Studies on the Synthesis of Macrocyclic Allenes by Ring Closing Metathesis and Doering–Moore–Skattebøl Reaction

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Several efficient synthetic approaches to allenic cyclophanes of the general structure **2/3**, which are of interest as chiral ligands or host molecules, are described. The combination of the ruthenium-catalyzed ring-closing metathesis and the Doering–Moore–Skattebøl (DMS) reaction using the Seyferth reagent $PhHgCBr_3$ provided a straightforward access to the allenic cyclophane **8**. The macrocycles **13** and **17** with the allenic bridge between the aromatic units were also obtained efficiently by copper-promoted S_N2'-substitution of propargylic acetates and ring-closing metathesis. Alternatively, macrocyclic allenes can be synthesized by ring-closing metathesis of α,ω-bisallenes, as was demonstrated by the formation of the products **20**, **21**, and **23**.

Introduction

Due to their unique steric and electronic properties and high reactivity, allenes have emerged has highly interesting target molecules in organic synthesis.[1] Among the different structural types, cyclic allenes have been studied mainly in terms of their physical properties[2] and their participation in biological systems, e.g., the neocarzinostatin chromophore.[3] In contrast, the use of (macro)cyclic allenes as chiral ligand or host molecule has found only limited interest so far.[4,5] Recently, we have reported the synthesis of the first macrocyclic allene incorporating alternating aromatic rings and allenic bridges (allenophane **1**)[5] which represents a novel, highly promising type of ligand for transition metal chemistry. However, due to the rather long linear sequence of addition and substitution steps used, it is not suitable for the generation of larger amounts of the allenophane. We now report the results of a study on shorter, more efficient routes to allenic cyclophanes of the general structure **2/3** (Figure 1), taking advantage of the ruthenium-catalyzed ring closing metathesis (RCM) with Grubbs catalyst[6] and the Doering–Moore–Skattebøl (DMS) reaction (the addition of a dihalocarbene to an alkene, followed by base-mediated allene formation).[7]

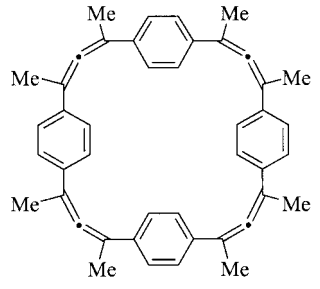

Figure 1. Allenophane **1** and macrocyclic allenes **2/3**.

Results and Discussion

The first route towards the target molecules **2/3** starts out from (*Z*)-4,4′-dibromostilbene (**4**) which was subjected to a nickel-catalyzed Kumada cross coupling with 8-bromomagnesiumoct-1-ene to furnish the desired hydrocarbon **5** with excellent yield (Scheme 1). Ring closing metathesis with the Grubbs-I catalyst under high dilution conditions also proceeded with high efficiency to give a 3:2 mixture of the cyclophanes **6** and **7**.[8] The configuration of the newly formed double bond of these symmetrical molecules was determined by measurement of the vicinal $^3J_{HH}$ coupling constant using long-range $^1H,^{13}C$ correlation with inverse

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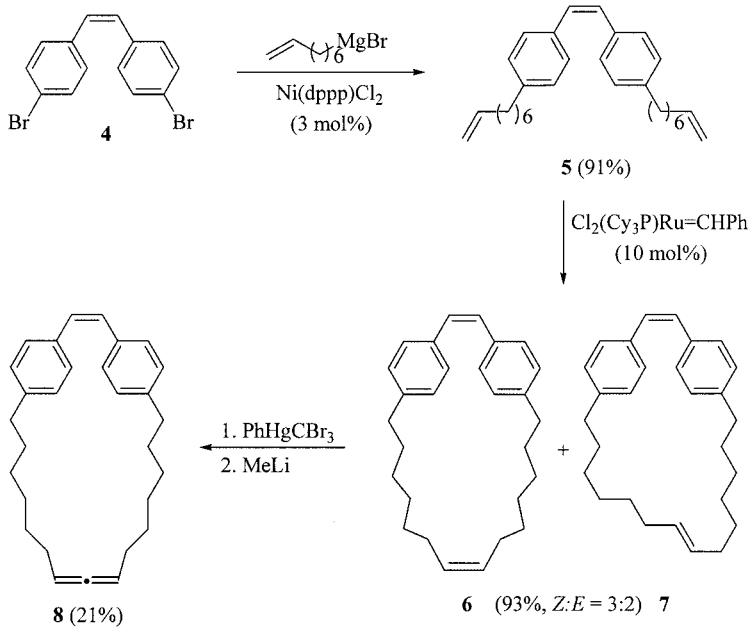
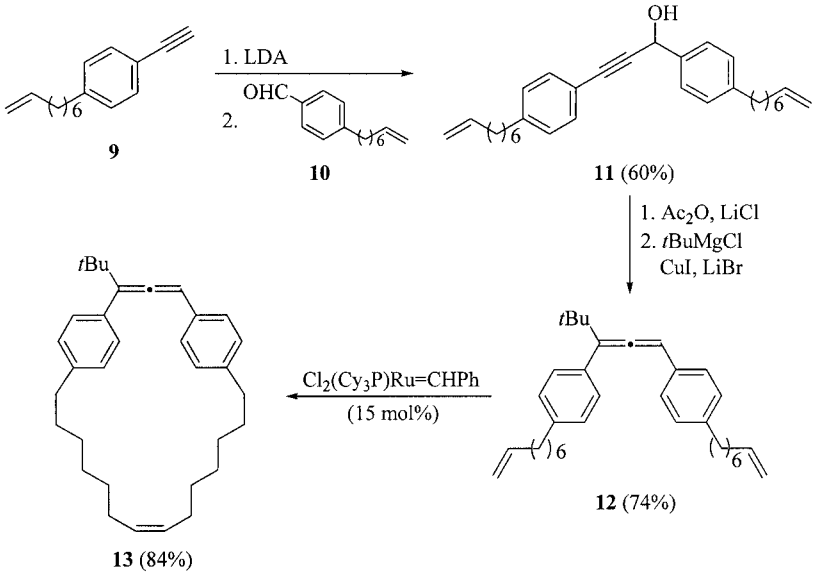


Scheme 1. Synthesis of macrocyclic allene **8**.

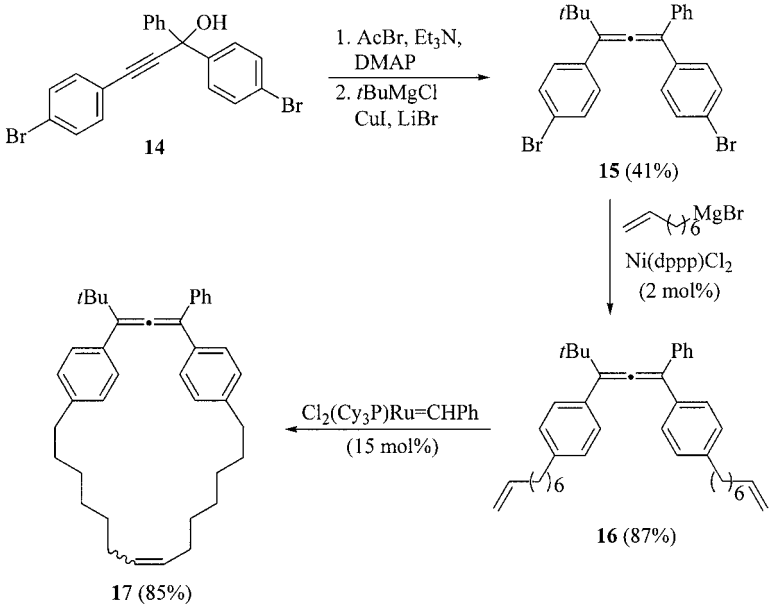
detection,[9] which gave values of 11 Hz and 17 Hz for **6** and **7**, respectively.

