Intramolecular Heck Couplings and Cycloisomerizations of Bromodienes and Enynes with 1′,1′-Disubstituted Methylenecyclopropane Terminators: Efficient Syntheses of [3]Dendralenes[‡]

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2-Bromoalka-1,*n*-dienes such as **9**, **30** and **14** (*n* = 7) with tetrasubstituted methylenecyclopropane end groups, under palladium catalysis, underwent cyclization with cyclopropane-ring opening to give 2-ethenyl-3-methylene-1-cycloalkenes **41** (*n* = 6), **42** (*n* = 7), and **43**, which are substituted monocyclic [3]dendralenes, in 65, 63 and 70 % yield, respectively. The same cross-conjugated trienes were isolated in good to excellent yields (77–92 %) from the corresponding 1,6- (**10**-H, **15**) and 1,7-enynes (**28**-H) by a more atom-economic, palladium-catalyzed cycloisomerization. The vinylpalladium halide intermediate generated by initial carbopalladation of the 1,6-enyne **10**-H with in situ generated phenylpalladium iodide also underwent the same cyclization cascade to yield the correspondingly phenyl-substituted cyclic [3]dendralene **41**-Ph (21 %). The palladium-catalyzed cycloisomerization of the alk-1-ene-7,12-diyne **33**-H gave the bicyclic cross-conjugated tetraene **50**-H (43 %). Key features of the mechanism of the palladium-catalyzed cycloisomerization were proved using the specially designed model system **20**-H. Like other cyclic [3]dendralenes, the ethenyl(methylene)cycloheptene **42** underwent a domino-Diels–Alder reaction with *N*-phenyltriazoline-3,5-dione to give a single diastereomer of the pentacyclic heterocycle **69** (77 % yield).

Introduction

So-called atom-economic processes[1] have received an ever increasing attention of the organic community for the last two decades.[2] The unsurpassable efficiency and environmental friendliness have made organic chemists search for new cascade reactions in which an ultimate number of bonds is formed chemo-, regio- and stereoselectively in a single operation. In short, the strive for the "ideal synthesis"[3] has only begun. In this context, palladium-catalyzed domino reactions coupled with a variety of other transformations do play a major role.[4]

In the course of our studies on various intramolecular Heck reaction cascades,[5] we examined all-intramolecular domino-Heck–Heck 6π-electrocyclizations leading to tricyclic skeletons[6] and intra-intermolecular domino Heck–Diels–Alder processes,[7] which easily led to bicyclo[4.3.0]nonene derivatives. In this latter context, we noticed that the intramolecular Heck reaction even proceeds with 2-bromo-1,*n*-dienes containing highly strained methylenecyclopropane end groups or (bromomethylene)cyclopropane starters[8] to yield spirocyclopropanebicyclo[4.3.0]nonene skeletons without opening of the three-membered ring.[6c] Although tetrasubstituted alkenes are frequently quoted – with a few exceptions[9] – to be unreactive in the Heck reaction, we were intrigued by the question, how methylenecyclopropane end groups with a tetrasubstituted double bond in a 2-bromoalka-1,*n*-diene or an enyne would behave under Heck reaction or cycloisomerization conditions.[6d] Herein, we give the full account of this investigation, and we present scope and limitations of this cascade reaction leading to monocyclic [3]dendralenes.[10]

Results and Discussion

When 2-bromo-1,6-dienes of type **1**[11] (R = H) with methylenecyclopropane end groups are treated with a suitable palladium catalyst cocktail in the presence of a dieno-

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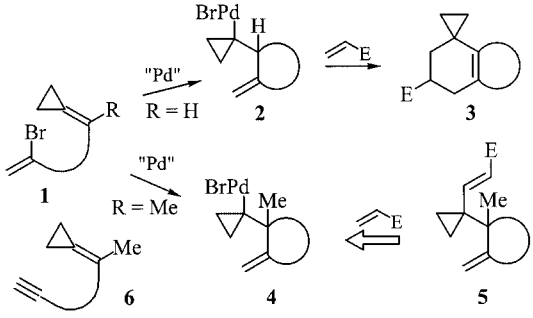
phile like methyl acrylate, they react in the usual way to give vicinal *exo*-dimethylenecycloalkanes, which immediately undergo a Diels–Alder reaction to yield products of type **3**.[11b] A different situation arises when R = Me in the bromodiene **1**, as the intermediate cyclopropylpalladium bromide **4** would probably be reluctant to undergo β-hydride elimination (to give a cyclopropene) and might prefer to couple with the added methyl acrylate. To prove this hypothesis, several bromodienes of type **1** (R = Me) were prepared, and subjected to the conditions of palladium-catalyzed cross-coupling reactions. In close analogy, several enynes of type **6** with a (1′-methylmethylene)cyclopropane end group were prepared and subjected to cycloisomerization conditions, since their cyclization intermediates were expected to encounter the very same situation as the intermediates **2** (Scheme 1).



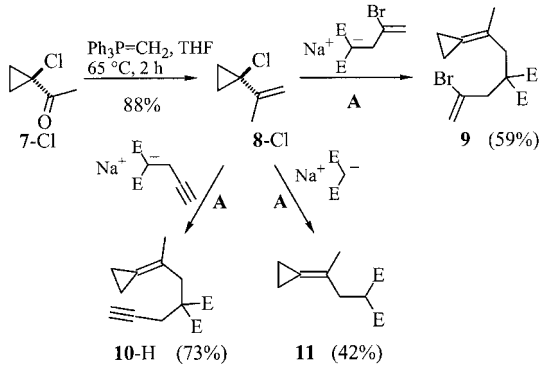
Scheme 1. The concept.

Preparation of Cyclization Precursors

The required methylenecyclopropane derivatives of types **1** and **6** with their tetrasubstituted double bonds were prepared either by a palladium-catalyzed allylic substitution on 1-(2′-propenyl)cyclopropyl chloride (**8**-Cl) – the corresponding tosylate **8**-OTs[11] – or, less elegantly, by Wittig olefination of a cyclopropanone hemiacetal.

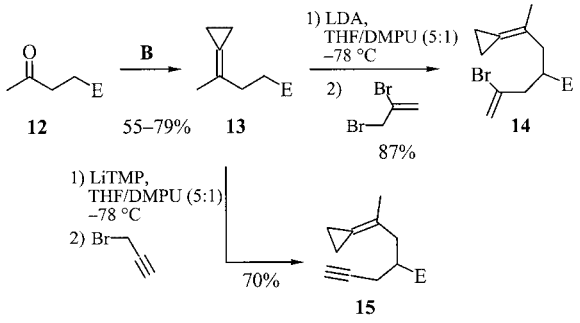
Thus, the cyclopropane derivative **8**-Cl is easily obtained in multigram quantities from (1′-chlorocyclopropyl) methyl ketone (**7**-Cl) by a Wittig olefination in 88% yield (Scheme 2).[12] The palladium-catalyzed substitution with the enolate of the appropriately substituted (2′-bromoprop-2′-enyl)malonate gave the 2-bromo-1,6-diene **9** (59%), while the reaction with dimethyl propargylmalonate enolate furnished the enyne **10**-H in 73% yield. The substitution of the chloride **8**-Cl with dimethyl malonate enolate gave the known diester **11** on an even larger scale (10 mmol) with only 0.01 mol-% palladium catalyst in up to 42% yield (not optimized).

The monoesters **14** and **15** with the same skeleton as **9** and **10**-H were synthesized by two-step sequences starting with Wittig olefination of methyl levulinate (**12**) with (3-bromopropyl)phosphonium bromide in benzene in the presence of 2.2 equiv. of potassium *tert*-butoxide (conditions **B**) [13] to give the methylenecyclopropane derivative **13** in up to 79% yield.[14] Subsequent alkylation of the enolate of **13** with 2,3-dibromopropene gave the bromodiene **14** in 87%



Scheme 2. **A**: 0.01–5 mol-% $Pd(dba)_2$, dppb, THF, 66 °C, 1–24 h. E = CO_2Me.

yield (Scheme 3). Under the same conditions, the alkylation of **13** with propargyl bromide yielded the enyne **15** (69%).

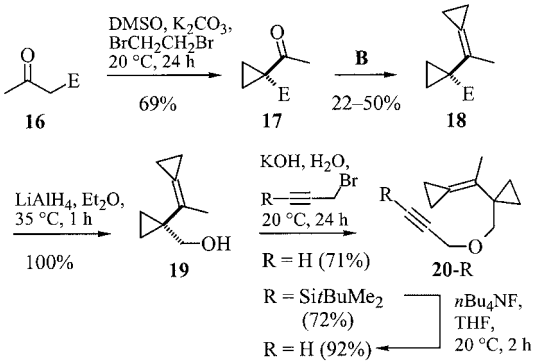


Scheme 3. **B**: $Br(CH_2)_3PPh_3Br$, KO*t*Bu, PhH, 70 °C, 4 h. E = CO_2Et.

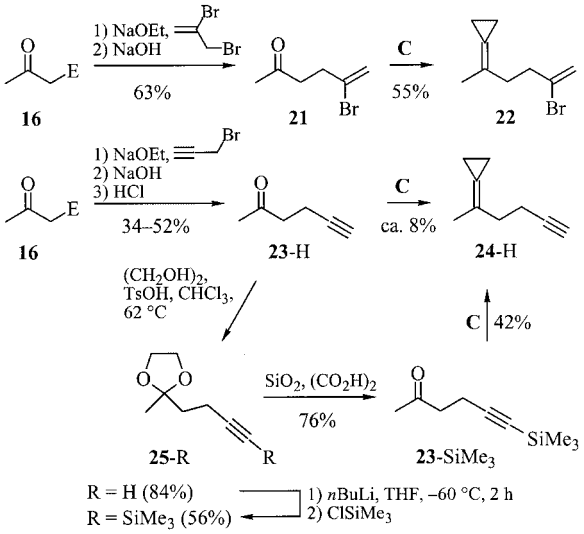
Another 1,7-enyne **20**-H, with a four-atom tether between the methylenecyclopropane end group and the triple bond, but with a 1,1-disubstituted cyclopropane moiety as a mechanistic probe adjacent to the double bond, was prepared from ethyl 1-acetylcyclopropanecarboxylate (**17**) which is accessible in good yield by cycloalkylation of ethyl acetoacetate (**16**) with 1,2-dibromoethane, analogous to a literature procedure (Scheme 4).[15] The olefination of **17** under the same conditions as applied to **12** gave the methylenecyclopropane derivative **18**. Reduction of **18** with lithium aluminum hydride and alkylation of the resulting alcohol **19** with propargyl bromide or better 3-(*tert*-butyldimethylsilyl)propargyl bromide, gave the ethers **20**-H and **20**-Si*t*BuMe$_2$, respectively. The latter was converted into the terminal alkyne **20**-H by protiodesilylation with *n*Bu$_4$NF in THF.

