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Versatile Synthesis of Bicyclo[4.3.0]nonenes and Bicyclo[4.4.0]decenes by a Domino Heck-Diels-Alder Reaction

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Abstract: Various 2-bromo-1,6- and 2-bromo-1,7-dienes were cyclized under palladium catalysis producing vicinal exodimethylenecycloalkanes which reacted with dienophiles (either present during the cyclization or added afterwards in a one-pot process) to give bicyclo[4.3.0]nonene and bicyclo[4.4.0]-decene derivatives in good to excellent yields. Among the examples reported are the first cases of intramolecular Heck reactions with a (bromomethylene)cyclopropane starter or/and a methylenecyclopropane terminator which occur without ring opening of the cyclopropyl group.

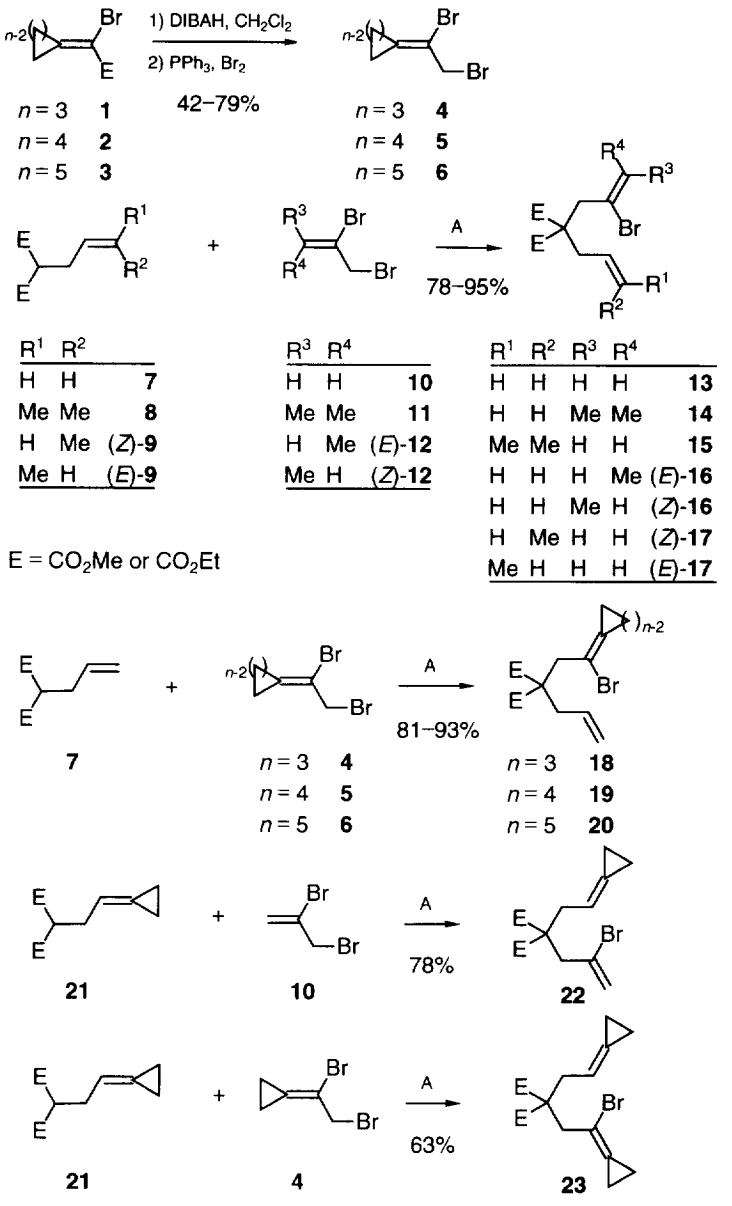
Over the last decade, palladium-catalyzed reactions have emerged as extremely versatile methods for the preparation of carbo- and heterocyclic systems with varying degrees of complexity.[1-8] An interesting sequence for the construction of bicyclic systems containing at least one six-membered ring arises when an intramolecular Heck reaction or palladium-catalyzed enyne cycloisomerization to give a vicinal exodimethylenecycloalkane is immediately followed by a Diels-Alder reaction.[9-10] The scope and limitations of the two possible variants of this sequential reaction – the one-[9] or two-pot procedures[10] – have been tested and are reported here.

Bromodienes **13–20**, **22**, **23** were synthesized by a straightforward sequential alkylation of diethyl or dimethyl malonate with allyl bromide or the appropriate substituted allyl bromide.[11] Allyl bromide, 2,3-dibromoprop-1-ene (**10**), prenyl bromide are commercially available and (*E*)/(*Z*)-1,2-dibromobut-2-ene [(*E*)/(*Z*)-**12**],[12] and 1,2-dibromo-3-methylbut-2-ene (**11**)[13] are known compounds, 1,2-dibromo-1-cyclopropylidenethane (**4**), 1,2-dibromo-1-cyclobutylidenethane (**5**), and 1,2-dibromo-1-cyclopentylidenethane (**6**) were prepared from the corresponding 2-bromo-2-cycloalkylideneacetic acid esters **1**, **2**, and **3**, respectively, by reduction with DIBAH[14] and subsequent conversion of the alcohols to the bromides with PPh_3/Br_2.[15] The α-bromoesters **2** and **3** were synthesized from the cyclic ketones by Horner-Wadsworth-Emmons reactions adopting the known procedure for the preparation of 2-bromo-2-cyclopropylideneacetate **1**.[16]

Table 1. Preparation of bromodienes **13–20**, **22**, and **23**.

Allylmalonate	Allyl Bromide	Product	E	Yield (%)	Mp[a] [°C]
7	**10**	**13**	CO_2Et	78	oil
7	**11**	**14**	CO_2Me	82	oil
8	**10**	**15**	CO_2Me	>95	65
7	(*E*)/(*Z*)-**12**	(*E*)/(*Z*)-**16**	CO_2Me	86	oil
(*E*)/(*Z*)-**9**	**10**	(*E*)/(*Z*)-**17**	CO_2Me	87	oil
7	**4**	**18**	CO_2Me	87	oil
7	**5**	**19**	CO_2Me	93	oil
7	**6**	**20**	CO_2Me	81	oil
21	**10**	**22**	CO_2Me	78	oil
21	**4**	**23**	CO_2Me	63	oil

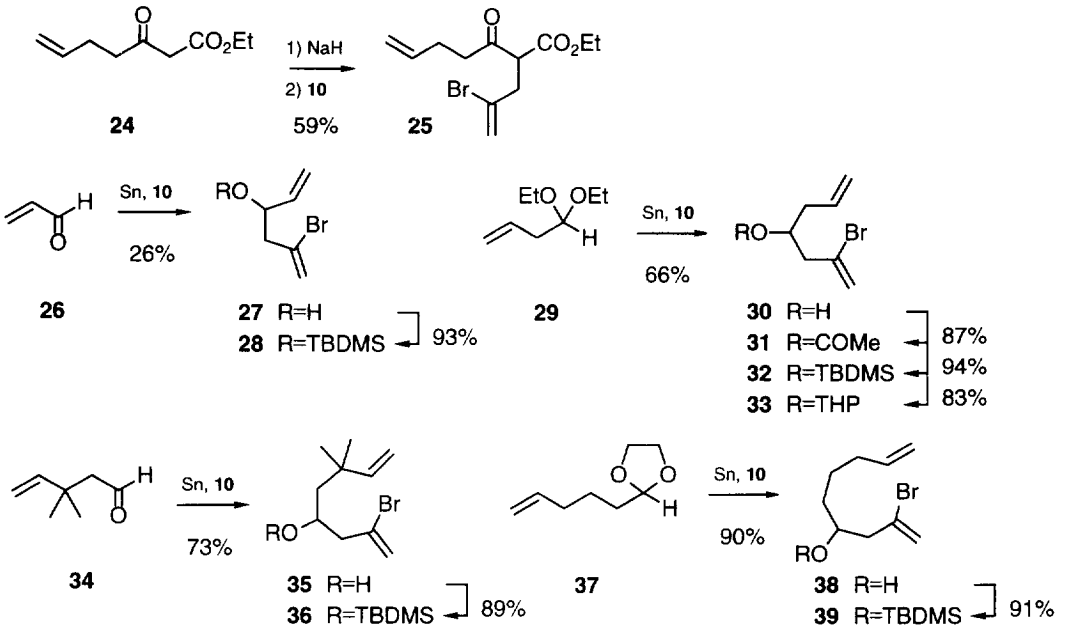
[a] Uncorrected.



Scheme 1. A: NaH (1.01 eq), THF, 0 °C→25 °C. E = CO_2Me or CO_2Et. For further details see **Table 1**.

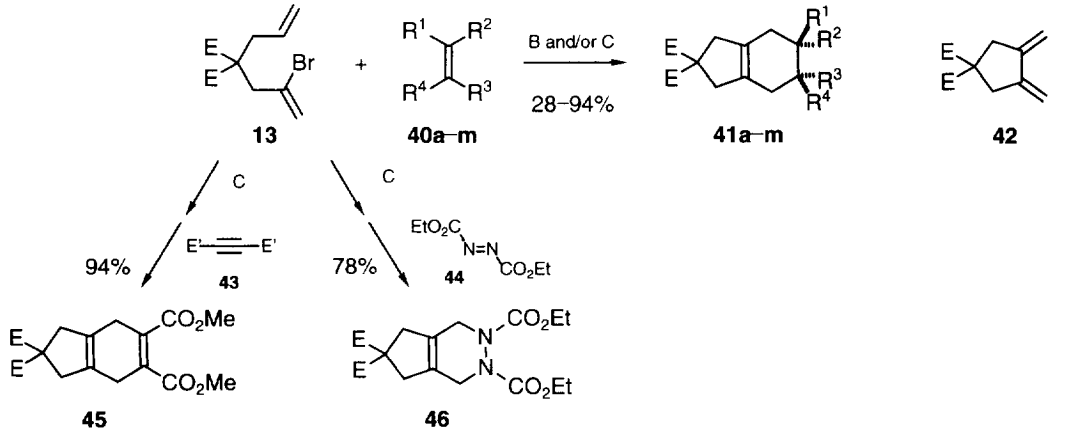
The 2-bromo-1,8-diene **25** was prepared from the known β-ketoester **24**[17] by alkylation with 2,3-dibromoprop-1-ene (**10**).

The oxygen-functionalized bromodienes **27**, **30**, **35**, and **38** were synthesized by tin-promoted coupling[18] of the aldehydes **26**, **34** or dialkyl acetals **29**, **37**, respectively, with 2,3-dibromoprop-1-ene (**10**). Protection of the hydroxy groups by standard methods[19] gave the tethered derivatives **28**, **31**–**33**, **36**, and **39** (**Scheme 2**).



Scheme 2.

Following the previously reported protocol,[9] various dienophiles were reacted with the terminally unsubstituted 2-bromo-1,6-diene **13**. Good to excellent yields were generally obtained (**Table 2**). While the cyclopropylideneacetates **40i**[20] and **40j**[21] gave the spirocyclopropane derivatives **41i** and **41j** in very good yields in both the one-step and the two-step procedure, strained methyl dimethylcyclopropene-carboxylate (**40m**)[22] and 1,2-dicyanocyclobut-1-ene (**40l**)[23] gave the expected tricyclic products **41m** and **41l** in only moderate yields (**Table 2**). These yields, however, could be increased by performing the second step under high pressure (10 kbar).



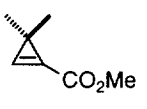
Scheme 3. B: $Pd(OAc)_2$, PPh_3, Ag_2CO_3, MeCN, 90 °C (one pot – one step). C: $Pd(OAc)_2$, PPh_3, Ag_2CO_3, MeCN, 90 °C (one pot – two steps). E = CO_2Et, E' = CO_2Me. For further details see **Table 2**.

Table 2. Heck-Diels-Alder products **41–83** prepared, yields in %; see **Schemes 3–7.**

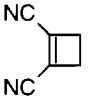
Bromo-diene[a]	Dieno-phile	Product[b]	R^1	R^2	R^3	R^4	R^5	Method[c]	One Step	Two Step
13	**40a**	**41a**	CN	H	H	H	–	B,C	83	70
13	**40b**	**41b**	COMe	H	H	H	–	B,C	81	70
13	**40c-Me**	**41c-Me**	CO_2Me	H	H	H	–	B,C	93	60
13	**40c-R***	**41c-R***[d]	CO_2R*[e]	H	H	H	–	C	–[f]	55
13[g]	**40c-X***	**41c-X***[d,g]	COX*[h]	H	H	H	–	C	–	52
13	**40d**	**41d**	CN	Cl	H	H	–	B	74	–[f]
13	**40e-Me**	**41e-Me**	CO_2Me	H	CO_2Me	H	–	B	85	–
13	**40e-Et**	**41e-Et**	CO_2Et	H	CO_2Et	H	–	D	88	–
13	**40e-Et**	**41e-Et**	CO_2Et	H	CO_2Et	H	–	B	94	–
13	**40f-Me**	**41f-Me**	CO_2Me	H	H	CO_2Me	–	B	93	–
13	**40g**	**41g**	CN	CN	CN	CN	–	C	–	79
13	**40h-Et**	**41h-Et**	CO_2Et	CO_2Et	CO_2Et	CO_2Et	–	B,C	78	48
13	**40i**	**41i**	$-CH_2-CH_2-$		CO_2Me	H	–	B,C	83	79
13	**40j**	**41j**	$-CH_2-CH_2-$		CO_2Me	Cl	–	B,C	83	61
13	**40k**	**41k**[d,i]	H	$-CH_2-CH_2-CO-$		H	–	C	–	30[j]
13	**40l**	**41l**	CN	$-CH_2-CH_2-$		CN	–	C	–	28 (71)[k]
13	**40m**	**41m**	H	$-C(CH_3)_2-$		CO_2Me	–	C	–	48 (60)[k]
13	**43**	**45**	–	–	–	–	–	C	–	94
13	**44**	**46**	–	–	–	–	–	C	–	78
13	**49**[l]	**50**	–	–	–	–	–	B	71	–
13	**49**[m]	**52**	–	–	–	–	–	B	43	–
13	**53**[n]	**54**	–	–	–	–	–	B	78	–
15[g]	**40c-Me**	**63c-Me**[g]	CO_2Me	H	H	H	–	F	24[o]	–
(*E*)-**16**[g]	**40c-Me**	**55c-Me**[g,p]	CO_2Me	H	H	H	–	B	60[q]	–
(*Z*)-**16**[g]	**40c-Me**	**55c-Me**[g,p]	CO_2Me	H	H	H	–	F	48[r]	–
17[g]	**40c-Me**	**55c-Me**[g,p]	CO_2Me	H	H	H	–	B	35	–
17[g]	**40e-Et**	**55e-Et**[g,s]	CO_2Et	H	CO_2Et	H	–	B	24[t]	–
22[g]	**40b**	**65b**[g]	COMe	H	H	H	–	B	86	–
22[g]	**40c-Me**	**65c-Me**[g]	CO_2Me	H	H	H	–	B	86	–
18[g]	**40c-*t*Bu**	**65c-*t*Bu**[d,g]	CO_2tBu	H	H	H	–	B	68	–
18[g]	**40c-X***	**65c-X***[d,g]	COX*[h]	H	H	H	–	C	–	57
19[g]	**40c-Me**	**66c-Me**[d,g]	CO_2Me	H	H	H	–	F	18	–
		67c-Me[d,g]	CO_2Me	H	H	H	–		32[u]	–
20[g]	**40c-Me**	**68c-Me**[d,g]	CO_2Me	H	H	H	–	F	43[v]	–
23[g]	**40e-Et**	**69e-Et**[d,g]	CO_2Et	H	CO_2Et	H	–	B	30	–
30	**40c-Me**	**77c-Me**[d,p]	CO_2Me	H	H	H	H	B	87	–
31	**40c-Me**	**78c-Me**[p]	CO_2Me	H	H	H	COMe	B	87	–
32	**40c-H**	**79c-H**[p]	CO_2H	H	H	H	TBDMS[w]	B	77	–
32	**40c-*t*Bu**	**79c-*t*Bu**[d,p]	CO_2tBu	H	H	H	TBDMS	B	73	–
32	**40f-Me**	**79f-Me**[x]	CO_2Me	H	H	CO_2Me	TBDMS	B	80	–
33	**40c-Me**	**80c-Me**[y]	CO_2Me	H	H	H	THP[z]	B	77	–
33	**40n-Me**	**80n-Me**	CO_2Me	Me	H	H	THP	B,C	86	87
36	**40c-Me**	**82c-Me**	CO_2Me	H	H	H	TBDMS	B,C	56	67
		83c-Me	CO_2Me	H	H	H	TBDMS			

Table 2, continued: [a] E = CO_2Et, unless otherwise stated. – [b] Satisfactory microanalyses were obtained: C ± 0.40, H ± 0.32. – [c] B: $Pd(OAc)_2$, PPh_3, MeCN, Ag_2CO_3, 90 °C, 45 min (one pot – one step). C: $Pd(OAc)_2$, PPh_3, MeCN, Ag_2CO_3, 1.) 90 °C, 45 min, 2.) 50 °C, 45 min (one pot – two steps). D: $Pd(OAc)_2$, dmphen, MeCN, Ag_2CO_3, 90 °C, 45 min. F: $Pd(OAc)_2$, PPh_3, MeCN, K_2CO_3, 90 °C, 45–180 min. – [d] Correct HRMS. – [e] R* = (*R*)-Myrtenyl. – [f] Not carried out, unless otherwise stated. – [g] E = CO_2Me (see **Table 1**). – [h] X* = Camphorsultam. – [i] As a 1:1 mixture of (*Z*)- and (*E*)-**41k**. – [j] In the presence of 1.0 equiv. of $AlCl_3$. – [k] Diels-Alder reaction at 10 kbar, 25 °C, 3 d. – [l] 0.5 Equiv. of **49** was used. – [m] 2.5 Equiv. of **49** was used. – [n] 1.2 Equiv. of **53** was used. – [o] 180 min; together with unreacted **15** (22%) and isomerized 1,3-diene **64** (44%). – [p] As a 1:2 mixture of diastereomers. – [q] Together with 18% of unreacted (*E*)-**16**. – [r] 90 min, together with 24% of isomerized 1,3-diene **59**. – [s] As a 1:1.8 mixture of diastereomers. – [t] Together with 11% of unreacted **17**. – [u] 90 min, together with 15% of **74**. – [v] Together with 45% of **75**. – [w] TBDMS = (*t*Bu)Me_2Si. – [x] As a 1:4 mixture of diastereomers. – [y] As a mixture of four diastereomers. – [z] THP = 2-tetrahydropyranyl.