Since the reactivity of the bisolefins **6/7** under the usual cyclopropanation conditions (bromoform or chloroform, aqueous NaOH, phase-transfer catalyst[7]) was very low, we treated the mixture with the Seyferth reagent $PhHgCBr_3$[10] and obtained the desired dibromocyclopropanes as a 3:2 *cis*/*trans* mixture which was converted into the 25-membered allene **8**[11] by treatment with methyllithium. Remarkably, a completely regioselective cyclopropanation of the "aliphatic" C–C double bond of the bisolefins **6/7** was observed. Regioselective dihalocyclopropanations of unsymmetrical, non-conjugated bisolefins have been reported occasionally in the literature[12] and were explained in terms of the electronic properties and steric accessibility of the different C–C double bonds. It seems reasonable to assume that the "aliphatic" C–C double bond of **6/7** is more electron-rich and sterically less hindered, compared to the "aromatic" double bond, and both factors favor the attack of the dibromocarbene at this position.

In order to synthesize macrocycles of type **3** with the allenic bridge between the aromatic units,[7] we used the well-established copper-promoted S_N2'-substitution of propargyl electrophiles[13,14] as the key step for the generation of the allene moiety (Scheme 2). Addition of the lithium acetylide of alkyne **9** to the aldehyde **10** furnished the propargylic alcohol **11**, which was converted into the corresponding acetate with acetanhydride and lithium chloride.



Scheme 2. Synthesis of macrocyclic allene **13**.

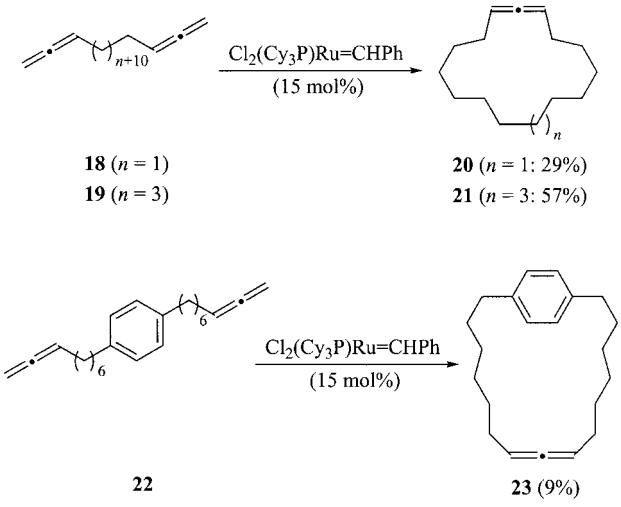


Scheme 3. Synthesis of macrocyclic allene **17**.

The S_N2'-substitution with the magnesium cuprate formed from *t*BuMgCl and CuI in the presence of LiBr[15] proceeded as expected to give the desired allene **12** with 74% yield over both steps. Finally, the Grubbs-I catalyst again induced a highly efficient ring-closing metathesis to the macrocyclic allene **13**. To the best of our knowledge, this is the first example of a ruthenium-catalyzed olefin metathesis in the presence of an allenic moiety; gratifyingly, the latter turned out to be inert under these conditions. The spectroscopic data of **13** indicate the presence of a single isomer with regard to the olefinic double bond, probably the less strained (*Z*) isomer.

In a similar fashion, we synthesized the allenic macrocycle **17** incorporating a tetrasubstituted allene bridge (Scheme 3). Again, the propargylic alcohol **14** (obtained by oxidation of the corresponding secondary alcohol and addition of phenyllithium) was converted into the allene **15** by esterification and S_N2'-substitution with a magnesium cuprate.[15] Double Kumada coupling with 8-bromomagnesiumoct-1-ene set the stage for the final ring closing metathesis of bisolefin **16** which, once more, furnished the desired allenic cyclophane **17** with high yield, as a 2:1 mixture of *E*/*Z* isomers. The spectroscopic data of the mixture did not allow an unambiguous assignment of the configuration of the olefinic double bond. It should be noted that all attempts to carry out a regioselective DMS synthesis by treating olefins **13** or **17** with the Seyferth reagent $PhHgCBr_3$[10] failed since only complex mixtures of cyclopropanated products were formed.

In order to gain even more flexibility in the introduction of allenic groups into (functionalized) macrocycles and cyclophanes, we also examined the ring-closing metathesis of α,ω-bisallenes. Whereas a single report on the cross-metathesis of mono-substituted allenes (giving symmetrical 1,3-disubstituted allenes with low to moderate yield in the presence of the Grubbs-I catalyst)[16,17] has appeared, there seems to be no precedent for the ring-closing metathesis of bisallenes. As reference substrates, we first prepared the α,ω-bisallenes **18** and **19** (by DMS synthesis of hexadeca-1,15-diene and octadeca-1,17-diene, respectively) and treated them with the Grubbs-I catalyst $Cl_2(Cy_3P)Ru=CHPh$ under high-dilution conditions (Scheme 4). Gratifyingly, the desired 15- and 17-membered allenes **20** and **21** were isolated with reasonably high yields of 29% and 57%, respectively. In contrast to this, the analogous reaction of bisallene **22** bearing an aromatic spacer (formed from 1,4-dibromobenzene by Kumada coupling with 8-bromomagnesiumoct-1-ene and subsequent DMS synthesis with $CHBr_3$/NaOH/MeLi) provided the allenic cyclophane **23** with only 9% yield (besides large amounts of polymeric products). Future experiments will have to show whether this yield difference reflects a dependence on the



Scheme 4. Ring-closing metathesis of bisallenes **18**, **19**, and **22**.

ring strain of the allenic macrocycle formed in the ring-closing metathesis.

Conclusions

Three different approaches to allenic cyclophanes of the general structure **2/3** are described in this paper. By combination of the ruthenium-catalyzed ring-closing metathesis and the Doering–Moore–Skattebøl (DMS) reaction using the Seyferth reagent $PhHgCBr_3$, the allenic cyclophane **8** was assembled in a straightforward manner. The second approach to the macrocycles **13** and **17** with the allenic bridge between the aromatic units took advantage of the copper-promoted S_N2'-substitution of propargylic acetates and ring-closing metathesis. A third alternative, which might be particular useful for accessing functionalized allenic macrocycles, involves the ring-closing metathesis of α,ω-bisallenes; by using simple test substrates, the products **20**, **21**, and **23** were obtained with low to average yields. Current studies are devoted towards the improvement of the efficiency of the allene ring-closing metathesis, the stereoselective synthesis of allenic macrocycles of the structure **2/3**, and their use as ligands in the formation of transition metal complexes.

Experimental Section

General Remarks: All reactions were carried out under an argon atmosphere using oven-dried glassware. THF and diethyl ether were distilled from sodium benzophenone ketyl. Lithium bromide was dried in vacuo at 120 °C and stored under an argon atmosphere. All other commercially available starting materials were used without further purification. The products were purified by column chromatography with Macherey&Nagel silica gel 60 (230–400 mesh) or by radial chromatography using a Harrison Research 8924 Chromatotron. Melting points were determined with a Büchi 510 capillary melting point apparatus and are uncorrected. ^1H and proton-decoupled ^{13}C NMR spectra were recorded with a Bruker DRX-400 spectrometer (400 MHz for protons, 100 MHz for carbon atoms) at room temperature in $CDCl_3$. Chemicals shifts were determined relative to the residual solvent peaks ($CHCl_3$: δ = 7.26 for protons, δ = 77.0 for carbon atoms). Carbon atoms were assigned with DEPT experiments [symbols used: (+) for CH_3,CH; (–) for CH_2; (×) for $C_{quat.}$]. Peaks for the major isomer of a mixture are marked with an asterisk (*). IR spectra were obtained with a Bruker IFS66 FT-IR spectrometer using KBr pellets or thin films between KBr plates. EI mass spectra (70 eV) and high-resolution mass spectra (HRMS) were measured with a Finnigan MAT 8230 or a Jeol SX102A spectrometer.

