The Twofold Heck Reaction on 1,2-Dihalocycloalkenes and Subsequent 6π-Electrocyclization of the Resulting (*E,Z,E*)-1,3,5-Hexatrienes: A New Formal {2+2+2}-Assembly of Six-Membered Rings☆

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1,6-Disubstituted (*E,Z,E*)-1,3,5-hexatrienes (**4** and **5**) were prepared by vicinal twofold Heck coupling reactions from 1,2-dibromocyclopentene (**1**), 1,2-dibromocyclohexene (**2**), 1,2-diiodocyclopentene (**8**), 1,2-diiodocyclohexene (**9**), 1-bromo-2-trifluoromethanesulfonyloxycyclohex-1-ene (**11**), or 1-chloro-2-nonafluorobutanesulfonyloxycyclohex-1-ene (**19**) with alkenes **3**, e. g. methyl, *tert*-butyl, menthyl, 8-phenylmenthyl acrylate, styrene, and alkenylsilanes, respectively, in moderate to mostly good and very good yields (20–92 %). The coupling of alkenylsilanes **3f−k** could only be achieved with the 1,2-diiodocycloalkenes **8** and **9**, respectively. The corresponding hexatrienes **5** with two different substituents in the 1- and 6-positions were prepared by a sequence of two coupling reactions with different alkenes from 1-chloro-2-nonafluorobutanesulfonyloxycyclohex-1-ene (**19**) or by Wittig-Horner-Emmons olefination of 2-bromocyclohexene-1-carbaldehyde (**24**) and subsequent Heck reaction of the resulting (*E,Z*)-bromodienes **25**. Several of the hexatrienes (**4aa**, **ee**, **5aa**, **ee**, **al**, **am**, **el**) readily underwent a 6π-electrocyclization upon heating in an inert atmosphere to give the 5- or 6-ring-annelated *cis*-5,6-disubstituted cyclohexadienes **26**, **27** (50–95 %). Starting from **5am** 2,3-disubstituted tetrahydronaphthalene **28am** was formed under oxidative conditions (air) in the reaction and in the work-up procedure. The bissilyl-substituted derivatives **4ff**, **jj**, **5ff** did not cyclize under thermal conditions, apparently due to the steric demand of the two silyl substituents which would have to end up *cis* with respect to each other in the cyclohexadiene products.

By far the most versatile method for the construction of carbo- and heterocyclic six-membered rings is the Diels-Alder reaction,[1] leading to cyclohexene derivatives by a [4+2] cycloaddition. The metal template-assisted {2+2+2} assembly of three alkynes or two alkynes and one nitrile has more recently been developed and popularized simultaneously by Vollhardt et al.[2] and Bönnemann et al.[3] as an attractive access to a vast array of arene and pyridine derivatives, respectively. This methodology can also be applied to assemble two alkyne and one alkene unit to give cyclohexadienes, yet not with the same broad scope.[2] In certain cases there is need for completely different convenient approaches to carbocyclic six-membered rings, as we encountered in the desire to prepare benzannelated and dibenzannelated [2.2]paracyclophane derivatives.[4] It occurred to us that the twofold palladium-catalyzed coupling − the so-called Heck reaction[5][6] − of vicinal dihalocycloalkenes with various alkenes and subsequent 6π-electrocyclization to yield cyclohexadienes, which was first applied by us towards that specific problem,[4] might be a useful complementing alternative to the existing arsenal of methodologies. We here report on a larger variety of 1,3,5-hexatrienes prepared by twofold Heck coupling reactions of 1,2-dihalocycloalkenes[7] as well as single Heck coupling of 1-bromodienes, and on the subsequent cyclization of the 1,2-dialkenylcycloalkenes to ring-annelated cyclohexadienes.

Results and Discussion

The palladium-catalyzed alkenylations of alkenyl and aryl halides often proceed in excellent yields, even when performed with oligohalogen derivatives.[5][6] However, the substitutive coupling of more than two vicinal halogen substituents on an arene moiety could only be achieved[7][8] under the modified conditions of Jeffery[9] [$Pd(OAc)_2$, K_2CO_3 or $NaHCO_3$, nBu$_4$NBr or nBu$_4$NCl, DMF or NMP]. Yet, for vicinal dibromoalkenes and dibromocycloalkenes application of the original Heck conditions[5] gave consistently higher yields of the resulting 1,6-disubstituted (*E,Z,E*)-1,3,5-hexatrienes which are versatile intermediates for further elaboration.[7]

Heck Reactions on 1,2-Dibromocycloalkenes 1, 2

Starting from easily accessible 1,2-dibromocyclopentene (**1**) and 1,2-dibromocyclohexene (**2**) the (*E,Z,E*)-1,3,5-hexatrienes **4**, **5** are available with various substituents in the 1,6-positions from the corresponding alkenes, according to the previously published procedure.[7f] Only a few examples

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of (*E,Z,E*)-1,3,5-hexatrienes have been synthesized,[10][11] though some of them show an interesting binding ability to the retinoid receptor.[12] Since the Heck reaction usually yields *trans*-configured alkenes, solely (*E,Z,E*)-configured products **4** and **5** were formed. These compounds were found to generally be solids and thus could easily be purified by recrystallization and/or chromatography (Table 1, entries 1−8). In the coupling of 1,2-dibromocyclohexene (**2**) with 8-phenylmenthyl acrylate **3d**, the yield was lower (43%, Table 1, entry 6) than with the other acrylates **3a−c** (Table 1, entries 2, 4, 5), but this most probably has to do with the fact that only 2.5 equiv. of acrylate **3d** was used instead of 5.0 equiv. in the other cases. Indeed, when only 2.5 equiv. of *tert*-butyl acrylate (**3b**) were used in the twofold Heck reaction of dibromocyclohexene (**2**) the yield of hexatriene **5bb** was lowered to 48 instead of 57% with 5.0 equiv. (Table 1, entry 4).

Anyhow, the couplings with these chiral, non-racemic acrylates **3c** and **3d** provide an easy access to 1,3,5-hexatrienes of types **4**, **5** with potent chiral auxiliaries on the 1- and 6-positions which may be useful in further transformations.[7]

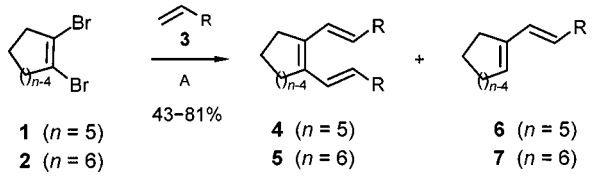
In the couplings of dibromocyclohexene (**2**) with acrylates **3a−d**, the monoalkenylated products **7**, resulting from partial reduction, were also isolated.[7f] The analogous compounds **6** derived from dibromocyclopentene (**1**) were not observed at all.

Table 1. Heck reaction of various alkenes **3a−e** with 1,2-dibromocyclopentene (**1**) or -hexene (**2**)

Entry	Dibromo-alkene	Alkene	Product	Reaction cond. (temp. [°C]/ time [h])	Yield[a] [%]
1	**1**	**3a**	**4aa**[7a]	100/40	81
2	**2**	**3a**	**5aa**[7a][7f]	100/72	55[b]
3	**1**	**3b**	**4bb**	100/20	56
4	**2**	**3b**	**5bb**[7f]	90/20	57[c]
5	**2**	**3c**	**5cc**	90/70	50[d]
6	**2**	**3d**	**5dd**	100/90	43[e]
7	**1**	**3e**	**4ee**[7a][10a]	90/40	73
8	**2**	**3e**	**5ee**[7a][11a]	90/92	69

[a] Isolated yield. − [b] Plus 16% of **7a**. − [c] Plus 41% of **7b**. − [d] Plus an unquantified amount of **7c**. − [e]Plus 11% of **7d**.

Scheme 1. For details see Table 1



Heck Reactions on 1,2-Diiodocycloalkenes 8 and 9 with Ethenylsilanes 3f−k

In Heck reactions of 1,2-dibromocyclopentene (**1**) and 1,2-dibromocyclohexene (**2**) with ethenylsilanes yields were rather poor, and desilylation was predominant; therefore **1** and **2** were converted to the corresponding 1,2-diiodocycloalkenes **8**, **9** by standard methods.[13] These diiodides with their better leaving groups did indeed undergo the Heck reaction more smoothly when carried out under slightly modified conditions adapted from those published by Hallberg et al.[14] [$Pd(OAc)_2$, no phosphane, $AgNO_3$, NEt_3 in DMSO], and gave the silyl-substituted (*E,Z,E*)-1,3,5-hexatrienes **4**, **5ff−kk** in moderate to high yields, depending on the bulkiness of the trialkylsilyl group. The reactions were usually over in 2 days at room temperature (conditions A) (Table 2), in several runs yields were found to be higher when the reactions were carried out under slightly elevated pressure (under 5 bar of argon, conditions C). When run at 100°C for 5 h to 2 days (conditions B, D) yields dropped (entries 2, 11, 12) or rose only slightly (entries 8, 17, 20). This decrease is apparently due to decomposition of the alkenylsilanes, as a sample reaction run at 100°C for 10 h with 10 equivalents of the alkenylsilane instead of 5 equivalents in the other cases gave a 92% yield (entry 13).

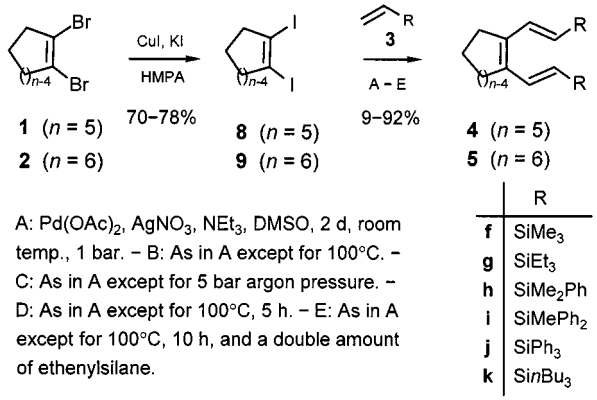
Table 2. Heck reactions of 1,2-diiodocyclopentene (**8**) and -hexene (**9**) with alkenylsilanes **3f−k**

Entry	Diiodo-alkene	Alkene	Conditions	Product	Yield[a] [%]
1	**8**	**3f**	A	**4ff**	80
2	**8**	**3f**	B	**4ff**	73
3	**8**	**3f**	C	**4ff**	90
4	**8**	**3g**	A	**4gg**	81
5	**8**	**3h**	A	**4hh**	53
6	**8**	**3i**	A	**4ii**	12
7	**8**	**3j**	A	**4jj**	30
8	**8**	**3j**	B	**4jj**	34
9	**8**	**3k**	A	**4kk**	71
10	**9**	**3f**	A	**5ff**	78
11	**9**	**3f**	B	**5ff**	72
12	**9**	**3f**	D	**5ff**	69
13	**9**	**3f**	E	**5ff**	92
14	**9**	**3g**	A	**5gg**	68
15	**9**	**3g**	C	**5gg**	80
16	**9**	**3h**	A	**5hh**	32
17	**9**	**3h**	B	**5hh**	40
18	**9**	**3h**	C	**5hh**	52
19	**9**	**3i**	A	**5ii**	9
20	**9**	**3i**	B	**5ii**	20
21	**9**	**3j**	A	**5jj**	38
22	**9**	**3k**	A	**5kk**	35

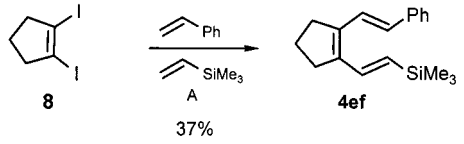
A: $Pd(OAc)_2$, $AgNO_3$, NEt_3, DMSO, 2 d, room temp., 1 bar. − B: As in A except for 100°C. − C: As in A except for 5 bar argon pressure. − D: As in A except for 100°C, 5 h. − E: As in A except for 100°C, 10 h, and a double amount of ethenylsilane. − [a] Isolated yields.

In a competition experiment carried out with 1 equivalent of 1,2-diiodocyclopentene (**8**), 12.5 equivalents of styrene (**3e**), and 2.5 equivalents of trimethylsilylethene (**3f**) the mixed product **4ef** was isolated in 37% yield. This shows that alkenylsilanes such as **3f** react much faster than styrene (**3e**) under these conditions.

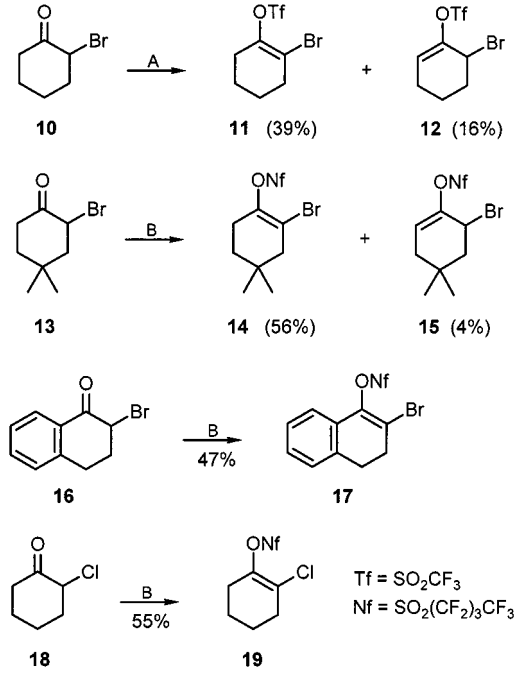
Scheme 2. For details see Table 2



Scheme 3



Scheme 4



Preparation of 1-Halo-2-perfluoroalkanesulfonyloxycycloalkenes 11, 14, 17, and 19 and Their Subsequent Heck Reactions

As the second Heck coupling step in the above twofold reactions is always considerably faster than the first one,[7a] it is not possible to produce 1,3,5-hexatrienes of type **4**, **5** with different substituents at the 1- and 6-position from 1,2-difunctionalized cycloalkenes with the same leaving groups via a sequence of two couplings with different alkenes. Alkenyl triflates are known to be more reactive in Heck reactions than alkenyl bromides, while alkenyl chlorides are unreactive under classical conditions.[6] Therefore, cycloalkenes **11**, **14**, **17**, and **19** were prepared with a trifluoromethanesulfonyloxy or a nonafluorobutanesulfonyloxy substituent as a very good leaving group and a bromo or a chloro substituent as a poor leaving group. This was achieved by trapping the enolate of the respective α-haloketone, generated with lithium hexamethyldisilazide (LiHMDS), with trifluoromethanesulfonic anhydride (Tf_2O) or nonafluorobutanesulfonyl fluoride (NfF). Reaction of 2-bromocyclohexanone (**10**) with Tf_2O gave the thermodynamic product **11** and the kinetic product **12** in a 2.4:1 ratio, whereas reactions with NfF gave only (**17**, **19**) or mainly (**14**) the thermodynamic products presumably due to the longer reaction time at a higher temperature.

The coupling of 1-halo-2-perfluoroalkanesulfonyloxycycloalkenes **11**, **14**, and **17** with acrylates **3a**,**b** gave higher yields of the twofold coupling products **5**, **20**, and **21** (Table 3, entries 1, 3, 4) than those starting from 1,2-dibromocyclohexene (**2**) (Table 1). On the other hand, the Heck reaction of the bromotriflate **11** with styrene (**3e**) gave a lower yield of hexatriene **5ee** compared to the coupling of dibromide **2** with **3e** (Table 3, entry 2 versus Table 1, entry 8). But a lower reactivity of styrene in Heck reactions with triflates using a palladium(II) catalyst has previously been reported.[15] Unfortunately, even at 60°C (Table 3, entry 4) the reactivity difference between nonaflate and bromide as leaving groups is overcompensated by the enhanced reactivity of the intermediate bromodiene towards Heck coupling. Even when using an excess of **11** in couplings with alkenes **3b** or **3e**, only starting material and the twofold coupling products were isolated.

For the selective preparation of monocoupling product the combination of a nonaflate and a chloro substituent is sufficient as compound **19** reacted with methyl acrylate at 60°C to give the chlorodiene **22a** in a 96% yield (Table 3, entry 5). The activation of the normally unreactive chloride by the acrylate functionality is so strong that it can act as leaving group in a following Heck coupling with styrene at 100°C to give the hexatriene **5ae** in 16% yield (68% starting material recovered). Under high pressure conditions (10 kbar)[7c] at 60°C compound **5ae** was obtained in 42% yield (38% starting material recovered). Couplings of **19** with methyl or *tert*-butyl acrylate at higher temperatures for longer reaction times gave mixtures of mono- and bis-coupled products (Table 3, entries 8, 9).