For cyclization precursors with shorter tethers between the methylenecyclopropane and bromoethenyl or ethynyl moiety, the synthesis started from ethyl acetoacetate (**16**) (Scheme 5). Alkylation of the enolate of **16** with 2,3-dibromopropene, hydrolysis of the ester and decarboxylation furnished 5-bromohex-5-en-2-one (**21**) in 63% yield (Scheme 5). Wittig olefination of **21** with (3-bromopropyl) phosphonium bromide in THF in the presence of sodium hydride (conditions **C**)[16] proceeded to give **22** in 55% yield.

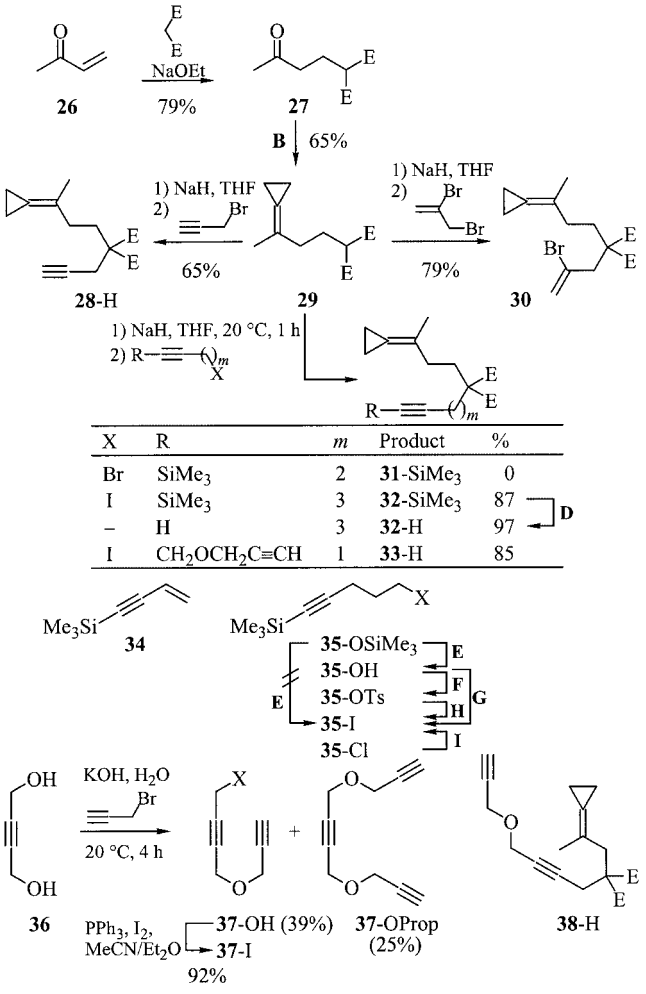
Hex-5-yn-2-one (**23**-H) was obtained by alkylation of **16** with propargyl bromide in 52% yield. Wittig olefination of



Scheme 4. **B**: $Br(CH_2)_3PPh_3Br$, KO*t*Bu, PhH or PhMe, 70 °C, 4 h. E = CO_2Et.



Scheme 5. **C**: $Br(CH_2)_3PPh_3Br$, NaH, THF or PhH, 66–70 °C. E = CO_2Et.



Scheme 6. **B**: $Br(CH_2)_3PPh_3Br$, KO*t*Bu, PhH, 70 °C, 4 h. **D**: $(nBu)_4NF$, THF, 25 °C, 3 h. **E**: NaI, Me_3SiCl, MeCN, 69%. **F**: TsCl, Py, 65%. **G**: I_2, PPh_3, MeCN/Et_2O, 81%. **H**: NaI, Me_2CO, 25 °C, 92%. **I**: NaI, Me_2CO, 25 °C, 90%. E = CO_2Et (CO_2Me for **38**-H).

23-H under the usual conditions (see above), gave only mixtures of different products. Therefore, the terminal alkyne moiety in **23**-H was protected by first converting **23**-H into the acetal **25**-H (84% yield), silylating the acetal at the terminus (56%) and then cleaving the acetal[17] to give **23**-$SiMe_3$ (76%). The silylated hexynone **23**-$SiMe_3$ underwent reasonably clean olefination, and the workup gave the desilylated enyne **24**-H in 42% yield.

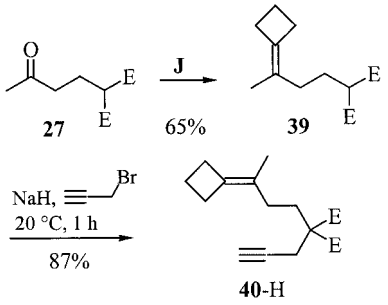
Two additional cyclization precursors were synthesized starting from methyl vinyl ketone (**26**) (Scheme 6). Michael addition of diethyl malonate gave diethyl (3′-oxobutyl)malonate (**27**),[18] which was in turn converted into the methylenecyclopropane derivative **29** under the same conditions as applied to **12** (see above). The obtained malonate derivative **29** was alkylated with 2,3-dibromopropene to yield the bromodiene **30** (79%) and with propargyl bromide to give the enyne **28**-H (65%). An attempt to alkylate **29** with 1-bromo-4-trimethylsilylbut-3-yne,[19] did not give the expected product **31**-$SiMe_3$, but 4-trimethylsilylbut-1-en-3-yne (**34**), resulting from dehydrobromination of the homopropargyl bromide.[20]

Alkylation of the malonate derivative **29** with 5-iodo-1-trimethylsilyl-1-pentyne (**35**-I) gave the enyne **32**-$SiMe_3$ in 87% yield, while with the tosylate **35**-OTs or the chloride **35**-Cl, even in the presence of tetrabutylammonium iodide, no conversion was observed. The iodide **35**-I[21,22] was obtained by treatment of the 5-silyloxy-1-pentyne **35**-$OSiMe_3$ with in situ generated trimethylsilyl iodide (TMSI)[23] to give the alcohol **35**-OH, and its subsequent treatment with triphenylphosphane/iodine. Alternatively, the alcohol **35**-OH was first converted into the tosylate **35**-OTs, which, by subsequent Finkelstein reaction, led to **35**-I. Finkelstein reaction of the corresponding chloride **35**-Cl also furnished the iodide **35**-I in multigram quantities. Protiodesilylation of **32**-$SiMe_3$ gave the unprotected enyne **32**-H in 97% yield (Scheme 6).

The 10-oxatridec-1-ene-7,12-diyne **33**-H was also prepared by alkylation of **29**, in this case with 4-oxaocta-1,6-diynyl iodide (**37**-I). The latter was obtained starting from but-2-yne-1,4-diol (**36**), the alkylation of which with propargyl bromide gave the diynol **37**-OH (39% yield) along

with the dipropargyl ether **37**-OProp (25%). Treatment of the alcohol **37**-OH with PPh_3/I_2 led to the corresponding iodide **37**-I (Scheme 6). Analogously, the 9-oxadodec-1-ene-6,11-diyne **38**-H was obtained by alkylation of dimethyl (2′-cyclopropylidenepropyl)malonate (**11**) with the extended propargyl iodide **37**-I.

For comparison with the methylenecyclopropane derivatives, the analogous methylenecyclobutane **40** was prepared from diethyl (3′-oxobutyl)malonate (**27**) by olefination with the ylide generated from (4-bromobutyl)phosphonium bromide[24] with potassium *tert*-butoxide in benzene and subsequent alkylation with propargyl bromide (Scheme 7).



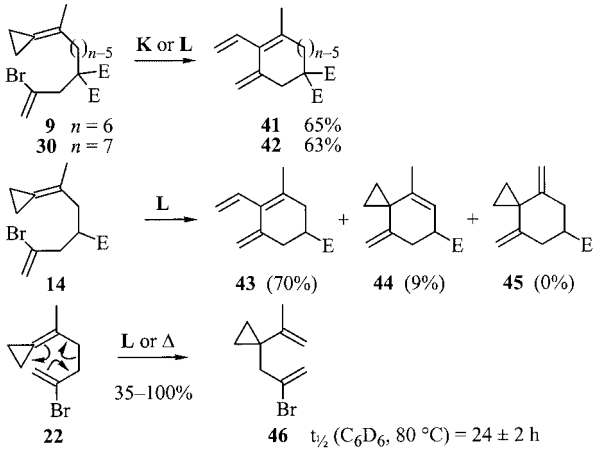
Scheme 7. **J**: $Br(CH_2)_4PPh_3Br$, KO*t*Bu, PhH, 70 °C, 4 h. E = CO_2Et.

Palladium-Catalyzed Cyclizations

The hypothesis put forward above (see Scheme 1) was first tested with the 2-bromo-1,6-diene **9**. Towards that end, **9** was treated with methyl acrylate under the conditions as previously optimized for the domino-Heck–Diels–Alder reaction [$Pd(OAc)_2$, PPh_3, Ag_2CO_3, MeCN].[6] However, no cyclization/cross-coupling product of type **5** was isolated, but rather a product which had no acrylate moiety incorporated. Under typical Heck conditions [$Pd(OAc)_2$, PPh_3, NEt_3], the new product could be isolated in 65% yield and identified as the cross-conjugated triene **41** (Scheme 8). Comparison with samples obtained from the first reaction of **9** showed that the dendralene **41** was also formed, but had slowly decomposed under those reaction conditions. The homologous 2-bromo-1,7-diene **30** gave the homologous methylene(vinyl)cycloheptane derivative **42** in 63% yield.

The 2-bromo-1,6-diene monoester **14** under the same reaction conditions gave, besides the triene **43** (70%) also the 8-methylenespiro[2.5]oct-4-ene-6-carboxylate **44** in 9% yield, but none of the double bond isomer **45**. The 2-bromo-1,5-diene **22** on the other hand led to a bromine-containing product, with the same composition as the starting material (according to MS).