(*E*)- and (*Z*)-4,4′-Dibromostilbene:[18] Sodium hydride (5.88 g, 0.147 mol) was added at 0 °C to a suspension of (4-bromobenzyl)triphenylphosphonium bromide[18,19] (20.0 g, 38.3 mmol) in THF (100 mL). The suspension was heated at reflux for 1 h and then cooled to room temperature. A solution of 4-bromobenzaldehyde (7.08 g, 38.2 mmol) in THF (50 mL) was added dropwise, and the mixture was stirred for 6 h at room temperature, followed by addition of water (50 mL). After extraction with pentane (150 mL), the organic layer was dried with Na_2SO_4 and concentrated in vacuo; the residue was subjected to a vacuum sublimation at 90 °C and 0.008 mbar to furnish 5.71 g (44%) of (*Z*)-4,4′-dibromostilbene (**4**) as a colorless solid (m.p. 49 °C). The residue was recrystallized from ethanol to provide 4.99 g (39%) of (*E*)-4,4′-dibromostilbene as a colorless solid (m.p. 210 °C).

(*E*)-4,4′-Dibromostilbene: ^1H NMR: δ = 7.48 (d, *J* = 8.5 Hz, 4 H, Ar-H), 7.36 (d, *J* = 8.5 Hz, 4 H, Ar-H), 7.02 (s, 2 H). ^{13}C NMR: δ = 137.4 (×), 133.3 (+), 129.6 (+), 129.5 (+), 123.0 (×). IR (KBr): $\tilde{\nu}$ = 3013, 1585 cm^{-1}. EI-MS: *m*/*z* (%) = 338 (100) [M^+], 178 (97). HR-EI-MS: calcd. for $C_{14}H_{10}Br_2$: 335.9149, found 335.9112.

(*Z*)-4,4′-Dibromostilbene (4): ^1H NMR: δ = 7.36 (d, *J* = 7.7 Hz, 4 H, Ar-H), 7.09 (d, *J* = 7.7 Hz, 4 H, Ar-H), 6.55 (s, 2 H). ^{13}C NMR: δ = 135.6 (×), 131.5 (+), 130.4 (+), 129.7 (+), 121.2 (×). IR (KBr): $\tilde{\nu}$ = 3005, 1636 cm^{-1}. EI-MS: *m*/*z* (%) = 338 (78) [M^+], 178 (100). HR-EI-MS: calcd. for $C_{14}H_{10}Br_2$: 335.9149, found 335. 9137.

(*Z*)-4,4′-Bis(oct-7-en-1-yl)stilbene (5): A solution of 8-bromooct-1-ene[20] (9.20 g, 45.0 mmol) in THF (15 mL) was added dropwise to magnesium turnings (1.27 g, 52.2 mmol) in THF (30 mL). After the exothermic reaction had ceased, the mixture was heated at reflux for 90 min. It was then cooled to room temperature and added dropwise to a suspension of **4** (6.25 g, 18.5 mmol) and 1,3-bis(diphenylphosphanyl)propanenickel(II) chloride (260 mg, 0.48 mmol) in diethyl ether (40 mL). After the exothermic reaction, the solution was heated at reflux for 3 h and stirred at room temperature for another 10 h. Addition of pentane (40 mL) was followed by stirring of the mixture under air for 2 h and filtration through silica gel (elution with pentane). The filtrate was concentrated in vacuo, and the crude product was purified by dry column chromatography (cyclohexane/ethyl acetate, 20:1) to give 6.80 g (91%) of **5** as a colorless oil. ^1H NMR: δ = 7.21 (d, *J* = 8.3 Hz, 4 H, Ar-H), 7.05 (d, *J* = 8.3 Hz, 4 H, Ar-H), 6.53 (s, 2 H), 5.87 (ddt, *J* = 16.9/10.3/6.8 Hz, 2 H), 5.02 (dd, *J* = 16.9/2.0 Hz, 2 H, C=CH_2), 4.97 (dd, *J* = 10.1/2.0 Hz, 2 H, C=CH_2), 2.58 (t, *J* = 7.5 Hz, 4 H), 2.09–2.00 (m, 4 H), 1.66–1.55 (m, 4 H), 1.43–1.25 (m, 12 H). ^{13}C NMR: δ = 141.9 (×), 139.3 (+), 134.1 (×), 129.7 (+), 128.9 (+), 128.3 (+), 114.4 (–), 35.8 (–), 33.9 (–), 31.41 (–), 29.3 (–), 29.1 (–), 29.0 (–). IR (neat): $\tilde{\nu}$ = 3012, 2928, 1640, 1463 cm^{-1}. EI-MS: *m*/*z* (%) = 400 (100) [M^+], 111 (25). HR-EI-MS: calcd. for $C_{30}H_{40}$: 400.3130, found 400.3134.

(*Z,Z*)- and (*1Z,15E*)-[2.14]Paracyclophan-1,15-diene (6/7): To a refluxing suspension of benzylidenedichlorobis(tricyclohexylphosphanyl)ruthenium (0.15 g, 0.18 mmol) in CH_2Cl_2 (400 mL) was added dropwise within 6 h a solution of **5** (2.03 g, 5.03 mmol) in CH_2Cl_2 (600 mL). During the reaction, the Grubbs-I catalyst (4 × 100 mg) was added after 2, 4, 6, and 8 h. After 10 h reaction time, the mixture was cooled to room temperature, silica gel (5 g) was added, and the solvent was removed in vacuo. The remaining loaded silica gel was used in dry column chromatography (pentane/diethyl ether, 1:1, then CH_2Cl_2) to give 1.10 g (58%) of **6** and 0.65 g (34%) of **7** as colorless oils.

(*Z,Z*)-[2.14]Paracyclophan-1,15-diene (6): ^1H NMR: δ = 7.19 (d, *J* = 8.3 Hz, 4 H, Ar-H), 7.04 (d, *J* = 8.3 Hz, 4 H, Ar-H), 6.52 (s, 2 H, 1-H, 2-H), 5.38 (m, 2 H, 15-H, 16-H), 2.56 (t, *J* = 7.7 Hz, 4 H), 2.05–1.91 (m, 4 H), 1.65–1.52 (m, 4 H), 1.40–1.20 (m, 12 H). ^{13}C NMR: δ = 141.8 (×), 134.7 (×), 130.3 (+), 129.5 (+), 128.7 (+), 128.2 (+), 35.7 (–), 32.6 (–), 31.3 (–), 29.5 (–), 29.2 (–), 29.0 (–). IR (neat): $\tilde{\nu}$ = 3017, 2926, 1652 cm^{-1}. EI-MS: *m*/*z* (%) = 372 (100) [M^+], 97 (45). HR-EI-MS: calcd. for $C_{28}H_{36}$: 372.2817, found 372.2825.