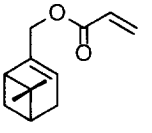
Chiral, non-racemic dienophiles were briefly examined: Reaction of **13** with (*R*)-myrtenyl acrylate (**40c-R***)[24] and the acryloylcamphorsultam **40c-X***[25] according to the two-step procedure gave the bicycles **41c-R*** and **41c-X*** with diastereomeric excesses of 82% and >95%, respectively.



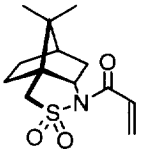
40m



40l

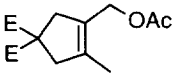


40c-R*

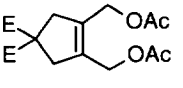


40c-X*

The effects of ligands derived from 1,10-phenanthroline have been compared to those of triphenylphosphane. The parent 1,10-phenanthroline completely suppressed the intramolecular Heck reaction. However, 2,9-dimethyl-1,10-phenanthroline (dmphen), which has so far been used in Heck arylations only,[26] under standard conditions [6 mol% $Pd(OAc)_2$, 10 mol% dmphen, 1.2 equiv. Ag_2CO_3] in the presence of **40e-Et** gave the Heck-Diels-Alder product **41e-Et** in 88% yield together with 12% of the formal 1,4-addition product **47** of acetic acid to the 1,3-diene **42**. Substituting silver carbonate by silver acetate or adding one equivalent of sodium acetate did not increase the yield of **47**. The formation of this compound was not observed with triarylphosphane ligands. In the presence of one equivalent of acetic acid, but without a dienophile, the 1,4-diacetoxylated compound **48**[27] was isolated in 10% yield together with the 1,3-diene **42** (78%). The yields of these products were approximately proportional to the amount of palladium acetate used.

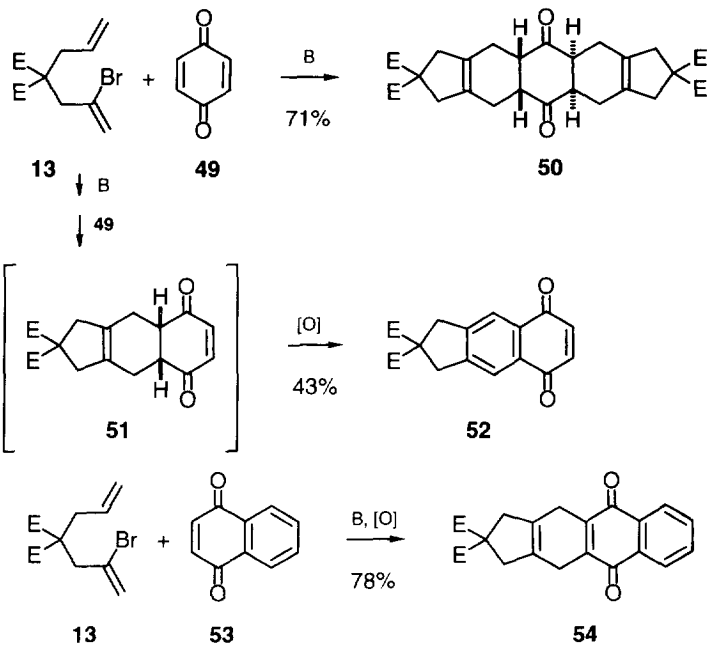


47



48

When 0.5 equiv. of *p*-benzoquinone (**49**) was used with **13**, the linearly annelated pentacycle **50** was isolated in 71% yield along with a trace of the tricyclic product **52**. Compound **52** presumably arises from the oxidation of the initially formed monocycloadduct **51** by *p*-benzoquinone. This was confirmed by the exclusive formation of **52** in an isolated yield of 43% when 2.5 equivalents of *p*-benzoquinone (**49**) were used. 1,4-Naphthoquinone (**53**) as a dienophile led to the tetracycle **54** (**Scheme 4**). The oxidation presumably took place during workup and purification by contact with air.



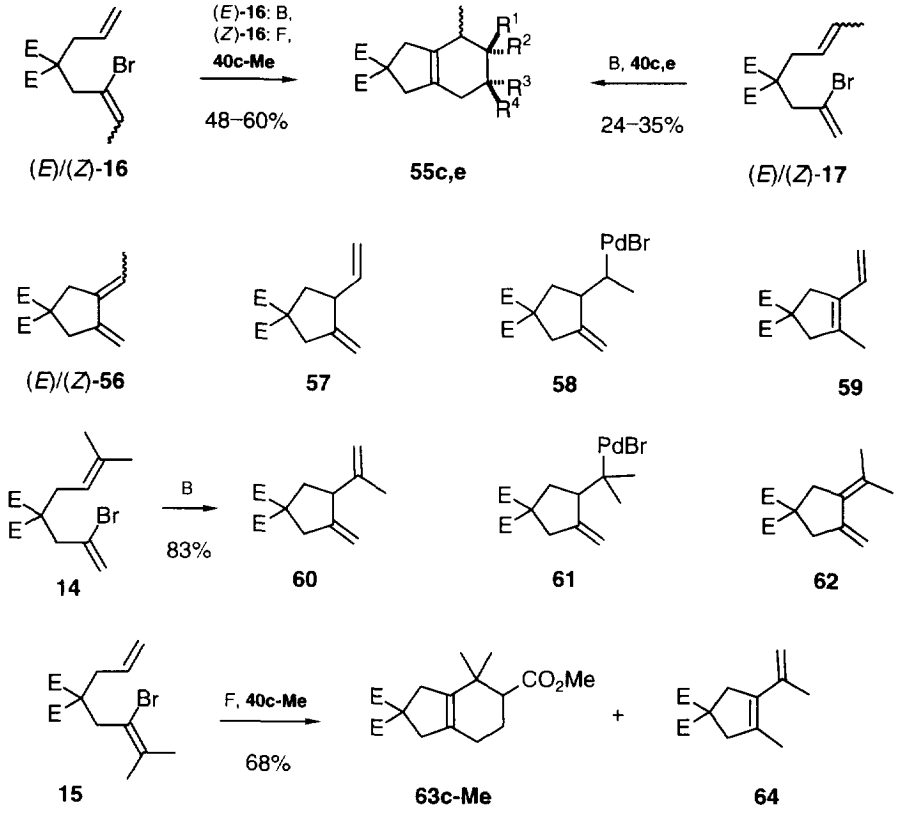
Scheme 4. B: $Pd(OAc)_2$, PPh_3, Ag_2CO_3, MeCN, 90 °C (one step).
E = CO_2Et. For further details see **Table 2**.

When the 2-bromo-1,6-dienes *(E)*/*(Z)*-**17**, which correspond to compound **13** with a methyl group on the alkene moiety, were treated in the usual manner [$Pd(OAc)_2$, PPh_3, Ag_2CO_3 plus a suitable dienophile **40**], the expected bicycles **55** were isolated only in moderate yields (24–35%) along with the known 1,4-diene **57**[28] (36–59%). Apparently, the σ-palladium bromide intermediate **58** is approximately twice as likely to undergo β-elimination to give **57** rather than the desired 1,3-diene *(E)*/*(Z)*-**56**. The use of Wilkinson's catalyst $Rh(PPh_3)_3Cl$ instead of $Pd(OAc)_2/PPh_3$[29] did not alter this ratio to a great extent. With a *gem*-dimethyl group on the alkene moiety as in **14**, the resulting σ-palladium species **61** underwent β-elimination in the undesired direction to give exclusively the 1,4-diene **60**.[30]

The same bicycles **55** were also obtained from the isomeric 3-bromo-2,7-diene *(E)*-**16**. With *(Z)*-**16** and the *gem*-dimethyl derivative **15** only unreacted starting material could be isolated when methods B, C, or D, i. e. silver carbonate as base, were used.[31] Since *(E)*-**16** did react under these conditions, the reason that compounds *(Z)*-**16** and **15** failed to react appears to be – at first sight – steric hindrance caused by the substituents on the bromoalkenyl moiety *cis* to bromine rather than an electronic effect of these substituents (**Scheme 5**).

With a cyclopropylidene group in place of the two methyl groups in either **14** or **15**, i. e. 1,6-dienes with a methylenecyclopropane terminator or starter, **22** and **18** were cyclized under Pd-catalysis and reacted with methyl vinyl ketone (**40b**) or methyl acrylate (**40c-Me**) as dienophiles to give the spirocyclopropane annelated bicyclo[4.3.0]nonenes **65b** and **65c-Me**, respectively, as single regioisomers in good yields. Even the highly unstable 3,4-bis(cyclopropylidene)cyclopentane diester **70**[32] could be generated from the 2-bromo-1,6-diene **23** with both a methylenecyclopropane moiety as a starter and a terminator and trapped by diethyl fumarate (**40e-Et**) to give **69e-Et** (**Scheme 6**).

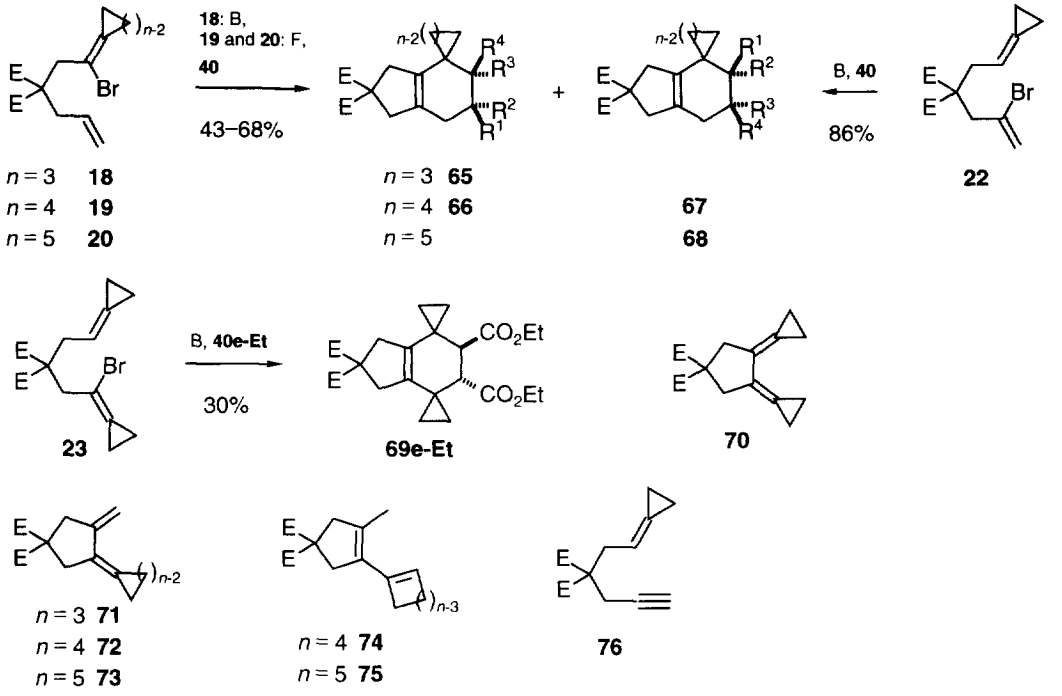
To the best of our knowledge, these are the first intramolecular palladium-catalyzed coupling reactions with methylenecyclopropane moieties which occur without opening of the three-membered ring (*cf.* ref.[33–37]). When Trost's protocol for the cycloisomerization of 1,6-enynes[6] was applied to the enyne **76**[38] with a methylenecyclopropane terminator neither the exocyclic diene **71** nor its cycloadduct **65c-Me** – in the presence of methyl acrylate (**40c-Me**) – were observed (*cf.* ref.[37]).



Scheme 5. B: $Pd(OAc)_2$, PPh_3, Ag_2CO_3, MeCN, 90 °C. F: $Pd(OAc)_2$, PPh_3, K_2CO_3, MeCN, 90 °C. E = CO_2Me. For further details see **Table 2**.

The higher homologues of **18** with methylenecyclobutane and methylenecyclopentane starters, **19** and **20**, respectively, did not cyclize when treated with the $Pd(OAc)_2/Ag_2CO_3$ system in the presence of a variety of ligands (PPh_3, dppe, dppf, 2,9-dimethyl-1,10-phenanthroline) or without added ligands. Surprisingly, when Ag_2CO_3 was replaced by K_2CO_3 (method F), both compounds **19** and **20** as well as (*Z*)-**16** and **15**, which did not react under the previously favored conditions, cyclized smoothly in a 5-*exo*-*trig* mode. One equivalent of silver salt with respect to palladium catalyst was sufficient to suppress the Heck reaction. The rationale of these unprecedented experimental results and the role of silver salts in this process are not clear at present.[39] Unfortunately, the 1,2-bis(exocyclic) 1,3-dienes (*Z*)-**56**, **62**, **72**, and **73** each isomerized to some extent to **59**,[40] **64**,[40] **74**, and **75**, respectively, possibly by readdition of a hydridopalladium species and β-hydride elimination in the other direction. It is also conceivable that, especially in the cases of compounds (*Z*)-**56**, **62**, **72**, and **73**, this rearrangement occurs by a suprafacial 1,5-hydrogen shift, which should be favored in such rigid coplanar systems.[41] Isomerizations of the 1,2-bis(exocyclic) 1,3-dienes and their Diels-Alder reactions with

methyl acrylate or dimethyl fumarate occurred with comparable rates. The isomerized 1,3-dienes **59**, **64**, **74**, and **75** did not react with methyl acrylate (**40c-Me**) under the conditions applied. It must also be mentioned that sensitive esters can hydrolyze to some extent under these conditions.

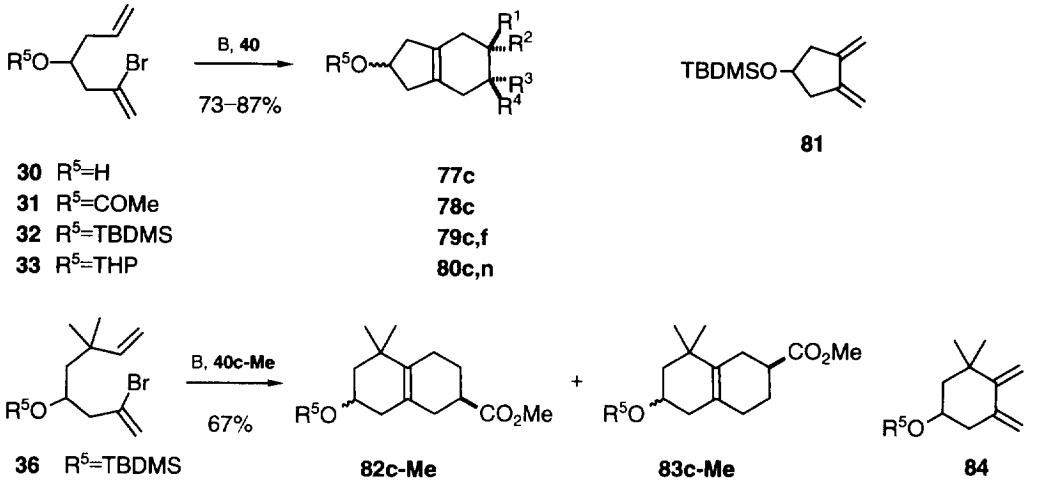


Scheme 6. B: $Pd(OAc)_2$, PPh_3, Ag_2CO_3, MeCN, 90 °C. F: $Pd(OAc)_2$, PPh_3, K_2CO_3, MeCN, 90 °C. E = CO_2Me. For further details see **Table 2**.