Successive Wittig-Horner-Emmons and Heck Reactions on 2-Bromocyclohexene-1-carbaldehyde (24)

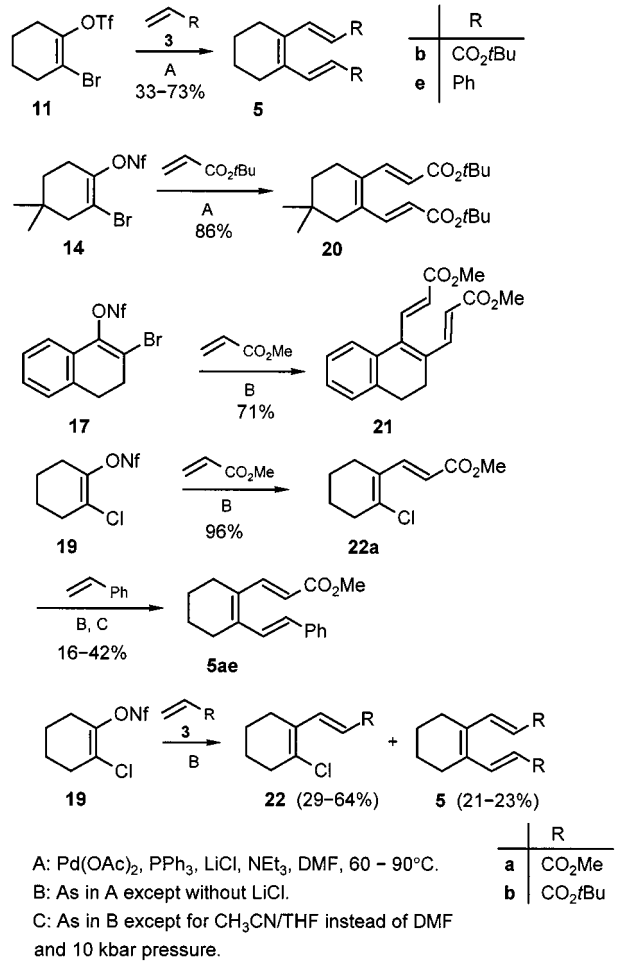
In view of the low yield of hexatriene **5ae** with two different terminal substituents by the above sequence, another method was deviced. Wittig-Horner-Emmons olefinations on 2-bromocyclohexene-1-carbaldehyde (**24**)[16] were carried out with different phosphonates to give the 1-alkenyl-2-bromocyclohexenes **25-R** with terminal alkoxycarbonyl

Table 3. Heck reactions of alkenes **3a**,**b**,**e** with triflate **11** and nonaflates **14**, **17**, and **19**

Entry	Triflate/ Nonaflate/ Chloride	Alkene	Product	Reaction cond. (temp. [°C]/ time [h])	Yield[a] [%]
1	**11**	**3b**	**5bb**[7f]	A: 90/96	73
2	**11**	**3e**	**5ee**[7a][11a]	A: 90/96	33
3	**14**	**3b**	**20**	A: 90/40	86
4	**17**	**3a**	**21**	B: 60/24	71
5	**19**	**3a**	**22a**	B: 60/12	96
6	**22a**	**3e**	**5ae**	B: 100/48	16[b]
7	**22a**	**3e**	**5ae**	C: 60/72	42[c]
8	**19**	**3a**	**5aa**[7a][f]	B: 75/192[d]	23[e]
9	**19**	**3b**	**5bb**[7f]	B: 70/20	21[f]

A: $Pd(OAc)_2$, PPh_3, NEt_3, LiCl, DMF. – B: As in A except without LiCl. – C: As in B except for CH_3CN/THF instead of DMF and 10 kbar pressure. – [a] Isolated yield. – [b] Plus 68% of **22a**. – [c] Plus 38% of **22a**. – [d] $PdCl_2(PPh_3)_2$ was used instead of $Pd(OAc)_2$, PPh_3. – [e] Plus 64% of **22a**. – [f] Plus 29% of **22b** and 22% of nonaflate **19**.

Scheme 5. For details see Table 3



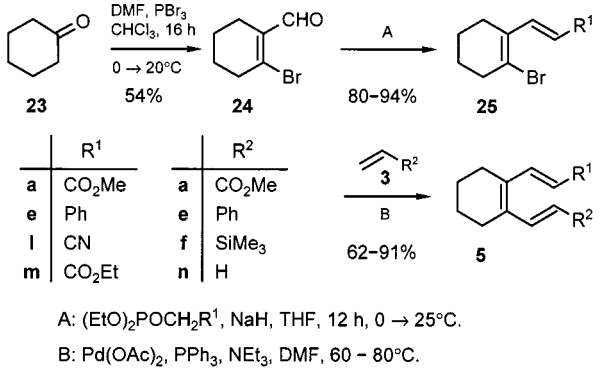
(**25a**, **25m**), phenyl (**25e**), and nitrile (**25l**) substituents, respectively (see Table 4). In most cases, solely the *trans*-configured isomer was obtained except for the acrylonitrile derivative **25l**. The two diastereomers of **25l** were isolated as a mixture with an *E*/*Z* ratio of 2:1, they were separable by column chromatography.

Table 4. Wittig-Horner-Emmons olefinations of 2-bromocyclohexene-1-carbaldehyde (**24**)

Entry	Phosphonate	Product	Yield[a] [%]
1	$(EtO)_2POCH_2CO_2Me$	**25a**	93
2	$(EtO)_2POCH_2Ph$	**25e**	80[b]
3	$(EtO)_2POCH_2CN$	**25l**	94[c]
4	$(EtO)_2POCH_2CO_2Et$	**25m**	88

[a] Isolated yields. – [b] Non-separable mixture of (*E*) and (*Z*) isomers with (*E*)/(*Z*) = 20:1. – [c] Obtained as a separable mixture of (*E*) and (*Z*) isomers with (*E*)/(*Z*) = 2:1.

Scheme 6. For details see Tables 4 and 5



The Heck coupling reactions of bromodienes **25-R** proceeded with very high yields (Table 5, entries 1–9), giving the corresponding 1,6-disubstituted (*E,Z,E*)-1,3,5-hexatrienes **5** with two different terminal substituents. Even when starting from (*Z*)-**25l**, only the (*E,Z,E*) product could be isolated after extended reaction times (Table 5, entries 5 and 7). The (*Z*)-configured double bond apparently isomerizes by an addition-elimination sequence of the hydridopalladium halide species as is known for the Heck reaction conditions.[5][6] The coupling of trimethylsilylethene (**3f**) with **25a** and **25l** gave only mixtures of silylated (**5af**, **5fl**) and non-silylated products (**5an**, **5ln**) at the terminal position, with the latter ones predominating (Table 5, entries 3 and 8).

Table 5. Heck reactions of bromobutadienes **25** with alkenes **3**

Entry	Bromobutadiene[a]	Alkene	Reaction cond. (temp. [°C]/ time [h])	Product	Yield[b] [%]
1	**25a**	**3a**	80/20	**5aa**	85
2	**25a**	**3e**	60/120	**5ae**	74
3	**25a**	**3f**	70/12	**5an/5af**	70/14
4	**25l**	**3a**	80/12	**5al**	80
5	(*Z*)-**25l**	**3a**	80/36	**5al**	63
6	**25l**	**3e**	80/20	**5el**	74
7	(*Z*)-**25l**	**3e**	80/45	**5el**	62
8	**25l**	**3f**	80/12	**5ln/5fl**	64/11
9	**25m**	**3a**	80/20	**5am**	91

[a] Always the (*E*) isomer unless otherwise stated. – [b] Isolated yields.

6π-Electrocyclizations of (*E,Z,E*)-1,3,5-Hexatrienes 4, 5

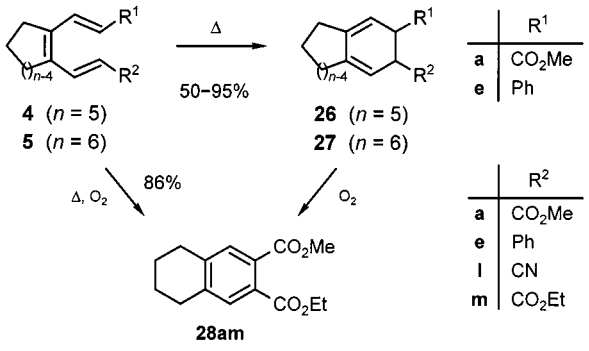
The (*E,Z,E*)-1,3,5-hexatrienes **4**, **5** thus prepared are perfectly set up for a thermal 6π-electrocyclization[11] to produce functionalized ring-annelated cyclohexa-1,3-dienes **26**, **27**. Indeed, this electrocyclization proceeded smoothly for the alkoxycarbonyl- (**4aa**, **5aa**, **5am**), cyano- (**5al**), and phenyl-substituted trienes (**5el**, **5ee**) upon heating to 130−150°C in deoxygenated xylene or di-*n*-butyl ether for several hours (Table 6, entries 1−7), and the products could be purified by column chromatography on deoxygenated silica gel. The two substituents from the former 1- and 6-positions have a stereochemical *cis* relationship in the products due to the disrotatory ring closure under thermal conditions. When the solvent for chromatography and/or the silica gel were not purged with nitrogen prior to use as in a reaction of hexatriene **5am** only the aromatized product **28am** was isolated. The electrocyclization was also be brought about by heating the neat compound **4ee** in a kugelrohr apparatus to 180°C at 3 mbar for 8 min, followed by kugelrohr distillation of the desired product at 150°C (Table 6, entry 8).[11a]

Table 6. 6π-Electrocyclizations of the 1,3,5-(*E,Z,E*)-Hexatrienes **4**, **5** in nBu_2O or xylene

Entry	Hexatriene	Reaction cond. (temp. [°C]/ time [h])	Product	Yield[a] [%]
1	**4aa**	A: 140/7	**26aa**[7a]	94
2	**5aa**	B: 140/5	**27aa**[7a]	89
3	**5al**	B: 140/20	**27al**	74[b]
4	**5am**	B: 150/12	**27am**	84
5	**5am**	B: 150/12	**28am**	86[c]
6	**5ee**	B: 140/2	**27ee**[7a][11a]	95
7	**5el**	B: 130/15	**27el**	81
8	**4ee**	C	**26ee**[7a]	50

[a] Isolated yields. − [b] 20% of isomerized product. − [c] Solvent for chromatography and silica gel not degassed. − A: Heating in nBu_2O. − B: Heating in xylene. − C: 180°C, 3 mbar, 8 min, kugelrohr.

Scheme 7. For details see Table 6



The silyl-substituted cyclohexadienes **26**, **27ff−kk** were not produced by these methods. Heating of the (*E,Z,E*)-1,3,5-hexatriene **4ff** under the above conditions or to 260°C in a sealed tube in xylene, or even subjecting them to flash vacuum pyrolysis at temperatures ranging from 400 to 650°C at a pressure of $4 \cdot 10^{-3}$ bar did not lead to any change in the starting material. This must be due to the steric bulk of the trimethylsilyl groups which raises the energy of the transition state for the disrotatory ring closure.

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Experimental Section

General: ^1H NMR spectra: Varian VXR 200 (200 MHz) or Bruker AW 250 (250 MHz). Chemical shifts in $CDCl_3$ are reported as δ values relative to tetramethylsilane (δ = 0.00) or chloroform (δ = 7.26) as internal reference unless stated otherwise. − ^{13}C-NMR spectra: Varian VXR 200 (50.3 MHz) or Bruker AW 250 (62.9 MHz). Chemical shifts in $CDCl_3$ are reported as δ values relative to $CDCl_3$ (δ = 77.00); the multiplicity of the signals was determined by the DEPT technique and quoted as (+) for CH_3 and CH groups, (−) for CH_2 and (C_{quat}) for quaternary carbon atoms. − IR spectra: Perkin-Elmer 1720 FTIR or a Bruker IFS 66. − Low-resolution EI mass spectra: Varian MAT CH-7 with Varian Aerograph 1740, ionizing voltage 70 eV. − High-resolution mass spectra: VG-70-250S. − Elemental analyses: Mikroanalytisches Labor der Universität Göttingen, Germany. − Melting points are uncorrected. − Solvents for extraction and chromatography were of technical grade and distilled before use. − Flash chromatography: Merck Kieselgel 60 (200−400 mesh). − All reactions were carried out under dry nitrogen or argon in oven- and/or flame-dried glassware. − Organolithium compounds were titrated according to the method of Suffert.[17] − Tetrahydrofuran, di-*n*-butyl ether, and xylene were distilled from sodium benzophenone ketyl. − DMF, CH_3CN, DMSO, NEt_3, and HMDS were distilled from CaH_2. − Sodium hydride was used as an 80% suspension in mineral oil. − Ethenylsilanes **3g**,**j**,**k** were prepared according to literature procedures[18a], **3h**,**i** were made analogously and their analytical data were identical with those in ref.[18b][18c]. 1,2-Dibromocyclohexene (**2**) was prepared following literature protocol[19] with slight modifications (see below), 2-bromocyclohexanone (**10**)[20a], 2-bromo-4,4-dimethylcyclohexanone (**13**)[20b], 2-bromotetralone (**16**)[20c], 2-bromocyclohexene-1-carbaldehyde (**24**)[16], (1*R*,2*S*,5*R*)-8-phenylmenthol[21], menthyl- and 8-phenylmenthyl acrylate (**3c**,**d**)[22] were prepared according to literature procedures. 1,2-Dibromocyclopentene (**1**) was prepared by the same method as dibromocyclohexene (**2**) but is also commercially available from Aldrich.

Dibromocyclohexene (**2**)[19]: To a suspension of phosphorous pentachloride (403 g, 1.93 mol) in 1 l of chloroform was added cyclohexanone (**23**) (183 g, 1.86 mol) in 600 ml of chloroform at 0°C over a period of 1 h. The mixture was stirred for 2 h at 25°C and 2 h at reflux and poured onto 1 kg of ice, followed by neutralization by adding solid $NaHCO_3$ (Caution! Extensive gas evolution!). The organic phase was separated, washed with sat. $NaHCO_3$ solution (500 ml), dried with $MgSO_4$, and concentrated in vacuo. The residue was dissolved in 100 ml of dichloromethane, and a solution of bromine (183 g, 1.15 mol) in 70 ml of dichloromethane was added dropwise at −5°C at such a rate that not too much bromine accumulated in the solution. The mixture was washed with $Na_2S_2O_3$ solution (100 ml) and dried with $MgSO_4$.

The solvent was removed in a rotatory evaporator, and the residue was distilled under reduced pressure (70−73°C, 0.05 mbar) to give 152 g (30%) of 1,2-dibromo-1-chlorocyclohexane as a colorless solid. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.45 (m_c, 1 H), 1.75 (m_c, 3 H), 2.15 (m_c, 1 H), 2.29 (m_c, 1 H), 2.45 (m_c, 1 H), 2.87 (m_c, 1 H), 4.57 (m_c, 1 H, 2-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 23.53 [−, C-4(5)], 34.21 [−, C-3(6)], 62.67 (+, C-2), 82.77 (C_{quat}, C-1). To a solution of KOH (45 g, 0.80 mol) in 200 ml of methanol, kept under reflux, was added dropwise a solution of 1,2-dibromo-1-chlorocyclohexane (112 g, 0.405 mol) in 200 ml of methanol. The refluxing reaction mixture was kept stirred for an additional 3 h, cooled down to room temp., neutralized with half-concentrated hydrochloric acid, and extracted with dichloromethane (4 × 200 ml). The organic phase was dried with $MgSO_4$, the solvent was removed in vacuo, and the residue was recrystallized from methanol to yield 69.2 g (71%) of **2** as a colorless solid. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.74 [m_c, 4 H, 4(5)-H], 2.55 [m_c, 4 H, 3(6)-H]. − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 24.02 [−, C-4(5)], 37.26 [−, C-3(6)], 122.93 [C_{quat}, C-1(2)].