(*1Z,15E*)-[2.14]Paracyclophan-1,15-diene (7): ^1H NMR: δ = 7.04 (d, *J* = 8.0 Hz, 4 H, Ar-H), 7.00 (d, *J* = 8.0 Hz, Ar-H), 6.64 (s, 2 H, 1-H, 2-H), 5.40 (m, 2 H, 15-H, 16-H), 2.59 (t, *J* = 6.9 Hz, 4 H), 2.06–1.92 (m, 4 H), 1.65–1.54 (m, 4 H), 1.40–1.15 (m, 12 H). ^{13}C

NMR: δ = 141.3 (×), 135.0 (×), 130.6 (+), 130.3 (+), 128.7 (+), 128.3 (+), 34.6 (–), 32.2 (–), 30.5 (–), 29.3 (–), 27.9 (–), 27.5 (–). IR (neat): $\tilde{\nu}$ = 3013, 2925, 2853, 1652 cm^{-1}. EI-MS: *m/z* (%) = 372 (100) [M^+], 97 (40). HR-EI-MS: calcd. for $C_{28}H_{36}$: 372.2817, found 372.2788.

(*Z*)-[2.15]Paracyclophan-1,15,16-triene (8): To a solution of the 3:2 mixture of **6/7** (200 mg, 0.54 mmol) in benzene (3 mL) was added $PhHgCBr_3$[10] (454 mg, 0.86 mmol), and the mixture was heated at reflux for 6 h. The solvent was removed at 40 °C under reduced pressure, and the residue was treated with petroleum ether and CH_2Cl_2 (20:1). Filtration was followed by removal of the solvent in vacuo and purification of the crude product by radial chromatography (petroleum ether/CH_2Cl_2, 20:1). The resulting dibromocyclopropane (90 mg) was dissolved in diethyl ether (10 mL), and to the cooled solution (–78 °C) was added MeLi (0.14 mL, 0.2 mmol, 1.39 M solution in diethyl ether) dropwise within 10 min. After warming to 0 °C, water (10 mL) was added, and the mixture was washed with diethyl ether (2 × 20 mL). The combined organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified by radial chromatography (petroleum ether/CH_2Cl_2, 20:1) to yield 43 mg (21% over both steps) of **8** as a colorless solid (m.p. 104 °C). ^1H NMR: δ = 7.07 (d, *J* = 8.3 Hz, 4 H, Ar-H), 7.00 (d, *J* = 8.3 Hz, 4 H, Ar-H), 6.60 (s, 2 H, 1-H, 2-H), 5.38 (qi, *J* = 4.7 Hz, 2 H, 15-H, 17-H), 2.59 (t, *J* = 6.9 Hz, 4 H), 1.96–1.80 (m, 4 H), 1.59 (tt, *J* = 7.1/7.3 Hz, 4 H), 1.40–1.15 (m, 12 H). ^{13}C NMR: δ = 203.6 (×, C-16), 141.3 (×), 134.9 (×). 130.1 (+), 128.8 (+), 128.3 (+), 91.5 (+, C-15, C-17), 34.9 (–), 30.4 (–), 28.5 (–), 28.9 (–), 28.7 (–), 27.7 (–). IR (KBr): $\tilde{\nu}$ = 3018, 2925, 1957, 1606 cm^{-1}. EI-MS: *m/z* (%) = 384 (100) [M^+], 219 (78). HR-EI-MS: calcd. for $C_{29}H_{36}$: 384.2817, found 384.2818.

1-Bromo-4-(oct-7-en-1-yl)benzene: From 8-bromooct-1-ene[20] (6.90 g, 36.0 mmol) in diethyl ether (40 mL), magnesium turnings (0.88 g, 36.0 mmol) in diethyl ether (20 mL), 1,1′-bis(diphenylphosphanyl)ferrocenepalladium(II) chloride (386 mg, 0.45 mmol) and 1,4-dibromobenzene (7.10 g, 30.4 mmol) in THF (10 mL) according to the synthesis of **5**. The crude product was purified by dry column chromatography (pentane); yield: 6.90 g (87%) of 1-bromo-4-(oct-7-en-1-yl)benzene as a colorless oil. ^1H NMR: δ = 7.40 (d, *J* = 8.2 Hz, 2 H, Ar-H), 7.06 (d, *J* = 8.2 Hz, 2 H, Ar-H), 5.83 (ddt, *J* = 17.1/10.1/6.5 Hz, 1 H), 5.02 (dd, *J* = 17.1/1.5 Hz, 1 H, C=CH_2), 4.96 (dd, *J* = 10.1/1.5 Hz, 1 H, C=CH_2), 2.57 (t, *J* = 8.0 Hz, 2 H), 2.06 (td, *J* = 7.2/6.5 Hz, 2 H), 1.61 (m, 2 H), 1.36 (m, 6 H). ^{13}C NMR: δ = 141.7 (×), 139.2 (+), 131.2 (+), 130.1 (+), 119.3 (×), 114.2 (–), 35.3 (–), 33.7 (–), 31.2 (–), 29.0 (–), 28.9 (–), 28.8 (–). IR (neat): $\tilde{\nu}$ = 2927, 1640, 1073 cm^{-1}. EI-MS: *m/z* (%) = 266/268 (33) [M^+], 182 (62), 171 (100). HR-EI-MS: calcd. for $C_{14}H_{19}Br$: 266.0670, found 266.0653.

1-(Trimethylsilylethynyl)-4-(oct-7-en-1-yl)benzene: A mixture of bis(diphenylphosphanyl)palladium(II) chloride (210 mg, 0.29 mmol), 1,3-dimesityl-4,5-dihydro-1H-imidazolium chloride (256 mg, 0.75 mmol) and diisopropylamine (15 mL) was heated at reflux for 1 h. To this suspension were added copper(I) iodide (142 mg, 0.75 mmol) and 1-bromo-4-(oct-7-en-1-yl)benzene (3.28 g, 12.3 mmol). Then trimethylsilylacetylene (2.21 g, 22.4 mmol) was added dropwise within 10 min, and the mixture was heated at reflux for 2 h. After cooling to room temperature and removal of the solvent in vacuo, cyclohexane (200 mL) was added, and the mixture was filtered through a short pad of silica gel. The solvent was removed in vacuo to give 3.48 g (99%) of 1-(trimethylsilylethynyl)-4-(oct-7-en-1-yl)benzene as a pale yellow oil. ^1H NMR: δ = 7.39 (d, *J* = 7.9 Hz, 2 H, Ar-H), 7.11 (d, *J* = 7.9 Hz, 2 H, Ar-H), 5.81 (ddt, *J* = 17.0/10.2/6.6 Hz, 1 H), 5.00 (d, *J* = 17.0 Hz, 1 H, C=CH_2), 4.95 (d, *J* = 10.2 Hz, 1 H, C=CH_2), 2.59 (t, *J* = 7.5 Hz, 2 H), 2.05 (m, 2 H), 1.65–1.55 (m, 2 H), 1.42–1.27 (m, 6 H), 0.26 (s, 9 H). ^{13}C NMR: δ = 143.5 (×), 139.0 (+), 131.9 (+), 128.3 (+), 120.3 (×), 114.2 (–), 105.4 (×), 93.2 (×), 35.8 (–), 33.7 (–), 31.1 (–), 29.0 (–), 28.9 (–), 28.8 (–), 0.0 (+). IR (neat): $\tilde{\nu}$ = 2928, 2158, 1641 cm^{-1}. EI-MS: *m/z* (%) = 284 (100) [M^+], 269 (90). HR-EI-MS: calcd. for $C_{19}H_{28}Si$: 284.1960, found 284.1955.