While the dimethyl compound **15**, the methylenecyclopropane derivatives **18** and **22** as well as the methylenecyclopentane derivative **20** each yielded only one regioisomer **63c-Me**, **65c-Me**,[42] and **68c-Me**, respectively, in the Diels-Alder reaction with methyl acrylate, the corresponding methylenecyclobutane compound **19** gave two isomers **66c-Me** and **67c-Me** in a ratio of about 1:1.7.[43]

The fact that the bromodienes **30–33** without the geminal diester grouping gave, when subjected to the standard conditions (see above), the corresponding bicycles **77–80** in good yields, indicates that the Thorpe-Ingold effect[44] is not essential for the success of the intramolecular Heck reaction (**Scheme 7**).

The sequential reaction can also be applied to the synthesis of bicyclo[4.4.0]dec-1(6)-enes. With 2-bromo-1,7-diene **36** as the starting material the general procedure (see above) gave a mixture of the two regioisomeric products **82c-Me** and **83c-Me** in good yield (together 67%); however, neither the regioisomers nor the diastereomers could be separated (**Scheme 7**).



Scheme 7. B: $Pd(OAc)_2$, PPh_3, Ag_2CO_3, MeCN, 90 °C. For further details see **Table 2**.

Attempts to build bicyclo[4.2.0]octenes and bicyclo[5.4.0]undecenes from 2-bromo-1,5-diene **28** and 2-bromo-1,8-dienes **25**, **38**, **39** were not successful, as the starting materials simply did not cyclize under the standard conditions, and prolonged heating resulted in decomposition.

Conclusion

In essence, the Heck reaction of 2-bromo-1,6- and 2-bromo-1,7-dienes – to yield vicinal exodialkylidenecycloalkanes – which is immediately followed by a Diels-Alder reaction, provides a versatile synthesis of bicyclo[4.3.0]nonenes and bicyclo[4.4.0]decenes. The yields in this one-pot process are generally significantly higher than in a two-step procedure with isolation of the exodialkylidenecycloalkanes. With this current method, even very sensitive 1,3-dienes can be generated and reacted *in situ* with dienophiles. Several of these 1,3-dienes are not accessible *via* cycloisomerization of the corresponding enynes, and even methylenecyclopropane moieties are compatible with these Heck coupling conditions leading to activated dienes as compared to a dimethylvinyl group in the same position in the subsequent Diels-Alder reaction. Silver salts are efficient to prevent double bond isomerization in the exodimethylenecycloalkanes, but they completely suppress the Heck reaction when the bromoalkenyl moiety is sterically congested.

Experimental Part

^1H NMR spectra were recorded on either a Bruker AM 250 (250 MHz) or a Varian VXR 500 (500 MHz) at ambient temperature in $CDCl_3$ with tetramethylsilane as internal standard (unless otherwise stated). The line positions or centres of multiplets are given in ppm (δ) and the coupling constants (*J*) are given as absolute values in Hertz, while the signal multiplicities are abbreviated as follows: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), dq (doublet of quartets), quint (quintet), m (multiplet), m_c (centered multiplet), AB (AB system), *p* (*pseudo*), and b (broad). ^{13}C NMR spectra were recorded on either a Bruker AM 250 (62.9 MHz) or a Varian VXR 500 (125 MHz). Infrared spectra were recorded on a Bruker FT-IR instrument of type IFS 66. Mass spectra were recorded using electron impact ionization at 70 eV. High resolution mass spectra (HRMS) data were obtained using preselected ion peak matching at R~10000 to be within ±2 ppm. All melting points were determined on a Reichert microscopic hot stage apparatus and are

uncorrected. Boiling points were determined upon fractional distillation and are uncorrected. Elemental analyses were performed by the Mikroanalytisches Labor der Universität Göttingen, Germany.

Solvents and reagents were dried and purified according to standard methods[45]. All solvents for chromatography or recrystallizations were distilled prior to use, while dry diethyl ether and tetrahydrofuran (THF) were distilled from sodiumbenzophenone ketyl under nitrogen immediately before use.

Ethyl 2-Bromo-2-cyclobutylideneacetate (2): To a stirred suspension of sodium hydride (453 mg, 10.0 mmol, 53% oil suspension) in dry DME (10 mL) was added triethyl 2-bromophosphonoacetate[46] (3.03 g, 10.0 mmol) at 0 °C and the mixture stirred at room temperature until evolution of hydrogen ceased. Cyclobutanone (701 mg, 10.0 mmol) was added dropwise, maintaining the temperature between 20 and 30 °C by occasional cooling with an ice bath. The reaction mixture was briefly heated to 50 °C and then cooled to room temperature during which time a precipitate had formed. Water (40 mL) was added and the mixture extracted with ether (5 × 30 mL). The combined ether layers were washed with brine (10 mL), dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*. Purification of the residue by column chromatography on silica gel (75 g, eluting with petroleum ether/ether 25:1) yielded 1.06 g (48%) of **2**; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.31 (t, *J* = 7.1, 3 H), 2.06 (quint, *J* = 8.0, 2 H), 2.75–2.84 (m, 2 H), 3.03–3.12 (m, 2 H), 4.23 (q, *J* = 7.1, 2 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 14.19 (+), 15.65 (–), 34.09 (–), 61.65 (–), 105.33 (C_{quat}), 162.33 (C_{quat}), 164.56 (C_{quat}); IR (film): ν = 3026 cm^{-1}, 2888, 1725, 1653, 1260, 1124, 1017, 804; MS (70 eV), *m/z*: 220/218 (11/11) [M^+], 192/190 (98/100), 147/145 (11/10), 119/117 (12/11), 111 (66), 93 (6), 66 (37), 65 (47); $C_8H_{11}BrO_2$ Calcd: 217.9942 (HRMS correct).

Methyl 2-Bromo-2-cyclopentylideneacetate (3): To a cooled (–5 °C) solution of methyl cyclopentylideneacetate[47] (6.31 g, 45 mmol), prepared from cyclopentanone and trimethyl phosphonoacetate according to ref.[48], in $CHCl_3$ (20 mL) was added a solution of bromine (7.51 g, 2.42 mL, 47 mmol) in $CHCl_3$ (5 mL) so that the temperature remained below 5 °C. After the mixture had been stirred at room temperature for 15 min, it was washed with brine (15 mL) containing $Na_2S_2O_3$, dried, and the solvent was evaporated. The residue was dissolved in dry methanol (15 mL) and the solution was cooled to 0 °C. A solution of NaOMe, freshly prepared by dissolving sodium metal (1.04 g, 45 mmol) in dry methanol (15 mL), was added dropwise, and the mixture was stirred at 0 °C for 3 h. After evaporation of methanol, the residue was taken up with water and saturated aqueous $NaHCO_3$ (10 mL each) and extracted with ether (4 × 20 mL). After washing with brine (10 mL), drying over $MgSO_4$ and evaporation of the solvents, the crude ester was distilled *in vacuo* (53–55 °C / 0.2 mm Hg), yielding 8.17 g (83%) of **3**; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.72 (b quint, *J* = 6.9, 2 H), 1.84 (b quint, *J* = 6.9, 2 H), 2.54 (bt, *J* = 7.1, 2 H), 2.78 (bt, *J* = 7.0, 2 H), 3.79 (s, 3 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 25.09 (–), 27.91 (–), 35.74 (–), 39.57 (–), 52.48 (+), 104.67 (C_{quat}), 163.42 (C_{quat}), 166.18 (C_{quat}); IR (film): ν = 2954 cm^{-1}, 2873, 1710, 1653, 1616, 1435, 1256, 1134, 1038, 861, 753; MS (70 eV), *m/z*: 220/218 (33/34) [M^+], 205/203 (5/5), 189/187 (17/14), 188/186 (24/22), 139 (25), 107 (36), 79 (100); $C_8H_{11}BrO_2$ Calcd: 217.9942 (HRMS correct).

General Procedure for the Synthesis of 2,3-Dibromo-1-alkenes from α,β-Unsaturated α-Bromoesters (GP1):[6,14] To a solution of diisobutylaluminum hydride (1.0 M in hexane, 57 ml, 57 mmol) in dry CH_2Cl_2 (60 mL) at –65 °C under nitrogen was added a solution of the ester **1**, **2** or **3** (25 mmol) in dry CH_2Cl_2 (40 mL). The reaction mixture was warmed to –20 °C over 2 h and quenched with 2 mL of methanol and 100 mL of a saturated solution of sodium potassium tartrate. After the mixture had been stirred for approx. 1 h, the two layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (4 × 50 mL). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, concentrated and, if necessary, purified by column chromatography on silica gel.

The alcohol (20 mmol), thus obtained, was added to a mixture of PPh_3 (5.77 g, 22 mmol) and bromine (3.48 g, 21.8 mmol) in dry CH_2Cl_2 (90 mL) at 0 °C. After the mixture had been stirred for 2 h at room temperature, hexane (90 mL) was added, the organic phase was washed with saturated aqueous solution of

$NaHCO_3$ containing $Na_2S_2O_3$ (20 mL) and brine (20 mL), dried over $MgSO_4$, filtered and evaporated to leave an oil and a solid, which was filtered off and washed with pentane. The solvent was evaporated and, if necessary, the crude product purified by distillation.

General Procedure for the Synthesis of 2-Bromo-1,6-dienes by Alkylation of Dimethyl or Diethyl Allylmalonates 13–20, 22, or 23 (GP2, method A in Scheme 1):[11] To a suspension of 363 mg (12.1 mmol, 80% suspension in oil) of sodium hydride in 30 mL of THF at 0 °C was added dropwise 12.0 mmol of the appropriate allylmalonate **7–9** or **21**. The cooling bath was removed and the mixture stirred at room temperature until the evolution of hydrogen ceased. After recooling the mixture to 0 °C, 12.0 mmol of the respective 2,3-dibromo-1-alkene **4–6** or **10–12** was added dropwise, and stirring was continued at room temperature until the reaction was complete as judged by TLC (1 h usually suffices). THF was removed under reduced pressure, and the residue was taken up in 15 mL of ether and 10 mL each of saturated NaCl and $NaHCO_3$ solution. The ether layer was separated, and the aqueous layer was extracted with ether (3 × 15 mL). The combined organic layers were dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on 100 g of silica gel eluting with petroleum ether/ether 10:1, yielding the malonates as colorless oils or, in the case of **15**, as colorless crystals.

2-Bromo-1,8-diene **25** was prepared in the same way, starting with ester **24**[17] and 2,3-dibromoprop-1-ene (**10**).

Diethyl Allyl-2-bromoallylmalonate (13): ^1H NMR, IR, MS data, and elemental analysis have already been reported[10a]; ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.88 (+), 35.88 (–), 42.79 (–), 56.71 (C_{quat}), 61.46 (–), 119.42 (–), 121.86 (–), 127.16 (C_{quat}), 132.03 (+), 169.95 (C_{quat}).

Dimethyl 2-Bromoallylprenylmalonate (14): ^1H NMR (250 MHz, $CDCl_3$): δ = 1.55 (s, 3 H), 1.65 (s, 3 H), 2.70 (d, *J* = 7.2, 2 H), 3.12 (s, 2 H), 3.70 (s, 6 H), 4.92 (t, *J* = 7.2, 1 H), 5.55 (s, 1 H), 5.60 (s, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.29 (+), 25.63 (+), 36.55 (–), 39.39 (–), 52.32 (+), 57.89 (C_{quat}), 114.81 (C_{quat}), 118.78 (–), 132.71 (+), 135.49 (C_{quat}), 170.97 (C_{quat}); IR (film): ν = 3079 cm^{-1}, 3038, 2999, 2975, 2917, 2855, 1734 (C=O), 1641, 1436, 1328, 1289, 1230, 1165, 1066, 924, 861, 591.

Dimethyl Allyl-2-bromoprenylmalonate (15): mp. 65 °C; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.80 (s, 3 H), 1.87 (s, 3 H), 2.71 (dt, *J* = 7.2, 0.9, 2 H), 3.30 (s, 2 H), 3.71 (s, 6 H), 5.00–5.10 (m, 2 H), 5.70–5.90 (m, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.39 (+), 25.73 (+), 36.61 (–), 39.46 (–), 52.44 (+), 57.97 (C_{quat}), 114.86 (C_{quat}), 118.89 (–), 132.78 (+), 135.61 (C_{quat}), 171.11 (C_{quat}); MS (70 eV), *m/z*: 239 (30), 207 (25), 179 (100), 167 (73), 135 (75); IR (KBr): ν = 3079 cm^{-1}, 3001, 2951, 1734 (C=O), 1701, 1640, 1436, 1327, 1289, 1214, 1133, 1065, 1042, 924, 861, 589. Anal. Calcd. for $C_{13}H_{19}BrO_4$: C, 48.92; H, 6.00; Br, 25.03. Found: C, 48.81; H, 5.99; Br, 24.97.

Dimethyl Allyl-2-bromocrotylmalonate [(*E*)/(*Z*)-16]: (*E*)-Isomer: ^1H NMR (250 MHz, $CDCl_3$): δ = 1.66 (d, *J* = 7.2, 3 H), 2.76 (dt, *J* = 7.3, 1.1, 2 H), 3.21 (s, 2 H), 3.73 (s, 6 H), 5.07–5.15 (m, 2 H), 5.58–5.79 (m, 1 H), 6.12 (q, *J* = 7.2, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 15.64 (+), 36.70 (–), 37.22 (–), 52.43 (+), 57.71 (C_{quat}), 118.68 (C_{quat}), 119.10 (–), 132.14 (+), 132.59 (+), 170.82 (C_{quat}); (*Z*)-Isomer: ^1H NMR (250 MHz, $CDCl_3$): δ = 1.73 (dt, *J* = 6.5, 0.8, 3 H), 2.72 (dt, *J* = 7.3, 1.1, 2 H), 3.16 (t, *J* = 0.8, 2 H), 3.73 (s, 6 H), 5.05–5.15 (m, 2 H), 5.67 (ddt, *J* = 17.5, 9.6, 7.3, 1 H), 5.84 (qt, *J* = 6.5, 0.8, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 17.09 (+), 36.35 (–), 43.55 (–), 52.41 (+), 57.50 (C_{quat}), 119.17 (–), 121.79 (C_{quat}), 129.01 (+), 132.47 (+), 170.76 (C_{quat}); mixture: MS (70 eV), *m/z*: 275/273 (3/3), 243/241 (13/12), 225 (100), 215/213 (11/11), 193 (23), 165 (64), 151 (27), 133 (59), 105 (100), 91 (23); IR (film): ν = 2953 cm^{-1}, 1739, 1653, 1559, 1436, 1280, 1217, 1131, 1056, 995, 923, 853; Anal. Calcd. for $C_{12}H_{17}BrO_4$: C, 47.23; H, 5.61. Found: C, 47.10; H, 5.57.

Dimethyl 2-Bromoallylcrotylmalonate [(*E*)/(*Z*)-17]: (*E*)-Isomer: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.73 (dd, *J* = 6.4, 1.2, 3 H), 2.69 (bd, *J* = 7.3, 2 H), 3.12 (s, 2 H), 3.72 (s, 6 H), 5.15–5.30 (m, 1 H), 5.45–5.60 (m, 1 H), 5.58 (d, *J* = 1.6, 1 H), 5.66 (d, *J* = 1.0, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 17.95 (+), 35.13 (–), 43.15 (–), 52.44 (+), 57.46 (C_{quat}), 121.78 (–), 124.36 (+), 127.32 (C_{quat}), 130.29 (+), 170.63 (C_{quat}); (*Z*)-Isomer: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.63 (bd, *J* = 6.4, 3 H), 2.77 (bd, *J* = 7.5, 2 H), 3.14 (s, 2 H), 3.72 (s, 6 H), 5.15–5.30 (m, 1 H), 5.45–5.60 (m, 1 H), 5.58 (d, *J* = 1.6, 1 H), 5.64 (*p*d, *J* = 1.0, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 12.97 (+), 29.33 (–), 43.25 (–), 52.53 (+), 57.14 (C_{quat}), 121.78 (–), 123.29 (+), 127.24 (C_{quat}), 128.21 (+), 170.72 (C_{quat}); mixture: MS (70 eV), *m/z*: 274/272 (4/4), 225 (82), 193 (10), 185 (29), 165 (100), 153 (69), 133 (18), 121 (36), 91 (39); IR (film): ν = 3038 cm^{-1}, 2953, 1734, 1626, 1436, 1214, 1150, 972; Anal. Calcd. for $C_{12}H_{17}BrO_4$: C, 47.23; H, 5.61. Found: C, 47.05; H, 5.59.