General Procedure for the Twofold Heck Coupling of 1,2-Dibromocyclopentene (**1**) *and 1,2-Dibromocyclohexene* (**2**) *with Alkenes (GP 1)*[7f]: In a Pyrex bottle containing a magnetic stirring bar were placed $Pd(OAc)_2$ (18 mg, 0.08 mmol, 4 mol-% per Br), PPh_3 (105 mg, 0.40 mmol), and 1,2-dibromocyclopentene (**1**) or 1,2-dibromocyclohexene (**2**) (1.00 mmol). DMF (20 ml) was added and the resulting suspension was purged with Argon in an ultrasound bath until it became a clear yellow solution. To the stirred solution were added NEt_3 (0.56 ml, 4.0 mmol) and the alkene (5.00 mmol, 2.5 equiv. per Br). The Pyrex bottle was heated under vigorous stirring for the stated time at 90−100°C. Then the reaction mixture was cooled down to room temp. and poured into Et_2O and H_2O (50 ml each). The organic layer was washed three times with water (20 ml) and the aqueous layer was extracted back once with Et_2O (20 ml). The combined organic layers were dried with $MgSO_4$, concentrated in vacuo, and the residue was purified by column chromatography (CC) on silica gel and/or recrystallization.

Methyl (3E)-3-{2-[(E)-2-(Methoxycarbonyl)ethenyl]-1-cyclopenten-1-yl}acrylate (**4aa**): 1,2-Dibromocyclopentene (**1**) (5.0 g, 22 mmol) was treated with methyl acrylate (**3a**) (10.0 ml, 0.11 mol) for 40 h at 100°C according to GP 1. After CC on silica gel (150 g, petroleum ether/EtOAc, 4:1) and recrystallization from EtOH/acetone (1:1), 4.21 g (81%) of **4aa** was obtained as colorless crystals, m. p. 89°C. − IR (KBr): ν = 2941 cm^{-1}, 1715, 1614, 1437, 1312, 1276, 1174, 1012, 977, 928, 851, 747, 716. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.98 (quint, *J* = 7.0 Hz, 2 H, 4′′-H), 2.69 [t, *J* = 7.0 Hz, 4 H, 3′′(5′′)-H], 3.80 (s, 6 H, OCH_3), 5.93 [d, *J* = 15.6 Hz, 2 H, 2(2′)-H], 7.86 [d, *J* = 15.6 Hz, 2 H, 3(3′)-H]. − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.28 (−, C-4′′), 33.59 [−, C-3′′(5′′)], 51.71 (+, OCH_3), 120.76 [+, C-2(2′)], 136.01 [+, C-3(3′)], 144.28 [C_{quat}, C-1′′(2′′)], 167.32 [C_{quat}, C-1(1′)]. − MS; *m/z* (%): 236 (47) [M^+], 204 (67), 177 (29) [$M^+ - CO_2CH_3$], 172 (33), 145 (45), 117 (100), 59 (8) [$CO_2CH_3^+$]. − $C_{13}H_{16}O_4$ (236.3): calcd. C 66.09, H 6.83; found C 66.10, H 6.75.

tert-Butyl (3E)-3-{2-[(E)-2-(tert-Butoxycarbonyl)ethenyl]-1-cyclopenten-1-yl}acrylate (**4bb**): 1,2-Dibromocyclopentene (**1**) (2.26 g, 10.0 mmol) was treated with *tert*-butyl acrylate (**3b**) (6.40 g, 49.9 mmol) in DMF (50 ml) for 20 h at 100°C according to GP 1. After CC on silica gel (80 g, petroleum ether/EtOAc, 100:3) and recrystallization from hexane, 1.78 g (56%) of **4bb** was obtained as a colorless solid, m. p. 110°C. − IR (KBr): ν = 2981 cm^{-1}, 1700, 1621, 1460, 1368, 1289, 1212, 1125, 1008, 968, 853, 758. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.51 [s, 18 H, $C(CH_3)_3$], 1.94 (quint, *J* = 7.6 Hz, 2 H, 4′′-H), 2.64 [t, *J* = 7.6 Hz, 4 H, 3′′(5′′)-H], 5.83 [d, *J* = 15.5 Hz, 2 H, 2(2′)-H], 7.73 [d, *J* = 15.5 Hz, 2 H, 3(3′)-H]. − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.32 (−, C-4′′), 28.14 [+, $C(CH_3)_3$], 33.66 [−, C-3′′(5′′)], 80.56 [C_{quat}, $C(CH_3)_3$], 122.89 [+, C-2(2′)], 134.96 [+, C-3(3′)], 143.71 [C_{quat}, C-1′′(2′′)], 166.32 [C_{quat}, C-1(1′)]. − MS; *m/z* (%): 320 (26) [M^+], 208 (44) [$M^+ - 2\ C_4H_8$], 190 (82) [$M^+ - OC_4H_9 - C_4H_9$], 163 (30) [$M^+ - CO_2C_4H_9 - C_4H_8$], 146 (78) [$M^+ - CO_2C_4H_9 - OC_4H_9$], 117 (46), 84 (38), 57 (100) [$C_4H_9^+$], 41 (55). − $C_{19}H_{28}O_4$ (320.4): calcd. C 71.22, H 8.81; found C 71.05, H 8.76.

(1R,2S,5R)-Menthyl (3E)-3-{2-[(E)-2-((1R,2S,5R)-Menthoxycarbonyl)ethenyl]-1-cyclohexen-1-yl}acrylate (**5cc**): 1,2-Dibromocyclohexene (**2**) (1.20 g, 5.00 mmol) was treated with (1*R*,2*S*,5*R*)-menthyl acrylate (**3c**) (2.63 g, 12.5 mmol) in DMF (50 ml) for 70 h at 90°C according to GP 1. After CC on silica gel (85 g, petroleum ether/EtOAc, 50:1), 879 mg (4.18 mmol) of (1*R*,2*S*,5*R*)-menthyl acrylate (**3c**) (R_f = 0.38), 313 mg of an unseparable mixture of an unknown impurity and **7c** (R_f = 0.32) as a colorless oil, and 1.25 g (50%) of pure **5cc** (R_f = 0.25) as a colorless foam were obtained. − **7c**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.74−1.15 (m, 11 H), 1.34−1.80 (m, 9 H), 1.85−2.20 (m, 6 H), 4.81 (m_c, 1 H, OCH), 5.75 (d, *J* = 15.7 Hz, 1 H, 2-H), 6.14 (m_c, 1 H, 2′-H), 7.27 (d, *J* = 15.7 Hz, 1 H, 3-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 16.24 (+, CH_3), 20.58 (+, CH_3), 21.88 [+/−, CH_3/C-4′(5′)], 23.36 (−, CH_2), 23.96 (−, C-3′), 26.12 (+, CH), 26.22 (−, C-6′), 31.21 (+, CH), 34.14 (−, CH_2), 40.88 (−, CH_2), 47.02 (+, CH), 73.45 (+, OCH), 114.88 (+, C-2), 134.73 (C_{quat}, C-1′), 138.21 (+, C-3), 147.58 (+, C-2′), 166.91 (C_{quat}, C-1). − MS; *m/z* (%): 290 (5) [M^+], 262 (1), 196 (3), 153 (19) [$M^+ - C_{10}H_{17}$], 138 (100) [$C_{10}H_{18}^+$], 95 (15) [$C_7H_{11}^+$]. − **5cc**: $[\alpha]_D^{20}$ = −73.8 (*c* = 1.00, $CHCl_3$). − IR (film): ν = 2954 cm^{-1}, 2868, 1709, 1612, 1456, 1303, 1275, 1173, 1012, 976. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.77 (d, *J* = 7.0 Hz, 6 H, CH_3), 0.89 (d, *J* = 7.0 Hz, 6 H, CH_3), 0.90 (d, *J* = 6.5 Hz, 6 H, CH_3), 0.94−1.10 (m, 4 H, CH_2), 1.38−1.79 [m, 14 H, 4′′(5′′)-H, CH_2, CH], 1.81−1.90 (m, 2 H, CH), 1.99−2.04 (m, 2 H, CH), 2.34 [br. s, 4 H, 3′′(6′′)-H], 4.79 (dt, *J* = 4.4, *J* = 10.8 Hz, 2 H, OCH), 5.97 [d, *J* = 15.6 Hz, 2 H, 2(2′)-H], 8.05 [d, *J* = 15.6 Hz, 2 H, 3(3′)-H]. − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 16.54 (+, CH_3), 20.67 (+, CH_3), 21.83 [−, C-4′′(5′′)], 21.98 (+, CH_3), 23.64 (−, CH_2), 26.42 (+, CH), 26.64 [−, C-3′′(6′′)], 31.36 (+, CH), 34.25 (−, CH_2), 40.96 (−, CH_2), 47.15 (+, CH), 74.13 (+, OCH), 119.38 [+, C-2(2′)], 137.84 [C_{quat}, C-1′′(2′′)], 139.69 [+, C-3(3′)], 166.60 [C_{quat}, C-1(1′)]. − MS; *m/z* (%): 498 (2) [M^+], 360 (3) [$M^+ - C_{10}H_{18}$], 342 (7), 230 (10), 222 (64), 204 (100), 177 (72) [$M^+ - C_{10}H_{18} - C_{10}H_{19} - CO_2$], 138 (58) [$C_{10}H_{18}^+$], 95 (27), 83 (76), 55 (24). − $C_{32}H_{50}O_4$ (498.8): calcd. C 77.06, H 10.10; found C 76.96, H 10.15; calcd. 498.3709 (correct HR-MS).

(1R,2S,5R)-8-Phenylmenthyl (3E)-3-{2-[(E)-2-((1R,2S,5R)-8-Phenylmenthylcarbonyl)ethenyl]-1-cyclohexen-1-yl}acrylate (**5dd**): 1,2-Dibromocyclohexene (**2**) (480 mg, 2.00 mmol) was treated with (*1R,2S,5R*)-8-phenylmenthyl acrylate (**3d**) (1.43 g, 5.00 mmol) in DMF (20 ml) for 90 h at 100°C according to GP 1. After CC on silica gel (85 g, petroleum ether/EtOAc, 30:1), 453 mg (1.58 mmol) of (1*R*,2*S*,5*R*)-8-phenylmenthyl acrylate (**3d**) (R_f = 0.39), 79 mg (11%) of **7d** (R_f = 0.33) as a colorless oil containing an unknown impurity, and 556 mg (43%) of **5dd** (R_f = 0.26) as a colorless foam were obtained. − **7d**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.86−2.19 (m, 19 H), 1.23 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 4.87 (m_c, 1 H, OCH), 5.18 (d, *J* = 15.7 Hz, 1 H, 2-H), 6.07 (m_c, 1 H, 2′-H), 6.93 (d, *J* = 15.7 Hz, 1 H, 3-H), 7.13−7.38 (m, 5 H, aromatic H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.74 (+, CH_3), 21.98 [−, C-4′(5′)], 23.93 (−, C-3′), 25.08 (+, CH_3), 26.31 (−, CH_2), 26.52 (−, C-6′), 27.59 (+, CH_3), 31.19 (+, CH), 34.55 (−, CH_2), 39.59 [C_{quat},

C$(CH_3)_2$Ph], 41.68 (−, CH_2), 50.58 (+, CH), 73.87 (+, OCH), 115.10 (+, C-2), 124.74 (+, aromatic C), 125.32 (+, aromatic C), 127.89 (+, aromatic C), 134.76 (C_{quat}, C-1′), 138.22 (+, C-3), 147.23 (+, C-2′), 151.62 (C_{quat}, aromatic C), 166.70 (C_{quat}, C-1). − **5dd**: $[\alpha]_D^{20}$ = +53.5 (*c* = 1.00, $CHCl_3$). − IR (Film): ν = 2952 cm^{-1}, 2925, 1700, 1612, 1457, 1304, 1275, 1241, 1176, 1006, 975, 909, 764, 732, 700. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.89 (d, *J* = 6.4 Hz, 6 H, CH_3), 0.94−1.83 [m, 16 H, 4′′(5′′)-H, CH_2], 1.24 (s, 6 H, CH_3), 1.35 (s, 6 H, CH_3), 1.91−1.96 (m, 2 H, CH), 2.08−2.19 [m, 6 H, 3′′(6′′)-H, CH], 4.93 (dt, *J* = 4.2, *J* = 10.7 Hz, 2 H, OCH), 5.34 [d, *J* = 15.6 Hz, 2 H, 2(2′)-H], 7.04 (m_c, 2 H, aromatic H), 7.21−7.31 (m, 8 H, aromatic H), 7.54 [d, *J* = 15.6 Hz, 2 H, 3(3′)-H]. − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.77 (+, CH_3), 21.88 [−, C-4′′(5′′)], 24.37 (+, CH_3), 26.43 (−, CH_2), 26.50 [−, C-3′′(6′′)], 28.38 (+, CH_3), 31.28 (+, CH), 34.61 (−, CH_2), 39.60 [C_{quat}, *C*$(CH_3)_2$Ph], 41.75 (−, CH_2), 50.67 (+, CH), 74.16 (+, OCH), 119.07 [+, C-2(2′)], 124.71 (+, aromatic C), 125.33 (+, aromatic C), 127.89 (+, aromatic C), 137.50 [C_{quat}, C-1′′(2′′)], 139.30 [+, C-3(3′)], 151.71 (C_{quat}, aromatic C), 166.15 [C_{quat}, C-1(1′)]. − MS; *m/z* (%): 650 (4) [M^+], 532 (1) [M^+ + H − $C(CH_3)_2$Ph], 436 (4) [M^+ − $C_{16}H_{22}$], 392 (1) [M^+ − $C_{16}H_{22}$ − CO_2], 317 (4) [M^+ − $C_{16}H_{22}$ − $C(CH_3)_2$Ph], 222 (33), 215 (20) [$C_{16}H_{23}^+$], 119 (100) [$C(CH_3)_2Ph^+$], 105 (56), 91 (39). − $C_{44}H_{58}O_4$ (650.9): calcd. C 81.19, H 8.98; found C 81.04, H 8.93; calcd. 650.4335 (correct HR-MS).

1,2-(E,E)-Distyrylcyclopentene (**4ee**): 1,2-Dibromocyclopentene (**1**) (5.0 g, 22 mmol) was treated with styrene (**3e**) (10 ml, 87 mmol) for 40 h at 90°C according to GP 1. After filtration through silica gel (10 g, petroleum ether/Et_2O, 4:1) and recrystallization from EtOH, 4.4 g (73%) of **4ee** was obtained as yellow crystals, m. p. 133°C. − IR (KBr): ν = 3028 cm^{-1}, 2958, 2898, 2848, 1593, 1489, 1446, 962, 747. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.88 (quint, *J* = 6.7 Hz, 2 H, 4-H), 2.67 [t, *J* = 6.7 Hz, 4 H, 3(5)-H], 6.55 [d, *J* = 16.0 Hz, 2 H, 2′(2′′)-H], 7.18−7.51 [m, 12 H, 1′(1′′)-H, aromatic H]. − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.58 (−, C-4), 33.87 [−, C-3(5)], 122.35 [+, C-2′(2′′)], 126.49 (+, aromatic C), 127.41 (+, aromatic C), 128.69 (+, aromatic C), 129.71 [+, C-1′(1′′)], 137.93 (C_{quat}, aromatic C), 139.00 [C_{quat}, C-1(2)]. − MS; *m/z* (%): 272 (100) [M^+], 181 (19), 91 (10). − $C_{21}H_{20}$ (272.4): calcd. C 92.60, H 7.40; found C 92.61, H 7.36.