1-Ethynyl-4-(oct-7-en-1-yl)benzene (9): A solution of 1-(trimethylsilylethynyl)-4-(oct-7-en-1-yl)benzene (1.89 g, 6.64 mmol) in methanol (10 mL) was treated with K_2CO_3 (500 mg) and stirred for 1 h. After addition of brine (100 mL) and diethyl ether (100 mL), the organic layer was separated and washed with water (2 × 50 mL) and brine (2 × 50 mL). Drying with Na_2SO_4 was followed by concentration to 20 mL under reduced pressure, filtration through a short plug of silica gel, and removal of the solvent under reduced pressure, affording 1.37 g (97%) of **9** as a reddish oil. ^1H NMR: δ = 7.41 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.13 (d, *J* = 8.0 Hz, 2 H Ar-H), 5.81 (ddt, *J* = 17.1/10.3/6.8 Hz, 1 H), 5.00 (d, *J* = 17.1 Hz, 1 H, C=CH_2), 4.94 (d, *J* = 10.3 Hz, 1 H, C=CH_2), 3.04 (s, 1 H), 2.61 (t, *J* = 7.4 Hz, 2 H), 2.05 (m, 2 H), 1.63–1.54 (m, 2 H), 1.41–1.23 (m, 6 H). ^{13}C NMR: δ = 143.9 (×), 139.1 (+), 132.0 (+), 128.4 (+), 119.2 (×), 114.2 (–), 83.8 (×), 76.4 (+), 35.8 (–), 33.7 (–), 31.1 (–), 29.0 (–), 28.9 (–), 28.8 (–). IR (neat): $\tilde{\nu}$ = 3299, 2927, 2109, 1641 cm^{-1}. EI-MS: *m/z* (%) = 212 (17) [M^+], 115 (100). HR-EI-MS: calcd. for $C_{16}H_{20}$: 212.1565, found 212.1565.

4-(Oct-7-en-1-yl)benzaldehyde (10): To a stirred solution of 1-bromo-4-(oct-7-en-1-yl)benzene (6.00 g, 22.5 mmol) in THF (25 mL) was added dropwise *n*BuLi (22 mL, 33 mmol, 1.5 M solution in hexane) at –78 °C. Stirring at this temperature was continued for 1 h before addition of *N*,*N*-dimethylformamide (6.56 g, 89.8 mmol) in THF (20 mL). After warming up to room temperature the mixture was hydrolyzed with 6 N hydrochloric acid (50 mL) and diluted with diethyl ether (100 mL). The mixture was then neutralized with a satd. $NaHCO_3$ solution. The organic layer was separated, washed with water (4 × 50 mL), and dried with Na_2SO_4. The solvent was removed under reduced pressure to furnish 4.10 g (84%) of **10** as a colorless oil. ^1H NMR: δ = 9.96 (s, 1 H, CHO), 7.79 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.33 (d, *J* = 8.0 Hz, 2 H, Ar-H), 5.80 (ddt, *J* = 17.0/10.2/6.2 Hz, 1 H), 4.98 (d, *J* = 17.0 Hz, 1 H, C=CH_2), 4.93 (d, *J* = 10.2 Hz, 1 H, C=CH_2), 2.68 (t, *J* = 8.2 Hz, 2 H), 2.07–1.95 (m, 2 H,), 1.64–1.47 (m, 2 H), 1.36–1.21 (m, 6 H). ^{13}C NMR: δ = 191.9 (+, CHO), 150.3 (×), 138.9 (+), 134.4 (×), 129.8 (+), 129.0 (+), 114.2 (–), 36.1 (-,), 33.6 (–), 30.9 (–), 29.0 (–), 28.8 (–), 28.7 (–). IR (neat): $\tilde{\nu}$ = 2928, 1702, 1640 cm^{-1}. EI-MS: *m/z* (%) = 216 [M^+, 97], 132 (100). HR-EI-MS: calcd. for $C_{15}H_{20}O$: 216.1514, found 216.1515.

1,3-Bis[(4-oct-7-en-1-yl)phenyl]prop-2-yn-1-ol (11): To a stirred solution of **9** (647 mg, 3.05 mmol) in THF (5 mL) was added dropwise LDA (1.68 mL, 3.36 mmol, 2 M suspension in hexane) at –78 °C. The mixture stirred for 1 h at –50 °C, followed by addition of **10** (660 mg, 3.05 mmol) in THF (2 mL). After stirring for 12 h at room temperature, the mixture was hydrolyzed with water (50 mL) and washed with diethyl ether (3 × 50 mL). The combined organic layers were dried with Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by radial chromatography (pentane/CH_2Cl_2), providing 887 mg (60%) of **11** as a colorless oil. ^1H NMR: δ = 7.53 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.39 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.22 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.13 (d, *J* = 8.0 Hz, 2 H, Ar-H), 5.81 (m, 2 H), 5.65 (d, *J* = 6.1 Hz, 1 H), 5.00 (d, *J* = 17.1 Hz, 2 H), 4.94 (d, *J* = 10.3 Hz, 2 H), 2.61 (m, 4 H,), 2.27 (d, *J* = 6.1 Hz, 1 H), 2.05 (m, 4 H), 1.65–1.54 (m, 4 H), 1.42–1.26 (m, 12 H). ^{13}C NMR: δ = 143.6 (×), 143.2

(×), 139.1 (+), 139.0 (+), 138.1 (×), 131.6 (+), 128.7 (+), 128.4 (+), 126.7 (+), 119.6 (×), 114.2 (–), 114.1 (–), 88.2 (×), 86.7 (×), 65.0 (+), 35.8 (–), 35.6 (–), 33.8 (–), 33,7 (–), 31.4 (–), 31.1 (–), 29.1 (–), 29.0 (–), 28.9 (–), 28.8 (–), 28.7 (–), 28.6 (–). IR (neat): $\tilde{\nu}$ = 3408, 2928, 2159, 1640 cm^{-1}. EI-MS: *m*/*z* (%) = 428 (6) [M$^+$], 411 (100). HR-EI-MS: calcd. for $C_{31}H_{40}O$: 428.3079, found 428.3107.

1-{1-(1,1-Dimethylethyl)-3-[4-(oct-7-en-1-yl)phenyl]propa-1,2-dienyl}-4-(oct-7-en-1-yl)benzene (12): A mixture of **11** (177 mg, 0.41 mmol), LiCl (150 mg, 3.5 mmol) and acetanhydride (10.1 g, 97.9 mmol) was stirred for 12 h at room temperature. Hydrolysis with a satd. $NaHCO_3$ solution (200 mL) was followed by extraction with diethyl ether (3 × 50 mL). The combined organic layers were dried with Na_2SO_4 and the solvent was in vacuo. The crude product was purified by radial chromatography (cyclohexane/ethyl acetate, 4:1), affording the acetate of **11** (157 mg, 82%) as a colorless oil. To a solution of LiBr (443 mg, 5.1 mmol) and CuI (974 mg, 5.1 mmol) in THF (8 mL) was added dropwise at 0 °C *t*BuMgCl (3.2 mL, 5.1 mmol, 1.6 M solution in diethyl ether). After stirring for 10 min at 0 °C, the above mentioned acetate (401 mg, 0.81 mmol) in THF (2 mL) was added dropwise. The mixture was stirred for 30 min at 0 °C. A satd. NH_4Cl solution (containing 15% conc. ammonia) and diethyl ether (40 mL) were added, the organic phase was separated and washed with the NH_4Cl/NH_3 solution until the aqueous layer remained colorless. The organic layer was dried with Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (cyclohexane/ ethyl acetate, 5:1), providing 361 mg (90%) of **12** as a colorless oil. ^{1}H NMR: δ = 7.22 (m, 4 H,), 7.09 (m, 4 H), 6.18 (s, 1 H), 5.79 (m, 2 H), 4.98 (m, 2 H), 4.92 (m, 2 H), 2.56 (t, *J* = 7.7 Hz, 2 H, 2.03 (m, 4 H), 1.63–1.54 (m, 4 H), 1.41–1.28 (m, 12 H), 1.21, (s, 9 H, $(CH_3)_3C$). ^{13}C NMR: δ = 209.7 (×), 141.4, 141.3(×), 139.1 (+), 134.5 (×), 132.7 (×), 129.0 (+), 128.7 (+), 127.9 (+), 126.3 (+), 119.5 (×), 114.2 (–), 94.8 (+), 35.6 (–), 35.5 (–), 35.2 (×), 33.8 (–), 31.4 (–), 31.3 (–), 30.0 (+), 29.2 (–), 29.1 (–), 29.0 (–), 28.8 (–). IR (neat): $\tilde{\nu}$ = 2928, 1942, 1641 cm^{-1}. EI-MS: *m*/*z* (%) = 468 (13) [M$^+$], 411 (100). HR-EI-MS: calcd. for $C_{35}H_{48}$: 468.3756, found 468.3743.