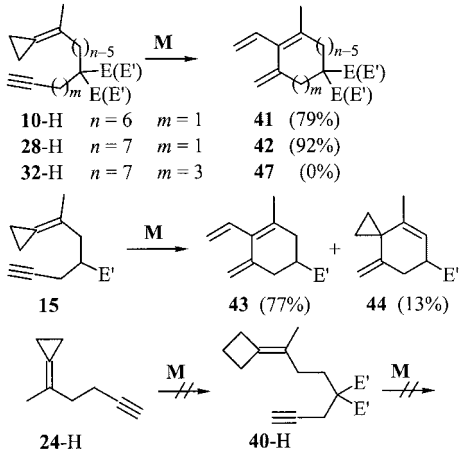
The NMR spectra revealed that the product was actually the bromodiene **46**, resulting from a Cope rearrangement[25] of **22**. The comparison with the NMR spectra of the starting material showed that this rearrangement is even detectable under the conditions for the preparation of **22**. This rearrangement also proceeds smoothly in the absence of



Scheme 8. **K**: $Pd(OAc)_2$, PPh_3, Ag_2CO_3, MeCN, methyl acrylate, 80 °C, 48 h. **L**: $Pd(OAc)_2$, PPh_3, NEt_3, DMF, 80 °C, 60 h or 100 °C, 24 h. E = CO_2Me or CO_2Et.

palladium acetate. By monitoring the purely thermal rearrangement of **22** in C_6D_6 by ^1H NMR spectroscopy, the half-reaction time was estimated to be approx. 24 h at 80 °C. This corresponds to a remarkably low activation energy for a Cope rearrangement. Even the single other reported example[26] of a Cope rearrangement of a 1,5-diene with a methylenecyclopropane end group most probably has a higher activation energy.

Since its development by Trost et al.,[27,28] the cycloisomerization of 1-ene-6-ynes has found wide application, because it yields the same products as the intramolecular Heck reaction of 2-halo-1,6-dienes, but with optimal atom economy. Thus, the enynes **10**-H and **28**-H in benzene were treated with a catalytic amount of the $Pd_2(dba)_3{\cdot}CHCl_3$ complex in the presence of acetic acid according to an established protocol. After 12 h at 25 °C, no starting materials could be detected, and after column chromatography, the cross-conjugated trienes **41** and **42** were isolated in 79 and 92% yield, respectively (Scheme 9). In the case of **10**-H, the product **41** was spectroscopically pure after filtration

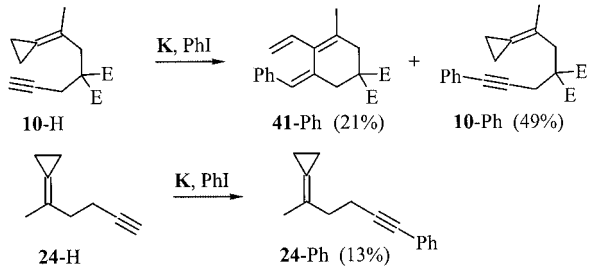


Scheme 9. **M**: $Pd_2(dba)_3{\cdot}CHCl_3$, P(*o*Tol)$_3$, HOAc, PhH, 25 °C, 12 h. E = CO_2Me, E′ = CO_2Et.

through Celite and removal of the solvent. The enyne **15** could be converted, like the bromodiene **14**, to the triene **43** in 77% and the spiro[2.5]octene **44** in 13% yield.

While the reaction of the bromodienes **9** and **30** proceeded smoothly with almost the same yields even in the presence of methyl acrylate, the reactions of the enynes **10**-H and **28**-H were drastically slower or even completely inhibited by added acrylate. Apparently, the palladium ion is coordinated by the acrylate and thus not catalytically active. The 1-en-9-yne **32**-H and the 1-en-5-yne **24**-H as well as the methylenecyclobutane derivative **40**-H under the same conditions, did not give any identified products.

Instead of a hydridopalladium species, an arylpalladium halide can also initiate the cyclization of an enyne. Therefore, the enyne **10**-H was heated with iodobenzene under Heck conditions [$Pd(OAc)_2$, PPh_3, NEt_3]. After 12 h at 80 °C, two isomeric products could be isolated in 21 and 49% yield, respectively. The first one was identified as the cross-conjugated triene **41**-Ph with a (*Z*)-configured phenyl-substituted *exo*-methylene moiety (according to an NOESY spectrum). The other one was the terminally aryl-substituted enyne **10**-Ph (Scheme 10). The arylation of alkynes with haloarenes is well established,[29] but normally proceeds well only in the presence of copper salts. Purely palladium-catalyzed couplings have rarely been reported.[30]

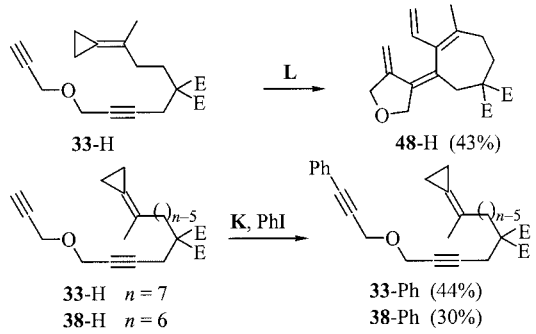


Scheme 10. **K**: $Pd(OAc)_2$, PPh_3, NEt_3, DMF, 80–100 °C, 12–20 h. E = CO_2Me.

The enyne **24**-H under the same conditions gave only the terminally arylated enyne **24**-Ph (13%) along with polymeric material.

Metal-catalyzed oligocyclizations of oligo-unsaturated, open-chain compounds have been used for an elegant and efficient assembly of oligocyclic systems.[31] Therefore, the enediyne **33**-H (Scheme 11) was treated with a palladium catalyst under standard conditions [$Pd_2(dba)_3{\cdot}CHCl_3$, HOAc, P(*o*Tol)$_3$, PhH, 25 °C]. After 12 h, the cross-conjugated tetraene **48**-H was isolated in 43% yield. According to a NOESY-NMR spectrum, the double bond between the two rings in **48**-H is (*Z*)-configured.

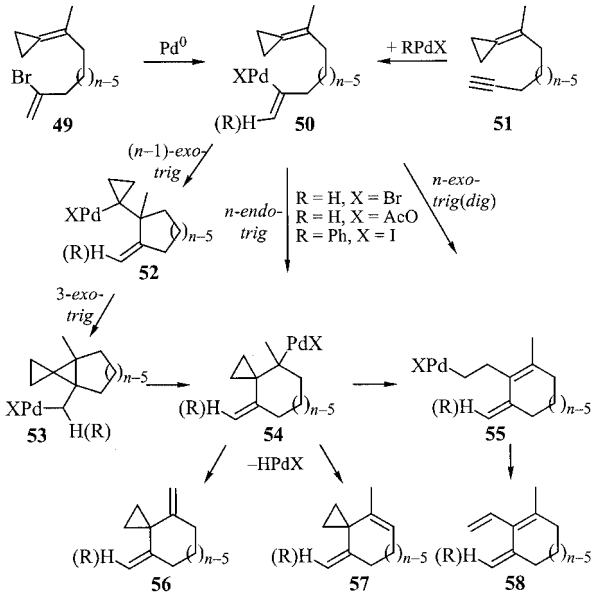
In the presence of iodobenzene and a palladium catalyst [$Pd(OAc)_2$, PPh_3, NEt_3] in DMF at 100 °C the enediyne **33**-H and its lower analogue **38**-H did not yield any phenyl-substituted cross-conjugated tetraene of type **48**-H, but only the terminally phenylated enediynes **33**-Ph (44%) and **38**-Ph (30%), respectively.



Scheme 11. **K**: $Pd(OAc)_2$, PPh_3, NEt_3, DMF, 100 °C, 12 h. **L**: $Pd_2(dba)_3{\cdot}CHCl_3$, P(*o*Tol)$_3$, HOAc, PhH, 25 °C, 72 h. E = CO_2Me or CO_2Et.

Discussion and Outlook

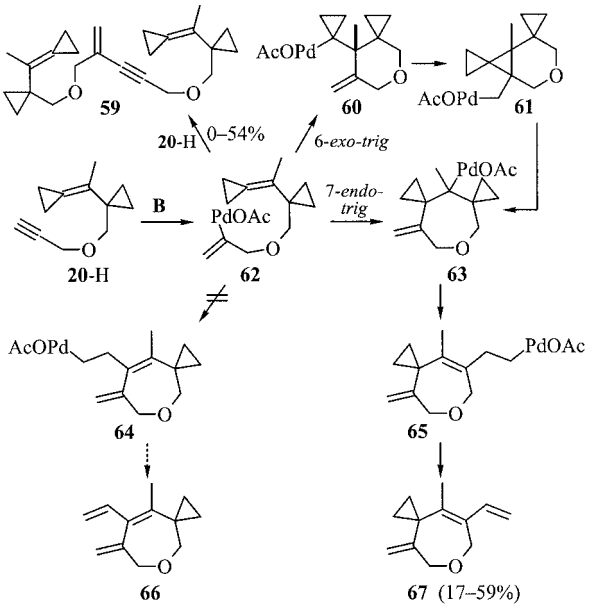
All of the cross-conjugated trienes and tetraenes discussed above are obviously formed with ring opening of the three-membered ring in the methylenecyclopropane unit of the bromodiene or enyne precursor. Going by the products only, this may occur by three mechanistic options. The most straightforward, yet intriguing mode would be a direct carbopalladation across the single bond of the three-membered ring in the intermediate **50** in an *n-exo-trig*(*dig*) mode to yield the homoallylpalladium species **55** which, by β-hydride elimination, would give the final product of type **58** (Scheme 12). It is more likely though, that the latter intermediate is formed by a cyclopropylcarbynyl-to-homoallyl rearrangement in **54**, as is well documented to rapidly occur with all kinds of cyclopropylcarbynylmetal derivatives.[32] There is experimental evidence, in fact, that **54** is an intermediate en route to **55**, as in one case a methylenespiro[2.5]oct-4-ene derivative of type **57**, apparently formed by β-dehydropalladation from an intermediate of type **54**, was isolated as a by-product. The intermediate **54** could arise from



Scheme 12. Mechanistic rationalization of the [3]dendralene formation.

an *n-endo-trig* cyclization of **50**, but, according to literature precedence and a stereochemical proof on a model system for the formation of formal *n-endo-trig* products,[33] the most probable route to **54** is by (*n*–1)-*exo-trig* cyclization of **50** to give the cyclopropylpalladium intermediate **52**, which would not want to undergo β-dehydropalladation, but rather a 3-*exo-trig* cyclization, and the resulting highly strained [(spiropentyl)methyl]palladium species **53** would rapidly open one ring to yield **54** as a homoallylpalladium species.