1,2-(E,E)-Distyrylcyclohexene (**5ee**): 1,2-Dibromocyclohexene (**2**) (3.0 g, 12.5 mmol) was treated with styrene (**3e**) (5.4 g, 52 mmol) for 92 h at 90°C according to GP 1. After CC on silica gel (150 g, petroleum ether), 2.45 g (69%) of **5ee** was obtained as colorless crystals, m. p. 68°C. − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.60 [−, C-4(5)], 26.88 [−, C-3(6)], 126.44 [+, C-2′(2′′)], 127.27 (+, aromatic C), 128.67 (+, aromatic C), 129.02 (+, aromatic C), 129.77 [+, C-1′(1′′)], 133.80 (C_{quat}, aromatic C), 138.24 [C_{quat}, C-1(2)]. − MS; *m/z* (%): 286 (100) [M^+], 195 (39), 91 (14). The other spectroscopic data were identical with those reported in ref.[11a]

1,2-Diiodocyclopentene (**8**)[13a]: To a solution of 1,2-dibromocyclopentene (**1**) (3.61 g, 16.0 mmol) in HMPA (36 ml) were added KI (25.6 g, 154 mmol) and CuI (15.2 g, 79.8 mmol). The reaction mixture was heated to 120°C for 9 h. After the reaction mixture had cooled down to room temp., 2 N HCl (160 ml) and then benzene (160 ml) were added. The organic phase was washed successively with Na_2SO_3 aq. (80 ml) and water (80 ml), dried with $MgSO_4$, concentrated, and chromatographed on silica gel (50 g, petroleum ether) to give 3.59 g (70%) of **8**. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.02 (quint, *J* = 7.8 Hz, 2 H, 4-H), 2.70 [t, *J* = 7.8 Hz, 4 H, 3(5)-H]. − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 25.28 (−, C-4), 44.29 [−, C-3(5)], 106.91 [C_{quat}, C-1(2)].

1,2-Diiodocyclohexene (**9**)[13a]: To a solution of 1,2-dibromocyclohexene (**2**) (4.80 g, 20.0 mmol) in HMPA (50 ml) were added KI (33.2 g, 200 mmol) and CuI (19.0 g, 100 mmol). The reaction mixture was heated to 120°C for 15 h. After the reaction mixture had cooled down to room temp., 2 N HCl (200 ml) and then benzene (200 ml) were added. The organic phase was washed successively with Na_2SO_3 aq. (80 ml) and water (80 ml), dried with $MgSO_4$, concentrated, and chromatographed on silica gel (50 g, petroleum ether) to give 5.20 g (78%) of **9**. Spectroscopic data were identical with those reported in ref.[13b]

General Procedure for the Twofold Heck Coupling of 1,2-Diiodocyclopentene (**8**) *and 1,2-Diiodocyclohexene* (**9**) *with Ethenylsilanes* **3f−k** (*GP 2*): A mixture consisting of $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), $AgNO_3$ (340 mg, 2.00 mmol), 1,2-diiodocyclopentene (**8**) or 1,2-diiodocyclohexene (**9**) (1.00 mmol), NEt_3 (0.84 ml, 6.0 mmol), trialkylethenylsilane (5 mmol in the cases of methods A−D, 10 mmol in the case of method E), and DMSO (10 ml) was placed in a Pyrex bottle and purged with Argon for several minutes, before the bottle was sealed with a screw cap. The suspension in the bottle was stirred at room temp. for 2 d (Method A) or heated to 100°C for 2 d (Method B), 5 h (Method D), or 10 h (Method E). After having been cooled down to room temp., the reacting mixture was added to H_2O (50 ml) and extracted with pentane (3 × 40 ml). The organic layer was dried ($MgSO_4$) and chromatographed on silica gel. The reactions at 5 bar were carried out in a hydrogenation vessel under Argon at room temp. for 2 d, a pressure of 5 bar was exerted on the apparatus and the apparatus was sealed (Method C).

1,2-Bis[(2E)-2-trimethylsilylethenyl]cyclopentene (**4ff**): 1,2-Diiodocyclopentene (**8**) (0.32 g, 1.0 mmol) was treated with trimethylethenylsilane (**3f**) (0.50 g, 5.0 mmol) in DMSO (10 ml) according to GP 2, Methods A−C. After CC on silica gel (25 g, petroleum ether) and recrystallization from petroleum ether/EtOH (4:1), **4ff** was obtained in 73−90% yield (see Table 2). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.06 (s, 18 H, $SiMe_3$), 1.97 (quint, *J* = 7.5 Hz, 2 H, 4-H), 2.63 [t, *J* = 7.5 Hz, 4 H, 3(5)-H], 5.89 [d, *J* = 15.5 Hz, 2 H, 2′(2′′)-H], 7.26 [d, *J* = 15.5 Hz, 2 H, 1′(1′′)-H]. − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = −1.19 (+, $SiMe_3$), 21.17 (−, C-4), 33.66 [−, C-3(5)], 131.36 [+, C-2′(2′′)], 136.78 [+, C-1′(1′′)], 140.15 [C_{quat}, C-1(2)]. − $C_{15}H_{28}Si_2$ (264.6): calcd. C 68.10, H 10.67; found C 68.19, H 10.77.

1,2-Bis[(2E)-2-triethylsilylethenyl]cyclopentene (**4gg**): 1,2-Diiodocyclopentene (**8**) (0.32 g, 1.0 mmol) was treated with triethylethenylsilane (**3g**) (0.71 g, 5.0 mmol) in DMSO (10 ml) according to GP 2, Method A. After CC on silica gel (25 g, petroleum ether), **4gg** was obtained as a clear oil in 81% yield (see Table 2). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.63 (q, *J* = 7.8 Hz, 12 H, $SiCH_2$), 0.99 (t, *J* = 7.8 Hz, 18 H, CH_3), 1.87 (quint, *J* = 7.5 Hz, 2 H, 4-H), 2.65 [t, *J* = 7.5 Hz, 4 H, 3(5)-H], 5.76 [d, *J* = 15.7 Hz, 2 H, 2′(2′′)-H], 7.13 [d, *J* = 15.7 Hz, 2 H, 1′(1′′)-H]. − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 3.56 (+, CH_3), 7.24 (−, $SiCH_2$), 21.11 (−, C-4), 33.56 [−, C-3(5)], 127.71 [+, C-2′(2′′)], 138.13 [+, C-1′(1′′)], 140.11 [C_{quat}, C-1(2)]. − $C_{21}H_{40}Si_2$ (348.7): calcd. C 72.33, H 11.56; found C 72.13, H 11.55.

1,2-Bis[(2E)-2-dimethylphenylsilylethenyl]cyclopentene (**4hh**): 1,2-Diiodocyclopentene (**8**) (0.32 g, 1.0 mmol) was treated with dimethylphenylethenylsilane (**3h**) (0.81 g, 5.0 mmol) in DMSO (10 ml) according to GP 2, Method A. After CC on silica gel (25 g, petroleum ether), 53% of **4hh** was obtained (see Table 2). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.38 (s, 12 H, CH_3), 1.85 (m_c, 2 H, 4-H), 2.63 [t, *J* = 7.5 Hz, 4 H, 3(5)-H], 5.90 [d, *J* = 15.7 Hz, 2 H, 2′(2′′)-H], 7.06 [d, *J* = 15.7 Hz, 2 H, 1′(1′′)-H], 7.26−7.56 (m, 10

H, aromatic H). − $C_{25}H_{32}Si_2$ (388.7): calcd. C 77.25, H 8.30; found C 77.13, H 8.39.

1,2-Bis[(2E)-2-methyldiphenylsilylethenyl]cyclopentene (**4ii**): 1,2-Diiodocyclopentene (**8**) (0.32 g, 1.0 mmol) was treated with methyldiphenylethenylsilane (**3i**) (1.12 g, 5.0 mmol) in DMSO (10 ml) for 2 d at 25°C according to GP 2, Method A. After CC on silica gel (25 g, petroleum ether), 60 mg (12%) of **4ii** was obtained (see Table 2). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.70 (s, 6 H, CH_3), 2.50 (quint, *J* = 7.5 Hz, 2 H, 4-H), 2.90 [t, *J* = 7.5 Hz, 4 H, 3(5)-H], 6.20 [d, *J* = 15.7 Hz, 2 H, 2′(2′′)-H], 6.90 [d, *J* = 15.7 Hz, 2 H, 1′(1′′)-H], 7.26−7.55 (m, 20 H, aromatic H).

1,2-Bis[(2E)-2-triphenylsilylethenyl]cyclopentene (**4jj**): 1,2-Diiodocyclopentene (**8**) (0.32 g, 1.0 mmol) was treated with triphenylethenylsilane (**3j**) (1.43 g, 5.0 mmol) in DMSO (10 ml) according to GP 2, Methods A and B. After CC on silica gel (25 g, petroleum ether/ethyl acetate, 100:1), **4jj** was obtained in 30−34% yield (see Table 2). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.95 (quint, *J* = 7.5 Hz, 2 H, 4-H), 2.78 [t, *J* = 7.5 Hz, 4 H, 3(5)-H], 6.31 [d, *J* = 15.7 Hz, 2 H, 2′(2′′)-H], 7.03 [d, *J* = 15.7 Hz, 2 H, 1′(1′′)-H], 7.31−7.53 (m, 30 H, aromatic H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 26.93 (−, C-4), 33.83 [−, C-3(5)], 125.19 [+, C-2′(2′′)], 127.81 (+, aromatic C), 129.47 (+, aromatic C), 134.58 [+, C-1′(1′′)], 134.88 (+, aromatic C), 141.53 (C_{quat}, aromatic C), 141.78 [C_{quat}, C-1(2)]. − $C_{45}H_{40}Si_2$ (637.0): calcd. C 84.85, H 6.33; found C 84.63, H 6.39.

1,2-Bis[(2E)-2-tri-n-butylsilylethenyl]cyclopentene (**4kk**): 1,2-Diiodocyclopentene (**8**) (0.32 g, 1.0 mmol) was treated with tri-*n*-butylethenylsilane (**3k**) (1.13 g, 5.0 mmol) in DMSO (10 ml) according to GP 2, Method A. After CC on silica gel (25 g, petroleum ether), **4kk** was obtained as a clear oil in 71% yield (see Table 2). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.62 (m_c, 12 H, $SiCH_2$), 0.90 (t, *J* = 6.9 Hz, 18 H, CH_3), 1.34 (m_c, 24 H, CH_2), 1.85 (quint, *J* = 7.5 Hz, 2 H, 4-H), 2.63 [t, *J* = 7.5 Hz, 4 H, 3(5)-H], 5.78 [d, *J* = 15.7 Hz, 2 H, 2′(2′′)-H], 7.15 [d, *J* = 15.7 Hz, 2 H, 1′(1′′)-H]. − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 12.38 (−, $SiCH_2$), 13.81 (+, CH_3), 21.08 (−, C-4), 26.16 (−, CH_2), 26.77 (−, CH_2), 33.62 [−, C-3(5)], 128.69 [+, C-2′(2′′)], 137.75 [+, C-1′(1′′)], 140.07 [C_{quat}, C-1(2)]. − $C_{33}H_{64}Si_2$ (517.0): calcd. C 76.66, H 12.48; found C 76.71, H 12.46.

1,2-Bis[(2E)-2-trimethylsilylethenyl]cyclohexene (**5ff**): 1,2-Diiodocyclohexene (**9**) (0.33 g, 1.0 mmol) was treated with trimethylethenylsilane (**3f**) (0.50 g, 5.0 mmol in the cases of methods A, B, and D, 1.0 g, 10 mmol in the case of method E) in DMSO (10 ml) according to GP 2, Methods A, B, D, and E. After CC on silica gel (30 g, petroleum ether), **5ff** was obtained as a colorless solid in 69−92% yield (see Table 2). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.14 (s, 18 H, $SiMe_3$), 1.67 (m_c, 4 H, 4(5)-H], 2.32 [m_c, 4 H, 3(6)-H], 5.94 [d, *J* = 18.7 Hz, 2 H, 2′(2′′)-H], 7.40 [d, *J* = 18.7 Hz, 2 H, 1′(1′′)-H]. − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = −1.18 (+, $SiMe_3$), 22.58 [−, C-4(5)], 26.14 [−, C-3(6)], 128.20 [+, C-2′(2′′)], 134.46 [C_{quat}, C-1(2)], 140.76 [+, C-1′(1′′)]. − $C_{16}H_{30}Si_2$ (278.6): calcd. C 68.99, H 10.85; found C 68.79, H 10.69.

1,2-Bis[(2E)-2-triethylsilylethenyl]cyclohexene (**5gg**): 1,2-Diiodocyclohexene (**9**) (0.33 g, 1.0 mmol) was treated with triethylethenylsilane (**3g**) (0.71 g, 5.0 mmol) in DMSO (10 ml) according to GP 2, Methods A and C. After CC on silica gel (30 g, petroleum ether), **5gg** was obtained as a clear oil in 68−80% yield (see Table 2). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.62 (q, *J* = 7.6 Hz, 12 H, $SiCH_2$), 0.97 (t, *J* = 7.6 Hz, 18 H, CH_3), 1.65 [m_c, 4 H, 4(5)-H], 2.31 [m_c, 4 H, 3(6)-H], 5.81 [d, *J* = 19.0 Hz, 2 H, 2′(2′′)-H], 7.33 [d, *J* = 19.0 Hz, 2 H, 1′(1′′)-H]. − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 3.71 (−, $SiCH_2$), 7.42 (+, CH_3), 22.59 [−, C-4(5)], 26.15 [−, C-3(6)], 124.50 [+, C-2′(2′′)], 134.47 [C_{quat}, C-1(2)], 142.32 [+, C-1′(1′′)].

1,2-Bis[(2E)-2-dimethylphenylsilylethenyl]cyclohexene (**5hh**): 1,2-Diiodocyclohexene (**9**) (0.33 g, 1.0 mmol) was treated with dimethylphenylethenylsilane (**3h**) (0.81 g, 5.0 mmol) in DMSO (10 ml) according to GP 2, Methods A, B, and C. After CC on silica gel (30 g, petroleum ether), **5hh** was obtained as colorless crystals in 32−52% yield (see Table 2). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.41 (s, 12 H, CH_3), 1.69 [m_c, 4 H, 4(5)-H], 2.37 [m_c, 4 H, 3(6)-H], 6.03 [d, *J* = 18.6 Hz, 2 H, 2′(2′′)-H], 7.33 [d, *J* = 18.6 Hz, 2 H, 1′(1′′)-H], 7.39−7.61 (m, 10 H, aromatic H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = −2.48 (+, CH_3), 22.49 [−, C-4(5)], 26.13 [−, C-3(6)], 126.07 (+, aromatic C), 127.78 (+, aromatic C), 128.96 [+, C-2′(2′′)], 133.88 (+, aromatic C), 134.89 [C_{quat}, C-1(2)], 138.99 [C_{quat}, aromatic C], 142.34 [+, C-1′(1′′)]. − $C_{26}H_{34}Si_2$ (402.7): calcd. C 77.54, H 8.51; found C 77.69, H 8.66.

1,2-Bis[(2E)-2-methyldiphenylsilylethenyl)cyclohexene (**5ii**): 1,2-Diiodocyclohexene (**9**) (0.33 g, 1.0 mmol) was treated with methyldiphenylethenylsilane (**3i**) (1.12 g, 5.0 mmol) in DMSO (10 ml) according to GP 2, Methods A and B. After CC on silica gel (30 g, petroleum ether), **5ii** was obtained as colorless crystals in 9−20% yield (see Table 2). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.58 (s, 6 H, CH_3), 1.67 [m_c, 4 H, 4(5)-H], 2.38 [m_c, 4 H, 3(6)-H], 6.16 [d, *J* = 18.7 Hz, 2 H, 2′(2′′)-H], 7.26 [d, *J* = 18.7 Hz, 2 H, 1′(1′′)-H], 7.27−7.54 (m, 20 H, aromatic H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = −3.74 (+, CH_3), 22.48 [−, C-4(5)], 26.25 [−, C-3(6)], 123.96 [+, C-2′(2′′)], 127.81 (+, aromatic C), 129.21 (+, aromatic C), 134.83 (+, aromatic C), 135.34 [C_{quat}, C-1(2)], 136.81 (C_{quat}, aromatic C), 144.14 [+, C-1′(1′′)]. − $C_{36}H_{38}Si_2$ (526.9): calcd. C 82.07, H 7.27; found C 82.06, H 7.31.