1-(1,1-Dimethylethyl)[3.14]paracyclophan-1,2,16-triene (13): To a refluxing solution of **12** (100 mg, 0.21 mmol) in CH_2Cl_2 (70 mL) was added benzylidenedichlorobis(tricyclohexylphosphanyl)ruthenium (27 mg, 0.03 mmol), and refluxing was continued for 6 h. After cooling to room temperature, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (hexane/ethyl acetate, 25:1) to give 78 mg (84%) of **13** as a colorless oil. ^{1}H NMR: δ = 7.20 (m, 4 H), 7.07 (m, 4 H,), 6.17 (s, 1 H), 5.34 (m, 2 H), 2.53, (t, *J* = 7.6 Hz, 4 H), 1.93 (m, 4 H), 1.56 (m, 4 H) 1.35–1.24 (m, 12 H), 1.19 (s, 9 H, $(CH_3)_3C$). ^{13}C NMR: δ = 202.9 (×), 141.3 (×), 141.2 (×), 134.4 (×), 132.6 (×), 130.2 (+), 128.9 (+), 128.6 (+), 127.8 (+), 126.2 (+), 119.4 (×), 94.7 (+), 35.6 (–), 35.5 (–), 35.1 (×), 32.5 (–), 31.4, 31.3 (–), 29.9 (+), 29.5 (–), 29.1 (–), 29.0 (–), 28.9 (–). IR (neat): $\tilde{\nu}$ = 2970, 2928, 1937 cm^{-1}. EI-MS: *m*/*z* (%) = 440 (32) [M$^+$], 383 (100). HR-EI-MS: calcd. for $C_{33}H_{44}$: 440.3443, found 440.3412.

1,3-Bis(4-bromophenyl)prop-2-yn-1-ol: From diisopropylamine (2.75 g, 27.1 mmol) in THF (20 mL), *n*BuLi (10.1 mL, 25.3 mmol, 2.5 M solution in hexane), 1-bromo-4-ethynylbenzene[21] (3.28 g, 18.1 mmol) in THF (5 mL) and 4-bromobenzaldehyde (3.35 g, 18.0 mmol) in THF (20 mL) according to the preparation of **11**. Yield: 5.04 g (76%) of 1,3-bis(4-bromophenyl)prop-2-yn-1-ol as a brownish solid (m.p. 60 °C). ^{1}H NMR: δ = 7.53 (d, *J* = 8.5 Hz, 2 H, Ar-H), 7.46 (d, *J* = 8.5 Hz, 2 H, Ar-H), 7.45 (d, *J* = 8.5 Hz, 2 H, Ar-H), 7.31 (d, *J* = 8.5 Hz, 2 H, Ar-H), 5.63 (s, 1 H), 2.54 (s, 1 H, OH). ^{13}C NMR: δ = 139.4 (×), 133.1 (+), 131.8 (+), 131.6 (+), 128.3 (+), 123.1 (×), 122.5 (×), 121.0 (×), 89.3 (×), 85.8 (×), 64.4 (+). IR (neat): $\tilde{\nu}$ = 3390, 3084, 2201 cm^{-1}. EI-MS: *m*/*z* (%) = 285/287 (3, M$^+$-Br), 77 (100). HR-EI-MS: calcd. for $C_{15}H_{10}Br_2O$: 363.9098, found 363.9068.

1,3-Bis(4-bromophenyl)-1-phenylprop-2-yn-1-ol (14): A mixture of 1,3-bis(4-bromophenyl)prop-2-yn-1-ol (4.00 g, 10.9 mmol) and IBX (4.59 g, 16.4 mmol) in DMSO (15 mL) was stirred for 3 h at room temperature. Addition of water (100 mL) was followed by extraction with diethyl ether (3 × 50 mL), washing of the combined organic layers with brine (4 × 50 mL) and filtration through a plug of silica gel and Na_2SO_4. The solvent was removed under reduced pressure and the residue was crystallized from ethanol to furnish 1,3-bis(4-bromophenyl)prop2-yn-1one (2.51 g, 64%) as a pale brown solid (m.p. 178 °C). To a solution of 1,3-bis(4-bromophenyl) prop2-yn-1one (0.31 g, 0.82 mmol) in THF (3 mL) was added dropwise at –50 °C PhLi (0.47 mL, 0.94 mmol, 2 M in cyclohexane/diethyl ether). The mixture was stirred for 2 h at –50 °C and then warmed up to room temperature. It was hydrolyzed with a satd. NH_4Cl solution and washed with diethyl ether (3 × 50 mL). The combined organic layers were washed with brine (2 × 30 mL) and dried with Na_2SO_4. The solvent was removed in vacuo affording 0.35 g (96%) of **14** as a pale yellow oil. ^{1}H NMR: δ = 7.64–7.30 (m, 13 H), 2.94 (s, 1 H, OH). ^{13}C NMR: δ = 144.2 (×), 143.9 (×), 133.1 (+), 131.6 (+), 131.3 (+), 128.4 (+), 128.0 (+), 127.7 (+), 125.8 (+), 123.1 (×), 121.9 (×), 121.0 (×), 92.1 (×), 86.3 (×), 74.3 (×). IR (neat): $\tilde{\nu}$ = 3407, 3060, 2223 cm^{-1}. EI-MS: *m*/*z* (%) = 442 (1) [M$^+$], 363 (3), 98 (100). HR-EI-MS: calcd. for $C_{21}H_{14}Br_2O$: 439.9411, found 439.9448.

1-Bromo-4-[3-(4-bromophenyl)-1-(1,1-dimethylethyl)-3-phenylpropa-1,2-dienyl]benzene (15): To a mixture of acetyl bromide (0.15 g,1.2 mmol), triethylamine (0.15 g, 1.4 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (8 mg, 0.07 mmol) in CH_2Cl_2 (5 mL) was added **14** (0.29 g, 0.65 mmol). After stirring for 12 h at room temperature, water (5 mL) was added, and the mixture was washed with diethyl ether (3 × 50 mL). The combined organic layers were washed with brine and dried with Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (cyclohexane/ethyl acetate, 5:1) to furnish 0.19 g (60%) of the acetate of **14** as a reddish oil. According to the synthesis of **12**, the acetate (0.34 g, 0.70 mmol) was treated with LiBr (0.37 g, 4.2 mmol) and CuI (0.80 g (4.2 mmol) in THF (8 mL), *t*BuMgCl (2.6 mL, 4.2 mmol, 1.6 M solution in diethyl ether). The crude product was purified by flash chromatography (cyclohexane/ethyl acetate, 4:1); yield: 0.23 g (68%) of **15** as a pale yellow oil. ^{1}H NMR: δ = 7.64–7.15 (m, 13 H, Ar-H), 1.22 (s, 9 H, $(CH_3)_3C$). ^{13}C NMR: δ = 202.6 (×), 136.6 (×), 136.3 (×), 135.8 (×), 131.4 (+), 131.0 (+), 130.9 (+), 129.6 (+), 128.6 (+), 128.4 (+), 127.9 (+), 121.0 (×), 120.8 (×), 118.1 (×), 109.1 (×), 35.7 (×), 29.6 (+). IR (neat): $\tilde{\nu}$ = 3059, 1939 cm^{-1}. EI-MS: *m*/*z* (%) = 482 (12) [M$^+$], 425 (100). HR-EI-MS: calcd. for $C_{25}H_{22}Br_2$: 480.0088, found 480.0086.