Additional evidence could be expected from the cyclization of a model precursor such as **20**-H which, by either of the two latter discussed reaction modes, would have to unequivocally yield a (cyclopropylcarbynyl)palladium species. Under the established reaction conditions, the enyne **20**-H did indeed give two products, the ratio of which strongly depended on the dilution of the starting material. The more polar one was identified as the trienyne **59**, a dimer of **20**-H. Apparently, a coupling of the hydridopalladation product from **20**-H with the acetylene terminus of a second molecule **20**-H took place. This type of reaction has previously been observed.[34] An unambiguous characterization of the other product from **20**-H as the non-cross-conjugated triene **67** was possible only on the basis of 2D-NMR spectra since, according to the ^{1}H and ^{13}C NMR spectra, the two different constitutions **66** and **67** would have been possible. Hence, the formation of the product **67** must proceed via the intermediate **63** (Scheme 13). Whether this is formed directly by a 7-*endo-trig*-carbopalladation or the sequence of 6-*exo-trig*-, 3-*exo-trig*-carbopalladation and cyclopropylcarbynyl-to-homoallyl rearrangement, i.e. via **60** and **61**, remains an open question. In the formation of six- and seven-membered rings *n-exo*- as well as *n-endo*-ring closure modes are known to occur.[35]

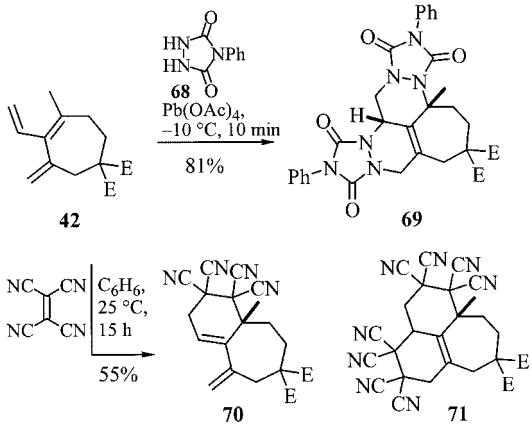


Scheme 13. **B**: Br(CH$_2$)$_3$PPh$_3$Br, KO*t*Bu, PhH, 80 °C, 4 h.

The ring opening in conjunction with the Heck coupling of such methylenecyclopropanes as discussed above leads to 2-substituted 1,3-butadienes. In analogous Heck reactions of butadienes, the initial carbopalladation occurs with the opposite regioselectivity to form a π-allylpalladium intermediate.[5] Methylenecyclopropanes can thus be considered as suitable precursors to substituted buta-1,3-dienes complementing the recently found access by palladium-catalyzed ring opening of 2-halomethylenecyclopropanes.[36]

Cross-conjugated trienes such as the ones accessible by this new palladium-catalyzed cascade reaction, are so-called [3]dendralenes.[37] As such, they should be able to undergo a sequential Diels–Alder reaction, a so-called transmissive cycloaddition.[38] To test this possibility, the triene **42** was treated with the very reactive dienophile *N*-phenyltriazoline-3,5-dione (PTAD),[39] in situ prepared by oxidation of the urazole **68** with lead tetraacetate in dichloromethane at –10 °C. The conversion of **42** was complete within 10 min, and chromatography gave the pentacyclic compound **69** as a single diastereomer in 81% yield.

On the other hand, the reaction of **42** with tetracyanoethylene (TCNE) at room temperature within 15 h only led to the bicyclo[5.4.0]undecene derivative **70** (Scheme 14), which did not react any further to the tricycle **71**, not even at 80 °C. The structure of **70** was rigorously proved by an X-ray crystal structure analysis (Figure 1).[40] Other dieno-



Scheme 14. E = CO_2Et.

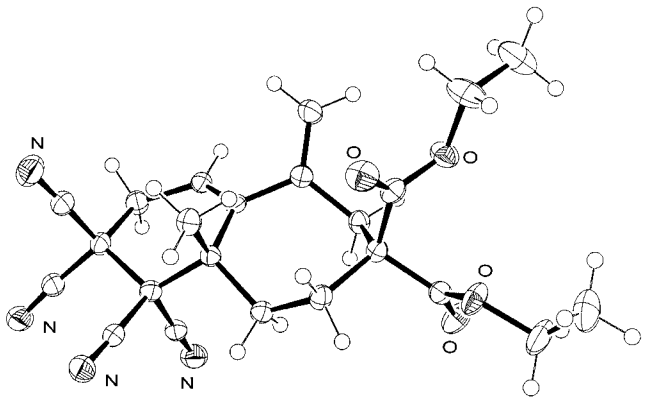


Figure 1. Structure of diethyl 8,8,9,9-tetracyano-7-methyl-2-methylenebicyclo[5.4.0]undec-11-ene-4,4-dicarboxylate (**70**) in the crystal.[40]

philes [dimethyl maleate, (*E*)-1,2-bis(phenylsulfonyl)ethene] did not at all react with **42**, neither at elevated temperature nor under high pressure.[41]

Experimental Section

General Remarks: ^{1}H and ^{13}C NMR spectra were recorded with Bruker AW 250, WM 500 or Varian Mercury 300, Inova 600 instruments at 250, 300, 500 or 600 MHz and 62.9, 75.6, 125.0 or 150.8 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 registered with a Perkin–Elmer 1720 FT-IR or a Bruker IFS 66. Low-resolution EI and DCI MS (EI at 70 eV, DCI with NH_3): Finnigan MAT 95 spectrometer. High-resolution MS: Finnigan MAT 95. HRMS: Preselected ion peak matching at $R \approx 10000$ to be within ±2 ppm of the exact masses. ESI MS: Finnigan LCQ. ESI HRMS: APEX IV 7T FTICR, Bruker Daltonic. Elemental analyses were performed by the Mikroanalytisches Laboratorium des Instituts für Organische und Biomolekulare Chemie 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 dry nitrogen or argon in oven- and/or flame-dried glassware. Unless otherwise specified, solutions of NH_4Cl and $NaHCO_3$ are saturated aqueous solutions. Tetrahydrofuran was distilled from potassium benzophenone ketyl, and DMF and MeCN were distilled from CaH_2. (3-Bromopropyl) triphenylphosphonium bromide[24b] and **35**-OSiMe$_3$[42] were prepared according to published procedures.

General Procedure for Palladium-Catalyzed Substitutions on Allyl Sulfonates and Halides (GP 1): A solution of bis(dibenzylideneacetone)palladium(0) [Pd(dba)$_2$] (5.8 mg, 10 μmol, 2.0 mol-%) and 11 μmol of a bidentate phosphane in 1 mL of THF was stirred at ambient temp. for 5 min, and subsequently the mixture was treated with 0.5 mmol of the allyl sulfonate or allyl halide. After ca. 5–10 min, the reaction mixture turned green, and then a solution of 0.5–1.5 mmol of the sodium malonate in 5 mL of anhydrous THF, prepared by addition of 0.5–1.5 mmol of the dialkyl malonate in 1.5 mL of anhydrous THF to 0.5–1.5 mmol of sodium hydride in 3.5 mL of anhydrous THF, was added dropwise. The reaction mixture was stirred until the allyl component had been consumed completely (TLC control). The mixture was added to 10 mL of diethyl ether and 20 mL of a 10% NH_4Cl solution, the phases were separated, the aqueous phase was extracted with diethyl ether (3 × 5 mL), the combined organic phases were washed with 5 mL of brine and dried. After removal of the solvent, the residue was purified by flash chromatography.

General Procedure for the Alkylation of Dialkyl Malonates and Substituted Dialkyl Malonates (GP 2): A solution of the corresponding malonate in THF (0.1 M, if not otherwise stated) was treated with 1.1–2.0 equiv. of sodium hydride, the mixture was stirred for 10 min, and subsequently 1.0–2.0 equiv. of the respective alkyl halide was added. After complete conversion (TLC or GC, 1–24 h), the mixture was filtered, and the residue washed with water. The combined organic layers were added to water, the aqueous layer extracted with diethyl ether (3 × 50 mL) and the combined extracts were washed twice with 20 mL each of water and brine. After having been dried ($MgSO_4$), the mixture was fractionally distilled or the residue after removal of the solvent was subjected to chromatography on silica gel. Alternatively, the reaction mixture can be directly chromatographed or recrystallized after filtration.

General Procedure for Intramolecular Heck Reactions of Bromodienes with Methylenecyclopropane End Groups (GP 3): A 50-mL Pyrex bottle was charged under argon with anhydrous acetonitrile (10 mL), 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, then 1.00 mmol of the respective bromodiene and silver(I) carbonate (552 mg, 2.00 mmol) were added. The bottle was closed with a screw cap, and the mixture was stirred at the given temperature for the given time, then cooled to ambient temp., extracted with pentane (5 × 50 mL), the combined organic phases were washed with 15 mL of water and dried ($MgSO_4$). After removal of the solvent in a rotary evaporator, the residue was subjected to chromatography on silica gel eluting with petroleum ether/ether (10:1 → 5:1).

Alternative General Procedure for Intramolecular Heck Reactions of Bromodienes with Methylenecyclopropane End Groups (GP 4): A 50-mL Pyrex bottle was charged under argon with anhydrous DMF (10 mL), 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, then 1.00 mmol of the respective bromodiene and triethylamine (202 mg, 2.00 mmol) were added. The bottle was closed with a screw cap, and the mixture was stirred at the given temperature for the given time, then the mixture was cooled to room temp., extracted with pentane (5 × 50 mL), the combined organic phases were washed with 15 mL of water and dried ($MgSO_4$). After removal of the solvent in a rotary evaporator, the residue was subjected to chromatography on silica gel eluting with petroleum ether/ether (10:1 → 5:1).