1,2-Bis[(2E)-2-triphenylsilylethenyl]cyclohexene (**5jj**): 1,2-Diiodocyclohexene (**9**) (0.33 g, 1.0 mmol) was treated with triphenylethenylsilane (**3j**) (1.43 g, 5.0 mmol) in DMSO (10 ml) according to GP 2, Method A. After CC on silica gel (30 g, petroleum ether/ethyl acetate, 100:1) and recrystallization from petroleum ether/ethyl acetate, 2:1, **5jj** was obtained as colorless crystals in 38% yield (see Table 2). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.59 [m_c, 4 H, 4(5)-H], 2.33 [m_c, 4 H, 3(6)-H], 6.25 [d, *J* = 18.8 Hz, 2 H, 2′(2′′)-H], 7.14−7.37 [m, 32 H, aromatic H, 1′(1′′)-H]. − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.45 [−, C-4(5)], 26.39 [−, C-3(6)], 122.19 [+, C-2′(2′′)], 127.78 (+, aromatic C), 129.39 (+, aromatic C), 134.79 (C_{quat}, aromatic C), 135.03 [C_{quat}, C-1(2)], 135.85 (+, aromatic C), 146.12 [+, C-1′(1′′)].

1,2-Bis[(2E)-2-tri-n-butylsilylethenyl]cyclohexene (**5kk**): 1,2-Diiodocyclohexene (**9**) (0.33 g, 1.0 mmol) was treated with tri-*n*-butylethenylsilane (**3k**) (1.13 g, 5.0 mmol) in DMSO (10 ml) according to GP 2, Method A. After CC on silica gel (30 g, petroleum ether) and kugelrohr distillation (150°C, 1 Torr), **5kk** was obtained as a clear oil in 35% yield (see Table 2). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.62 (m_c, 12 H, $SiCH_2$), 0.90 (t, *J* = 7.0 Hz, 18 H, CH_3), 1.34 (m_c, 24 H, CH_2), 1.70 [m_c, 4 H, 4(5)-H], 2.30 [m_c, 4 H, 3(6)-H], 5.90 [d, *J* = 18.7 Hz, 2 H, 2′(2′′)-H], 7.40 [d, *J* = 18.7 Hz, 2 H, 1′(1′′)-H].

(2E)-2-{2-[(2E)-2-Trimethylsilylethenyl]cyclopent-1-enyl}ethenylbenzene (**4ef**): 1,2-Diiodocyclopentene (**8**) (0.32 g, 1.00 mmol) was treated with trimethylethenylsilane (**3f**) (0.25 g, 2.5 mmol) and styrene (**3e**) (1.44 ml, 12.5 mmol) in DMSO (10 ml) according to GP 2, Method B. After CC on silica gel (30 g, petroleum ether), 100 mg (37%) of **4ef** was obtained as colorless crystals. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.16 (s, 9 H, $SiMe_3$), 1.95 (quint, *J* = 7.5 Hz, 2 H, 4′-H), 2.65 [t, *J* = 7.5 Hz, 4 H, 3′(5′)-H], 5.84 (d, *J* = 18.7 Hz, 1 H, 2′′-H), 6.50 (d, *J* = 15.9 Hz, 1 H, 1-H),

7.15−7.49 [m, 7 H, 2(1′′)-H, aromatic H]. − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = −1.13 [+, $SiMe_3$], 21.30 (−, C-4′), 33.51 (−, C-5′), 33.94 (−, C-3′), 122.22 (+, C-1), 126.36 (+, aromatic C), 127.32 (+, aromatic C), 128.57 (+, aromatic C), 129.75 (+, C-2), 131.30 (+, C-2′′), 136.74 (+, C-1′′), 137.79 (C_{quat}, aromatic C), 138.74 (C_{quat}, C-1′), 140.88 (C_{quat}, C-2′).

General Procedure (GP 3) for the Preparation of 1-Halo-2-perfluoroalkanesulfonyloxycycloalk-1-enes: n-Butyllithium (1.05 mmol, 2.36 M in hexane) was added to hexamethyldisilazane (HMDS) (1.1 mmol) in THF (4 ml) at −78°C. After 10 min, the respective halo ketone (1.0 mmol) in THF (3 ml) was added dropwise within 5 min. The reaction was quenched 11 min later by addition of the perfluoroalkanesulfonic acid derivative (3.0 mmol). After stirring for the stated time at the stated temperature, the mixture was diluted with Et_2O (80 ml), extracted with H_2O (3 × 20 ml), dried ($MgSO_4$), and the solvents were evaporated. The crude product was chromatographed on silica gel.

1-Bromo-2-trifluoromethanesulfonyloxycyclohex-1-ene (**11**): 2-Bromocyclohexanone (**10**) (177 mg, 1.00 mmol) was treated with trifluoromethanesulfonic anhydride (846 mg, 3.00 mmol) for 30 min at −78°C according to GP 3. After CC on silica gel (20 g, petroleum ether/Et_2O, 20:1), 119 mg (39%) of **11** (R_f = 0.52) as a clear oil and 49 mg (16%) of 3-bromo-2-trifluoromethanesulfonyloxycyclohex-1-ene (**12**) (R_f = 0.40) as a clear oil were obtained. − **11**: IR (film): ν = 2935 cm^{-1}, 1415, 1218, 1137, 1090, 1049, 998, 892, 840, 796, 760, 614. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.68−1.89 [m, 4 H, 4(5)-H], 2.36−2.45 (m, 2 H, 6-H), 2.57−2.67 (m, 2 H, 3-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.30 (−, C-5), 23.32 (−, C-4), 28.14 (−, C-6), 29.35 (−, C-3), 122.77 (C_{quat}, C-1), 118.30 (q, J = 320 Hz, CF_3), 145.37 (C_{quat}, C-2). − MS; *m/z* (%): 310/308 (39/38) [M^+], 229 (28) [M^+ − Br], 177/175 (26/25) [M^+ − SO_2CF_3], 149/147 (22/22), 121/119 (23/23), 79 (20), 67 (100). − $C_7H_8BrF_3O_3S$ (309.1): calcd. 307.9323 (correct HR-MS). − **12**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.69−1.88 (m, 2 H, 5-H), 2.36−2.67 [m, 4 H, 4(6)-H], 4.76 (m_c, 1 H, 3-H), 5.96 (m_c, 1 H, 1-H).

2-Bromo-1-nonafluorobutanesulfonyloxy-4,4-dimethylcyclohex-1-ene (**14**): 2-Bromo-4,4-dimethylcyclohexanone (**13**) (1.03 g, 5.02 mmol) was treated with nonafluorobutanesulfonic fluoride (4.53 g, 15.0 mmol) for 48 h at room temp. according to GP 3. After CC on silica gel (65 g, petroleum ether/Et_2O, 40:1), 1.36 g (56%) of **14** (R_f = 0.53) as a clear oil and 102 mg (4%) of 3-bromo-2-nonafluorobutanesulfonyloxy-5,5-dimethylcyclohex-1-ene (**15**) (R_f = 0.35) as a clear oil were obtained. − **14**: IR (film): ν = 2962 cm^{-1}, 1424, 1353, 1240, 1201, 1145, 1073, 1033, 864, 792, 737, 651, 615, 600, 585. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.02 (s, 6 H, CH_3), 1.59 (m_c, 2 H, 5-H), 2.38−2.42 [m, 4 H, 3(6)-H]. − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 26.54 (−, C-6), 27.26 (+, CH_3), 31.74 (C_{quat}, C-4), 35.02 (−, C-5), 48.22 (−, C-3), 105−120 (m, C_{quat}, C_4F_9), 115.14 (C_{quat}, C-2), 144.55 (C_{quat}, C-1). − MS; *m/z* (%): 488/486 (10/9) [M^+], 407 (1) [M^+ − Br], 327 (4), 219 (10) [$C_4F_9^+$], 205/203 (23/24) [M^+ − $C_4F_9O_2S$], 133 (24), 123 (100) [M^+ − $C_4F_9O_2S$ − HBr], 95 (50), 69 (29). − $C_{12}H_{12}BrF_9O_3S$ (487.2): calcd. C 29.59, H 2.48; found C 30.09, H 2.57; calcd. 485.9546 (correct HR-MS). − **15**: IR (film): ν = 2962 cm^{-1}, 1423, 1353, 1240, 1202, 1144, 1049, 1033, 867, 797, 590. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.99 (s, 3 H, CH_3), 1.09 (s, 3 H, CH_3), 1.94−2.30 [m, 4 H, 4(6)-H], 4.76 (m_c, 1 H, 3-H), 5.95 (m_c, 1 H, 1-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 25.75 (+, CH_3), 29.34 (+, CH_3), 31.51 (C_{quat}, C-5), 38.06 (−, C-6), 42.74 (+, C-3), 47.14 (−, C-4), 105−120 (m, C_{quat}, C_4F_9), 122.46 (+, C-1), 145.38 (C_{quat}, C-2).

2-Bromo-1-nonafluorobutanesulfonyloxy-3,4-dihydronaphthalene (**17**): 2-Bromotetralone (**16**) (225 mg, 1.00 mmol) was treated with nonafluorobutanesulfonic fluoride (906 mg, 3.00 mmol) for 48 h at room temp. according to GP 3. After CC on silica gel (20 g, petroleum ether/Et_2O, 20:1), 238 mg (47%) of **17** was obtained as colorless crystals, m. p. 76°C. − IR (KBr): ν = 2990 cm^{-1}, 1628, 1407, 1348, 1198, 1140, 1093, 1011, 898, 762. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.83−3.01 [m, 4 H, 3(4)-H], 7.06−7.19 (m, 1 H, 5-H), 7.19−7.30 [m, 2 H, 6(7)-H], 7.32−7.40 (m, 1 H, 8-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 28.41 (−, C-3), 34.13 (−, C-4), 105−120 (m, C_{quat}, C_4F_9), 117.14 (C_{quat}, C-2), 121.66 (+, C-5), 126.98 (+, C-6), 127.62 (+, C-7), 129.00 (C_{quat}, C-10), 129.20 (+, C-8), 134.61 (C_{quat}, C-9), 143.49 (C_{quat}, C-1). − MS; *m/z* (%): 508/506 (33/33) [M^+], 225/223 (31/31) [M^+ − $SO_2C_4F_9$], 187/185 (20/20), 143 (42) [$C_{10}H_7O^+$], 115 (100). − $C_{14}H_8BrF_9O_3S$ (507.2): calcd. 505.9233 (correct HR-MS).

1-Chloro-2-nonafluorobutanesulfonyloxycyclohex-1-ene (**19**): 2-Chlorocyclohexanone (**18**) (133 mg, 1.00 mmol) was treated with nonafluorobutanesulfonic fluoride (906 mg, 3.00 mmol) for 48 h at room temp. according to GP 3. After CC on silica gel (20 g, petroleum ether/Et_2O, 20:1), 228 mg (55%) of **19** was obtained as a clear oil. − IR (film): ν = 2935 cm^{-1}, 2853, 1675, 1617, 1415, 1346, 1200, 1139, 1047, 880, 840, 775, 726. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.68−1.89 [m, 4 H, 4(5)-H], 2.36−2.47 (m, 2 H, 6-H), 2.47−2.55 (m, 2 H, 3-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.40 (−, C-5), 22.44 (−, C-4), 28.44 (−, C-6), 32.62 (−, C-3), 105−120 (m, C_{quat}, C_4F_9), 125.69 (C_{quat}, C-1), 143.51 (C_{quat}, C-2). − MS; *m/z* (%): 416/414 (13/38) [M^+], 379 (1) [M^+ − Cl], 219 (11) [$C_4F_9^+$], 133/131 (23/68) [M^+ − $SO_2C_4F_9$], 67 (100). − $C_{10}H_8ClF_9O_3S$ (414.7): calcd. 413.9738 (correct HR-MS).

tert-Butyl (3E)-3-{2-[(E)-2-(tert-Butoxycarbonyl)ethenyl]-1-cyclohexen-1-yl}acrylate (**5bb**): 1-Bromo-2-trifluoromethanesulfonyloxycyclohex-1-ene (**11**) (147 mg, 0.476 mmol) was treated with *tert*-butyl acrylate (**3b**) (305 mg, 2.38 mmol) in the presence of $Pd(OAc)_2$ (9 mg, 40 μmol), PPh_3 (30 mg, 0.11 mmol), LiCl (16 mg, 0.38 mmol), and NEt_3 (0.265 ml, 1.90 mmol) in DMF (7 ml) for 4 d at 90°C according to GP 1. After CC on silica gel (20 g, petroleum ether/EtOAc, 25:1), 116 mg (73%) of **5bb** was obtained as colorless crystals. Analytical data of **5bb** were identical with those reported in ref.[7f]

1,2-(E,E)-Distyrylcyclohexene (**5ee**): 1-Bromo-2-trifluoromethanesulfonyloxycyclohex-1-ene (**11**) (213 mg, 0.689 mmol) was treated with styrene (**3e**) (359 mg, 3.45 mmol) in the presence of $Pd(OAc)_2$ (12 mg, 53 μmol), PPh_3 (43 mg, 0.16 mmol), LiCl (23 mg, 0.54 mmol), and NEt_3 (0.385 ml, 2.76 mmol) in DMF (7 ml) for 4 d at 90°C according to GP 1. After CC on silica gel (25 g, petroleum ether/CH_2Cl_2, 20:1), 65 mg (33%) of **5ee** was obtained as colorless crystals. Analytical data of **5ee** were identical with those reported in ref.[11a]

tert-Butyl (3E)-3-{2-[(E)-2-tert-Butoxycarbonylethenyl]-4,4-dimethylcyclohex-1-en-1-yl}acrylate (**20**): 2-Bromo-1-nonafluorobutanesulfonyloxy-4,4-dimethylcyclohex-1-ene (**14**) (1.60 g, 3.28 mmol) was treated with *tert*-butyl acrylate (**3b**) (2.11 g, 16.5 mmol) in the presence of $Pd(OAc)_2$ (59 mg, 0.26 mmol), PPh_3 (207 mg, 0.790 mmol), LiCl (112 mg, 2.64 mmol), and NEt_3 (1.8 ml, 13 mmol) in DMF (30 ml) for 40 h at 90°C according to GP 1. CC on silica gel (78 g, petroleum ether/EtOAc, 40:1) yielded 1.02 g (86%) of **20** as colorless crystals, m. p. 114°C. − IR (KBr): ν = 2975 cm^{-1}, 2928, 1713, 1615, 1392, 1366, 1320, 1150, 967, 848. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.92 (s, 6 H, CH_3), 1.38−1.50 (m, 2 H, 5′′-H), 1.50 [s, 18 H, $C(CH_3)_3$], 2.09 (s, 2 H, 3′′-H), 2.35 (m_c, 2 H, 6′′-H), 5.90 (d, J = 15.6 Hz, 1 H, 2-H), 5.92 (d, J = 15.6 Hz, 1 H, 2′-H), 7.98 [d, J = 15.6 Hz, 2 H, 3(3′)-H]. − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 24.39 (−, C-6′′), 28.01 (+, CH_3), 28.13

[+, C(CH_3)$_3$], 28.52 (C_{quat}, C-4′′), 34.40 (−, C-5′′), 40.42 (−, C-3′′), 80.35 [C_{quat}, $C(CH_3)_3$], 120.71 (+, C-2), 120.89 (+, C-2′), 136.08 (C_{quat}, C-1′′), 136.56 (C_{quat}, C-2′′), 138.77 (+, C-3), 139.28 (+, C-3′), 166.38 [C_{quat}, C-1(1′)]. − MS; *m/z* (%): 362 (< 1) [M^+], 250 (4), 204 (8) [$M^+ - CO_2 - 2\ C(CH_3)_3$], 159 (8), 148 (11), 105 (12), 91 (21), 57 (100) [$C(CH_3)_3^+$]. − $C_{22}H_{34}O_4$ (362.5): cacld. C 72.89, H 9.45; found C 72.79, H 9.31.