1-{1-(1,1-Dimethylethyl)-3-[4-(oct-7-en-1-yl)phenyl]-3-phenylpropa-1,2-dienyl}-4-(oct-7-en-1-yl)benzene (16): According to the synthesis of **5**, **15** (0.11 g, 0.26 mmol) and 1,3-bis(diphenylphosphanyl)propanenickel(II) chloride (4.2 mg, 7.7 μmol) in diethyl ether (1 mL) was treated with 8-bromomagnesiumoct-1-ene (0.8 mL, 0.8 mmol, 1 M solution in diethyl ether). The crude product was purified by flash chromatography (cyclohexane/ethyl acetate, 10:1); yield: 0.12 g (87%) of **16** as a colorless oil. ^{1}H NMR: δ = 7.37–7.05 (m, 13 H), 5.80 (ddt, *J* = 17.0/10.2/6.7 Hz, 2 H), 4.98 (d, *J* = 17.0 Hz, 2 H), 4.91 (d, *J* = 10.2 Hz 2 H), 2.58 (m, 4 H), 2.03 (m, 4 H), 1.66–1.55 (m, 4 H), 1.40–1.24 (m, 12 H), 1.21 (s, 9 H, $(CH_3)_3C$). ^{13}C NMR: δ = 203.0 (×), 141.4 (×), 141.3 (×), 139.1 (+), 137.9 (×),

134.8 (×), 134.5 (×), 129.2 (+), 128.3 (+), 128.2 (+), 128.1 (+), 128.0 (+), 127.8 (+), 126.6 (+), 118.3 (×), 114.2 (–), 109.2 (×), 35.8 (×), 35.6 (–), 33.8 (–), 31.4 (–), 29.9 (+), 29.2 (–), 29.0 (–), 28.8 (–). IR (neat): $\tilde{\nu}$ = 3077, 2926, 1940, 1641 cm^{-1}. EI-MS: *m/z* (%) = 544 (9) [M^+], 487 (100). HR-EI-MS: calcd. for $C_{41}H_{52}$: 544.4069, found 544.4049.

1-(1,1-Dimethylethyl)-3-phenyl[3.14]paracyclophan-1,2,16-triene (17): To a refluxing solution of **16** (110 mg, 0.20 mmol) in CH_2Cl_2 (100 mL) was added benzylidenedichlorobis(tricyclohexylphosphanyl)ruthenium (25 mg, 0.03 mmol), and refluxing was continued for 3 h. After cooling to room temperature, cyclohexane (50 mL) was added, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (cyclohexane/ethyl acetate, 20:1) to give 90 mg (85%) of **17** (2:1 mixture of *E*/*Z* isomers) as a colorless oil. ^{1}H NMR: δ = 7.49–7.05 (m, 13 H), 5.37/5.32 (2m, 2 H), 2.63 (m, 4 H), 2.08–1.93 (m, 4 H), 1.68–1.54 (m, 4 H), 1.49–1.25 (m, 12 H), 1.30 (s, 9 H, $(CH_3)_3C$). ^{13}C NMR: δ = 204.5*/203.0 (2×), 141.2 (×), 140.1 (×), 140.9 (×), 140.7 (×), 137.9/137.4* (2×), 134.7 (×), 134.6 (×), 134.5 (×), 134.4 (×), 131.6 (+), 130.3 (+), 130.0 (+), 129.2 (+), 128.9 (+), 128.7 (+), 128.4 (+), 128.3 (+), 128.2 (+), 128.0 (+), 127.5 (+), 126.7 (+), 118.7 (×), 118.3 (×), 109.4*/109.2 (2×), 35.8 (×), 35.7 (–) 35.4 (×), 30.1 (+), 29.9 (+); numerous additional peaks between 29.9 and 22.6 could not be assigned. IR (neat): $\tilde{\nu}$ = 3058, 2926, 1938, 1646 cm^{-1}. EI-MS: *m/z* (%) = 516 (19) [M^+], 459 (77), 57 (100). HR-EI-MS: calcd. for $C_{39}H_{48}$: 516.3756, found 516.3777.

Octadeca-1,2,16,17-tetraene (18): To a solution of hexadeca-1,15-diene[22] (10.2 g, 45.9 mmol) in CH_2Cl_2 (40 mL) was added $CHBr_3$ (41.4 g, 0.17 mol), triethylbenzylammonium chloride (1.10 g, 4.8 mmol) and 50% aqueous NaOH (30 mL). The mixture was stirred for 8 h with an *Ultra Turrax* stirrer and then diluted with pentane (300 mL) and brine (250 mL). The organic layer was separated, washed with brine (3 × 100 mL), dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by dry column chromatography (pentane) to furnish 22.6 g (87%) of the α,ω-bis(dibromocyclopropane) as a colorless waxy solid. To a solution of the α,ω-bis(dibromocyclopropane) (3.50 g, 6.2 mmol) in diethyl ether (25 mL) was added dropwise at –65 °C MeLi (8.5 mL, 13.6 mmol, 1.6 M solution in diethyl ether). The mixture was warmed to 0 °C and poured into ice water. The organic layer was separated and the aqueous layer was washed with pentane (3 × 30 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed in vacuo. The crude product was purified by flash chromatography (pentane), affording 1.24 g (81%) of **18** as a colorless oil. ^{1}H NMR: δ = 5.09 (qi, *J* = 6.7 Hz 2 H), 4.65 (dt, *J* = 6.7/3.2 Hz, 4 H), 2.00 (m, 4 H), 1.45–1.38 (m, 4 H), 1.35–1.23 (m, 16 H). ^{13}C NMR: δ = 208.5 (×), 90.1 (+), 74.5 (–), 29.6 (–), 29.6 (–), 29.4 (–), 29.2 (–), 29.1 (–), 28.3 (–). IR (neat): $\tilde{\nu}$ = 2926, 1956, 1464 cm^{-1}. EI-MS: *m/z* (%) = 246 (23) [M^+], 231 (28), 81 (100). HR-EI-MS: calcd. for $C_{18}H_{30}$: 246.2348, found 246.2327.

Eicosa-1,2,18,19-tetraene (19): According to the preparation of **18**, octadeca-1,17-diene[22] (11.0 g, 43.9 mmol) in CH_2Cl_2 (40 mL) was treated with $CHBr_3$ (33.4 g, 0.13 mol), triethylbenzylammonium chloride (1.05 g, 4.6 mmol) and 50% aqueous NaOH (50 mL). Yield: 21.9 g (84%) of the α,ω-bis(dibromocyclopropane) as a pale yellow solid (m.p. 42–46 °C). The α,ω-bis(dibromocyclopropane (3.53 g, 5.94 mmol) was treated with MeLi (8.6 mL, 13.7 mmol, 1.6 M solution in diethyl ether) to give 1.04 g (64%) of **19** as a colorless oil. ^{1}H NMR: δ = 5.09 (qi, *J* = 6.7 Hz 2 H), 4.65 (dt, *J* = 6.7/3.3 Hz, 4 H), 2.00 (m, 4 H), 1.45–1.38 (m, 4 H), 1.35–1.23 (m, 20 H). ^{13}C NMR: δ = 208.5 (×), 90.1 (+), 74.5 (–), 29.7 (–), 29.6 (–), 29.5 (–), 29.1 (–), 29.1 (–), 28.3 (–). IR (neat): $\tilde{\nu}$ = 2927, 1956, 1464 cm^{-1}. EI-MS: *m/z* (%) = 274 (14) [M^+], 259 (8), 81 (100). HR-EI-MS: calcd. for $C_{20}H_{34}$: 274.2661, found 274.2607.