Dimethyl 4-Ethenyl-5-methyl-3-methylenecyclohex-4-ene-1,1-dicarboxylate (41-H). a) By Enyne Cycloisomerization: To a solution of dimethyl (2′-cyclopropylidenepropyl)(prop-2-ynyl)malonate (**10**-H) (250 mg, 1.00 mmol) in benzene (10 mL) were added tris(dibenzylideneacetone)dipalladium–chloroform complex (51.8 mg, 50.0 μmol, 5.0 mol-%), tris(*o*-tolyl)phosphane (15.2 mg, 49.9 μmol, 5 mol-%) and acetic acid (3 μL, 3 mg, 0.05 mmol, 5 mol-%), and the mixture was stirred under argon at ambient temp. for 15 h. Chromatography on silica gel (column 1 × 20 cm, petroleum ether/ether, 10:1) gave 198 mg (79%) of **41**-H as a colorless, unstable oil, R_f = 0.26. IR (film): $\tilde{\nu}$ = 3060 cm^{-1}, 1740 (C=O), 1670 (C=C), 1655, 1625, 1570, 1090, 830, 755, 740, 710, 650. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.83 (s, 3 H, CH_3), 2.66 (s, 2 H, CH_2), 2.84 (s, 2 H, CH_2), 3.69 (s, 6 H, OCH_3), 4.86 (s, 1 H, C=CH_2), 4.97 (s, 1 H, C=CH_2), 5.07 (dd, ^2J = 2.1, ^3J = 15.8 Hz, 1 H, CH=CH_2), 5.31 (dd, ^2J = 2.1, ^3J = 11.2 Hz, 1 H, CH=CH_2), 6.24 (dd, ^3J = 15.8, ^3J = 11.2 Hz, 1 H, CH=CH_2) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 20.8 (+, CH_3), 37.6 (–, CH_2), 37.4 (–, CH_2), 53.6 (+, OCH_3), 59.6 [C_{quat}, $C(CO_2)_2$], 112.0 (–, CH_2), 119.2 (–, CH_2), 131.2 (C_{quat}, C=C), 131.5 (C_{quat}, C=C), 133.5 (+, CH=C), 139.4 (C_{quat}, C=C), 171.2 (C_{quat}, CO) ppm. MS (70 eV, EI): *m*/*z* (%) = 250 (12) [M$^+$], 204 (100) [M$^+$ – C_2H_6O]. $C_{14}H_{18}O_4$ (250.3): calcd. C 67.18, H 7.25; found C 67.52, H 7.01. **b) By Intramolecular Heck Reaction of 9 in the Presence of NEt$_3$:** According to GP 4, bromodiene **9** (113 mg, 0.342 mmol) in acetonitrile (10 mL) in the presence of triethylamine (69.0 mg, 0.682 mmol) was treated with $Pd(OAc)_2$ (3.8 mg, 17 μmol) and triphenylphosphane (11.1 mg, 42 μmol) at 100 °C for 24 h. Workup and purification gave 55.5 mg (65%) of **41**-H with spectroscopic data as above.

Diethyl 4-Ethenyl-5-methyl-3-methylenecyclohept-4-ene-1,1-dicarboxylate (42). a) By Enyne Cycloisomerization: To a solution of

diethyl (3′-cyclopropylidenebutyl)(2′′-propynyl)malonate (**28**-H, 1.87 g, 6.40 mmol) in 90 mL of benzene were added tris(dibenzylideneacetone)dipalladium–chloroform complex (190 mg, 186.3 μmol, 2.9 mol-%), tris(*o*-tolyl)phosphane (111 mg, 364.4 μmol, 6 mol-%) and acetic acid (22 μL, 0.05 mmol, 6 mol-%), and the mixture was stirred under argon at ambient temp. for 15 h. Chromatography on silica gel (2×20 cm, pentane/ether, 10:1) gave 1.25 g (67%) of **42** as a colorless oil, R_f = 0.32. IR (film): $\tilde{\nu}$ = 2981 cm^{-1}, 2937, 1731 (C=O), 1642 (C=C), 1446, 1367, 1239, 1178, 1063, 906, 859, 704. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.24 (t, ^3J = 7.6 Hz, 6 H, OCH_2CH_3), 1.81 (s, 3 H, CH_3), 2.08–2.13 (m, 2 H, 7-H), 2.26–2.30 (m, 2 H, 6-H), 2.84 (s, 2 H, 2-H), 4.16 (q, ^3J = 7.6 Hz, 4 H, OCH_2CH_3), 4.89 (d, ^2J = 1.9 Hz, 1 H, 1′-H), 5.08 (dd, ^2J = 1.8, ^3J = 10.8 Hz, 1 H, 2′′-H_E), 5.14 (dd, ^2J = 1.8, ^3J = 17.2 Hz, 1 H, 2′′-H_Z), 5.18 (d, ^2J = 1.9 Hz, 1 H, 1′-H), 6.50 (dd, ^3J = 17.2, ^3J = 10.8 Hz, 1 H, 1′′-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 14.0 (+, OCH_2CH_3), 21.0 (+, CH_3), 30.2 (–, CH_2), 32.4 (–, CH_2), 39.5 (–, CH_2), 58.2 (C_{quat}, C-1), 61.2 (–, OCH_2CH_3), 115.3 (–, C=CH_2), 118.0 (–, C=CH_2), 134.6 (+, C-1′′), 135.7 (C_{quat}, C-3*), 136.7 (C_{quat}, C-4*), 141.8 (C_{quat}, C-5*), 171.4 (C_{quat}, CO) ppm. MS (70 eV, EI): *m*/*z* (%) = 292 (12) [M^+], 246 (54) [$M^+ - C_2H_6O$], 218 (35) [$M^+ - C_2H_5OH - CO$], 201 (15), 189 (20), 173 (18), 145 (100) [$M^+ - C_2H_5OH - CO - C_2H_5CO_2$]. $C_{17}H_{24}O_4$ (292.37): calcd. C 69.84, H 8.27; found C 69.79, H 8.03. **b) By Enyne Cycloisomerization in the Presence of *tert*-Butyl Acrylate:** A solution of diethyl (3′-cyclopropylidenebutyl)(2′′-propynyl)malonate (**28**-H, 145 mg 0.496 mmol) in 5 mL of benzene was stirred with tris(dibenzylideneacetone)dipalladium–chloroform complex (12.7 mg, 12.3 μmol, 2.5 mol-%), tris(*o*-tolyl)phosphane (3.8 mg, 12 μmol), *tert*-butyl acrylate (630 mg, 4.92 mmol) and acetic acid (2 μL, 2 mg, 0.03 mmol, 7 mol-%) under argon at ambient temp. for 15 h. After removal of the solvents under reduced pressure, chromatography on silica gel (column 2×20 cm, pentane/ether, 10:1) gave 200 mg (69%) of **42**; R_f = 0.32. As a second fraction, 9.3 mg (6%) of tetraethyl 2,14-bis(cyclopropylidene)-9-methylenepentadeca-7-yne-5,5,11,11-tetracarboxylate was obtained as a colorless oil; R_f = 0.08. IR (film): $\tilde{\nu}$ = 3023 cm^{-1}, 2878, 2856, 1734 (C=O), 1684 (C=C), 1448, 1368, 1277, 1127, 1032, 832, 668, 527. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.8–1.0 (m, 8 H, cPr-H), 1.15–1.25 (m, 12 H, OCH_2CH_3), 1.4–1.5 [m, 4 H, 4(12)-H], 1.75 [s, 6 H, 1(15)-H], 1.90–2.15 [m, 8 H, 3(6,10,13)-H], 4.1–4.2 (m, 8 H, OCH_2CH_3), 5.5–5.6 (m, 2 H, CH_2=C) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 1.3 (–, cPr-C), 2.7 (–, cPr-C), 13.9 (+, OCH_2CH_3), 22.5 [+, C-1(15)], 29.6 (–, CH_2), 30.2 (–, CH_2), 56.5 [C_{quat}, C-5(11)], 60.9 (–, OCH_2CH_3), 95.1 (C_{quat}, C-7*), 108.8 (C_{quat}, C-8*), 115.8 (C_{quat}, cPr-C), 117.3 (–, CH_2), 123.0 [C_{quat}, C-2(14)], 125.5 (C_{quat}, C-9*), 170.0 (C_{quat}, CO) ppm. MS (70 eV, EI): *m*/*z* (%) = 513 (26), 436 (33), 422 (100), 392 (80), 378 (45), 91 (76). **c) By Intramolecular Heck Reaction in the Presence of Ag_2CO_3:** According to GP 3, a mixture of diethyl (2′-bromoprop-2′-enyl)(3′′-cyclopropylidenebutyl)malonate (**30**, 373 mg, 1.00 mmol), $Pd(OAc)_2$ (11.6 mg 51.7 μmol), PPh_3 (26.3 mg, 100 μmol), Ag_2CO_3 (572 mg, 2.07 mmol), and *tert*-butyl acrylate (455 mg, 3.55 mmol) was heated at 80 °C for 48 h. According to TLC and ^1H NMR an intermediate product **42** was present (ca. 10%), but this decomposed after prolonged reaction time. **d) By Intramolecular Heck Reaction in the Presence of NEt_3:** According to GP 4, a mixture of the bromodiene **30** (127 mg, 0.340 mmol), $Pd(OAc)_2$ (3.8 mg, 17 μmol), PPh_3 (11.1 mg, 42.3 μmol), NEt_3 (69.0 mg, 0.682 mmol) and *tert*-butyl acrylate (135 mg, 1.05 mmol) was heated at 100 °C for 24 h. Workup yielded 40 mg (40%) of **42**. The same reaction at 80 °C after 60 h gave **42** in 63% yield.