1,2-Bis[(2E)-2-methoxycarbonylethenyl]-3,4-dihydronaphthalene (**21**): 2-Bromo-1-nonafluorobutanesulfonyloxy-3,4-dihydronaphthalene (**17**) (507 mg, 1.00 mmol) was treated with methyl acrylate (**3a**) (431 mg, 5.00 mmol) in the presence of $Pd(OAc)_2$ (23 mg, 0.10 mmol), PPh_3 (68 mg, 0.26 mmol), and NEt_3 (0.56 ml, 4.0 mmol) in DMF (10 ml) for 24 h at 60°C according to GP 1. CC on silica gel (30 g, petroleum ether/EtOAc, 10:1) yielded 212 mg (71%) of **21** as orange crystals, m. p. 118°C. − IR (KBr): ν = 2940 cm^{-1}, 1712, 1605, 1429, 1320, 1272, 1161, 1023, 976, 856, 749. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.49−2.59 (m, 2 H, 3-H), 2.76−2.87 (m, 2 H, 4-H), 3.79 (s, 3 H, CH_3), 3.84 (s, 3 H, CH_3), 6.12 (d, *J* = 16 Hz, 1 H, 2′′-H), 6.15 (d, *J* = 16 Hz, 1 H, 2′-H), 7.17−7.33 (m, 4 H, aromatic H), 7.38 (d, *J* = 16 Hz, 1 H, 1′-H), 7.92 (d, *J* = 16 Hz, 1 H, 1′′-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 24.55 (−, C-3), 27.48 (−, C-4), 51.63 (+, CH_3), 51.78 (+, CH_3), 118.48 (+, C-2′′), 126.29 (+, C-5), 126.36 (+, C-6), 126.50 (+, C-7), 127.49 (+, C-8), 128.64 (+, C-2′), 133.41 (C_{quat}, C-10), 134.48 (C_{quat}, C-9), 137.00 (C_{quat}, C-2), 137.82 (C_{quat}, C-1), 140.30 (+, C-1′′), 141.75 (+, C-1′), 166.52 (C_{quat}, C-3′′), 167.58 (C_{quat}, C-3′). − MS; *m/z* (%): 298 (4) [M^+], 267 (1) [$M^+ - OCH_3$], 179 (37), 165 (28), 152 (23), 84 (100), 59 (8) [$CO_2CH_3^+$]. − $C_{18}H_{18}O_4$ (298.3): calcd. 298.1205 (correct HR-MS).

Methyl (3E)-3-(2-Chloro-1-cyclohexen-1-yl)acrylate (**22a**): 1-Chloro-2-nonafluorobutanesulfonyloxycyclohex-1-ene (**19**) (415 mg, 1.00 mmol) was treated with methyl acrylate (**3a**) (215 mg, 2.50 mmol) in the presence of $Pd(OAc)_2$ (11 mg, 0.05 mmol), PPh_3 (34 mg, 0.13 mmol), and NEt_3 (0.28 ml, 2.0 mmol) in DMF (5 ml) for 12 h at 60°C according to GP 1. After CC on silica gel (30 g, petroleum ether/EtOAc, 10:1), 192 mg (96%) of **22a** was obtained as a yellow oil. − IR (film): ν = 2915 cm^{-1}, 1715, 1612, 1426, 1287, 1161, 1089, 1062, 980, 850, 739. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.59−1.73 [m, 4 H, 4′(5′)-H], 2.12−2.21 (m, 2 H, 3′-H), 2.40−2.49 (m, 2 H, 6′-H), 3.70 (s, 3 H, OCH_3), 5.83 (d, *J* = 16.0 Hz, 1 H, 2-H), 7.88 (d, *J* = 16.0 Hz, 1 H, 3-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.54 (−, C-4′), 23.16 (−, C-5′), 25.99 (−, C-3′), 35.03 (−, C-6′), 51.33 (+, OCH_3), 117.58 (+, C-2), 128.48 (C_{quat}, C-1′), 139.24 (C_{quat}, C-2′), 141.33 (+, C-3), 167.27 (C_{quat}, C-1). − MS; *m/z* (%): 202/200 (5/16) [M^+], 171/169 (2/6) [$M^+ - OCH_3$], 165 (100) [M^+ − Cl], 154 (27), 133 (7), 122 (4), 105 (17) [$C_8H_9^+$], 91 (8), 77 (19) [$C_6H_5^+$], 51 (9). − $C_{10}H_{13}ClO_2$ (200.7): calcd. 200.0604 (correct HR-MS).

Methyl (3E)-3-[2-(E)-Styryl-1-cyclohexen-1-yl]acrylate (**5ae**): Methyl (3*E*)-3-(2-chloro-1-cyclohexen-1-yl)acrylate (**22a**) (192 mg, 0.96 mmol) was treated with styrene (**3e**) (260 mg, 2.50 mmol) in the presence of $Pd(OAc)_2$ (11 mg, 0.05 mmol), PPh_3 (34 mg, 0.13 mmol), and NEt_3 (0.28 ml, 2.0 mmol) in DMF (5 ml) for 48 h at 100°C according to GP 1. After CC on silica gel (30 g, petroleum ether/EtOAc, 10:1), 42 mg (16%) of **5ae** (R_f = 0.58) as yellow crystals, m. p. 71°C, and 131 mg (68%) of **22a** (R_f = 0.31) as a yellow oil were obtained. − IR (KBr): ν = 3030 cm^{-1}, 2930, 1715, 1605, 1435, 1305, 1275, 1250, 1195, 1175, 1155, 1075, 1040, 1015, 970, 865, 845, 750, 695, 650. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.70 [m_c, 4 H, 4′(5′)-H], 2.31 (m_c, 2 H, 3′-H), 2.48 (m_c, 2 H, 6′-H), 3.79 (s, 3 H, OCH_3), 5.92 (d, *J* = 15.5 Hz, 1 H, 2-H), 6.71 (d, *J* = 16.0 Hz, 1 H, 2′′-H), 7.20−7.51 (m, 5 H, aromatic H), 7.57 (d, *J* = 16.0 Hz, 1 H, 1′′-H), 8.23 (d, *J* = 15.5 Hz, 1 H, 3-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.97 (−, C-4′), 22.02 (−, C-5′), 26.17 (−, C-3′), 26.86 (−, C-6′), 51.27 (+, OCH_3), 115.66 (+, C-2), 125.06 (+, C-2′′), 126.58 (+, aromatic C), 127.68 (+, aromatic C), 128.47 (+, aromatic C), 129.80 (+, C-1′′), 131.44 (C_{quat}, C-2′), 137.21 (C_{quat}, C-1′), 140.62 (C_{quat}, aromatic C), 141.08 (+, C-3), 167.96 (C_{quat}, C-1). − MS; *m/z* (%): 268 (2) [M^+], 209 (4) [$M^+ - CO_2CH_3$], 165 (100) [$M^+ - C_8H_7$], 105 (22), 91 (17) [$C_7H_7^+$], 77 (20) [$C_6H_5^+$]. − $C_{18}H_{20}O_2$ (268.4): calcd. 268.1463 (correct HR-MS).

Methyl (3E)-3-[2-(E)-Styryl-1-cyclohexen-1-yl]acrylate (**5ae**): A suspension of $Pd(OAc)_2$ (11 mg, 0.05 mmol) and PPh_3 (37 mg, 0.10 mmol) in a 1:3 mixture of dry THF and acetonitrile (4 ml) was purged with Argon in an ultrasound bath until it became a yellow solution. To the stirred solution were added NEt_3 (101 mg, 1.00 mmol), styrene (**3e**) (130 mg, 1.25 mmol), and methyl (3*E*)-3-(2-chloro-1-cyclohexen-1-yl)acrylate (**22a**) (100 mg, 0.50 mmol). The mixture was sealed in a teflon tube and subjected to 10 kbar at 60°C for 3 d. Then dichloromethane (20 ml) was added, and the organic layer was washed with water (3 × 10 ml). The solution was dried with $MgSO_4$, the solvent removed, and the residue chromatographed on silica gel (15 g, petroleum ether/EtOAc, 20:1) to yield 56 mg (42%) of **5ae** and 38 mg (38%) of **22a**.

Methyl (3E)-3-{2-[(E)-2-(Methoxycarbonyl)ethenyl]-1-cyclohexen-1-yl}acrylate (**5aa**) *and Methyl (3E)-3-(2-Chloro-1-cyclohexen-1-yl)acrylate* (**22a**): 1-Chloro-2-nonafluorobutanesulfonyloxycyclohex-1-ene (**19**) (725 mg, 1.75 mmol) was treated with methyl acrylate (**3a**) (500 mg, 5.81 mmol) in the presence of $PdCl_2(PPh_3)_2$ (38 mg, 54 μmol) and NEt_3 (921 mg, 9.10 mmol) in DMF (10 ml) for 8 d at 75°C according to GP 1. After CC on silica gel (30 g, petroleum ether/EtOAc, 10:1), 225 mg (64%) of **22a** as a yellow oil (fraction 1) and 100 mg (23%) of **5aa** as colorless crystals (fraction 2) were obtained. Analytical data of **5aa** were identical with those reported in ref.[7f]

tert-Butyl (3E)-3-{2-[(E)-2-(tert-Butoxycarbonyl)ethenyl]-1-cyclohexen-1-yl}acrylate (**5bb**) *and tert-Butyl (3E)-3-(2-Chloro-1-cyclohexen-1-yl)acrylate* (**22b**): 1-Chloro-2-nonafluorobutanesulfonyloxycyclohex-1-ene (**19**) (415 mg, 1.00 mmol) was treated with *tert*-butyl acrylate (**3b**) (320 mg, 2.50 mmol) in the presence of $Pd(OAc)_2$ (9 mg, 40 μmol), PPh_3 (52 mg, 0.20 mmol), and NEt_3 (202 mg, 2.00 mmol) in DMF (10 ml) for 20 h at 70°C according to GP 1. After CC on silica gel (30 g, petroleum ether/EtOAc, 25:1), 90 mg (22%) of starting material **19** (fraction 1), 70 mg (29%) of **22b** as a colorless oil (fraction 2), and 70 mg (21%) of **5bb** as colorless crystals (fraction 3) were obtained. Analytical data of **5bb** were identical with those reported in ref.[7f] − **22b**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.46 [s, 9 H, $C(CH_3)_3$], 1.49−1.65 [m, 4 H, 4′(5′)-H], 1.95−2.04 (m, 2 H, 3′-H), 2.28−2.36 (m, 2 H, 6′-H), 5.76 (d, *J* = 15.9 Hz, 1 H, 2-H), 7.49 (d, *J* = 15.9 Hz, 1 H, 3-H).

General Procedure (GP 4) for the Wittig-Horner-Emmons Olefinations of 2-Bromocyclohexene-1-carbaldehyde (**24**): The diethyl phosphonate (12 mmol) in THF (10 ml) was added to a suspension of NaH (11 mmol) in THF (10 ml) at 0°C, the mixture warmed up to room temp., and stirred for 45 min. After having cooled the mixture down to 0°C again, a solution of **24** (10 mmol) in THF (10 ml) was added slowly. After stirring at room temp. for 12 h, the reaction mixture was diluted with Et_2O (100 ml), and extracted with H_2O (2 × 100 ml), dried ($MgSO_4$), and the solvents were evaporated. The crude product was chromatographed on silica gel.

Methyl (3E)-3-(2-Bromo-1-cyclohexen-1-yl)acrylate (**25a**): Diethyl methoxycarbonylmethylphosphonate (12.6 g, 60.0 mmol) in THF (20 ml) was treated with NaH (1.76 g, 58.0 mmol, 80% sus-

pension in mineral oil) in THF (20 ml) and **24** (10.0 g, 52.9 mmol) according to GP 4. Without further purification 12.0 g (93%) of pure **25a** was obtained. − IR (film): ν = 2945 cm^{-1}, 1715, 1640, 1450, 1315, 1270, 1180, 1100, 1090, 980, 865, 770, 715, 685. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.73 [m_c, 4 H, 4′(5′)-H], 2.36 (m_c, 2 H, 6′-H), 2.70 (m_c, 2 H, 3′-H), 3.74 (s, 3 H, CH_3), 5.90 (d, *J* = 15.9 Hz, 1 H, 2-H), 7.85 (d, *J* = 15.9 Hz, 1 H, 3-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.83 (−, C-5′), 24.31 (−, C-4′), 27.19 (−, C-6′), 38.16 (−, C-3′), 51.39 (+, CH_3), 118.89 (+, C-2), 131.22 (C_{quat}, C-2′), 132.68 (C_{quat}, C-1′), 144.28 (+, C-3), 167.07 (C_{quat}, C-1). − MS; *m/z* (%): 246/244 (39/37) [M^+], 215/213 (17/16) [$M^+ - OCH_3$], 165 (100) [$M^+ - Br$], 133 (22), 105 (39). − $C_{10}H_{13}BrO_2$ (245.1): calcd. 244.0099 (correct HR-MS).

1-Bromo-2-styrylcyclohex-1-ene (**25e**): Diethyl benzylphosphonate (4.6 g, 20 mmol) in THF (10 ml) was treated with NaH (0.59 g, 19 mmol, 80% suspension in mineral oil) in THF (10 ml) and **24** (3.3 g, 17.5 mmol) according to GP 4. CC on silica gel (50 g, hexane/dichloromethane, 20:1) yielded 3.68 g (80%) of **25e** as a mixture of diastereomers (*E*/*Z* = 20:1). − IR (film): ν = 3020 cm^{-1}, 2940, 1680, 1620, 1600, 1495, 1450, 1340, 960, 810, 750, 690. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.77 [m_c, 4 H, 4(5)-H], 2.42 (m_c, 2 H, 3-H), 2.69 (m_c, 2 H, 6-H), 6.58 (d, *J* = 16.5 Hz, 1 H, 2′-H), 7.17−7.48 (m_c, 6 H, aromatic H, 1′-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.20 (−, C-4), 24.69 (−, C-5), 27.46 (−, C-3), 38.81 (−, C-6), 125.91 (C_{quat}, C-2), 126.59 (+, C-2′), 127.58 (+, aromatic C), 128.62 (+, aromatic C), 129.00 (+, aromatic C), 129.37 (+, C-1′), 132.06 (C_{quat}, C-1), 137.51 (C_{quat}, aromatic C).

3-(2-Bromo-1-cyclohexen-1-yl)acrylonitrile [(*E*/*Z*)-**25l**]: Diethyl cyanomethylphosphonate (10.0 g, 56.5 mmol) in THF (20 ml) was treated with NaH (1.60 g, 52.0 mmol, 80% suspension in mineral oil) in THF (30 ml) and **24** (8.90 g, 47.1 mmol) according to GP 4. **25l** was formed as a mixture of the (*E*) and (*Z*) diastereomer in a ratio of 2:1. CC on silica gel (50 g, petroleum ether/Et_2O, 15:1) yielded 6.3 g (63%) of (*E*)-**25l** (R_f = 0.10) and 3.1 g (31%) of (*Z*)-**25l** (R_f = 0.23). − (*E*)-**25l**: ^1H NMR (250 MHz, $CDCl_3$): δ = 1.71 [m_c, 4 H, 4′(5′)-H], 2.17 (m_c, 2 H, 6′-H), 2.69 (m_c, 2 H, 3′-H), 5.46 (d, *J* = 16.5 Hz, 1 H, 2-H), 7.49 (d, *J* = 16.5 Hz, 1 H, 3-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.33 (−, C-5′), 23.90 (−, C-4′), 27.22 (−, C-6′), 37.92 (−, C-3′), 96.44 (+, C-2), 118.25 (C_{quat}, CN), 130.64 (C_{quat}, C-2′), 134.00 (C_{quat}, C-1′), 149.97 (+, C-3). − MS; *m/z* (%): 213/211 (24/22) [M^+], 132 (100) [$M^+ - Br$], 117 (32), 105 (23), 104 (25), 91 (9), 77 (22), 51 (17). − $C_9H_{10}BrN$ (212.1): calcd. 210.9997 (correct HR-MS). − (*Z*)-**25l**: ^1H NMR (250 MHz, $CDCl_3$): δ = 1.69 [m_c, 4 H, 4′(5′)-H], 2.66 [m_c, 4 H, 3′(6′)-H], 5.23 (d, *J* = 12.2 Hz, 1 H, 2-H), 7.19 (d, *J* = 12.2 Hz, 1 H, 3-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.64 (−, C-5′), 23.77 (−, C-4′), 28.18 (−, C-6′), 37.86 (−, C-3′), 95.09 (+, C-2), 117.08 (C_{quat}, CN), 131.70 (C_{quat}, C-2′), 133.57 (C_{quat}, C-1′), 148.24 (+, C-3).