Dimethyl Allyl-2-bromo-2-cyclopropylideneethylmalonate (18): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.20–1.45 (m, 4 H), 2.53 (d, *J* = 7.3, 2 H), 3.22 (s, 2 H), 3.68 (s, 6 H), 5.0–5.1 (m, 2 H), 5.5–5.9 (m, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 7.40 (–), 10.66 (–), 32.28 (–), 38.23 (–), 52.33 (+), 57.52 (C_{quat}), 108.00 (C_{quat}), 118.84 (–), 132.26 (+), 135.81 (C_{quat}), 170.58 (C_{quat}); MS (70 eV), *m/z*: 318/316 (1/1) [M$^+$], 237 (31), 177 (88), 117 (100); Anal. Calcd. for $C_{13}H_{17}BrO_4$: C, 49.23; H, 5.40; Br, 25.19. Found: C, 49.51; H, 5.49; Br, 25.01.

Dimethyl Allyl-2-bromo-2-cyclobutylideneethylmalonate (19): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.90 (quint, *J* = 8.0, 2 H), 2.63 (m_c, 4 H), 2.73 (dt, *J* = 7.3, 1.2, 2 H), 3.04 (s, 2 H), 3.72 (s, 6 H), 5.09 (dt, *J* = 10.1, 1.1, 1 H), 5.11 (dt, *J* = 17.1, 1.1, 1 H), 5.70 (ddt, *J* = 17.0, 10.1, 7.3, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.59 (–), 30.11 (–), 32.58 (–), 36.42 (–), 37.86 (–), 52.38 (+), 57.55 (C_{quat}), 109.72 (C_{quat}), 118.88 (–), 132.53 (+), 144.62 (C_{quat}), 170.82 (C_{quat}); MS (70 eV), *m/z*: 251 (100), 241/239 (2/2), 191 (12), 159 (6), 131 (10), 111 (7), 91 (5); IR (film): ν = 2953 cm^{-1}, 1737, 1640, 1436, 1290, 1219, 1137, 1058, 995, 961, 928, 860; Anal. Calcd. for $C_{14}H_{19}BrO_4$: C, 50.77; H, 5.78. Found: C, 50.64; H, 5.71.

Dimethyl Allyl-2-bromo-2-cyclopentylideneethylmalonate (20): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.90 (m_c, 4 H), 2.30 (m_c, 4 H), 2.71 (d, *J* = 7.3, 2 H), 3.20 (s, 2 H), 3.69 (s, 6 H), 5.05 (d, *J* = 10.6, 1 H), 5.06 (d, *J* = 16.3, 1 H), 5.71 (ddt, *J* = 16.3, 10.6, 7.3, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 25.72 (–), 27.78 (–), 32.58 (–), 36.37 (–), 36.71 (–), 40.72 (–), 52.38 (+), 57.94 (C_{quat}), 110.53 (C_{quat}), 118.78 (–), 132.87 (+), 148.24 (C_{quat}), 171.04 (C_{quat}); MS (70 eV), *m/z*: 315/313 (1/1), 265 (100), 255/253 (3/3), 233 (1), 205 (76), 173 (35), 145 (83), 108 (51), 105 (34), 91 (74); IR (film): ν = 2954 cm^{-1}, 1739, 1435, 1233, 992, 934; Anal. Calcd. for $C_{15}H_{21}BrO_4$: C, 52.19; H, 6.13; Br, 23.14. Found: C, 52.24; H, 6.03; Br, 23.18.

Dimethyl 2'-Bromoallyl-2-cyclopropylideneethylmalonate (22): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.9–1.25 (m, 4 H), 2.80 (d, *J* = 7.3, 2 H), 3.18 (s, 2 H), 3.72 (s, 6 H), 5.6–5.7 (m, 2 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 2.02 (–), 2.86 (–), 34.31 (–), 43.12 (–), 52.57 (+), 57.26 (C_{quat}), 111.56 (+), 121.76 (–), 126.80 (C_{quat}), 127.23 (C_{quat}), 170.72 (C_{quat}); MS (70 eV), *m/z*: 318/316 (1/1) [M$^+$], 237 (31), 177 (59), 117 (100). Anal. Calcd. for $C_{13}H_{17}BrO_4$: C, 49.23; H, 5.40; Br, 25.19. Found: C, 49.51; H, 5.49; Br, 25.01.

Dimethyl 2'-Bromo-2'-cyclopropylideneethyl-2-cyclopropylideneethylmalonate (23): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.91–1.02 (AA'BB', 4 H), 1.22–1.30 and 1.38–1.60 (AA'BB', 4 H), 2.87 (dt, *J* = 7.3, 1.1, 2 H), 3.34 (s, 2 H), 3.72 (s, 6 H), 5.6–5.7 (tt, *J* = 7.2, 2.0, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 2.04 (–), 2.90 (–), 7.56 (–), 10.72 (–), 34.61 (–), 42.02 (–), 52.55 (+), 57.51 (C_{quat}), 108.26 (C_{quat}), 111.84 (+), 127.19 (C_{quat}), 136.04 (C_{quat}), 171.41 (C_{quat}); IR (film): ν = 3030 cm^{-1}, 2982, 2952, 2841, 1736, 1436, 1286, 1207, 1084, 945, 899, 860.

3,3-Dimethyl-4-pentenal (34): In analogy to a described procedure[45] 35.0 mL (0.35 mol) of 3-methyl-2-butene-1-ol, 50.3 g (0.354 mol) of 1,4-butanediol divinyl ether and 2.077 g (6.52 mmol) of $Hg(OAc)_2$ were

heated to 120 °C under N_2 for 48 h. The reaction mixture was cooled to room temperature and partitioned between water (140 mL) and Et_2O (120 mL). The ether layer was separated, washed with water and dried. After distillation of the solvent at normal pressure, the remaining liquid was carefully fractionated using a 40 cm Vigreux column at partial vacuum. The main fraction boiling at 72–76 °C/160–166 Torr was 90% pure aldehyde (the remaining impurity was 3-methyl-2-buten-1-yl vinyl ether). Yield: 17.1 g (0.152 mol, 42%).

General Procedure for the Tin-promoted Coupling of Aldehydes or Acetals with 2,3-Dibromoprop-1-ene (10) (GP3):[16] To a solution of the aldehydes **26**, **34** or the dialkyl acetals **29**, **37** (40.0 mmol) in 50 mL of ether were added 20 mL of water, 4.75 mL (48.0 mmol) of 2,3-dibromoprop-1-ene (**10**), 5.93 g (50.0 mmol) of tin powder and 6 drops of 48% HBr. The reaction flask was immersed in a water bath at room temperature and the mixture vigorously stirred until the starting aldehyde had disappeared (3–18 hours). A milky aqueous lower layer resulted. The phases were separated and the aqueous phase (containing a white solid) extracted with ether (the yields obtained in this reaction have been found strongly dependent on this tedious extraction, care should be taken to ensure that all the product has been extracted from the aqueous layer). The combined organic extracts were washed with small portions of water (2 × 2 mL) and dried over Na_2SO_4 containing a spatula tip of Na_2CO_3. After evaporation of the solvent, the residue was purified by chromatography on silica gel eluting with petroleum ether/ether mixtures and yielded the bromodienols as colorless oils.

2-Bromo-1,5-hexadien-4-ol (27): Following GP3, 1.92 g (34.2 mmol) of acrolein, 8.39 g (42 mmol) of 2,3-dibromoprop-1-ene (**10**) and 6.36 g (53.6 mmol) of Sn in water/ether containing two drops of 48% HBr were allowed to react for 14 h. After column chromatography (petroleum ether/ether 3:1) 1.585 g (8.95 mmol, 26%) of pure compound were obtained. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.7–1.8 (bs, 1 H), 2.54 (d, J = 6.1, 2 H), 4.47 (q, J = 6.1, 1 H), 5.18 (dt, J = 10.4, 1.5, 1 H), 5.33 (dt, J = 17.1, 1.5, 1 H), 5.50 (d, J = 1.6, 1 H), 5.66 (bs, 1 H), 5.89 (ddd, J = 5.8, 10.4, 17.1, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 48.95, 70.18, 115.56, 119.87, 129.78, 139.00; MS (70 eV), *m/z*: 162/160 (3/3), 147/145 (4/4), 122/120 (3/3), 97 (5), 57 (100); Anal. Calcd. for C_6H_9BrO: C, 40.71; H 5.12. Found: C, 40.79; H 5.12.

2-Bromo-1,6-heptadien-4-ol (30): According to GP3, from 13.48 g (93.46 mmol) of the diethyl acetal **29** and 22.32 g (112 mmol) of 2,3-dibromoprop-1-ene (**10**) dissolved in 100 mL of ether, 12.20 g (103 mmol) of Sn and a solution of 0.5 mL of 48% HBr in 20 mL of water was obtained after 12 h 11.78 g (61.65 mmol, 66%) of **30**. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.73 (bs, 1 H), 2.4–2.6 (m, 2 H), 2.54 (d, J = 6.1, 2 H), 4.4–4.5 (m, 1 H), 5.1–5.4 (m, 2 H), 5.50 (d, J = 1.6, 1 H), 5.66 (bs, 1 H), 5.8–6.0 (m, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 40.74, 48.52, 68.08, 118.50, 119.64, 130.44, 134.04; IR (film): ν = 3600–3300 cm^{-1}, 3082, 2950–2750, 1630, 1414, 1380, 1160–1003, 890; Anal. Calcd. for $C_7H_{11}BrO$: C, 44.00; H, 5.80; Br, 41.82. Found: C, 43.85; H, 5.82; Br, 41.57.

2-Bromo-6,6-dimethyl-1,7-octadien-4-ol (35): According to GP3, from 1.14 g (10.2 mmol) of the aldehyde **34** and 4.05 g (20.3 mmol) of 2,3-dibromoprop-1-ene (**10**) dissolved in 10 mL of ether, 1.80 g (15.1 mmol) of Sn and two drops of 48% HBr in 10 mL of water was obtained after 3 h 1.73 g (7.72 mmol, 73%) of **35**. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.07 (s, 3 H), 1.10 (s, 3 H), 1.4–1.6 (m, 2 H), 1.96 (d, J = 2.9, 1 H), 2.4–2.6 (m, 2 H), 4.0–4.1 (m, 1 H), 4.95–5.10 (m, 2 H), 5.50 (d, J = 1.6, 1 H), 5.66 (bs, 1 H), 5.94 (dd, J = 15.6, 10.7, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 25.86 (+), 28.51 (+), 36.22 (C_{quat}), 48.85 (–) 50.15 (–), 66.81 (+), 111.31 (–), 119.35 (–), 130.68 (C_{quat}), 148.59 (+); IR (film): ν = 3600–3300 cm^{-1}, 3082, 2950–2750, 1630, 1414, 1380, 1160–1003, 890; Anal. Calcd. for $C_{10}H_{17}BrO$: C, 51.52; H, 7.35; Br, 34.27. Found: C, 51.62; H, 7.24; Br, 34.34.

2-Bromo-1,8-nonadien-4-ol (38): Following GP3, 710 mg (4.99 mmol) of 4-pentenyl-1,3-dioxolane (**37**), 1.55 g (7.75 mmol) of 2,3-dibromoprop-1-ene (**10**) and 733 mg of Sn (6.17 mmol) in water/ether

containing two drops of 48% HBr were allowed to react for 18 h. After column chromatography on silica gel (petroleum ether/*t*BuOMe 15:2), 986 mg (4.50 mmol, 90%) of pure compound were obtained. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.4–1.7 (m, 5 H), 2.05–2.15 (m, 2 H), 2.4–2.6 (m, 2 H), 3.9–4.0 (m, 1 H), 4.9–5.1 (m, 2 H), 5.41 (d, *J* = 1.5, 1 H), 5.60 (bs, 1 H), 5.81 (ddt, *J* = 17.0, 10.2, 6.7, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 24.82 (–), 33.55 (–), 35.72 (–), 49.40 (–), 68.86 (+), 114.75 (–), 119.64 (–), 130.72 (C_{quat}), 138.48 (+); IR (film): ν = 3600–3200 cm^{-1}, 3076, 2980–2850, 1631, 1558, 1506, 1209, 1082, 995, 911, 890; Anal. Calcd. for $C_9H_{15}BrO$: C, 49.33; H, 6.90; Br, 36.47. Found: C, 49.05; H, 6.95; Br, 36.22.

General Procedure for the Protection of Alcohols as TBDMS Ethers (GP4): To a solution of the alcohol (21.5 mmol) in 20 mL of dry DMF were added TBDMSCl (3.57 g, 23.7 mmol) and imidazole (1.76 g, 25.8 mmol). The reaction mixture was stirred at room temperature until all the alcohol had reacted (usually 4–5 hours). Water (40 mL) and Et_2O were added, the phases separated and the aqueous one extracted with Et_2O (2 × 10 mL). The combined extracts were washed with water (3 × 15 mL), 1 N HCl (5 mL), sat. $NaHCO_3$ (10 mL) and sat. NaCl (10 mL). Drying and evaporation afforded a crude protected alcohol that was filtered through a short flash silica column eluting with petroleum ether/ Et_2O 40:1 to give the pure ether as a colorless oil.

2-Bromo-1,5-hexadien-4-yl *t*-Butyldimethylsilyl Ether (28): According to GP4, from 461 mg (2.60 mmol) of the alcohol **27** was obtained 703 mg (2.41 mmol, 93%) of the corresponding silyl ether **28**. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.06 (s, 3 H), 0.07 (s, 3 H), 0.96 (s, 9 H), 2.54 (m, 2 H), 4.4–4.5 (m, 1 H), 5.1–5.4 (m, 2 H), 5.50 (d, *J* = 1.6, 1 H), 5.66 (bs, 1 H), 5.8–6.0 (m, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –4.85 (+), –4.43 (+), 18.23 (C_{quat}), 25.83 (+), 50.36 (–), 71.29 (+), 114.53 (–), 119.39 (–), 130.39 (C_{quat}), 140.17 (+); IR (film): ν = 3080 cm^{-1}, 2960–2850, 1632, 1472, 1361, 1252, 1085–1005, 924, 887, 836, 810, 776; MS (70 eV), *m/z*: 235/233 (29/29), 195/193 (100/100), 171 (94), 139/137 (36/36), 115 (14), 99 (14), 73 (82); Anal. Calcd. for $C_{12}H_{23}BrOSi$: C, 49.48; H, 7.96. Found: C, 49.79; H, 8.00.

2-Bromo-1,6-heptadien-4-yl *t*-Butyldimethylsilyl Ether (32): According to GP4, from 5.66 g (29.6 mmol) of the alcohol **30** was obtained 8.51 g (27.9 mmol, 94%) of the corresponding silyl ether **32**. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.05 (s, 6 H), 0.96 (s, 9 H), 2.4–2.6 (m, 2 H), 2.54 (d, *J* = 6.1, 2 H), 4.4–4.5 (m, 1 H), 5.1–5.4 (m, 2 H), 5.5 (d, *J* = 1.6, 1 H), 5.66 (bs, 1 H), 5.8–6.0 (m, 1 H); IR (film): ν = 3076 cm^{-1}, 2950–2750, 1640, 1409, 1143, 1030, 994, 912; Anal. Calcd. for $C_{13}H_{25}BrOSi$: C, 51.14; H, 8.25; Br, 26.17. Found: C, 49.79; H, 8.00; Br, 26.10.

2-Bromo-6,6-dimethyl-1,7-octadien-4-yl *t*-Butyldimethylsilyl Ether (36): According to GP4, from 1.04 g (4.46 mmol) of the alcohol **35** was obtained 1.37 g (3.95 mmol, 89%) of the corresponding silyl ether **36**. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.08 (s, 6 H), 0.87 (s, 9 H), 1.02 (s, 3 H), 1.06 (s, 3 H), 1.51–1.57 (m, 2 H), 2.46 and 2.57 (AB part of ABX, *J* = 16.0, 6.7, 5.3, 2 H), 3.99 (q, *J* = 5.9, 1 H), 4.89–4.97 (m, 2 H), 5.41 (d, *J* = 1.4, 1 H), 5.59 (s, 1 H), 5.89 (dd, *J* = 17.7, 10.4, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –4.60 (+), –4.41 (+), 18.01 (C_{quat}), 25.73 (+), 25.99 (+), 26.88 (+), 35.95 (C_{quat}), 49.61 (–), 50.95 (–), 67.93 (+), 110.70 (–), 118.91 (–), 131.68 (C_{quat}), 148.33 (+); Anal. Calcd. for $C_{16}H_{31}BrOSi$: C, 55.32; H, 8.99; Br 23.00. Found: C, 55.89; H, 9.13; Br 22.60.