Cyclopentadeca-1,2-diene (20): To a refluxing solution of **18** (201 mg, 0.81 mmol) in CH_2Cl_2 (165 mL) was added benzylidenedichlorobis(tricyclohexylphosphanyl)ruthenium (100 mg, 0.12 mmol), and refluxing was continued for 18 h. After cooling to room temperature, cyclohexane (100 mL) was added, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (cyclohexane) to give 48 mg (29%) of **20** as a colorless oil. ^{1}H NMR: δ = 5.08 (m, 2 H), 1.99 (m, 4 H), 1.45–1.10 (m, 20 H). ^{13}C NMR: δ = 204.4 (×), 91.2 (+), 28.3 (–), 28.2 (–), 27.6 (–), 27.2 (–), 27.1 (–), 26.5 (–). IR (neat): $\tilde{\nu}$ = 2924, 1959, 1465 cm^{-1}. EI-MS: *m/z* (%) = 206 (2) [M^+], 81 (100). HR-EI-MS: calcd. for $C_{15}H_{26}$: 206.2035, found 206.2051.

Cycloheptadeca-1,2-diene (21): To a refluxing solution of **19** (200 mg, 0.73 mmol) in CH_2Cl_2 (145 mL) was added benzylidenedichlorobis(tricyclohexylphosphanyl)ruthenium (90 mg, 0.12 mmol), and refluxing was continued for 18 h. After cooling to room temperature, cyclohexane (100 mL) was added, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (cyclohexane) to give 98 mg (57%) of **21** as a colorless oil. ^{1}H NMR: δ = 5.09 (m, 2 H), 1.99 (m, 4 H), 1.45–1.20 (m, 2 H). ^{13}C NMR: δ = 204.1 (×), 91.1 (+), 28.7 (–), 28.3 (–), 28.1 (–), 27.9 (–), 27.5 (–), 27.1 (–), 27.0 (–). IR (neat): $\tilde{\nu}$ = 2925, 1957, 1458 cm^{-1}. EI-MS: *m/z* (%) = 234 (27) [M^+], 81 (100). HR-EI-MS: calcd. for $C_{17}H_{30}$: 234.2348, found 234.2343.

1,4-Di(oct-7-en-1-yl)benzene: According to the synthesis of **5**, 1,4-dibromobenzene (6.02 g, 25.5 mmol) and 1,3-bis(diphenylphosphanyl)propanenickel(II) chloride (276 mg, 0.51 mmol) in diethyl ether (20 mL) was treated with the Grignard reagent prepared from 8-bromooct-1-ene (13.1 g, 68.5 mmol) and magnesium turnings (1.67 g, 68.7 mmol) in diethyl ether (70 mL). The crude product was purified by kugelrohr distillation (40–90 °C, 0.01 mbar); yield: 4.90 g (65%) of 1,4-di(oct-7-en-1-yl)benzene as a colorless oil. ^{1}H NMR: δ = 7.11 (s, 4 H, Ar-H), 5.83 (ddt, *J* = 17.2/10.1/6.7 Hz, 2 H), 5.02 (d, *J* = 17.2 Hz, 2 H), 4.96 (d, *J* = 10.1 Hz, 2 H), 2.60 (t, *J* = 7.7 Hz, 4 H), 2.07 (q, *J* = 6.7 Hz, 4 H), 1.63 (m, 4 H), 1.38 (m, 12 H). ^{13}C NMR: δ = 140.0 (×), 139.1 (+), 128.2 (+), 114.1 (–), 35.5 (–), 33.8 (–), 31.5 (–), 29.2 (–), 29.0 (–), 28.8 (–). IR (neat): $\tilde{\nu}$ = 2927, 1640 cm^{-1}. EI-MS: *m/z* (%) = 298 (74) [M^+], 129 (87), 117 (100). HR-EI-MS: calcd. for $C_{22}H_{34}$: 298.2661, found 298.2661.

1,4-Di(nona-7,8-dien-1-yl)benzene (22): According to the preparation of **18**, 1,4-di(oct-7-en-1-yl)benzene (1.08 g, 3.7 mmol) in CH_2Cl_2 (20 mL) was treated with $CHBr_3$ (3.01 g, 11.9 mmol), triethylbenzylammonium chloride (105 mg, 0.46 mmol) and 50% aqueous NaOH (20 mL). Yield: 2.14 g (91%) of the bis(dibromocyclopropane) as a yellow oil. The bis(dibromocyclopropane) (1.50 g, 3.26 mmol) was treated with MeLi (3.3 mL, 5.2 mmol, 1.6 M solution in diethyl ether) to give 698 mg (90%) of **22** as a reddish oil. ^{1}H NMR: δ = 7.10 (s, 4 H, Ar-H), 5.10 (qi, *J* = 6.7 Hz, 4 H), 4.66 (dt, *J* = 6.7/3.3 Hz, 4 H), 2.59 (t, *J* = 7.5 Hz, 4 H), 2.00 (m, 4 H), 1.68–1.55 (m, 4 H), 1.50–1.32 (m, 12 H). ^{13}C NMR: δ = 208.5 (×), 140.0 (×), 128.2 (+), 90.0 (+), 74.5 (–), 35.5 (–), 31.5 (–), 29.1 (–), 29.0 (–), 28.9 (–), 28.2 (–). IR (neat): $\tilde{\nu}$ = 3044, 2928, 1956, 1458 cm^{-1}. EI-MS: *m/z* (%) = 322 (44) [M^+], 199 (46), 117 (100). HR-EI-MS: calcd. for $C_{24}H_{34}$: 322.2661, found 322.2642.

[15]Paracyclophan-7,8-diene (23): To a refluxing solution of **22** (200 mg, 0.62 mmol) in CH_2Cl_2 (125 mL) was added benzylidenedichlorobis(tricyclohexylphosphanyl)ruthenium (76 mg, 0.09 mmol), and refluxing was continued for 18 h. After cooling to room temperature, cyclohexane (100 mL) was added, the solvent was re-

moved under reduced pressure and the crude product was purified by flash chromatography (cyclohexane) to give 19 mg (9%) of **23** as a colorless oil. ^{1}H NMR: δ = 7.05 (s, 4 H, Ar-H), 5.08 (m, 2 H), 2.66–2.53 (m, 4 H), 2.09–1.91 (m, 4 H), 1.45–1.24 (m, 16 H). ^{13}C NMR: δ = 203.6 (×), 139.5 (×), 128.6 (+), 90.8 (+), 35.0 (–), 30.3 (–), 28.5 (–), 28.0 (–), 27.7 (–), 26.8 (–). IR (neat): $\tilde{\nu}$ = 3044, 2925, 1959, 1458 cm^{-1}. EI-MS: *m*/*z* (%) = 282 (60) [M$^+$], 117 (100). HR-EI-MS: calcd. for $C_{21}H_{30}$: 282.2348, found 282.2344.

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