7.66; found C 74.86, H 7.42.

Dimethyl Spiro[cyclopropane-1,5'-(2',3',4',5'-tetrahydro-1'-H-cyclopenta[*a*]naphthalene-2',2'-dicarboxylate)] (32): According to GP2, Pd(OAc)₂ (16.8 mg, 74.8 μmol, 10 mol %), PPh₃ (59.0 mg, 225 μmol, 30 mol %), K₂CO₃ (414 mg, 3.00 mmol) and dimethyl 2-(2'-bromoallyl)-2-[(*E*)-5'-methoxy-4'-penten-2''-ynyl]malonate (**28c**, 259 mg, 750 μmol) were stirred in DMF (10 mL) with bicyclopropylidene (120 mg, 1.50 mmol) at 110 °C for 14 h. Column chromatography on silica gel (100 g, 3 × 30 cm, pentane/diethyl ether, 10:1, *R*_f = 0.50) yielded **32** (75 mg, 32%) as a yellowish oil. IR (film): $\tilde{\nu}$ = 3071, 3001, 2953, 2844, 1735, 1491, 1435, 1263, 1200, 1164, 1098, 1074, 969, 911, 756, 733, 648 cm^{–1}. ¹H NMR (250 MHz, CDCl₃): δ = 0.74 (m_c, 2 H, Cpr-H), 0.94 (m_c, 2 H, Cpr-H), 2.26 (br. s, 2 H, 4'-H), 3.14–3.19 (m, 2 H, 3'-H), 3.39–3.44 (m, 2 H, 1'-H), 3.77 (s, 6 H, OCH₃), 6.77–6.84 (m, 1 H, 9'-H), 6.99–7.17 (m, 3 H, 6'-H, 7'-H, 8'-H) ppm. ¹³C NMR (62.9 MHz, CDCl₃, DEPT): δ = 17.43 (–, 2 C, Cpr-C), 17.70 (C_{quat}, Cpr-C), 35.43 (–, C-4'), 39.71 (–, C-3'), 44.02 (–, C-1'), 52.93 (+, 2 C, OCH₃), 58.25 (C_{quat}, C-2'), 121.03 (+, C-6'), 122.63 (+, C-9'*), 125.45 (+, C-8'*), 126.95 (+, C-7'), 130.66 (C_{quat}, C-3a'), 133.14 (C_{quat}, C-9a**), 134.60 (C_{quat}, C-9b**), 139.49 (C_{quat}, C-5a'), 172.57 (C_{quat}, 2 C, C=O) ppm. MS (EI, 70 eV): *m/z* (%) = 312 (57) [M⁺], 284 (29) [M⁺ – C₂H₄], 252 (67) [M⁺ – C₂H₄ – CH₃OH], 224 (71) [M⁺ – HCO₂CH₃ – C₂H₄], 193 (46), 165 (38), 83 (100). C₁₉H₂₀O₄ (312.4): calcd. C 73.06, H 6.45; found C 72.91, H 6.17.

Supporting Information Available: Preparation and full characterization of compounds **6-TMS**, **7-TMS**, **6-TBDMS**, **7-TBDMS**, **6-ThDMS**, **7-ThDMS**, **6-Hept**, **7-Hept**, **5-Cpr**, **5-*t*Bu**, **5-Ph**, **5-TMS**, **5-TBDMS**, **5-Hept**, **9-Ph**, **9-TBDMS**, **11-Ph**, **11-TBDMS**, **5-SnBu₃**, **5-ThDMS**, **28a**, **28b** and **28c** (See also footnote on the first page of this article).

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