2-Bromo-1,8-nonadien-4-yl *t*-Butyldimethylsilyl Ether (39): According to GP4, from 925 mg (4.22 mmol) of the alcohol **38** was obtained 1.272 g (3.82 mmol, 91%) of the corresponding silyl ether **39**; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.07 (s, 6 H), 0.90 (s, 9 H), 1.4–1.8 (m, 4 H), 1.9–2.1 (m, 2 H), 2.49–2.51 (m, 2 H), 3.9–4.0 (m, 1 H), 4.9–5.1 (m, 2 H), 5.5 (bs, 1 H), 5.6 (bs, 1 H), 5.7–5.9 (m, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –4.49 (+), –4.41 (+), 18.08 (C_{quat}), 24.17 (–), 25.87 (+), 33.73 (–), 36.05 (–), 49.38 (–), 69.76 (+), 114.54 (–), 118.96 (–), 131.38 (C_{quat}), 138.71 (+); IR (film): ν = 3077 cm^{-1}, 2960–2850, 1632, 1562, 1472, 1388, 1256, 1186, 1096, 1005, 933, 911, 887, 836, 808, 775; MS (70 eV), *m/z*: 277/275 (12/12),

237/235 (2/2), 213 (5), 171 (3), 155 (3), 139/137 (13/13), 81 (100), 73 (31); Anal. Calcd. for $C_{15}H_{29}BrOSi$: C, 54.04; H, 8.77; Br, 23.97. Found: C, 54.24; H, 8.75; Br, 23.99.

2-Bromo-1,6-heptadien-4-yl Acetate (31): A mixture of the alcohol **30** (512 mg, 2.68 mmol), 515 mg (5.04 mmol) of acetic anhydride and 15 mg of DMAP in 5 mL of dry CH_2Cl_2 and 0.6 mL of dry pyridine was stirred at 15 °C for 1 h. The reaction mixture was diluted with ether (20 mL) and extracted with a sat. solution of $NaHCO_3$ (4 × 5 mL). The organic layer was washed with water (10 mL), 1 N HCl (2 × 5 mL), sat. solution of $NaHCO_3$ (2 × 15 mL) and brine (10 mL). Drying over Na_2SO_4, evaporation and column chromatography on silica (petroleum ether/tBuOMe 20:1) afforded **31** as a clear oil (542 mg, 2.32 mmol, 87%); ^1H NMR (250 MHz, $CDCl_3$): δ = 2.03 (s, 3 H), 2.3–2.5 (m, 2 H), 2.6–2.8 (m, 2 H), 5.08 (bs, 1 H), 5.13 (bs, 1 H), 5.2–5.3 (m, 1 H), 5.49 (d, *J* = 1.6, 1 H), 5.63 (bs, 1 H), 5.6–5.8 (m, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.00 (+), 37.84 (–), 45.17 (–), 70.55 (+), 118.38 (–), 119.43 (–), 129.06 (C_{quat}), 132.88 (+), 170.27 (C_{quat}); IR (film): ν = 3079 cm^{-1}, 2979, 1740, 1631, 1435, 1374, 1234, 1032, 894; Anal. Calcd. for $C_9H_{13}BrO_2$: C, 46.37; H, 5.62. Found: C, 46.43; H, 5.58.

2-Bromo-1,6-heptadien-4-yl 2-Tetrahydropyranyl Ether (33): A mixture of the alcohol **30** (920 mg, 4.81 mmol), dihydro-2*H*-pyran (672 mg, 7.99 mmol) and 18 mg of PPTS in 10 mL of CH_2Cl_2 was stirred at room temperature for 16 h. The reaction mixture was diluted with ether (30 mL) and extracted with a saturated solution of $NaHCO_3$ (3 × 15 mL). The organic layer was washed with water (10 mL) and brine (10 mL). Drying over Na_2SO_4, evaporation and column chromatography on silica (petroleum ether/*t*BuOMe 10:1) afforded **33** as a clear oil (1.102 g, 4.00 mmol, 83%, 1:1 mixture of diastereomers); ^1H NMR (250 MHz, $CDCl_3$): δ = 1.6–2.0 (m, 6 H), 2.2–2.7 (m, 4 H), 3.5–3.6 (m, 1 H), 3.9–4.1 (m, 2 H), 4.71 and 4.78 (bs, 1 H), 5.0–5.2 (m, 2 H), 5.46 and 5.48 (d, *J* = 1.4, 1 H), 5.65 and 5.70 (bs, 1 H), 5.8–6.0 (m, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 19.27 (–), 19.75 (–), 25.47 (–), 30.73 (–), 30.81 (–), 36.94 (–), 39.62 (–), 46.39 (–), 46.65 (–), 62.08 (–), 62.73 (–), 72.62 (+), 74.37 (+), 96.47 (+), 99.03 (+), 117.44 (–), 117.76 (–), 119.05 (–), 119.17 (–), 130.94 (C_{quat}), 133.95 (+), 134.51 (+); IR (film): ν = 3075 cm^{-1}, 2900–2750, 1630, 1466, 1453, 1440, 1382, 1260, 1183, 992, 915, 888, 870, 814; MS (70 eV), *m/z*: 235/233 (2/2), 195 (1), 155/153 (3/4), 107 (7), 93 (11), 85 (100), 41 (17); Anal. Calcd. for $C_{12}H_{19}BrOSi$: C, 52.38; H, 6.96; Br, 29.04. Found: C, 52.70; H, 6.98; Br, 28.90.

General Procedure for the Domino Heck-Diels-Alder Reaction of 2-Bromo-1,6- and 2-Bromo-1,7-dienes in One Pot (GP5): *Method B*: To a solution of 2-bromo-1,6-diene or 2-bromo-1,7-diene (0.627 mmol) in acetonitrile (5 mL) in a screw-capped Pyrex bottle were added $Pd(OAc)_2$ (5 mg, 3.5 mol%), PPh_3 (12.8 mg, 8 mol%), silver carbonate (207 mg, 0.75 mmol), and the respective dienophile (0.74 mmol). The solution was purged with argon and then stirred in the sealed bottle at 90 °C for 45 min unless stated otherwise. The reaction mixture was filtered through a bed of charcoal and celite, and the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel (6.0 g, column 1.7 × 6 cm) and recrystallization if possible.

Method D: 2,9-Dimethyl-1,10-phenanthroline (dmphen) (10.4 mg, 8 mol%) was used instead of PPh_3.

Method F: Potassium carbonate (104 mg, 0.75 mmol) was used instead of silver carbonate.

General Procedure for the Domino Heck-Diels-Alder Reaction of 2-Bromo-1,6- and 2-Bromo-1,7-dienes in One Pot, But Two Steps (GP6): *Method C*: To a solution of 2-bromo-1,6-diene or 2-bromo-1,7-diene (0.627 mmol) in acetonitrile (5 mL) in a screw-capped Pyrex bottle were added $Pd(OAc)_2$ (5 mg, 3.5 mol%), PPh_3 (12.8 mg, 8 mol%), and silver carbonate (207 mg, 0.75 mmol). The solution was purged with argon, and then stirred in the sealed bottle at 90 °C for 45 min. After the mixture had been cooled down to room temp., the dienophile (0.74 mmol) was added, and the mixture was stirred at 50 °C for further 45 min unless stated otherwise. Workup and purification were done as described in GP5.

For performing the second step under high pressure (compounds **41l**, **41m**), the cooled mixture was filtered directly into a teflon tube which was sealed and subjected to 10 kbar at 25 °C for 3 d.

Diethyl 3-Cyanobicyclo[4.3.0]non-1(6)-ene-8,8-dicarboxylate (41a): Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.15 (t, *J* = 7.0, 6 H), 2.10–2.25 (m, 4 H), 2.50–2.65 (m, 2 H), 2.75–2.90 (m, 1 H), 2.85 (bs, 4 H), 4.15 (q, *J* = 7.0, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.77, 22.89, 24.69, 25.48, 28.21, 43.13, 43.33, 57.35, 61.35, 121.99, 127.98, 131.56, 171.64, 171.91; MS (70 eV), *m/z*: 291 (7) [M$^+$], 246 (2), 220 (28), 217 (29), 205 (100), 177 (6) 153 (12), 117 (10), 91 (22); IR (film): ν = 2982 cm^{-1}, 2934, 2254, 1728, 1653, 1558, 1441, 1367, 1260, 1186, 1160, 1073, 913; Anal. Calcd. for $C_{16}H_{21}NO_4$: C, 65.96; H, 7.26. Found: C, 65.83; H, 7.48.

Diethyl 3-Acetylbicyclo[4.3.0]non-1(6)-ene-8,8-dicarboxylate (41b): Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7.0, 6 H), 1.55–1.70 (m, 1 H), 2.05–2.20 (m, 3 H), 2.18 (s, 3 H), 2.19–2.34 (m, 2 H), 2.61–2.76 (m, 1 H), 2.91–3.06 (m, 4 H), 4.20 (q, *J* = 7.0, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.82 (+), 24.51 (–), 24.77 (–), 26.73 (–), 28.01 (+), 43.43 (–), 43.55 (–), 47.60 (+), 57.73 (C_{quat}), 61.26 (–), 130.00 (C_{quat}), 131.24 (C_{quat}), 172.11 (C_{quat}), 172.31 (C_{quat}), 211.13 (C_{quat}); MS (70 eV), *m/z*: 308 (9) [M$^+$], 234 (26), 191 (57), 165 (52), 164 (41), 137 (14), 117 (41), 91 (50), 43 (100); IR (film): ν = 2991 cm^{-1}, 1720, 1480; Anal. Calcd. for $C_{17}H_{24}O_5$: C, 66.21; H, 7.84. Found: C, 65.97; H, 7.78.

Diethyl 3-Methoxycarbonylbicyclo[4.3.0]non-1(6)-ene-8,8-dicarboxylate (41c-Me): Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7.5, 6 H), 1.69–1.84 (m, 1 H), 2.04–2.19 (m, 3 H), 2.21–2.35 (m, 2 H), 2.52–2.60 (m, 1 H), 2.75–3.08 (m, 4 H), 3.36 (s, 3 H), 4.17 (q, *J* = 7.5, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.79 (+), 24.14 (–), 25.22 (–), 27.37 (–), 39.48 (+), 43.39 (–), 43.41 (–), 51.34 (+), 57.60 (C_{quat}), 61.18 (–), 129.81 (C_{quat}), 131.08 (C_{quat}), 171.98 (C_{quat}), 172.09 (C_{quat}), 175.66 (C_{quat}); MS (70 eV), *m/z*: 324 (5) [M$^+$], 250 (27), 220 (13), 205 (72), 190 (30), 165 (100), 164 (81), 137 (28), 117 (19), 91 (32); IR (film): ν = 2981 cm^{-1}, 2936, 1733, 1440, 1367, 1256, 1183, 1119, 1070; Anal. Calcd. for $C_{17}H_{24}O_6$: C, 62.94; H, 7.45. Found: C, 62.72; H, 7.48.

Diethyl 3-Myrtenyloxybicyclo[4.3.0]non-1(6)-ene-8,8-dicarboxylate (41c-R*): Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.84 (s, 3 H), 1.18 (dd, *J* = 8.8, 1.5, 1 H), 1.27 (t, *J* = 7.2, 6 H), 1.31 (s, 3 H), 1.66–1.72 (m, 1 H), 1.99–2.08 (m, 4 H), 2.11 (dd, *J* = 5.8, 1.3, 2 H), 2.18–2.24 (m, 2 H), 2.26 (dddd, *J* = 5.5, 1.5, 5.5, 1.5, 1 H), 2.29–3.31 (m, 1 H), 2.41 (ddd, *J* = 8.8, 5.5, 5.5, 1 H), 2.56 (dddd, *J* = 11.3, 1.1, 7.9, 3.0, 1 H), 2.90–2.98 (m, 3 H), 4.19 (q, *J* = 7.2, 4 H), 4.47 (d, *J* = 1.4, 2 H), 5.55 (ddt, *J* = 4.5, 4.5, 1.4, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.97 (+), 21.05 (+), 24.35 (–), 25.39 (–), 26.10 (+), 27.60 (–), 31.19 (–), 31.41 (–), 37.97 (C_{quat}), 39.90 (+), 40.69 (+), 43.50 (–), 43.58 (–), 57.47 (C_{quat}), 61.39 (–), 66.89 (–), 121.26 (+), 130.08 (C_{quat}), 131.25 (C_{quat}), 143.07 (C_{quat}), 172.24 (C_{quat}), 172.38 (C_{quat}), 175.32 (C_{quat}); MS (70 eV), *m/z*: 444 (7) [M$^+$], 399 (10), 311 (31), 265 (20), 236 (64), 235 (100), 191 (32), 163 (20), 134 (50), 119 (34); $C_{26}H_{36}O_6$ Calcd: 444.2512 (HRMS correct).

4-(3'*S*,7*R*)-{8',8'-Bis(methoxycarbonyl)bicyclo[4.3.0]non-1'(6')-enyl-3'-carbonyl}-4-aza-10,10-dimethyl-5-thiatricyclo[5.2.1.0^{3,7}]decane-5,5-dioxide (41c-X*): Colorless crystals, mp. 89 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.94 (s, 3 H), 1.11 (s, 3 H), 1.83–2.00 (m, 17 H), 2.86–3.07 (m, 1 H), 3.40 and 3.48 (AB, $^2J_{AB}$ = 13.8, 2 H), 3.68 (s, 3 H), 3.69 (s, 3 H), 3.85 (dd, ^3J = 6.2, 6.3, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 19.73 (+), 20.77 (+), 23.98 (–), 24.51 (–), 26.32 (–), 28.95 (–), 32.70 (–), 38.41 (–), 40.72 (–), 43.55 (–), 43.65 (+), 44.53 (+), 47.60 (C_{quat}), 48.20 (C_{quat}), 52.61 (+), 52.99 (–), 57.69 (C_{quat}), 65.08 (+), 129.39 (C_{quat}), 131.45 (C_{quat}), 172.50 (C_{quat}), 172.68 (C_{quat}), 175.20 (C_{quat}); IR (KBr): ν = 2983 cm^{-1}, 2867, 1734, 1431, 1250, 1070, 986, 842, 761, 699, 642; MS (70 eV), *m/z* : 479 (58) [M$^+$], 419 (33), 236 (50), 176 (63), 83 (100); $C_{24}H_{33}NO_7S$ Calcd: 479.1977 (HRMS correct).

Diethyl 3-Chloro-3-cyanobicyclo[4.3.0]non-1(6)-ene-8,8-dicarboxylate (41d): Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.18 (t, *J* = 7.0, 6 H), 2.22 (m, 4 H), 2.65 (bd, *J* = 13.5, 1 H), 2.88 (bd, *J* = 13.5, 1 H), 2.92 (bs, 4 H), 4.17 (q, *J* = 7.0, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.94 (+), 22.81 (–), 35.93 (–), 39.87 (–), 42.82 (–), 43.01 (–), 54.27 (C_{quat}), 57.89 (C_{quat}), 61.67 (–), 119.25 (C_{quat}), 126.65 (C_{quat}), 131.56 (C_{quat}), 171.53 (C_{quat}), 171.75 (C_{quat}); MS (70 eV), *m/z*: 327/325 (6/18) [M$^+$], 290 (2), 282/280 (3/8), 253/251 (37/100), 208 (19), 171 (90), 165 (59), 164 (49), 139 (37), 91 (56); IR (film): ν = 2980 cm^{-1}, 2928, 2239, 1732, 1558; Anal. Calcd. for $C_{16}H_{20}ClNO_4$: C, 58.99; H, 6.19; N, 4.30. Found: C, 58.83; H, 6.13; N, 4.33.

Tetraethyl (3*R,4*R**)-Bicyclo[4.3.0]non-1(6)-ene-3,4,8,8-tetracarboxylate (41e-Et):** Colorless crystals, mp. 51 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.241, 1.242 (t, *J* = 7.1, 12 H), 2.05–2.2 (m, 2 H), 2.36 (bd, *J* = 17.7, 2 H), 2.75–3.05 (m, 6 H), 4.13, 4.19 (q, *J* = 7.1, 8 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.94 (+), 14.07 (+), 27.95 (–), 41.96 (+), 43.26 (–), 58.20 (C_{quat}), 60.52 (–), 61.48 (–), 130.12 (C_{quat}), 172.01 (C_{quat}), 174.46 (C_{quat}); MS (70 eV), *m/z*: 410 (16) [M$^+$], 365 (33), 364 (15), 336 (26), 290 (16), 263 (95), 262 (100), 217 (29), 189 (53), 173 (24), 145 (16), 117 (49), 115 (18), 91 (12); IR (KBr): ν = 2982 cm^{-1}, 2937, 1734, 1446, 1296, 1255, 1186, 1070, 861, 734; Anal. Calcd. for $C_{21}H_{30}O_8$: C, 61.45; H, 7.37. Found: C, 61.62; H, 7.39.

Diethyl (3*R,4*R**)-Bis(methoxycarbonyl)bicyclo[4.3.0]non-1(6)-ene-8,8-dicarboxylate (41e-Me):** Colorless crystals, mp. 80–81 °C; ^{1}H NMR (250 MHz, C_6D_6): δ = 0.92 (t, *J* = 7.1, 6 H), 1.75–1.95 (m, 2 H), 2.07 (bd, *J* = 17.3, 2 H), 2.83–2.90 (m, 2 H), 3.00, 3.07 (bAB, *J* = 16.7, 4 H), 3.33 (s, 6 H), 3.98 (q, *J* = 7.1, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.00 (+), 27.93 (–), 41.83 (+), 43.25 (–), 51.88 (+), 58.11 (C_{quat}), 61.56 (–), 130.06 (C_{quat}), 172.05 (C_{quat}), 175.02 (C_{quat}); IR (KBr): ν = 2985 cm^{-1}, 1734, 1443, 1339, 1220, 1128, 1085, 1003, 909; MS (70 eV), *m/z*: 382 (15) [M$^+$], 351 (15), 337 (6), 322 (10), 308 (19), 277 (10), 276 (16), 263 (22), 249 (34), 248 (100), 217 (10), 189 (31), 175 (12), 173 (10), 117 (30), 115 (15), 91 (7); Anal. Calcd. for $C_{19}H_{26}O_8$: C, 59.68; H, 6.85. Found: C, 59.64; H, 6.80.