Ethyl 4-Ethenyl-3-methyl-5-methylenecyclohex-3-enecarboxylate (43) and Ethyl 4-Methyl-8-methylenespiro[2.5]octane-6-carboxylate (44). a) By Enyne Cycloisomerization: To a solution of ethyl 2-(2′-cyclopropylidenepropyl)pentynoate (**15**, 207 mg, 1.00 mmol) in 40 mL of benzene were added tris(dibenzylideneacetone)dipalladium–chloroform complex (21.6 mg, 20.9 μmol, 2 mol-%), tris(*o*-tolyl)phosphane (12.7 mg, 41.7 μmol, 4 mol-%) and acetic acid (2 mL, 2 mg, 0.03 mmol, 3 mol-%), and the mixture was stirred under argon at ambient temp. for 36 h. After removal of the solvents under reduced pressure, chromatography on silica gel (column 2×20 cm, petroleum ether/ether, 10:1) gave three fractions: Fraction I: 5.3 mg (3%) of **15**, R_f = 0.28. Fraction II: 160 mg (77%) of **43** as a colorless oil, R_f = 0.26. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.54 (t, ^3J = 7.2 Hz, 3 H, OCH_2CH_3), 1.83 (s, 3 H, CH_3), 2.50–2.60 (m, 1 H), 2.60–2.70 (m, 2 H, CH_2), 2.80–2.90 (m, 2 H, CH_2), 3.54 (q, ^3J = 7.2 Hz, 2 H, OCH_2CH_3), 4.86 (s, 1 H, C=CH_2), 4.97 (s, 1 H, C=CH_2), 5.07 (dd, ^2J = 2.1, ^3J = 15.8 Hz, 1 H, 2′′-H_Z), 5.31 (dd, ^2J = 2.1, ^3J = 11.2 Hz, 1 H, 2′′-H_E), 6.24 (dd, ^3J = 15.8, ^3J = 11.2 Hz, 1 H, 1′′-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 15.4 (+, OCH_2CH_3), 20.8 (+, CH_3), 37.6 (–, CH_2), 37.4 (–, CH_2), 59.6 (C_{quat}, C-5), 65.5 (–, OCH_2CH_3), 112.0 (–, CH_2), 119.2 (–, CH_2), 131.2 (C_{quat}, C-1*), 131.5 (C_{quat}, C-2*), 133.5 (+, *C*H=C), 139.4 (C_{quat}, C-3*), 171.2 (C_{quat}, CO) ppm. Fraction III: 27.5 mg (13%) of **44** as a yellow oil, contaminated with dibenzylideneacetone, R_f = 0.24. IR (film): $\tilde{\nu}$ = 2990 cm^{-1}, 1735 (C=O), 1670 (C=C), 1090, 890, 830, 750. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.85–0.90 (m_c, 2 H, cPr-H), 1.03–1.08 (m_c, 2 H, cPr-H), 1.51 (d, ^4J = 1.1 Hz, 3 H, CH_3), 1.62 (t, ^3J = 7.2 Hz, 3 H, OCH_2CH_3), 2.93 (s, 2 H, CH_2), 3.79 (q, ^3J = 7.2 Hz, 2 H, OCH_2CH_3), 4.62 (s, 1 H, C=CH_2), 4.71 (s, 1 H, C=CH_2), 5.68 (s, 1 H, C=CH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 12.4 (–, cPr-C), 13.3 (–, cPr-C), 15.11 (+, OCH_2CH_3), 20.9 (+, CH_3), 36.2 (–, CH_2), 42.5 (+, CH), 59.6 (C_{quat}, C-3), 66.8 (–, OCH_2CH_3), 112.7 (–, CH_2), 129.4 (C_{quat}, C-4*), 132.7 (C_{quat}, C-8*), 133.5 (+, *C*H=C), 171.8 (C_{quat}, CO) ppm. MS (70 eV, EI): *m*/*z* (%) = 206 (100) [M^+]. **b) By Enyne Cycloisomerization in the Presence of Methyl Acrylate:** To a solution of of ethyl 2-(2′-cyclopropylidenepropyl)pentynoate (**15**, 164 mg, 795 μmol) in 40 mL of benzene were added tris(dibenzylideneacetone)dipalladium–chloroform complex (17.0 mg, 16.4 μmol, 2 mol-%), tris(*o*-tolyl)phosphane (10.0 mg, 32.9 μmol, 4 mol-%), acetic acid (2 mL, 2 mg, 0.03 mmol, 4 mol-%), methyl acrylate (172 mg, 2.00 mmol), and the mixture was stirred under argon at ambient temp. for 36 h. After removal of the solvents under reduced pressure, chromatography on silica gel (column 2×20 cm, petroleum ether/ether, 10:1) gave three fractions: Fraction I: 25 mg (15%) of **15**, R_f = 0.28. Fraction II: 58 mg (35%) of **43** as a colorless oil, R_f = 0.26. Fraction III: 14 mg (9%) of **44**, contaminated with dibenzylideneacetone as a yellow oil, R_f = 0.24. **c) By Intramolecular Heck Reaction in the Presence of NEt_3:** According to GP 4, ethyl 4-bromo-2-(2′-cyclopropylidenepropyl)pent-4-enoate (**14**, 287 mg, 1.00 mmol), of $Pd(OAc)_2$ (3.8 mg, 17 μmol), PPh_3 (11.1 mg, 42.3 μmol) and NEt_3 (69.0 mg, 682 μmol) were heated at 100 °C for 24 h. After aqueous workup, chromatography on silica gel (column 2×20 cm, petroleum ether/ether, 10:1) gave two fractions: Fraction I: 145 mg (70%) of **43** as a colorless oil, R_f = 0.26. Fraction II: 18.5 mg (9%) of **44** as a colorless oil, R_f = 0.24.

1-(2′-Bromoprop-2′-enyl)-1-(1′′-methylethenyl)cyclopropane (46): In an NMR tube, a solution of 2-bromo-5-cyclopropylidenehexene (**22**, 20 mg, 99 mmol) in 0.5 mL of [D_6]benzene was heated at 80 °C. After certain time intervals, ^1H NMR spectra were recorded, indicating a conversion of **22** to **46** with a half-life of 24±2 h (15 h: 35% conversion, 40 h: 65% conversion). ^1H NMR (250 MHz, $CDCl_3$): δ = 0.50–0.55 [m, 2 H, 2(3)-H], 0.75–0.80 [m, 2 H, 2(3)-H], 1.75 (s, 3 H, CH_3), 2.45 (s, 2 H, 1′-H), 4.85 (br. s, 2 H, C=CH_2), 5.25 (s, 1 H, C=CH_2), 5.30 (s, 1 H, C=CH_2) ppm. ^{13}C NMR

(62.9 MHz, $CDCl_3$, DEPT): δ = 12.9 [–, C-2(3)], 20.8 (+, CH_3), 24.5 (C_{quat}, C-1), 39.7 (–, C-1′), 110.4 (–, C=*C*H_2), 113.1 (–, C=*C*H_2), 145.5 (C_{quat}, *C*=CH_2), 147.8 (C_{quat}, *C*=CH_2) ppm. MS (70 eV, EI): *m/z* (%) = 202/200 (0.1/0.1) [M^+], 174/172 (12/12) [$M^+ - C_2H_4$], 121 (43) [M^+ – Br], 93 (53) [M^+ – Br – C_2H_4], 79 (100) [M^+ – Br – C_3H_6].

Dimethyl (*Z*)-4-Ethenyl-3-methyl-5-(phenylmethylene)cyclohex-3-ene-1,1-dicarboxylate (41-Ph) and Dimethyl (2′-Cyclopropylidenepropyl)(3′′-phenylprop-2′′-ynyl)malonate (10-Ph): Argon was bubbled through a solution of of dimethyl (2′-cyclopropylidenepropyl)(prop-2′′-ynyl)malonate (**10**-H, 85.3 mg, 341 μmol), $Pd(OAc)_2$ (4.0 mg, 18 μmol, 5 mol-%) and PPh_3 (14.0 mg, 53.4 μmol) in 3 mL of DMF for 10 min, to the mixture were then added NEt_3 (50.0 mg, 494 μmol) and iodobenzene (102 mg, 500 μmol), and it was stirred at 100 °C for 12 h. After being cooled to ambient temp., the mixture was extracted with pentane (3 × 10 mL), the combined organic phases were washed three times with 10 mL each of water and brine, dried ($MgSO_4$), and the solvent was removed in a rotary evaporator. The residue was subjected to chromatography on silica gel (column 1 × 20 cm, pentane/ether, 15:1). Fraction I: Iodobenzene, not completely evaporated, R_f = 0.90. Fraction II: 54.5 mg (49%) of **10**-Ph as a colorless oil, R_f = 0.31. IR (film): $\tilde{\nu}$ = 3070 cm^{-1}, 2210, 1740 (C=O), 1670 (C=C), 1080, 900, 830, 780, 745, 705, 680. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.04–1.07 (m_c, 4 H, cPr-H), 1.76 (s, 3 H, 3′-H), 3.00 (s, 2 H, 1′-H*), 3.07 (s, 2 H, 1′′-H*), 3.75 (s, 6 H, CH_3O), 7.26–7.28 (m, 3 H, Ar-H), 7.34–7.38 (s, 2 H, Ar-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 2.7 (–, cPr-C), 3.8 (–, cPr-C), 21.4 (+, C-3′), 23.7 (–, C-1′′), 39.0 (–, C-1′), 52.7 (+, CH_3O), 57.2 (C_{quat}, C-1), 83.5 (C_{quat}, C-2′′*), 85.1 (C_{quat}, C-3′′*), 118.8 (C_{quat}, cPr-C*), 122.4 (C_{quat}, C-2′*), 123.4 (C_{quat}, Ar-C*), 127.9 (+, Ar-C), 128.2 (+, Ar-C), 131.6 (+, Ar-C), 171.0 (C_{quat}, CO) ppm. MS (70 eV, EI): *m/z* (%) = 326 (8) [M^+], 294 (70) [$M^+ - CH_4O$], 207 (100) [$M^+ - CH_3CO_2H - CH_3CO_2$], 77 (89) [$C_6H_5^+$]. $C_{20}H_{22}O_4$ (326.4): calcd. C 73.60, H 6.79; found C 73.45, H 6.45. Fraction III: 23.4 mg (21%) of **41**-Ph as a colorless oil; R_f = 0.28. IR (Film): $\tilde{\nu}$ = 3090 cm^{-1}, 1740 (C=O), 1680 (C=C), 1655, 1620 (C=C), 1585, 1080, 990, 920, 900, 830, 750, 740, 705, 650. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.88 (s, 3 H, CH_3), 2.72 (s, 2 H, 2-H), 3.09 (d, ^4J = 1.1 Hz, 2 H, 6-H), 3.62 (s, 6 H, CH_3O), 5.15 (dd, ^2J = 2.2, ^3J = 17.8 Hz, 1 H, CH=C*H*$_2$), 5.42 (dd, ^2J = 2.2, ^3J = 11.2 Hz, 1 H, CH=C*H*$_2$) 6.30 (dd, ^2J = 17.8, ^3J = 11.2 Hz, 1 H, C*H*=CH_2), 6.55 (s, 1 H, C*H*Ph=C), 7.17–7.35 (s, 2 H, Ar-H), 7.40–7.62 (m, 3 H, Ar-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 21.35 (+, CH_3), 31.57 (–, C-2*), 37.49 (–, C-6*), 52.43 (+, OCH_3), 53.99 (C_{quat}, C-1), 119.75 (–, *C*H_2=CH), 126.14 (+, C=*C*H), 127.17 (+, C=*C*H), 127.97 (+, C=CH), 128.82 (+, C=CH), 131.51 (C_{quat}), 132.35 (C_{quat}), 133.33 (C_{quat}), 134.00 (+, C=CH), 137.92 (C_{quat}), 171.20 (C_{quat}, CO) ppm. MS (70 eV, EI): *m/z* (%) = 326 (45) [M^+], 294 (20) [$M^+ - CH_4O$], 207 (100) [$M^+ - CH_3CO_2H - CH_3CO_2$], 77 (55) [$C_6H_5^+$]. $C_{20}H_{22}O_4$ (326.4): calcd. C 73.60, H 6.79; found C 73.25, H 6.23.