Ethyl (3E)-3-(2-Bromo-1-cyclohexen-1-yl)acrylate (**25m**): Diethyl ethoxycarbonylmethylphosphonate (1.32 g, 5.9 mmol) in THF (5 ml) was treated with NaH (176 mg, 5.80 mmol, 80% suspension in mineral oil) in THF (5 ml) and **24** (1.00 g, 5.29 mmol) according to GP 4. Filtration through silica gel (10 g, petroleum ether/ethyl acetate, 5:1) yielded 1.20 g (88%) of **25m**. − IR (film): ν = 2938 cm^{-1}, 1714, 1622, 1448, 1366, 1291, 1176, 1095, 1070, 1036, 979, 860, 810, 736, 653. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.31 (t, *J* = 7.5 Hz, 3 H, CH_3), 1.75 [m_c, 4 H, 4′(5′)-H], 2.28 (m_c, 2 H, 6′-H), 2.69 (m_c, 2 H, 3′-H), 4.22 (q, *J* = 7.5 Hz, 2 H, OCH_2), 5.91 (d, *J* = 16.0 Hz, 1 H, 2-H), 7.87 (d, *J* = 16.0 Hz, 1 H, 3-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.29 (+, CH_3), 21.83 (−, C-5′), 24.30 (−, C-4′), 27.22 (−, C-6′), 38.07 (−, C-3′), 60.41 (−, OCH_2), 118.89 (+, C-2), 131.22 (C_{quat}, C-2′), 132.68 (C_{quat}, C-1′), 144.28 (+, C-3), 167.07 (C_{quat}, C-1). − MS; *m/z* (%): 260/258 (60/62) [M^+], 215/213 (22/21) [$M^+ - OC_2H_5$], 179 (100) [$M^+ - Br$], 133 (32), 105 (51). − $C_{11}H_{15}BrO_2$ (259.1): calcd. 258.0256 (correct HR-MS).

General Procedure for the Heck Coupling of Bromobutadienes **25** *with Alkenes (GP 5):* In a Pyrex bottle were placed the bromobutadiene (10.0 mmol), NEt_3 (2.80 ml, 20.0 mmol), the alkene (25.0 mmol), and DMF (20 ml) and the mixture was purged for 3 min with nitrogen. $Pd(OAc)_2$ (90 mg, 0.4 mmol) and PPh_3 (262 mg, 1.0 mmol) were added and the reaction mixture was stirred at 20°C for 10 min, then heated to 50°C (30 min) and then for the stated time to 60−80°C. When the reaction mixture had been cooled down to room temp., it was poured into Et_2O (200 ml) and the solution extracted with H_2O (5 × 80 ml). The combined aqueous layers were extracted back once with Et_2O (100 ml). The combined organic layers were dried with $MgSO_4$, concentrated in vacuo, and the residue was purified by CC on silica gel and/or recrystallization.

Methyl (3E)-3-{2-[(E)-2-(Methoxycarbonyl)ethenyl]-1-cyclohexen-1-yl}acrylate (**5aa**): Methyl (3*E*)-3-(2-bromo-1-cyclohexen-1-yl)acrylate (**25a**) (4.00 g, 16.3 mmol) was treated with methyl acrylate (**3a**) (4.0 ml, 44 mmol) at 80°C for 20 h according to GP 5. After filtration through silica gel (10 g, petroleum ether/ethyl acetate, 4:1) and recrystallization from acetone, 3.47 g (85%) of **5aa** was obtained as colorless crystals. Spectroscopic data were identical with those reported in ref.[7f]

Methyl (3E)-3-[2-(E)-Styryl-1-cyclohexen-1-yl]acrylate (**5ae**): Methyl (3*E*)-3-(2-bromo-1-cyclohexen-1-yl)acrylate (**25a**) (2.00 g, 8.2 mmol) was treated with styrene (**3e**) (2.0 ml, 17 mmol) for 5 d at 60°C according to GP 5. After CC on silica gel (50 g, petroleum ether/Et_2O, 20:1), 1.62 g (74%) of **5ae** was obtained as yellow crystals, m. p. 71°C. − IR (KBr): ν = 3030 cm^{-1}, 2930, 1715, 1605, 1435, 1305, 1275, 1250, 1195, 1175, 1155, 1075, 1040, 1015, 970, 865, 845, 750, 695, 650. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.70 [m_c, 4 H, 4′(5′)-H], 2.31 (m_c, 2 H, 3′-H), 2.48 (m_c, 2 H, 6′-H), 3.79 (s, 3 H, OCH_3), 5.92 (d, *J* = 15.5 Hz, 1 H, 2-H), 6.71 (d, *J* = 16.0 Hz, 1 H, 2′′-H), 7.20−7.51 (m, 5 H, aromatic H), 7.57 (d, *J* = 16.0 Hz, 1 H, 1′′-H), 8.23 (d, *J* = 15.5 Hz, 1 H, 3-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.97 (−, C-4′), 22.02 (−, C-5′), 26.17 (−, C-3′), 26.86 (−, C-6′), 51.27 (+, OCH_3), 115.66 (+, C-2), 125.06 (+, C-2′′), 126.58 (+, aromatic C), 127.68 (+, aromatic C), 128.47 (+, aromatic C), 129.80 (+, C-1′′), 131.44 (C_{quat}, C-2′), 137.21 (C_{quat}, C-1′), 140.62 (C_{quat}, aromatic C), 141.08 (+, C-3), 167.96 (C_{quat}, C-1). − MS; *m/z* (%): 268 (2) [M^+], 209 (4) [$M^+ - CO_2CH_3$], 165 (100) [$M^+ - C_8H_7$], 105 (22), 91 (17) [$C_7H_7^+$], 77 (20) [$C_6H_5^+$]. − $C_{18}H_{20}O_2$ (268.4): calcd. 268.1463 (correct HR-MS).

Methyl (3E)-3-{2-[2-(E)-Trimethylsilylethenyl]-1-cyclohexen-1-yl}acrylate (**5af**) *and Methyl (3E)-3-(2-Ethenyl-1-cyclohexen-1-yl)-acrylate* (**5an**): Methyl (3*E*)-3-(2-bromo-1-cyclohexen-1-yl)acrylate (**25a**) (1.00 g, 4.08 mmol) was treated with trimethylethenylsilane (**3f**) (1.0 ml, 6.9 mmol) for 12 h at 70°C according to GP 5. After CC on silica gel (80 g, petroleum ether/ethyl acetate, 10:1), 150 mg (14%) of **5af** was obtained as colorless crystals (R_f = 0.47), m. p. 63°C, and 550 mg (70%) of **5an** as a colorless oil (R_f = 0.40). − **5af**: IR (KBr): ν = 2920 cm^{-1}, 1705, 1600, 1425, 1295, 1270, 1240, 1185, 1145, 1065, 1010, 975, 835, 750, 735, 690. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.12 [s, 9 H, $Si(CH_3)_3$], 1.69 [m_c, 4 H, 4′(5′)-H], 2.28 (m_c, 2 H, 6′-H), 2.33 (m_c, 2 H, 3′-H), 3.77 (s, 3 H, OCH_3), 5.89 (d, *J* = 15.6 Hz, 1 H, 2-H), 6.08 (d, *J* = 18.8 Hz, 1 H, 2′′-H), 7.30 (d, *J* = 18.8 Hz, 1 H, 1′′-H), 8.14 (d, *J* = 15.6 Hz, 1 H, 3-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = −1.2 [+, $Si(CH_3)_3$], 22.2 [−, C-4′(5′)], 26.2 (−, C-6′), 26.8 (−, C-3′), 51.5 (+, OCH_3), 115.9

(+, C-2), 131.3 (C_{quat}, C-2′), 132.1 (+, C-2′′), 139.8 (+, C-1′′), 141.6 (+, C-3), 141.9 (C_{quat}, C-1′), 168.2 (C_{quat}, C-1). − MS; *m/z* (%): 264 (2) [M^+], 205 (7) [$M^+ - CO_2CH_3$], 160 (18) [$M^+ - Si(CH_3)_3 - OCH_3$], 73 (100) [$Si(CH_3)_3^+$], 59 (18) [$CO_2CH_3^+$]. − $C_{15}H_{24}O_2Si$ (264.4): calcd. 264.1545 (correct HR-MS). − **5an**: IR (film): ν = 2920 cm^{-1}, 1710, 1610, 1430, 1295, 1250, 1160, 1060, 1040, 1010, 965, 850, 750, 725. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.66 [m_c, 4 H, 4′(5′)-H], 2.28 (m_c, 2 H, 6′-H), 2.33 (m_c, 2 H, 3′-H), 3.75 (s, 3 H, OCH_3), 5.22 (d, *J* = 11.1 Hz, 1 H, 2′′-H), 5.37 (d, *J* = 17.1 Hz, 1 H, 2′′-H), 5.88 (d, *J* = 15.6 Hz, 1 H, 2-H), 7.14 (dd, *J* = 11.1, *J* = 17.1 Hz, 1 H, 1′′-H), 8.07 (d, *J* = 15.6 Hz, 1 H, 3-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.05 (−, C-4′), 22.15 (−, C-5′), 26.02 (−, C-6′), 26.37 (−, C-3′), 51.49 (+, OCH_3), 115.31 (−, C-2′′), 115.89 (+, C-2), 131.07 (C_{quat}, C-2′), 133.37 (+, C-1′′), 140.95 (C_{quat}, C-1′), 141.45 (+, C-3), 168.11 (C_{quat}, C-1). − MS; *m/z* (%): 192 (42) [M^+], 165 (98) [$M^+ - CH{=}CH_2$], 135 (100). − $C_{12}H_{16}O_2$ (192.3): calcd. 192.1150 (correct HR-MS).

Methyl (3E)-3-{2-[(E)-2-Cyanoethenyl]-1-cyclohexen-1-yl}acrylate (**5al**): (3*E*)-3-(2-Bromo-1-cyclohexen-1-yl)acrylonitrile [(*E*)-**25l**] (1.0 g, 4.7 mmol) was treated with methyl acrylate (**3a**) (1.50 ml, 16.6 mmol) for 12 h at 80°C according to GP 5. After filtration through silica gel (10 g, petroleum ether/Et_2O/ethyl acetate, 10:1:1) and recrystallization from EtOH, 820 mg (80%) of **5al** was obtained as yellow crystals, m. p. 68°C. − IR (KBr): ν = 2910 cm^{-1}, 2200, 1705, 1610, 1580, 1445, 1420, 1295, 1270, 1190, 1170, 1155, 1010, 955, 945, 860, 830, 805, 720, 710, 635. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.69 [m_c, 4 H, 4′(5′)-H], 2.38 (m_c, 2 H, 3′-H), 2.40 (m_c, 2 H, 6′-H), 3.78 (s, 3 H, OCH_3), 5.42 (d, *J* = 16.2 Hz, 1 H, 2′′-H), 6.01 (d, *J* = 15.6 Hz, 1 H, 2-H), 7.80 (d, *J* = 16.2 Hz, 1 H, 1′′-H), 7.89 (d, *J* = 15.6 Hz, 1 H, 3-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.45 (−, C-4′), 21.52 (−, C-5′), 25.65 (−, C-3′), 26.60 (−, C-6′), 51.76 (+, OCH_3), 96.65 (+, C-2′′), 118.53 (C_{quat}, CN), 119.82 (+, C-2), 136.66 (C_{quat}, C-2′), 139.03 (C_{quat}, C-1′), 139.10 (+, C-3), 145.85 (+, C-1′′), 167.13 (C_{quat}, C-1). − MS; *m/z* (%): 217 (27) [M^+], 202 (5) [$M^+ - CH_3$], 158 (100) [$M^+ - CO_2CH_3$], 129 (75), 116 (90), 77 (75). − $C_{13}H_{15}NO_2$ (217.3): calcd. C 71.87, H 6.96, N 6.45; found C 71.87, H 6.96, N 6.52.

Methyl (3E)-3-{2-[(E)-2-Cyanoethenyl]-1-cyclohexen-1-yl}acrylate (**5al**): (3*Z*)-3-(2-Bromo-1-cyclohexen-1-yl)acrylonitrile [(*Z*)-**25l**] (1.0 g, 4.7 mmol) was treated with methyl acrylate (**3a**) (1.50 ml, 16.6 mmol) for 36 h at 80°C according to GP 5. After CC on silica gel (50 g, petroleum ether/Et_2O/ethyl acetate, 10:1:1) and recrystallization from EtOH, 650 mg (63%) of **5al** was obtained as yellow crystals.

(3E)-3-[2-(E)-Styryl-1-cyclohexen-1-yl]acrylonitrile (**5el**): (3*E*)-3-(2-Bromo-1-cyclohexen-1-yl)acrylonitrile [(*E*)-**25l**] (1.0 g, 4.7 mmol) was treated with styrene (**3e**) (1.50 ml, 13.0 mmol) for 20 h at 80°C according to GP 5. After filtration through silica gel (10 g, petroleum ether/Et_2O, 10:1) and recrystallization from EtOH, 820 mg (74%) of **5el** was obtained as yellow crystals, m. p. 109°C. − IR (KBr): ν = 3040 cm^{-1}, 2920, 2205, 1585, 1485, 1445, 1360, 1295, 1275, 1245, 1160, 965, 820, 800, 750, 690. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.69 [m_c, 4 H, 4′(5′)-H], 2.21 (m_c, 2 H, 3′-H), 2.49 (m_c, 2 H, 6′-H), 5.31 (d, *J* = 16.2 Hz, 1 H, 2-H), 6.75 (d, *J* = 15.9 Hz, 1 H, 2′′-H), 7.21−7.50 (m_c, 6 H, aromatic H, 1′′-H), 7.88 (d, *J* = 16.2 Hz, 1 H, 3-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.80 (−, C-4′), 21.93 (−, C-5′), 25.41 (−, C-3′), 26.88 (−, C-6′), 93.59 (+, C-2), 119.47 (C_{quat}, CN), 124.40 (+, C-2′′), 126.74 (+, aromatic C), 128.20 (+, aromatic C), 128.71 (+, aromatic C), 130.69 (C_{quat}, C-2′), 131.29 (+, C-1′′), 136.90 (C_{quat}, C-1′), 141.78 (C_{quat}, aromatic C), 146.80 (+, C-3). − MS; *m/z* (%): 235 (100) [M^+], 206 (28), 193 (26), 167 (22), 144 (18), 91 (87) [$C_7H_7^+$], 77 (21) [$C_6H_5^+$]. − $C_{17}H_{17}N$ (235.3): calcd. C 86.77, H 7.28, N 5.95; found C 86.63, H 7.37, N 5.96.

(3E)-3-[2-(E)-Styryl-1-cyclohexen-1-yl]acrylonitrile (**5el**): (3*Z*)-3-(2-Bromo-1-cyclohexen-1-yl)acrylonitrile [(*Z*)-**25l**] (1.0 g, 4.7 mmol) was treated with styrene (**3e**) (1.50 ml, 13.0 mmol) for 45 h at 80°C according to GP 5. After CC on silica gel (50 g, petroleum ether/Et_2O, 10:1) and recrystallization from EtOH, 690 mg (62%) of **5el** was obtained as yellow crystals.