Diethyl (3*R,4*S**)-Bis(methoxycarbonyl)bicyclo[4.3.0]non-1(6)-ene-8,8-dicarboxylate (41f-Me):** Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.24 (t, *J* = 7.5, 6 H), 2.29 (bd, *J* = 16.0, 2 H), 2.48 (bd, *J* = 16.0, 2 H), 2.91–3.05 (m, 4 H), 3.06 (t, *J* = 5.0, 2 H), 3.40 (s, 6 H), 4.10 (q, *J* = 7.5, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.76 (+), 25.66 (–), 40.14 (+), 43.17 (–), 51.95 (+), 57.87 (C_{quat}), 61.23 (–), 129.96 (C_{quat}), 171.62 (C_{quat}), 172.03 (C_{quat}), 173.18 (C_{quat}); IR (KBr): ν = 2983 cm^{-1}, 1735, 1553; MS (70 eV), *m/z*: 382 (4) [M$^+$], 351 (11), 322 (11), 276 (6), 263 (63), 248 (100), 189 (54), 117 (59), 91 (25); Anal. Calcd. for $C_{19}H_{26}O_8$: C, 59.68; H, 6.85. Found: C, 59.54; H, 6.95.

Diethyl 3,3,4,4-Tetracyanobicyclo[4.3.0]non-1(6)-ene-8,8-dicarboxylate (41g): Colorless crystals, mp. 171–173 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (t, *J* = 7.0, 6 H), 3.107 (s, 4 H), 3.110 (s, 4 H), 4.23 (q, *J* = 7.0, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.96 (+), 33.08 (–), 38.23 (C_{quat}), 42.56 (–), 58.03 (C_{quat}), 62.29 (–), 110.42 (C_{quat}), 127.54 (C_{quat}), 170.47 (C_{quat}); MS (70 eV), *m/z*: 366 [M$^+$], 337, 293, 248, 189, 117; IR (KBr): ν = 2996 cm^{-1}, 2959, 2898, 2361, 2336, 1732, 1646, 1500, 1456, 1266, 1178, 1121, 1060, 908; Anal. Calcd. for $C_{19}H_{18}N_4O_4$: C, 62.29; H, 4.95. Found: C, 62.57; H, 5.38.

Hexaethyl Bicyclo[4.3.0]non-1(6)-ene-3,3,4,4,8,8-hexacarboxylate (41h-Et): Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.22–1.35 (m, 18 H), 2.15–2.30 (m, 4 H), 2.95 (bs, 4 H), 4.21–4.35 (m, 12 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.15, 13.36, 31.36, 41.01, 57.57, 57.63, 60.57, 60.94, 61.89, 134.83, 161.64, 171.02; MS (70 eV), *m/z*: 554 (9) [M$^+$], 509 (8), 435 (9), 407 (18), 361 (35), 311 (32), 239 (16), 164 (39), 107 (23), 91 (22), 43 (100); IR (film): ν = 2984 cm^{-1}, 1730, 1552; Anal. Calcd. for $C_{27}H_{38}O_{12}$: C, 58.48; H, 6.91. Found: C, 58.54; H, 7.05.

Diethyl 4'-Methoxycarbonylbicyclo[4.3.0]non-1'(6')-ene-3'-spiro-1-cyclopropane-8',8'-dicarboxylate (41i): Colorless oil; ^{1}H NMR (250 MHz, C_6D_6): δ = 0.09–0.19 (m, 2 H), 0.26–0.33 (m, 1 H), 0.65–0.70 (m, 1 H), 0.89 (t, *J* = 7.1, 3 H), 0.90 (t, *J* = 7.1, 3 H), 1.32 (bd, *J* = 16.7, 1 H), 1.88 (dd, *J* = 5.7, 4.4, 1 H), 1.96–2.20 (m, 2 H), 2.44 (bd, *J* = 16.9, 1 H), 3.10–3.25 (m, 4 H), 3.28 (s, 3 H), 3.94 (q, *J* = 7.1, 2 H) 3.96 (q, *J* = 7.1, 2 H); ^{13}C NMR (62.9 MHz, C_6D_6): δ = 11.15 (–), 12.75 (–), 13.99 (+), 17.92 (C_{quat}), 27.58 (–), 34.31 (–), 44.00 (–), 44.06 (–), 46.22 (+), 50.97 (+), 58.63 (C_{quat}), 61.27 (–), 130.48 (C_{quat}), 131.90 (C_{quat}), 171.93 (C_{quat}), 172.22 (C_{quat}), 173.52 (C_{quat}); MS (70 eV), *m/z*: 350 (11) [M$^+$], 305 (8), 291 (42), 276 (40), 245 (31), 217 (100), 201 (19), 189 (14), 171 (13), 143 (60), 129 (15), 117 (19), 91 (18); IR (film): ν = 2999 cm^{-1}, 2952, 1734, 1435; Anal. Calcd. for $C_{19}H_{26}O_6$: C, 65.13; H, 7.48. Found: C, 65.25; H, 7.52.

Diethyl 4'-Chloro-4'-methoxycarbonylbicyclo[4.3.0]non-1'(6')-ene-3'-spiro-1-cyclopropane-8',8'-dicarboxylate (41j): Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.31–0.40 (m, 1 H), 0.51–0.65 (m, 1 H), 0.88–1.00 (m, 1 H), 1.03–1.15 (m, 1 H), 1.25 (t, *J* = 7.3, 6 H), 1.75–1.90 (m, 1 H), 2.31–2.45 (m, 1 H), 2.45–2.60 (m, 1 H), 2.95–3.02 (m, 4 H), 3.05–3.20 (m, 1 H), 3.40 (s, 3 H), 4.17 (q, *J* = 7.3, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 9.66 (–), 10.48 (–), 14.03 (+), 22.00 (C_{quat}), 35.25 (–), 38.29 (–), 42.98 (–), 43.17 (–), 52.97 (+), 58.37 (C_{quat}), 61.55 (–), 70.68 (C_{quat}), 129.95 (C_{quat}), 131.55 (C_{quat}), 170.18 (C_{quat}), 171.91 (C_{quat}), 172.10 (C_{quat}); MS (70 eV), *m/z*: 386/384 (3/9) [M$^+$], 349 (9), 275 (17), 220 (23), 205 (89), 165 (28), 153 (60), 135 (68), 113 (95), 43 (100); IR (film): ν = 3011 cm^{-1}, 1731, 1620; Anal. Calcd. for $C_{19}H_{25}ClO_6$: C, 59.29; H, 6.55; Cl, 9.21. Found: C, 59.29; H, 6.62; Cl, 9.44.

Diethyl Tricyclo[7.3.0.0^{3,7}]dodec-1(9)-ene-4-one-11,11-dicarboxylate (41k): Colorless oil, mixture of *cis/trans*-isomers (1:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.238, 1.242, 1.248 (t, *J* = 7.1, 6 H), 2.45–2.65 (m, 10 H), 2.75–3.10 (m, 4 H), 4.176, 4.184, 4.191 (q, *J* = 7.1, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$, *cis/trans* assignments according to ref.[49]): δ = 14.00 (+), 21.76 (–), 24.95 (–), 26.38 (–), 26.51 (–), 27.50 (–), 31.94 (–), 34.14 (–), 38.12 (–), 43.40 (–), 43.67 (–), 43.93 (–), 46.28 (–), 57.75 (C_{quat}), 58.63 (C_{quat}), 61.42 (–), 61.45 (–), 129.46 (C_{quat}), 130.04 (C_{quat}), 131.53 (C_{quat}), 132.13 (C_{quat}), 172.08 (C_{quat}), 172.27 (C_{quat}), 172.46 (C_{quat}); *cis*: 33.19 (+), 47.79 (+), 218.52 (C_{quat}); *trans*: 39.97 (+), 52.37 (+), 217.45 (C_{quat}); MS (70 eV), *m/z*: 320 (36) [M$^+$], 275 (7), 247 (29), 246 (100), 202 (8), 201 (12), 200 (13), 192 (10), 173 (25), 172 (11), 164 (19), 91 (14); IR (film): ν = 2981 cm^{-1}, 1734, 1457, 1367, 1255, 1183, 1096, 1015, 917, 859, 733; $C_{18}H_{24}O_5$ Calcd: 320.16245 (HRMS correct).

Diethyl 1,9-Dicyanotricyclo[7.2.0.0^{3,7}]undec-3(7)-ene-5,5-dicarboxylate (41l): Colorless crystals, mp. 88–89 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.26, 1.27 (t, *J* = 7.1, 6 H), 2.05 (AA', 2 H), 2.42, 2.61 (bAB, *J* = 16.2, 4 H), 2.66 (BB', 2 H), 2.99, 3.11 (bAB, *J* = 16.4, 4 H), 4.21, 4.22 (q, *J* = 7.1, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.97 (+), 13.98 (+), 29.46 (–), 32.46 (–), 38.04 (C_{quat}), 43.72 (–), 58.09 (C_{quat}), 61.82 (–), 121.16 (C_{quat}), 129.54 (C_{quat}), 171.20 (C_{quat}), 171.85 (C_{quat}); MS (70 eV), *m/z*: 342 (17) [M$^+$], 297 (11), 268 (100), 250 (8), 240 (17), 223 (51), 196 (19), 167 (17), 141 (11), 119 (7), 91 (32); IR (KBr): ν = 2983 cm^{-1}, 2962, 2232, 1748, 1446, 1366, 1274, 1187, 1154, 1097, 1012, 863, 788; Anal. Calcd. for $C_{19}H_{22}N_2O_4$: C, 66.65; H, 6.48; N, 8.18. Found: C, 66.71; H, 6.49; N, 8.16.

Diethyl 10,10-Dimethyl-1-methoxycarbonyltricyclo[7.1.0.0^{3,7}]dec-3(7)-ene-5,5-dicarboxylate (41m): Colorless crystals, mp. 67–68 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.81 (s, 3 H), 1.06 (s, 3 H), 1.19, 1.20 (t, *J* = 7.1, 6 H), 1.66 (d, *J* = 7.7, 1 H), 1.90 (bd, *J* = 18.5, 1 H), 2.15 (bd, *J* = 19.8, 1 H), 2.23–2.40 (m, 1 H), 2.56 (bd, *J* = 19.8, 1 H), 2.78, 2.84 (bAB, *J* = 16.4, 4 H), 3.63 (s, 3 H), 4.13, 4.14 (q, *J* = 7.1, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.91 (+), 13.92 (+), 14.57 (+), 20.78 (–), 22.30 (+), 23.41 (–), 25.22 (+), 26.58 (C_{quat}), 29.65 (C_{quat}), 43.13 (–), 43.17 (–), 51.60 (+), 57.39 (C_{quat}), 61.34 (–), 61.37 (–), 129.14 (C_{quat}), 129.29 (C_{quat}), 172.09 (C_{quat}), 172.20 (C_{quat}), 174.71 (C_{quat}); MS (70 eV), *m/z*: 364 (100) [M$^+$], 333 (26), 332 (30), 321 (50), 319 (25), 290 (34), 275 (48), 247 (82), 231 (33), 217 (20), 185 (53), 175 (50), 157 (33),

117 (18), 115 (18), 91 (16); IR (KBr): ν = 2989 cm^{-1}, 2929, 1734, 1259, 1124, 1071; Anal. Calcd. for $C_{20}H_{28}O_6$: C, 65.92; H, 7.74. Found: C, 65.93; H, 7.72.

Diethyl 3,4-Bis(methoxycarbonyl)bicyclo[4.3.0]nona-1(6),3-diene-8,8-dicarboxylate (45): Colorless crystals, mp. 131–134 °C; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.26 (t, *J* = 7.0, 6 H), 2.98 (s, 8 H), 3.78 (s, 6 H), 4.19 (q, *J* = 7.0, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.99 (+), 28.64 (–), 42.83 (–), 52.20 (+), 57.92 (C_{quat}), 61.63 (–), 127.90 (C_{quat}), 132.90 (C_{quat}), 168.34 (C_{quat}), 171.91 (C_{quat}); MS (70 eV), *m/z*: 380 (18) [M^+], 349 (26), 333 (22), 275 (67), 274 (100), 247 (13), 216 (30), 201 (76), 143 (29), 115 (29); IR (KBr): ν = 2891 cm^{-1}, 2700, 1735, 1450; Anal. Calcd. for $C_{19}H_{24}O_8$: C, 59.99; H, 6.36. Found: C, 60.09; H, 6.48.

Tetraethyl 3,4-Diazabicyclo[4.3.0]non-1(6)-ene-3,4,8,8-tetracarboxylate (46): Colorless crystals, mp. 90 °C; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.21 (t, *J* = 7.1, 12 H), 2.90, 3.02 (bAB, *J* = 16.6, 4 H), 3.69 (bd, *J* = 16.0, 2 H), 4.16 (q, *J* = 7.1, 8 H), 4.38 (bd, *J* = 16.0, 2 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.97 (+), 14.52 (+), 41.12 (–), 44.31 (–), 58.20 (C_{quat}), 61.78 (–), 62.42 (–), 129.23 (C_{quat}), 155.39 (C_{quat}), 171.52 (C_{quat}); MS (70 eV), *m/z*: 412 (57) [M^+], 367 (21), 339 (45), 293 (13), 250 (100), 249 (76), 221 (13), 193 (19), 165 (27), 119 (16), 91 (29); IR (KBr): ν = 2987 cm^{-1}, 2908, 2860, 1742, 1730, 1420, 1378, 1298, 1259, 1175, 1143, 1118, 1022, 929, 860, 756; Anal. Calcd. for $C_{19}H_{28}N_2O_8$: C, 55.33; H, 6.84; N, 6.79. Found: C, 55.30; H, 6.86; N, 6.86.

Tetraethyl Pentacyclo[15.3.0.0.^{3,15}0.^{5,13}0^{7,11}]eicosa-1(17),7(11)-diene-4,14-dione-9,9,19,19-tetracarboxylate (50): Colorless crystals, mp. 208–211 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.22 (t, *J* = 7.0, 12 H), 2.18–2.30 (m, 8 H), 2.43–2.60 (m, 8 H) 3.00–3.15 (m, 4 H), 4.17–4.30 (m, 8 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.03 (+), 24.61 (–), 43.54 (–), 44.39 (+), 57.49 (C_{quat}), 61.61 (–), 129.49 (C_{quat}), 172.23 (C_{quat}), 209.52 (C_{quat}); MS (70 eV), *m/z*: 584 (100) [M^+], 539 (15), 510 (24), 464 (14), 437 (17), 390 (12), 363 (9), 346 (27), 272 (40), 165 (31), 145 (56), 117 (90); IR (KBr): ν = 2940 cm^{-1}, 1733, 1465; Anal. Calcd. for $C_{32}H_{40}O_{10}$: C, 65.74; H, 6.89. Found: C, 65.69; H, 6.99.

Diethyl 5,8-Dioxo-1,3,5,8-tetrahydrocyclopenta[*b*]naphthalene-2,2-dicarboxylate (52): Colorless crystals, mp. 142–145 °C; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7.1, 6 H), 3.69 (s, 4 H), 4.20 (q, *J* = 7.1, 4 H), 6.92 (s, 2 H), 7.90 (s, 2 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.90 (+), 40.42 (–), 60.07 (C_{quat}), 62.02 (–), 122.25 (+), 131.42 (C_{quat}), 138.41 (+), 146.89 (C_{quat}), 170.80 (C_{quat}), 184.90 (C_{quat}); MS (70 eV), *m/z*: 342 (59) [M^+], 269 (53), 268 (100), 241 (59), 223 (20), 196 (96); IR (KBr): ν = 2980 cm^{-1}, 1736, 1520; Anal. Calcd. for $C_{19}H_{18}O_6$: C, 66.66; H, 5.30. Found: C, 66.46; H, 5.43.