2-Cyclopropylidene-6-phenylhex-5-yne (24-Ph): In a screw-cap Pyrex bottle were placed 2-cyclopropylidenehex-5-yne (**24**-H, 460 mg, 3.83 mmol), iodobenzene (1.13 g, 5.54 mmol), triethylamine (602 mg, 5.95 mmol), triphenylphosphane (157 mg, 599 μmol), $Pd(OAc)_2$ (47.0 mg, 209 μmol) in 15 mL of DMF, and the mixture was heated under argon at 100 °C for 20 h. After being cooled to ambient temperature, the mixture was extracted with pentane (5 × 20 mL). The combined organic phases were extracted with 50 mL of water and dried ($MgSO_4$). The solvent was removed in a rotary evaporator at 20 °C and 300 Torr. Chromatography on silica gel (column 3 × 20 cm, pentane) yielded 100 mg (13%) of **24**-Ph as a colorless oil. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.97–1.16 (m_c, 4 H, cPr-H), 1.89 (t, ^4J = 1.5 Hz, 3 H, 1-H), 2.46–2.67 (m_c, 4 H, 3-H, 4-H), 7.25–7.42 (m_c, 5 H, C_6H_5) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 1.4 (–, cPr-C), 3.1 (–, cPr-C), 18.1 (–, C-4), 20.7 (+, C-1), 35.9 (–, C-3), 80.5 (C_{quat}, C-5), 90.5 (C_{quat}, C-6), 116.5 (C_{quat}, cPr-C), 122.7 (C_{quat}, C-1′), 124.1 (C_{quat}, C-2), 127.4 (+, C-4′), 128.1 (+, C-3′), 131.5 (+, C-2′) ppm. MS (70 eV, EI): *m/z* (%) = 195 (46) [M^+ – H], 181 (73) [$M^+ - CH_3$], 115 (100) [$C_9H_7^+$].

Diethyl (*Z*)-4-Ethenyl-5-methyl-3-(4′-methylenedihydrofuran-3′-ylidene)cycloheptyl-4-enedicarboxylate (48-H): A mixture of tris(dibenzylideneacetone)dipalladium–chloroform complex (6.8 mg (6.6 μmol), tris(*o*-tolyl)phosphane (4.0 mg, 13 μmol), of acetic acid (2 μL, 2 mg, 30 μmol), *tert*-butyl acrylate (200 mg, 1.56 mmol) and diethyl (3′′′-cyclopropylidenebutyl)[4′-(prop-2′′-ynyloxy)but-2′-ynyl]malonate (**33**-H, 90.0 mg, 250 μmol) in 50 mL of benzene was stirred under argon for 72 h. The solvent was removed under reduced pressure and the residue subjected to chromatography on silica gel (column 2 × 20 cm, light petroleum/ether, 20:1) to yield 39 mg (43%) of **48**-H as a yellowish oil, R_f = 0.25. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.20 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.25 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.85 (s, 3 H, CH_3C=C), 1.93–2.14 (m, 4 H, 6-H, 7-H), 2.80 (s, 2 H, 2-H), 4.02–4.27 (m, 4 H, OCH_2CH_3), 4.37 (br. s, 2 H, CH_2O), 4.47 (d, ^2J = 12.6 Hz, 1 H, CH_2O), 4.63 (d, ^2J = 12.6 Hz, 1 H, CH_2O), 4.90 (dd, ^2J = 1.8, ^3J = 10.4 Hz, 1 H, CH=C*H*$_2$), 4.93 (s, 1 H, CH_2), 5.02 (dd, ^2J = 1.8, ^3J = 17.1 Hz, 1 H, CH=C*H*$_2$), 5.10 (s, 1 H, CH_2), 6.45 (dd, ^3J = 17.1, ^3J = 10.4 Hz, 1 H, C*H*=CH_2) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 13.9 (+, OCH_2CH_3), 19.1 (+, CH_3C=C), 29.5 (–, C-7*), 32.0 (–, C-2*), 36.8 (–, C-6*), 56.8 (C_{quat}, C-1), 61.4 (–, OCH_2CH_3), 72.0 (–, CH_2O), 73.8 (–, CH_2O), 107.9 (–, CH_2=CH), 113.1 (–, CH_2=C), 128.3 (C_{quat}, C=C), 129.6 (+, CH=CH_2), 134.0 (C_{quat}, C=C), 135.8 (C_{quat}, C=C), 136.7 (C_{quat}, C=C), 142.9 (C_{quat}, C=C), 171.1 (C_{quat}, CO), 171.8 (C_{quat}, CO) ppm. MS (70 eV, EI): *m/z* (%) = 360 (100) [M^+], 332 (21) [M^+ – CO], 314 (32) [$M^+ - C_2H_5OH$], 287 (26) [$M^+ - C_2H_5CO_2$], 257 (23), 241 (20), 229 (14), 213 (44), 183 (39), 173 (28), 127 (21), 91 (14). $C_{21}H_{28}O_5$ (360.5): 360.1936 (correct HRMS).

Diethyl (3′′′-Cyclopropylidenebutyl)[4′-(3′′-phenylprop-2′′-ynyloxy)but-2′-ynyl]malonate (33-Ph): According to GP 4, a mixture of diethyl (3′′-cyclopropylidenebutyl)[4′-(prop-2′′-ynyloxy)but-2′-ynyl]malonate (**33**-H, 177 mg, 491 μmol), $Pd(OAc)_2$ (6.2 mg, 28 μmol, 6 mol-%), PPh_3 (21.9 mg, 83.5 μmol), NEt_3 (101 mg, 1.00 mmol) and iodobenzene (102 mg, 500 μmmol) was heated in 3 mL of DMF at 100 °C for 12 h. After cooling to ambient temp., the mixture was extracted with pentane (3 × 10 mL), the combined organic phases were washed three times with 10 mL each of water and brine, dried ($MgSO_4$), and the solvent was removed in a rotary evaporator. The residue was subjected to chromatography on silica gel (column 1 × 20 cm, pentane/ether, 15:1). Fraction I: Iodobenzene, not completely evaporated, R_f = 0.90. Fraction II: 94.5 mg (44%) of **33**-Ph as a colorless oil, R_f = 0.31. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.88–1.15 (m, 4 H, cPr-H), 1.20 (t, ^3J = 7.1 Hz, 6 H, OCH_2CH_3), 1.76 (t, ^4J = 1.5 Hz, 3 H, 4′′′-H), 1.99–2.10 (m, 2 H, 1′′′-H), 2.16–2.23 (m, 2 H, 2′′′-H), 2.84 (t, ^4J = 2.1 Hz, 2 H, 1′-H), 4.10–4.18 (m, 8 H, OCH_2CH_3, 1′′-H, 4′-H), 7.10–7.29 (m, 5 H, Ar-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 1.38 (–, C-cPr), 2.63 (–, C-cPr), 13.89 (+, OCH_2CH_3), 20.34 (–, C-1′′′), 22.78 (+, C-4′′′), 29.85 (–, C-2′′′), 30.89 (–, C-1′), 55.82 (C_{quat}, C-1), 55.99 (–, CH_2O), 56.51 (–, CH_2O), 61.32 (–, OCH_2CH_3), 74.61 (C_{quat}, C≡C), 77.77 (C_{quat}, C-3′′), 78.83 (C_{quat}, C≡C), 82.03 (C_{quat}, C≡C), 116.13 (C_{quat}, C-cPr), 122.77 (–, C-3′′′), 128.02 (+, C–Ar), 128.43 (+, C–Ar), 131.09 (+, C–Ar), 149.88 (C_{quat}), 170.88 (C_{quat}, CO), 170.07 (C_{quat}, CO) ppm.

Dimethyl (2′′′-Cyclopropylidenepropyl)[4′-(3′′-phenylprop-2′′-ynyloxy)but-2′-ynyl]malonate (38-Ph): According to GP 4, a mixture of dimethyl (2′′′-cyclopropylidenepropyl)[4′-(prop-2′′-ynyloxy)-but-2′-ynyl]malonate (**38**-H, 177 mg, 556 μmol), $Pd(OAc)_2$ (6.2 mg, 28 μmol, 5 mol-%), PPh_3 (21.9 mg, 83.5 μmol), NEt_3 (101 mg, 1.00 mmol) and iodobenzene (102 mg, 500 μmol) was heated in 3 mL of DMF at 100 °C for 12 h. After cooling to ambient temp., the mixture was extracted with pentane (3 × 10 mL), the combined organic phases were washed three times with 10 mL each of water and brine, dried ($MgSO_4$), and the solvent was removed in a rotary evaporator. The residue was subjected to chromatography on silica gel (column 1 × 20 cm, pentane/ether, 15:1). Fraction I: Iodobenzene R_f = 0.90. Fraction II: 60 mg (30%) of **38**-Ph as a colorless oil, R_f = 0.31. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.00–1.16 (m, 4 H, cPr-H), 1.73 (s, 3 H, 3′′′-H), 2.78 (s, 2 H, 1′-H), 3.04 (s, 2 H, 1′′′-H), 3.70 (s, 6 H, OCH_3), 4.32 (s, 2 H, 1′′-H), 4.45 (s, 2 H, 4′-H), 7.12–7.32 (m, 5 H, Ar-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 2.7 (–, cPr-C), 3.8 (–, cPr-C), 21.4 (+, C-3′′′), 23.2 (–, C-1′), 39.0 (–, C-1′′′), 52.7 (+, OCH_3), 56.8 (–, CH_2O), 56.9 (–, CH_2O), 62.0 (C_{quat}, C-1), 77.5 (C_{quat}, C≡C), 78.3 (C_{quat}, C≡C), 78.9 (C_{quat}, C≡C), 82.7 (C_{quat}, C≡C), 118.7 (C_{quat}, cPr-C), 122.4 (C_{quat}, C-2′′′), 128.3 (+, Ar-C), 128.5 (+, Ar-C), 131.8 (+, Ar-C), 149.2 ($C_{quat,}$ Ar-C), 170.9 (C_{quat}, CO) ppm.