(3E)-3-{2-[(E)-2-Trimethylsilylethenyl]-1-cyclohexen-1-yl}acrylonitrile (**5fl**) *and (3E)-3-(2-Ethenyl-1-cyclohexen-1-yl)acrylonitrile* (**5ln**): (3*E*)-3-(2-Bromo-1-cyclohexen-1-yl)acrylonitrile [(*E*)-**25l**] (1.0 g, 4.7 mmol) was treated with trimethylethenylsilane (**3f**) (1.0 ml, 6.9 mmol) for 12 h at 80°C according to GP 5. After CC on silica gel (80 g, petroleum ether), 116 mg (11%) of **5fl** was obtained as colorless crystals (R_f = 0.2), m. p. 48°C, and 480 mg (64%) of **5ln** as colorless crystals (R_f = 0.08), m. p. 36°C. − **5fl**: IR (KBr): ν = 2920 cm^{-1}, 2200, 1582, 1280, 1150, 970, 865, 850, 830. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.08 [s, 9 H, $Si(CH_3)_3$], 1.65 [m_c, 4 H, 4′(5′)-H], 2.20 (m_c, 2 H, 3′-H), 2.36 (m_c, 2 H, 6′-H), 5.26 (d, *J* = 16.2 Hz, 1 H, 2-H), 6.12 (d, *J* = 18.8 Hz, 1 H, 2′′-H), 7.10 (d, *J* = 18.8 Hz, 1 H, 1′′-H), 7.79 (d, *J* = 16.2 Hz, 1 H, 3-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = −1.31 [+, $Si(CH_3)_3$], 21.85 (−, C-5′), 21.95 (−, C-4′), 25.30 (−, C-3′), 26.80 (−, C-6′), 93.78 (+, C-2), 119.44 (C_{quat}, CN), 130.36 (C_{quat}, C-1′), 133.95 (+, C-2′′), 138.87 (+, C-1′′), 142.86 (C_{quat}, C-2′), 147.02 (+, C-3). − MS; *m/z* (%): 231 (27) [M^+], 214 (19), 203 (8), 159 (66), 132 (77) [$M^+ - Si(CH_3)_3 - CN$], 117 (93) [$M^+ - Si(CH_3)_3 - CH_3CN$], 104 (63), 91 (45), 73 (100) [$Si(CH_3)_3^+$]. − $C_{14}H_{21}NSi$ (231.4): calcd. 231.1443 (correct HR-MS). − **5ln**: IR (KBr): ν = 3080 cm^{-1}, 3060, 3025, 3005, 2920, 2850, 2820, 2200, 1570, 1440, 1425, 1345, 1275, 1245, 1155, 1130, 1015, 970, 945, 910, 830, 795, 725. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.68 [m_c, 4 H, 4′(5′)-H], 2.19 (m_c, 2 H, 3′-H), 2.36 (m_c, 2 H, 6′-H), 5.30 (d, *J* = 11.2 Hz, 1 H, 2′′-H), 5.31 (d, *J* = 16.3 Hz, 1 H, 2-H), 5.42 (d, *J* = 17.1 Hz, 1 H, 2′′-H), 6.93 (dd, *J* = 17.1, *J* = 11.2 Hz, 1 H, 1′′-H), 7.73 (d, *J* = 16.3 Hz, 1 H, 3-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.73 (−, C-4′), 21.75 (−, C-5′), 25.07 (−, C-3′), 26.44 (−, C-6′), 93.83 (+, C-2), 116.88 (−, C-2′′), 119.22 (C_{quat}, CN), 130.24 (C_{quat}, C-1′), 132.64 (+, C-1′′), 140.00 (C_{quat}, C-2′), 146.98 (+, C-3). − MS; *m/z* (%): 159 (93) [M^+], 144 (29), 131 (50), 130 (52), 119 (48), 104 (37), 91 (100), 80 (32), 79 (39), 78 (27), 77 (37), 65 (22), 41 (24). − $C_{11}H_{13}N$ (159.2): calcd. 159.1048 (correct HR-MS).

Ethyl (3E)-3-{2-[(E)-2-(Methoxycarbonyl)ethenyl]-1-cyclohexen-1-yl}acrylate (**5am**): Ethyl (3*E*)-3-(2-bromo-1-cyclohexen-1-yl)-acrylate (**25m**) (2.00 g, 7.72 mmol) was treated with methyl acrylate (**3a**) (2.0 ml, 22.2 mmol) for 20 h at 80°C according to GP 5. After filtration through silica gel (10 g, petroleum ether/ethyl acetate, 4:1) and recrystallization from EtOH, 1.85 g (91%) of **5am** was obtained as colorless crystals, m. p. 79°C. − IR (KBr): ν = 2946 cm^{-1}, 1718, 1612, 1427, 1365, 1312, 1274, 1171, 1034, 976, 846, 749, 715, 685, 618, 515. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.31 (t, *J* = 7.5 Hz, 3 H, CH_3), 1.69 [m_c, 4 H, 4′(5′)-H], 2.35 [m_c, 4 H, 3′(6′)-H], 3.79 (s, 3 H, OCH_3), 4.23 (q, *J* = 7.5 Hz, 2 H, OCH_2), 6.00 [d, *J* = 16.0 Hz, 2 H, 2(2′′)-H], 8.07 [d, *J* = 16.0 Hz, 2 H, 3(3′′)-H]. − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.31 (+, CH_2CH_3), 21.82 [−, C-4′(5′)], 26.63 (−, C-3′), 26.69 (−, C-6′), 51.68 (+, OCH_3), 60.51 (−, OCH_2), 118.59 (+, C-2), 119.14 (+, C-2′′), 137.90 (C_{quat}, C-1′), 138.14 (C_{quat}, C-2′), 139.91 (+, C-3), 140.18 (+, C-1′′), 167.15 (C_{quat}, C-1), 167.55 (C_{quat}, C-3′′). − MS; *m/z* (%): 264 (54) [M^+], 205 (25) [$M^+ - CO_2CH_3$], 131 (100) [$M^+ - CO_2C_2H_5 - CO_2CH_4$]. − $C_{15}H_{20}O_4$ (264.3): calcd. C 68.16, H 7.63; found C 68.22, H 7.53.

General Procedure for the 6π-Electrocyclizations of (E,Z,E)-1,3,5-Hexatrienes under Thermal Conditions (GP 6): A solution of the (*E,Z,E*)-1,3,5-hexatriene **4** or **5** (1 mmol) in deoxygenated xylene or di-*n*-butyl ether (nBu$_2$O) (100 ml) was stirred at the specified temperature. Removal of the solvent in vacuo gave the crude product, which was further purified.

Dimethyl 5,6-Dihydroindane-cis-5,6-dicarboxylate (**26aa**): Methyl (3*E*)-3-{2-[(*E*)-2-(methoxycarbonyl)ethenyl]-1-cyclopenten-1-yl}-acrylate (**4aa**) (190 mg, 0.804 mmol) was heated in nBu$_2$O (100 ml) for 7 h at 140°C. Removal of the solvent in vacuo yielded 179 mg (94%) of **26aa** as a colorless oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.67 (m_c, 2 H, 2-H), 2.28 [m_c, 4 H, 1(3)-H], 3.57 [m_c, 2 H, 5(6)-H], 3.62 (s, 6 H, OCH_3), 5.68 [m, 2 H, 4(7)-H]. – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 24.83 (–, C-2), 30.84 [–, C-1(3)], 42.15 [+, C-5(6)], 51.88 (+, OCH_3), 112.93 [+, C-4(7)], 141.63 [C_{quat}, C-8(9)], 172.44 (C_{quat}, CO_2).

Dimethyl 2,3,5,6,7,8-Hexahydronaphthalene-cis-2,3-dicarboxylate (**27aa**): Methyl (3*E*)-3-{2-[(*E*)-2-(methoxycarbonyl)ethenyl]-1-cyclohexen-1-yl}acrylate (**5aa**) (200 mg, 0.800 mmol) was heated in xylene at 140°C for 5 h according to GP 6. Purification of the crude product by CC on silica gel (30 g, pentane/ethyl acetate, 5:1) yielded 177 mg (89%) of **27aa** as a colorless oil. The solvent and the silica gel were degassed with nitrogen prior to use. – IR (film): ν = 3005 cm^{-1}, 2930, 2845, 1715, 1605, 1555, 1425, 1280, 1200, 1155, 1125, 1040, 965, 920, 815, 775, 755, 660. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.55 [m_c, 4 H, 6(7)-H], 2.28 [m_c, 4 H, 5(8)-H], 3.50 [m_c, 2 H, 2(3)-H], 3.64 (s, 6 H, OCH_3), 5.74 [m_c, 2 H, 1(4)-H]. – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 24.27 [–, C-6(7)], 30.81 [–, C-5(8)], 41.06 [+, C-2(3)], 51.78 (+, OCH_3), 117.18 [+, C-1(4)], 136.21 [C_{quat}, C-9(10)], 172.10 (C_{quat}, CO_2). – $C_{14}H_{18}O_4$ (250.3): calcd. C 67.18, H 7.25; found C 67.54, H 7.27.

cis-[3-(Methoxycarbonyl)-2,3,5,6,7,8-hexahydronaphthalene]-2-carbonitrile (**27al**): Methyl (3*E*)-3-{2-[(*E*)-2-(cyano)ethenyl]-1-cyclohexen-1-yl}acrylate (**5al**) (200 mg, 0.920 mmol) was heated in xylene at 140°C for 20 h according to GP 6. The crude product (148 mg, 74%) was a colorless oil, which gave a single spot on TLC but contained 20% of isomerized material according to the NMR spectra. – IR (film): ν = 2920 cm^{-1}, 2840, 2210, 1730, 1585, 1425, 1275, 1195, 1170, 1020, 975, 905, 820, 775, 695. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.40–1.82 [m, 4 H, 6(7)-H], 2.20–2.55 [m, 4 H, 5(8)-H], 3.38 (m_c, 1 H, 2-H), 3.57 (t, *J* = 6.5 Hz, 1 H, 3-H), 3.81 (s, 3 H, OCH_3), 5.55 (bd, *J* = 5.6 Hz, 1 H, 1-H), 5.83 (br. s, 1 H, 4-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 23.93 (–, C-6), 24.07 (–, C-7), 26.90 (+, C-2), 30.75 (–, C-5), 30.77 (–, C-8), 42.18 (+, C-3), 52.42 (+, OCH_3), 113.10 (+, C-1), 116.67 (+, C-4), 118.30 (C_{quat}, CN), 137.18 (C_{quat}, C-9), 140.28 (C_{quat}, C-10), 170.29 (C_{quat}, CO_2). – MS; *m/z* (%): 217 (25) [M$^+$], 190 (17), 158 (92) [M$^+$ – CO_2CH_3], 131 (48), 129 (64), 116 (100), 104 (38), 91 (57), 77 (38), 51 (17). – $C_{13}H_{15}NO_2$ (217.3): calcd. 217.1103 (correct HR-MS).

Ethyl cis-[3-(Methoxycarbonyl)-2,3,5,6,7,8-hexahydronaphthalene]-2-carboxylate (**27am**): Ethyl (3*E*)-3-{2-[(*E*)-2-(methoxycarbonyl)ethenyl]-1-cyclohexen-1-yl}acrylate (**5am**) (200 mg, 0.757 mmol) was heated in xylene at 150°C for 12 h according to GP 6. Purification of the crude product by CC on silica gel (30 g, pentane/ethyl acetate, 5:1) yielded 168 mg (84%) of **27am** as a colorless oil. The solvent and the silica gel were degassed with nitrogen prior to use. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.13 (t, *J* = 7.5 Hz, 3 H, CH_2CH_3), 1.49 [m_c, 4 H, 6(7)-H], 2.19 [m_c, 4 H, 5(8)-H], 3.40 [m_c, 2 H, 2(3)-H], 3.58 (s, 3 H, OCH_3), 4.05 (m_c, 2 H, CH_2CH_3), 5.63 [m_c, 2 H, 1(4)-H]. – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.87 (+, CH_2CH_3), 24.16 (–, C-6), 24.19 (–, C-7), 30.86 [–, C-5(8)], 40.94 (+, C-2), 41.06 (+, C-3), 51.50 (+, OCH_3), 60.34 (–, CH_2CH_3), 117.09 (+, C-1), 117.34 (+, C-4), 135.89 (C_{quat}, C-9), 136.09 (C_{quat}, C-10), 171.41 (C_{quat}, CO_2), 171.89 (C_{quat}, CO_2). – $C_{15}H_{20}O_4$ (264.3): calcd. C 68.16, H 7.63; found C 68.35, H 7.82.

Ethyl 3-(Methoxycarbonyl)-5,6,7,8-hexahydronaphthalene-2-carboxylate (**28am**): Ethyl (3*E*)-3-{2-[(*E*)-2-(methoxycarbonyl)-ethenyl]-1-cyclohexen-1-yl}acrylate (**5am**) (100 mg, 0.378 mmol) was heated in xylene at 150°C for 12 h according to GP 6. Purification of the crude product by CC on silica gel (20 g, pentane/ethyl acetate, 5:1) yielded 86 mg (86%) of **28am** as a colorless oil. The solvent and the silica gel were not degassed with nitrogen prior to use. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.37 (t, *J* = 7.5 Hz, 3 H, CH_2CH_3), 1.80 [m_c, 4 H, 6(7)-H], 2.79 [m_c, 4 H, 5(8)-H], 3.87 (s, 3 H, OCH_3), 4.32 (q, *J* = 7.5 Hz, 2 H, CH_2CH_3), 7.41 (s, 1 H, 1-H), 7.43 (s, 1 H, 4-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.08 (+, CH_2CH_3), 22.58 [–, C-6(7)], 29.18 [–, C-5(8)], 52.29 (+, OCH_3), 61.33 (–, CH_2CH_3), 128.91 (C_{quat}, C-9), 129.14 (C_{quat}, C-10), 129.66 [+, C-1(4)], 140.64 (C_{quat}, C-2), 140.68 (C_{quat}, C-3), 167.78 (C_{quat}, CO_2), 168.33 (C_{quat}, CO_2).

cis-2,3-Diphenyl-2,3,5,6,7,8-hexahydronaphthalene (**27ee**): 1,2-Di-(*E*)-styrylcyclohexene (**5ee**) (100 mg, 0.35 mmol) was heated in xylene at 140°C for 2 h. The crude product **27ee** (95 mg, 95%) was a colorless oil, which gave a single spot on TLC. – IR (film): ν = 3040 cm^{-1}, 3005, 2910, 2840, 1590, 1485, 1440, 1210, 1065, 1020, 955, 905, 660. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.71 [m_c, 4 H, 6(7)-H], 2.46 [m_c, 4 H, 5(8)-H], 3.78 [br. s, 2 H, 2(3)-H], 5.61 [m_c, 2 H, 1(4)-H], 6.72–7.04 (m, 10 H, aromatic H). – ^{13}C NMR (62.9 MHz, [D_6]acetone): δ = 25.66 [–, C-6(7)], 31.93 [–, C-5(8)], 47.66 [+, C-2(3)], 124.53 [+, C-1(4)], 126.94 (+, aromatic C), 128.26 (+, aromatic C), 130.64 (+, aromatic C), 136.88 [C_{quat}, C-9(10)], 140.91 (C_{quat}, aromatic C).

cis-(3-Phenyl-2,3,5,6,7,8-hexahydronaphthalene)-2-carbonitrile (**27el**): (3*E*)-3-[2-(*E*)-Styryl-1-cyclohexen-1-yl]acrylonitrile (**5el**) (200 mg, 0.85 mmol) was heated in xylene at 130°C for 15 h. The crude product **27el** (162 mg, 81%) was a colorless oil, which gave a single spot on TLC. – IR (film): ν = 3050 cm^{-1}, 3005, 2910, 2845, 2210, 1595, 1475, 1440, 1425, 1150, 1035, 920, 865. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.49–1.75 [m, 4 H, 6(7)-H], 2.25–2.50 [m, 4 H, 5(8)-H], 3.44 (t, *J* = 6.2 Hz, 1 H, 2-H), 3.71 (m_c, 1 H, 3-H), 5.44 (bd, *J* = 5.6 Hz, 1 H, 1-H), 5.72 (br. s, 1 H, 4-H), 7.21–7.45 (m, 5 H, aromatic H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 24.04 (–, C-6), 24.35 (–, C-7), 30.78 (–, C-5), 30.93 (–, C-8), 33.26 (+, C-3), 42.32 (+, C-2), 113.20 (+, C-4), 119.07 (C_{quat}, CN), 122.91 (+, C-1), 127.54 (+, aromatic C), 128.44 (+, aromatic C), 128.52 (+, aromatic C), 136.75 (C_{quat}, C-9), 138.62 (C_{quat}, C-10), 139.20 (C_{quat}, aromatic C). – MS; *m/z* (%): 235 (8) [M$^+$], 206 (3), 165 (4), 122 (11), 107 (15) 91 (32) [$C_7H_7^+$], 84 (100), 77 (18) [Ph$^+$], 47 (26).

cis-5,6-Diphenyl-5,6-dihydroindane (**26ee**): 1,2-Di-(*E*)-styrylcyclopentene (**4ee**) (50 mg, 0.18 mmol) was placed in a kugelrohr apparatus and heated to 180°C at 3 mbar for 8 min. The product was then distilled in the kugelrohr at 150°C/0.01 Torr to yield 25 mg (50%) of **26ee** as colorless crystals. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.90 (quint, *J* = 7.9 Hz, 2 H, 2-H), 2.50 [m_c, 4 H, 1(3)-H], 3.91 [m_c, 2 H, 5(6)-H], 5.60 [m_c, 2 H, 4(7)-H], 6.75–7.10 (m, 10 H, aromatic H).

☆ Dedicated to Professor *Mordecai Rabinovitz* on the occasion of his 65th birthday.

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