Diethyl 5,8-Dioxo-1,3,4,5,10,11-hexahydrocyclopenta[*b*]antracene-2,2-dicarboxylate (54): Colorless crystals, mp. 156–157 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.26 (t, *J* = 7.1, 6 H), 3.07 (s, 4 H), 3.20 (s, 4 H), 4.23 (q, *J* = 7.0, 4 H), 7.71–7.85 (m, 2 H), 8.08–8.15 (m, 2 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.02 (+), 25.73 (–), 43.12 (–), 57.72 (C_{quat}), 61.68 (–), 126.24 (+), 128.05 (C_{quat}), 131.97 (C_{quat}), 133.56 (+), 141.97 (C_{quat}), 172.08 (C_{quat}), 184.49 (C_{quat}); MS (70 eV), *m/z*: 394 (36) [M^+], 349 (6), 320 (100), 291 (15), 275 (7), 247 (95), 189 (9); IR (KBr): ν = 2991 cm^{-1}, 1732, 1514; Anal. Calcd. for $C_{23}H_{22}O_6$: C, 70.04; H, 5.62. Found: C, 70.07; H, 5.42.

Trimethyl 2-Methylbicyclo[4.3.0]non-1(6)-ene-3,8,8-tricarboxylate (55c-Me): Colorless oil, mixture of 2 isomers (A/B = 2:1); ^1H NMR (250 MHz, $CDCl_3$): Isomer A: δ = 0.88 (d, *J* = 7.0, 3 H); Isomer B: δ = 1.00 (d, *J* = 7.0, 3 H); 1.6–2.7 (m, 6 H), 2.7–3.2 (m, 4 H), 3.69 (s, 3 H), 3.73 (s, 6 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): Isomer A: δ = 14.33 (+), 19.56 (–), 24.65 (–), 31.53 (+), 42.32 (–), 43.75 (–), 44.30 (+), 51.26 (+), 58.04 (C_{quat}), 131.21 (C_{quat}), 135.43 (C_{quat}), 174.91 (C_{quat}); Isomer B: δ = 17.90 (+), 24.48 (–), 25.79 (–), 32.77 (+), 41.69 (–), 43.97 (–), 48.28 (+), 51.49 (+), 57.88 (C_{quat}), 131.01 (C_{quat}), 134.42 (C_{quat}), 176.10 (C_{quat}); δ = 52.68 (+), 172.69 (C_{quat}), 172.76 (C_{quat}), 172.80 (C_{quat}); MS (70 eV), *m/z*: 310 (17) [M^+], 279

(8), 250 (100), 224 (10), 192 (26), 191 (68), 190 (89), 165 (47), 164 (38), 159 (17), 131 (75), 105 (51), 91 (22); IR (film): ν = 2954 cm^{-1}, 1734, 1436, 1258, 1197, 1163, 1072, 1014, 959, 864; Anal. Calcd. for $C_{16}H_{22}O_6$: C, 61.92; H, 7.14. Found: C, 61.81; H, 7.11.

Dimethyl (3*R,4*R**)-Bis(ethoxycarbonyl)-2-methylbicyclo[4.3.0]non-1(6)-ene-8,8-dicarboxylate (55e-Et)**: Colorless oil, mixture of 2 isomers (A/B = 2:1); ^1H NMR (250 MHz, $CDCl_3$): Isomer A: δ = 0.88 (d, J = 6.8, 3 H), 1.24 (t, J = 7.1, 6 H), 4.13 (q, J = 7.1, 4 H); Isomer B: δ = 1.03 (d, J = 7.0, 3 H) 1.26 (t, J = 7.1, 6 H), 4.14 (q, J = 7.1, 4 H); δ = 1.9–2.7 (m, 5 H), 2.7–3.2 (m, 4 H), 3.73 (s, 6 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): Isomer A: δ = 14.83 (+), 28.93 (–), 31.44 (+), 37.58 (+), 42.04 (–), 43.26 (–), 46.44 (+), 52.75 (+), 58.13 (C_{quat}), 129.28 (C_{quat}), 135.69 (C_{quat}); Isomer B: δ = 17.29 (+), 31.55 (–), 34.68 (+), 41.34 (–), 43.17 (+), 43.59 (–), 50.53 (+), 52.74 (+), 58.01 (C_{quat}), 129.70 (C_{quat}), 134.57 (C_{quat}); δ = 14.00 (+), 14.10 (+), 14.17 (+), 60.38 (–), 60.47 (–), 60.60 (–), 172.41, 172.45, 172.47, 173.35, 174.00, 174.56, 175.27 (8 C, C_{quat}); mixture: MS (70 eV), *m/z*: 396 (1) [M^+], 351 (7), 350 (8), 322 (5), 262 (8), 217 (5), 189 (9), 140 (100), 105 (5); IR (film): ν = 2956 cm^{-1}, 1734, 1436, 1374, 1255, 1184, 1127, 1073, 1031, 958, 861; Anal. Calcd. for $C_{20}H_{28}O_8$: C, 60.59; H, 7.12. Found: C, 60.70; H, 7.19.

Trimethyl 2,2-Dimethylbicyclo[4.3.0]non-1(6)-ene-3,8,8-dicarboxylate (63c-Me): Colorless oil; ^1H NMR (250 MHz, C_6D_6): δ = 1.06 (s, 3 H), 1.16 (s, 3 H), 1.60–1.70 (m, 3 H), 1.80–1.93 (m, 1 H), 2.32 (dd, J = 2.7, 12.2, 1 H), 3.04 and 3.09 (bAB, J = 16.4, 2 H), 3.17 (bs, 2 H), 3.30 (s, 3 H), 3.32 (s, 6 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.22 (+), 22.49 (–), 24.47 (–), 26.74 (+), 34.86 (C_{quat}), 39.48 (–), 43.84 (–), 50.95 (+), 51.15 (+), 52.77 (+), 57.68 (C_{quat}), 130.31 (C_{quat}), 138.29 (C_{quat}), 172.66 (C_{quat}), 172.73 (C_{quat}), 174.91 (C_{quat}); MS (70 eV), *m/z*: 324 (14) [M^+], 292 (11), 264 (39), 239 (50), 215 (48), 213 (100), 211 (52), 205 (17), 204 (20), 189 (14), 179 (11), 147 (19), 128 (30), 117 (17), 94 (12); IR (film): ν = 2955 cm^{-1}, 1739, 1435, 1365, 1259, 1200, 1158, 1073, 1017, 960, 865; $C_{17}H_{24}O_6$ Calcd: 324.1573 (HRMS correct)

Dimethyl 4'-Acetylbicyclo[4.3.0]non-1'(6')-ene-2'-spiro-1-cyclopropane-8',8'-dicarboxylate (65b): Colorless oil; ^1H NMR (250 MHz, C_6D_6): δ = 0.1–0.26 (m, 2 H), 0.55–0.68 (m, 2 H), 1.10–1.40 (m, 2 H), 1.67 (s, 3 H), 1.60–2.50 (m, 3 H), 2.80–3.20 (m, 4 H), 3.35 (s, 6 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 10.95 (–), 12.51 (–), 18.62 (C_{quat}), 27.53 (+), 27.72 (–), 36.26 (–), 39.52 (–), 44.60 (–), 47.57 (+), 52.32 (+), 57.93 (C_{quat}), 130.94 (C_{quat}), 135.00 (C_{quat}), 172.32 (C_{quat}), 172.57 (C_{quat}), 208.29 (C_{quat}); MS (70 eV), *m/z*: 306 (10) [M^+], 263 (21), 246 (29), 231 (34), 203 (100), 143 (90), 128 (26), 115 (32), 91 (16); IR (film): ν = 3022 cm^{-1}, 1721, 1620, 1580, 1536, 1221, 1138; Anal. Calcd. for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24. Found: C, 66.52; H, 7.37.

Trimethyl Bicyclo[4.3.0]non-1'(6')-ene-2'-spiro-1-cyclopropane-4',8',8'-tricarboxylate (65c-Me): Colorless oil; ^1H NMR (500 MHz, C_6D_6): δ = 0.12–0.16 (m, 1 H), 0.23–0.28 (m, 1 H), 0.50–0.55 (m, 1 H), 0.60–0.65 (m, 1 H), 1.23 (dd, J = 3.0, 13.0, 1 H), 1.92 (t, J = 12.2, 1 H), 2.03–2.09 (m, 1 H), 2.18–2.26 (m, 1 H), 2.56–2.62 (m, 1 H), 2.76–2.79 (m, 2 H), 3.04 and 3.14 (AB, J = 16.5, 2 H), 3.27 (s, 6 H), 3.29 (s, 3 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 10.95 (–), 12.33 (–), 18.45 (C_{quat}), 28.34 (–), 36.93 (–), 39.51 (–), 39.88 (+), 44.51 (–), 51.08 (+), 52.30 (+), 57.88 (C_{quat}), 130.83 (C_{quat}), 134.91 (C_{quat}), 172.31 (C_{quat}), 172.46 (C_{quat}), 174.92 (C_{quat}); MS (70 eV), *m/z*: 322 (20) [M^+], 291 (3), 263 (40), 262 (50), 231 (28), 203 (100), 171 (19), 143 (78), 128 (22), 115 (24), 91 (36); IR (film): ν = 3000 cm^{-1}, 2953, 1735, 1653, 1435, 1259, 1198, 1171; Anal. Calcd. for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88. Found: C, 63.24; H, 6.92.

Dimethyl 4'-*tert*-Butoxycarbonylbicyclo[4.3.0]non-1'(6')-ene-2'-spiro-1-cyclopropane-8',8'-dicarboxylate (65c-*t*Bu): Colorless oil; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.20–0.82 (m, 4 H), 1.41 (s, 9 H), 1.80–2.35 (m, 2 H), 2.55–2.70 (m, 5 H), 2.90–3.10 (m, 2 H), 3.70–3.80 (m, 6 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 10.89 (–), 12.18 (–), 15.23 (+), 18.26 (C_{quat}), 28.04 (–), 36.57 (–), 39.06 (–), 40.85 (+), 44.17 (–), 52.75 (+), 57.56 (C_{quat}), 80.02 (C_{quat}), 130.55 (C_{quat}), 134.57 (C_{quat}), 172.68 (C_{quat}), 174.63 (C_{quat}); MS

(70 eV), *m/z*: 364 (12) [M+], 333 (3), 308 (42), 291 (18), 262 (60), 249 (49), 248 (100), 231 (26), 205 (67), 189 (45), 171 (19), 143 (59), 128 (20), 115 (18), 91 (28), 57 (31); IR (film): ν = 3027 cm^{-1}, 2879, 2845, 1734, 1701, 1457, 1368, 1259, 1073; $C_{20}H_{28}O_6$ Calcd: 364.1885 (HRMS correct).

4-(4''*S*,7*R*)-{8'',8''-Bis(methoxycarbonyl)bicyclo[4.3.0]non-1''(6'')-enyl-2''-(spiro-1'-cyclopropane)-4''-carbonyl}-4-aza-10,10-dimethyl-5-thiatricyclo[5.2.1.0^{3,7}]decane-5,5-dioxide (65c-X*): Colorless crystals, mp. 57 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.55–1.01 (m, 4 H), 0.94 (s, 3 H), 1.11 (s, 3 H), 1.55–2.10 (m, 15 H), 2.70–3.00 (m, 1 H), 3.45 and 3.55 (AB, $^2J_{AB}$ = 13.8, 2 H), 3.69 (s, 3 H), 3.73 (s, 3 H), 3.99 (dd, ^3J = 6.2, 6.3, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 10.24 (–), 12.83 (–), 18.02 (C_{quat}), 19.11 (+), 20.52 (+), 24.44 (–), 24.91 (–), 27.02 (–), 32.78 (–), 38.79 (–), 40.88 (–), 43.19 (–), 43.72 (+), 44.12 (+), 48.05 (C_{quat}), 48.12 (C_{quat}), 52.99 (+), 54.45 (–), 57.41 (C_{quat}), 65.48 (+), 129.77 (C_{quat}), 131.65 (C_{quat}), 172.55 (C_{quat}), 172.81 (C_{quat}), 175.43 (C_{quat}); IR (KBr): ν = 2988 cm^{-1}, 2867, 1730, 620; MS (70 eV), *m/z*: 505 (12) [M+], 437 (13), 236 (50), 176 (52), 83 (100); $C_{26}H_{35}NO_7S$ Calcd: 505.2134 (HRMS correct).

Trimethyl Bicyclo[4.3.0]non-1'(6')-ene-2'-spiro-1-cyclobutane-3',8',8'-tricarboxylate (66c-Me) and Trimethyl Bicyclo[4.3.0]non-1'(6')-ene-2'-spiro-1-cyclobutane-4',8',8'-tricarboxylate (67c-Me): Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$): Signals for **66c-Me** and **67c-Me**: δ = 1.60–2.35 (m, 10 H), 2.75–3.30 (overlapping AB systems, 4 H), 3.74 (s, 6 H); for **66c-Me**: δ = 2.40–2.60 (m, 1 H), 3.69 (s, 3 H); for **67c-Me**: δ = 2.65 (dd, *J* = 4.2, 7.2, 1 H), 3.68 (s, 3 H); **66c-Me**: ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 15.63 (–), 27.99 (–), 30.36 (–), 31.60 (–), 37.56 (+), 38.81 (–), 39.51 (C_{quat}), 40.06 (–), 43.76 (–), 51.57 (+), 52.69 (+), 57.62 (C_{quat}), 129.28 (C_{quat}), 137.28 (C_{quat}), 172.60 (C_{quat}), 172.67 (C_{quat}), 175.92 (C_{quat}); **67c-Me**: ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 15.48 (–), 22.61 (–), 23.65 (–), 28.37 (–), 30.69 (–), 40.41 (–), 41.14 (C_{quat}), 43.80 (–), 49.21 (+), 51.26 (+), 52.72 (+), 57.68 (C_{quat}), 129.79 (C_{quat}), 136.85 (C_{quat}), 172.52 (C_{quat}), 172.78 (C_{quat}), 174.69 (C_{quat}); mixture: MS (70 eV), *m/z*: 336 (3) [M+], 308 (24), 276 (10), 249 (100), 248 (33), 217 (48), 207 (27), 195 (33), 189 (72), 157 (21), 134 (55), 129 (59), 115 (18), 91 (24), 79 (34), 59 (42); IR (film): ν = 2953 cm^{-1}, 1741, 1435, 1364, 1260, 1200, 1169, 1073, 1010, 918, 864, 733; $C_{18}H_{24}O_6$ Calcd: 336.1573 (HRMS correct).

Trimethyl Bicyclo[4.3.0]non-1'(6')-ene-2'-spiro-1-cyclopentane-3',8',8'-tricarboxylate (68c-Me): Colorless oil; ^{1}H NMR (250 MHz, C_6D_6): δ = 1.40–1.90 (m, 11 H), 1.98–2.09 (m, 1 H), 2.44 (dd, *J* = 2.7, 9.6, 1 H), 3.086 and 3.092 (bAB, *J* = 15.6, 2 H), 3.21 (bs, 2 H), 3.30 (s, 3 H), 3.33 (s, 3 H), 3.34 (s, 3 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 24.01 (–), 24.16 (–), 26.57 (–), 26.94 (–), 33.66 (–), 36.43 (–), 39.98 (–), 43.69 (–), 45.52 (C_{quat}), 49.83 (+), 51.30 (+), 52.77 (+), 57.72 (C_{quat}), 129.43 (C_{quat}), 138.17 (C_{quat}), 172.67 (C_{quat}), 172.83 (C_{quat}), 175.29 (C_{quat}); MS (70 eV), *m/z*: 350 (15) [M+], 318 (8), 290 (47), 258 (8), 230 (40), 198 (39), 195 (48), 194 (44), 166 (35), 135 (49), 134 (100), 107 (44), 91 (26), 84 (51), 79 (45), 59 (46); IR (film): ν = 2952 cm^{-1}, 2868, 1734, 1653, 1559, 1436, 1364, 1257, 1199, 1074, 967; $C_{19}H_{26}O_6$ Calcd: 350.1729 (HRMS correct).

Dimethyl (3'*R,4'*R**)-Diethoxycarbonylbicyclo[4.3.0]non-1'(6')-ene-2',5'-di(spiro-1-cyclopropane)-8',8'-dicarboxylate (69e-Et):** Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.55–0.67 (m, 4 H), 0.71–0.77 (m, 2 H), 0.71–0.77 (m, 2 H), 1.23 (t, *J* = 7.1, 6 H), 2.74 (s, 4 H), 2.85 (s, 2 H), 3.71 (s, 6 H), 4.01–4.20 (m, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 9.79 (–), 11.54 (–), 14.13 (+), 18.36 (C_{quat}), 39.52 (–), 50.89 (+), 52.80 (+), 57.37 (C_{quat}), 60.49 (–), 133.17 (C_{quat}), 172.18 (C_{quat}), 172.60 (C_{quat}); MS (70 eV), *m/z*: 434 (23) [M+], 389 (6), 375 (11), 361 (50), 360 (43), 315 (100), 301 (88), 300 (37), 287 (25), 255 (24), 241 (16), 227 (25) 205 (25), 195 (13), 169 (44), 167 (25), 141 (25), 115 (18), 91 (37), 59 (24), 43 (40); IR (film): ν = 3082 cm^{-1}, 2982, 2955, 1737, 1435, 1370, 1258, 1175, 1030, 966, 861, 733; $C_{23}H_{30}O_8$ Calcd: 434.1940 (HRMS correct).