8-Ethenyl-9-methyl-4-methylene-6-oxaspiro[2.6]non-8-ene (67) and 1,5-Bis(3′-cyclopropylidene-2′,2′-ethanobutoxy)-4-methylenepent-2-yne (59). a) A mixture of tris(dibenzylideneacetone)dipalladium–chloroform complex (29.8 mg, 28.8 μmol), tris(*o*-tolyl)phosphane (17.5 mg, 57.5 μmol), acetic acid (2 μL, 2 mg, 0.03 mmol) and [1′-(1′′-cyclopropylideneethyl)cyclopropylmethyl] (prop-2′′-ynyl) ether (**20**-H, 203 mg, 1.15 mmol) in 7 mL of benzene was stirred under argon for 12 h. Chromatography on silica gel (column 2 × 20 cm, pentane → pentane/ether, 20:1) gave two fractions. Fraction I: 35.0 mg (17%) of **67** as a colorless oil, R_f = 0.30 (pentane/ether, 40:1). IR (film): $\tilde{\nu}$ = 3060 cm^{-1}, 1665 (C=C), 1650, 1090, 990, 885, 755, 740, 710. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.85–1.02 (m, 4 H, cPr-H), 1.72 (s, 3 H, CH_3), 4.26 (s, 2 H, 7-H), 4.53 (dd, ^4J = 1.0, ^4J = 1.0 Hz, 2 H, 5-H), 4.90 (t, ^4J = 1.0 Hz, 2 H, CH_2C=C<), 5.01 (d, ^3J = 11.3 Hz, 1 H, CH=CH_2), 5.15 (d, ^3J = 17.5 Hz, 1 H, CH=CH_2), 6.63 (dd, ^3J = 17.5, ^3J = 11.3 Hz, 1 H, CH=CH_2) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$, DEPT): δ = 14.2 (–, CH_2), 16.1 (+, CH_3), 29.5 (C_{quat}, cPr-C), 66.4 (–, OCH_2), 74.6 (–, OCH_2), 111.9 (–, C=CH_2), 112.4 (–, C=CH_2), 132.8 (C_{quat}, C=C), 134.6 (+, CH=C), 139.6 (C_{quat}, C=C), 149.1 (C_{quat}, C=C) ppm. MS (70 eV, EI): *m*/*z* (%) = 176 (100) [M$^+$], 148 (65) [M$^+$ – C_2H_4]. $C_{12}H_{16}O$ (176.3): calcd. C 81.77, H 9.15; found C 81.56, H 9.20. Fraction II: 110 mg (54%) of **59** as a colorless oil, R_f = 0.35 (pentane/ether, 20:1). IR (film): $\tilde{\nu}$ = 3117 cm^{-1}, 3038, 2944, 2856, 2115 (C≡C), 1675 (C=C), 1456, 1372, 1281, 1202, 1011, 980, 736, 526. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.53–0.59 (m, 4 H, cPr-H), 0.73–0.87 (m, 8 H, cPr-H), 1.09–1.17 (m, 4 H, cPr-H), 2.13 (br. s, 6 H, CH_3), 3.45 (s, 2 H, CH_2O), 3.51 (s, 2 H, CH_2O), 3.94 (s, 2 H, C=CCH_2O), 4.24 (s, 2 H, C≡CCH_2O), 5.43 (s, 1 H, CH_2=C), 5.45 (s, 1 H, CH_2=C) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 0.2 (–, 4 × cPr-C), 3.9, 4.1 (–, cPr–C), 10.3, 10.4 (–, cPr–C), 19.0, 19.1 (+, C-4′), 24.9, 25.2 (C_{quat}, C-2′), 57.8 (–, CH_2O), 72.1 (–, CH_2O), 75.0 (–, CH_2O), 75.7 (–, CH_2O), 84.4 (C_{quat}, C-2*), 86.1 (C_{quat}, C-3*), 116.8, 117.0 (C_{quat}, C-3′*), 121.5 (–, CH_2=C), 124.1, 124.3 (C_{quat}, cPr-C), 128.2 (C_{quat}, C-4) ppm. MS (70 eV, EI): *m*/*z* (%): = 320 (9), 305 (32), 79 (100). **b)** A mixture of tris(dibenzylideneacetone) dipalladium–chloroform complex (29.8 mg, 28.8 μmol), tris(*o*-tolyl) phosphane (17.5 mg, 57.5 μmol), acetic acid (2 μL, 2 mg, 0.03 mmol) and [1′-(1′′-(cyclopropylideneethyl)cyclopropylmethyl] (prop-2′′-ynyl) ether (**20**-H, 203 mg, 1.15 mmol) in 100 mL of benzene was stirred under argon for 36 h. Chromatography on silica gel (column 2 × 20 cm, pentane → pentane/ether, 20:1) gave 120 mg (59%) of **67** as a colorless oil.

Diethyl 13-Methyl-3,5,15,17-tetraoxo-4,16-diphenyl-2,4,6,14,16,18-hexaazapentacyclo[11.6.1.0^{2,6}.0^{8,20}.0^{14,18}]eicosa-8(20)-ene-10,10-dicarboxylate (69): To a solution of diethyl 4-ethenyl-5-methyl-3-methylenecyclohept-4-ene-1,1-dicarboxylate (**42**, 1.25 g, 4.28 mmol) and phenylurazole (1.73 g, 11.92 mmol) in 75 mL of dichloromethane was added at –10 °C lead(IV) acetate (4.57 g, 11.92 mmol, 95% + 5% AcOH) within 10 min. After an additional 30 min, the mixture was diluted with 500 mL of diethyl ether, filtered, and the filtrate washed three times with 100 mL each of water and brine, then dried ($MgSO_4$), and filtered while hot. After removal of the solvent, the residue was recrystallized from hexane/dichloromethane to give 2.18 g (81%) of **69** as light yellow crystals, m.p. 157–163 °C. IR (KBr): $\tilde{\nu}$ = 3455 cm^{-1}, 2979, 1715, 1410, 1254, 1202, 1134, 768, 689, 646. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.21 (t, ^3J = 7.1 Hz, 3 H, CH_3), 1.22 (t, ^3J = 7.1 Hz, 3 H, CH_3), 2.05 (dt, *J* = 14.1, *J* = 2.8 Hz, 1 H, CH), 2.30 (dt, *J* = 15.2, *J* = 3.1 Hz, 1 H, CH), 2.57 (dd, *J* = 16.3, *J* = 2.0 Hz, 1 H, CH), 2.64 (dq, *J* = 12.7, *J* = 2.5 Hz, 1 H, CH), 3.12 (dt, *J* = 16.0, *J* = 1.2 Hz, 1 H, CH), 3.39 (dd, *J* = 11.3, *J* = 9.2 Hz, 1 H, CH), 3.49 (ddd, *J* = 14.3, *J* = 5.0, *J* = 3.2 Hz, 1 H, CH), 4.0–4.24 (m, 6 H, CH_2, CH), 4.64 (dq, *J* = 9.1, *J* = 5.6 Hz, 1 H, CH), 4.93–4.95 (m, 1 H, CH), 7.15–7.25 (m, 10 H, Ar-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 14.0 (+, OCH_2CH_3), 14.1 (+, CCH_3), 28.7 (–, CH_2), 30.4 (–, CH_2), 35.1 (–, CH_2), 44.0 (–, CH_2), 49.7 (+, CH), 55.5 (–, CH_2), 61.9 (–, CH_2), 62.2 (–, CH_2), 69.7 (C_{quat}, C-10), 125.4 (+, Ar-Cr), 125.8 (+, Ar-C), 126.4 (C_{quat}, Ar-C), 128.4 (+, Ar-C), 129.7 (+, Ar-C), 129.3 (+, Ar-C), 130.9 (C_{quat}, Ar-C*), 131.0 (C_{quat}, C=C*), 133.6 (C_{quat}, C=C), 151.2 (C_{quat}, NCO), 151.7 (C_{quat}, NCO), 153.0 (C_{quat}, NCO), 169.4 (C_{quat}, CO_2), 171.0 (C_{quat}, CO_2) ppm. MS (70 eV, EI): *m*/*z* (%) = 642 (8) [M$^+$], 466 (23), 452 (41), 129 (72), 115 (100), 91 (55). $C_{33}H_{34}N_6O_8$ (642.2): calcd. C 61.67, H 5.33, N 13.08; found C 61.75, H 5.52, N 12.92.

Diethyl 8,8,9,9-Tetracyano-7-methyl-2-methylenebicyclo[5.4.0]undec-11-ene-4,4-dicarboxylate (70): To a solution of the ester **42** (800 mg, 2.87 mmol) in 50 mL of benzene was added tetracyanoethylene (290 mg, 2.29 mmol), and the mixture stirred for 15 h at ambient temperature. The solvent was removed under reduced pressure, and the residue recrystallized from benzene to give 533 mg (55%) of **70** as colorless crystals, m.p. 134 °C. IR (KBr): $\tilde{\nu}$ = 2979 cm^{-1}, 2914, 1772, 1715, 1599, 1504, 1410, 1290, 1254, 1202, 1134, 768, 689, 646. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.22 ppm (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.25 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.65 (s, 3 H, CH_3), 1.90–1.96 (ddd, *J* = 1.6, 8.5, 16.3 Hz, 1 H, 6*-H), 2.22–2.28 (ddd, *J* = 1.6, 10.6, 17.6 Hz, 1 H, 6*-H), 2.34–2.42 (m, 1 H, 5*-H), 2.73 (d, *J* = 15.0 Hz, 1 H, 3-H), 3.00 (d, *J* = 15.0 Hz, 1 H, 3-H), 3.17 (dd$_c$, *J* = 18.8, 3.5 Hz, 1 H, 10-H), 3.21 (dd$_c$, *J* = 18.8, 4.5 Hz, 1 H, 10-H), 4.12–4.23 (m, 4 H, OCH_2CH_3), 5.09 (d, *J* = 1.3 Hz, 1 H, =CH_2), 5.13 (d, *J* = 1.3 Hz, 1 H, =CH_2), 5.63 Hz (dd$_c$, *J* = 4.5, 3.4 Hz, 1 H, 11-H) ppm. ^{13}C NMR (150.82 MHz, $CDCl_3$, additional DEPT): δ = 13.90 ppm (+, OCH_2CH_3), 13.95 (+, OCH_2CH_3), 22.9 (+, CH_3), 27.4 (–, C-5), 32.6 (–, C-10), 34.0 (–, C-3), 36.4 (C_{quat}, C-7), 38.6 (–, C-6), 44.6 (C_{quat}, C-8*), 49.3 (C_{quat}, C-9*), 56.3 (C_{quat}, C-4), 61.82 (–, OCH_2CH_3), 61.84 (–, OCH_2CH_3), 110.2 (C_{quat},CN), 110.4 (C_{quat}, CN), 111.86 (C_{quat}, CN), 111.93 (C_{quat}, CN), 116.0 (+, C-11), 120.7 (–, =CH_2), 142.8 (C_{quat}, C-2*), 144.1 (C_{quat}, C-1*) 170.5 (–, COO), 170.7 (–, COO) ppm. MS (70 eV, EI): *m*/*z* (%) = 420 (27) [M$^+$], 375 (6) [M$^+$ – C_2H_5O], 347 (27) [M$^+$ – $CO_2C_2H_5$], 346 (33) [M$^+$ – C_2H_5OH – CO], 317 (33), 301 (46), 300 (100) [M$^+$ – 2 C_2H_5OH – CO], 273 (11), 246

(7). $C_{23}H_{24}N_4O_4$ (372.5): calcd. C 65.70, H 5.75, N 13.33; found C 66.04, H 5.83, N 13.18.

Supporting Information (see footnote on first page of this article): Detailed experimental procedures for cyclization precursors described in this article (19 pages).

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