Methyl 8-Hydroxybicyclo[4.3.0]non-1(6)-ene-3-carboxylate (77c-Me): Colorless oil, mixture of 2 isomers (2:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.65–1.85 (m, 1 H), 2.00–2.30 (m, 8 H), 2.50–2.70 (m, 3 H), 3.58 (s, 3 H), 4.50 (bs, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 24.59 (–), 24.82 (–), 25.59 (–), 27.93 (–), 28.01 (–), 39.72 (+), 39.91 (+), 45.82 (–), 45.88 (–), 45.93 (–), 51.90 (+), 70.80 (+), 70.87 (+), 130.26 (C_{quat}), 130.33 (C_{quat}), 131.57 (C_{quat}), 131.69 (C_{quat}), 176.28 (C_{quat}); MS (70 eV), *m/z*: 196 (9) [M$^+$], 178 (10), 165 (5), 146 (18), 136 (12), 119 (100), 118 (60), 91 (49); IR (film): ν = 3433 cm^{-1} (OH), 2916, 2838, 1734, 1437, 1226, 1194, 1170, 1030; $C_{11}H_{16}O_3$ Calcd: 196.4099 (HRMS correct).

Methyl 8-Acetoxybicyclo[4.3.0]non-1(6)-ene-3-carboxylate (78c-Me): Colorless oil, mixture of 2 isomers; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.70–1.85 (m, 1 H), 2.03 (s, 3 H), 2.00–2.08 (m, 3 H), 2.18–2.40 (m, 4 H), 2.55–2.80 (m, 3 H), 3.69 (s, 3 H), 5.30–5.35 (m, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.33 (+), 24.47 (–), 24.71 (–), 25.57 (–), 27.60 (–), 27.80 (–), 27.85 (–), 39.74 (+), 39.88 (+), 42.70 (–), 42.74 (–), 42.76 (–), 42.84 (–), 51.65 (+), 73.47 (+), 73.49 (+), 130.45 (C_{quat}), 130.53 (C_{quat}), 131.74 (C_{quat}), 131.80 (C_{quat}), 170.95 (C_{quat}), 171.00 (C_{quat}), 176.09 (C_{quat}), 176.12 (C_{quat}); IR (film): ν = 2911 cm^{-1}, 1731, 1461; Anal. Calcd. for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.66; H, 7.31.

8-*tert*-Butyldimethylsilyloxybicyclo[4.3.0]non-1(6)-ene-3-carboxylic Acid (79c-H): Colorless crystals, mp. 71–75 °C (decomp.); mixture of 2 isomers; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.05 (s, 6 H), 0.90 (s, 9 H), 1.60–2.70 (m, 12 H), 4.51–4.65 (m, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –4.72 (+), 18.31 (C_{quat}), 24.63 (–), 24.74 (–), 25.36 (–), 25.97 (+), 27.71 (–), 27.88 (–), 39.74 (+), 39.89 (+), 45.81 (–), 46.01 (–), 71.55 (+), 71.67 (+), 130.06 (C_{quat}), 131.68 (C_{quat}), 182.23 (C_{quat}); MS (70 eV), *m/z*: 296 (21) [M$^+$], 239 (97), 221 (16), 211 (5), 163 (10), 119 (100), 91 (25), 75 (61); IR (KBr): ν = 2931 cm^{-1}, 1701, 1531.

***tert*-Butyl 8-*tert*-Butyldimethylsilyloxybicyclo[4.3.0]non-1(6)-ene-3-carboxylate (79c-*t*Bu):** Colorless crystals, mp. 41–45 °C (decomp.); mixture of 2 isomers; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.06 (s, 6 H), 0.89 (s, 9 H), 1.44 (s, 9 H), 1.52–2.65 (m, 11 H), 4.54–4.70 (m, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –4.75 (+), 18.23 (C_{quat}), 24.76 (–), 25.66 (–), 25.92 (+), 28.03 (+), 28.20 (–), 40.84 (+), 41.01 (+), 45.78 (–), 45.98 (–), 71.58 (+), 77.70 (C_{quat}), 130.39 (C_{quat}), 131.41 (C_{quat}), 175.24 (C_{quat}); MS (70 eV), *m/z*: 315 (19), 295 (71), 279 (13), 239 (100), 221 (22), 185 (28), 163 (8), 119 (76); IR (KBr): ν = 2931 cm^{-1}, 1711, 1431; $C_{20}H_{36}O_3Si$ Calcd: 352.2434 (HRMS correct).

Dimethyl (3*R,4*S**)-8-*tert*-Butyldimethylsilyloxybicyclo[4.3.0]non-1(6)-ene-3,4-dicarboxylate (79f-Me):** Colorless oil, mixture of 2 isomers; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.07 (s, 6 H), 0.85 (s, 9 H), 2.12–2.65 (m, 8 H), 3.00–3.10 (m, 2 H), 3.63 (s, 6 H), 4.51 (m_c, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –4.72 (+), 18.22 (C_{quat}), 25.88 (+), 26.22 (–), 40.43 (+), 45.42 (–), 45.92 (–), 51.74 (+), 71.41 (+), 71.86 (+), 130.23 (C_{quat}), 130.38 (C_{quat}), 173.69 (C_{quat}), 173.80 (C_{quat}); MS (70 eV), *m/z*: 327 (1), 285 (4), 251 (2), 209 (100), 191 (8), 165 (7), 75 (12); IR (film): ν = 2911 cm^{-1}, 1731, 1459; Anal. Calcd. for $C_{19}H_{32}O_5Si$ (368.54): C, 61.92; H, 8.75. Found: C, 62.16; H, 8.73.

Methyl 8-(2-Tetrahydropyranyl)oxybicyclo[4.3.0]non-1(6)-ene-3-carboxylate (80c-Me): Colorless oil, mixture of 4 isomers; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.40–2.70 (m, 17 H), 3.45–3.60 (m, 1 H), 3.64 (s, 3 H), 3.87–4.00 (m, 1 H), 4.48–4.60 (m, 1 H), 4.61–4.75 (m, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 19.91 (–), 24.58 (–), 24.79 (–), 25.54 (–), 25.40 (–), 27.89 (–), 31.09 (–), 39.69 (+), 39.94 (+), 42.22 (–), 42.38 (–), 42.42 (–), 43.24 (–), 51.52 (+), 62.72 (–), 62.81 (–), 74.51 (+), 97.59 (+), 97.64 (+), 129.93 (C_{quat}), 130.68 (C_{quat}), 131.21 (C_{quat}), 131.99 (C_{quat}), 176.25 (C_{quat}); MS (70 eV), *m/z*: 249 (1), 178 (90), 146 (5), 119 (55), 118 (65), 85 (100); IR (film): ν = 2991 cm^{-1}, 1732, 1463; Anal. Calcd. for $C_{16}H_{24}O_4$: C, 68.55; H, 8.63. Found: C, 68.66; H, 8.66.

Methyl 3-Methyl-8-(2-tetrahydropyranyl)oxybicyclo[4.3.0]non-1(6)-ene-3-carboxylate (80n-Me): Colorless oil, mixture of 4 isomers; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.17, 1.21 (2 s, 3 H), 1.50–2.70 (m, 17 H), 3.49 (m, 1 H), 3.65, 3.66 (2 s, 3 H), 3.89–4.05 (m, 2 H), 4.63–4.80 (m, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 19.84 (–), 20.01 (–), 22.81 (–), 22.88 (–), 23.08 (–), 23.17 (–), 23.46 (–), 23.54 (+), 24.64 (+), 25.46 (–), 31.15 (–), 31.89 (–), 34.79 (–), 34.87 (–), 34.96 (–), 41.36 (C_{quart}), 41.79 (–), 41.84 (–), 42.01 (–), 42.11 (–), 42.17 (–), 42.33 (–), 42.48 (–), 43.07 (–), 43.20 (–), 43.40 (–), 43.49 (–), 51.70 (+), 62.72 (–), 62.87 (–), 62.91 (–), 74.80 (+), 97.64 (+), 97.73 (+), 129.71 (C_{quat}), 130.00 (C_{quat}), 130.06 (C_{quat}), 130.25 (C_{quat}), 130.49 (C_{quat}), 130.80 (C_{quat}), 130.85 (C_{quat}), 131.02 (C_{quat}), 178.13 (C_{quat}), 178.28 (C_{quat}); MS (70 eV), *m/z*: 294 (9) [M$^+$], 263 (1), 235 (1), 220 (2), 192 (70), 160 (7), 133 (85), 132 (71), 117 (10), 85 (100); IR (film): ν = 2930 cm^{-1}, 1734, 1463; Anal. Calcd. for $C_{17}H_{26}O_4$: C, 69.35; H, 8.90. Found: C, 69.65; H, 9.06.

Methyl 10,10-Dimethyl-8-*tert*-butyldimethylsilyloxybicyclo[4.4.0]dec-1(6)-ene-4-carboxylate (82c-Me) and Methyl 7,7-Dimethyl-9-*tert*-butyldimethylsilyloxybicyclo[4.4.0]dec-1(6)-ene-4-carboxylate (83c-Me): Colorless oil, mixture of 3 isomers; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.07 (2 s, 6 H), 0.90, 0.91 (2 s, 9 H), 0.91, 0.92, 0.97, 0.99, 1.00, 1.01 (6 s, 6 H), 1.40–1.65 (m, 3 H), 1.70–2.60 (m, 8 H), 3.67, 3.68, 3.69 (3 s, 3 H), 3.87–3.96 (m, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –4.51 (+), 18.20 (C_{quat}), 22.24 (–), 23.95 (–), 25.49 (–), 25.61 (–), 25.91 (+), 26.12 (–), 27.02 (–), 27.32 (+), 27.38 (–), 27.64 (+), 27.91 (+), 28.60 (+), 29.02 (+), 29.29 (+), 30.20 (–), 32.77 (–), 36.31 (C_{quat}), 36.48 (C_{quat}), 36.59 (C_{quat}), 39.14 (+), 39.88 (+), 40.48 (+), 41.09 (–), 41.15 (–), 41.59 (–), 48.76 (–), 51.53 (+), 65.69 (+), 123.21 (C_{quat}), 123.61 (C_{quat}), 124.86 (C_{quat}), 132.97 (C_{quat}), 134.23 (C_{quat}), 134.31 (C_{quat}), 176.02 (C_{quat}), 176.43 (C_{quat}), 176.63 (C_{quat}); MS (70 eV), *m/z*: 352 (1) [M$^+$], 337 (3), 295 (100), 264 (15), 239 (49), 211 (28), 161 (66), 131 (35), 117 (42), 105 (24), 75 (56); IR (film): ν = 2955 cm^{-1}, 2928, 2856, 1734, 1472, 1361, 1256, 1171, 849; Anal. Calcd. for $C_{20}H_{36}O_3Si$: C, 68.13; H, 10.29. Found: C, 68.27; H, 9.93.

Diethyl 3,4-Bis(methylene)cyclopentane-1,1-dicarboxylate (42): Colorless oil, ^{1}H NMR, MS data, and elemental analysis have already been reported;[10a] ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.76 (+), 40.82 (–), 57.35 (C_{quat}), 61.27 (–), 105.18 (–), 144.38 (C_{quat}), 171.39 (C_{quat}); IR (film): ν = 3084 cm^{-1}, 2983, 1733, 1628, 1446, 1390, 1247, 1192, 1069, 905, 862.

Diethyl 3-Acetoxymethyl-4-methyl-3-cyclopentene-1,1-dicarboxylate (47): Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.24 (t, *J* = 7.1, 6 H), 1.70 (bs, 3 H), 2.05 (s, 3 H), 2.99 (bs, 2 H), 3.04 (bs, 2 H), 4.19 (q, *J* = 7.1, 4 H), 4.58 (bs, 2 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.45 (+), 13.99 (+), 20.80 (+), 42.31 (–), 45.94 (–), 57.32 (C_{quat}), 60.09 (–), 61.51 (–), 127.32 (C_{quat}), 135.47 (C_{quat}), 168.14 (C_{quat}), 172.02 (C_{quat}); MS (70 eV), *m/z*: 298 (0.03) [M$^+$], 253 (1), 239 (2), 238 (8), 192 (17), 166 (24), 165 (89), 164 (56), 120 (20), 119 (19), 93 (67), 92 (22), 91 (50); IR (film): ν = 2982 cm^{-1}, 1734, 1652, 1437, 1367, 1259, 1184, 1074, 958, 861, 795.

Diethyl 3,4-Bis(acetoxymethyl)-3-cyclopentene-1,1-dicarboxylate (48): Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7.1, 6 H), 2.06 (s, 6 H), 3.11 (s, 4 H), 4.20 (q, *J* = 7.1, 4 H), 4.67 (s, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.98 (+), 20.69 (+), 42.47 (–), 57.39 (C_{quat}), 59.52 (–), 61.70 (–), 133.21 (C_{quat}), 170.56 (C_{quat}), 171.53 (C_{quat}); MS (70 eV), *m/z*: 311 (4), 296 (12), 254 (15), 236 (3), 224 (10), 223 (22), 208 (5), 164 (100), 163 (33), 91 (22); IR (film): ν = 2983 cm^{-1}, 1735, 1447, 1367, 1234, 1185, 1073, 963, 861.

Dimethyl 3-Cyclopentylidene-4-methylenecyclopentane-1,1-dicarboxylate (73): Colorless oil, mixture of **73** and **75** (1.4:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.59–1.79 (m, 4 H), 2.24–2.34 (m, 4 H), 2.94 (bs, 2 H), 3.04 (bs, 2 H), 3.720 (s, d, $^1J_{CH}$ = 147.4, 6 H), 4.98 (bs, 1 H), 5.01 (bs, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 25.91 (–), 27.26 (–), 32.60 (–), 33.87 (–), 40.47 (–), 43.14 (–), 52.65 (+), 57.65 (C_{quat}), 107.45 (–), 126.37 (C_{quat}), 141.83 (C_{quat}), 145.73 (C_{quat}), 171.98 (C_{quat}).

Dimethyl 3-Cyclopent-1'-enyl-4-methylcyclopent-3-ene-1,1-dicarboxylate (75): Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.83 (bs, 3 H), 1.88 (quint, *J* = 7.6, 2 H), 2.30–2.43 (m, 2 H), 2.55–2.65 (m, 2 H), 3.04 (bs, 2 H), 3.17 (q, *J* = 1.7, 2 H), 3.723 (s, d, $^1J_{CH}$ = 147.4, 6 H), 5.60 (bs, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 15.14 (+), 23.78 (–), 32.02 (–), 34.20 (–), 43.47 (–), 47.53 (–), 52.76 (+), 56.84 (C_{quat}), 128.42 (C_{quat}), 128.70 (+), 130.96 (C_{quat}), 139.43 (C_{quat}), 172.76 (C_{quat}); IR (film): ν = 2980 cm^{-1}, 2846, 1734, 1653, 1436, 1269, 1213, 1184, 1144, 1071, 801, 531; MS (70 eV), *m/z*: 264 (35) [M$^+$], 233 (5), 204 (100), 173 (9), 145 (49), 117 (8), 91 (10), 59 (6); Anal. Calcd. for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.01; H, 7.71.

3,4-Bis(methylene)cyclopent-1-yl *tert*-butyldimethylsilyl ether (81): Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.63 (s, 6 H), 0.94 (s, 9 H), 2.20–2.35 (m, 2 H), 2.65 (m, 2 H), 4.25–4.40 (m, 1 H), 4.90 (bs, 2 H), 5.38 (bs, 2 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –4.77 (+), 18.11 (C_{quat}), 25.80 (+), 43.51 (–), 70.90 (+), 104.65 (–), 145.92 (C_{quat}); IR (film): ν = 2911 cm^{-1}, 1713, 1529; Anal. Calcd. for $C_{13}H_{24}OSi$: C, 69.58; H, 10.78. Found: C, 69.18; H, 10.30.

3,3-Dimethyl-4,5-(bis)methylenecyclohex-1-yl *tert*-butyldimethylsilyl ether (84): Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.86 (s, 6 H), 0.89 (s, 9 H), 0.95 (s, 3 H), 1.15 (s, 3 H), 1.41–1.56 (m, 1 H), 1.67–1.82 (m, 1 H), 2.10–2.25 (m, 1 H), 2.55–2.70 (m, 1 H), 3.93–4.08 (m_c, 1 H), 4.71–4.90 (m, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –4.55 (+), 18.18 (C_{quat}), 25.87 (+), 28.09 (+), 28.76 (+), 36.60 (C_{quat}), 45.32 (–), 49.38 (–), 67.80 (+), 106.08 (–), 111.17 (–), 147.45 (C_{quat}), 156.81 (C_{quat}); MS (70 eV), *m/z*: 227 (6), 195 (10), 167 (5), 154 (20), 145 (100), 117 (6), 91 (16), 75 (30); IR (film): ν = 3081 cm^{-1}, 2958, 2928, 1635, 1472, 1464, 1087, 1005; Anal. Calcd. for $C_{16}H_{30}OSi$: C, 72.11; H, 11.35. Found: C, 71.92; H, 11.30.

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