1,6-Dibromohexa-1,3,5-triene − Stereocontrolled Synthesis of Monosubstituted and Disubstituted Hexatrienes by Palladium-Catalysed Cross-Coupling Reactions

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1,6-Dibromohexa-1,3,5-triene, previously described by us and easily obtained from 5-bromopenta-2,4-dienal by condensation with bromomethylene triphenylphosphorane, is a versatile precursor for the synthesis of conjugated 1,3,5-trienic derivatives of controlled configuration. In this paper, we describe the stereocontrolled synthesis of *E,E,Z*, *E,E,E* and *Z,E,Z* isomers of α-bromo-ω-substituted-1,3,5-hexatrienes and 1,6-disubstituted-1,3,5-hexatrienes. The synthesis is based on palladium-catalysed single or double cross-coupling reactions between the three isomers – 1*E*,3*E*,5*Z*, 1*E*,3*E*,5*E* and 1*Z*,3*E*,5*Z* – of the intermediate 1,6-dibromohexa-1,3,5-triene and various organozinc reagents.

Introduction

The conjugated 1,3,5-trienic structural unit has been found in numerous natural products, equally in the vegetable and animal kingdoms. These products possess generally important biological properties. For example, we can quote the large variety of all-*trans* heptatrienamides containing acetylenic linkages, isolated from plants of the *Asteraceae* family, and which have shown insecticidal and physiological properties.[1] Many fatty acids isolated from numerous plants have in their structure a conjugated trienic unit with *Z,E,E* or *Z,E,Z* geometry, and some of their derivatives have shown insecticidal activity.[2] Leukotrienes, isolated from leukocytes, constitute an important class of *Z,E,E*-conjugated trienic compounds, acting as biological mediators in inflammation and hypersensibility reactions.[3] As well as this, conjugated polyenes possessing disubstituted hexatrienics units are potentially useful compounds as nonlinear optical materials.[4] In view of the great importance of polyenic conjugated compounds and of our interest in this field, we have synthesized many products incorporating a stereodefined conjugated trienic unit. The work reported in this paper is focused on the synthesis of (*E,E,Z*)-, (*E,E,E*)- and (*Z,E,Z*)-α-bromo-ω-substituted hexatrienes[5] **1** and 1,6-disubstituted-1,3,5-hexatrienes **2** and **3** [possessing either identical (compounds **2**) or different (compounds **3**) groups] from the corresponding 1*E*,3*E*,5*Z* (**4a**) and 1*E*,3*E*,5*E* (**4b**) isomers, previously reported by us,[6] and from the new 1*Z*,3*E*,5*Z* isomer (**4c**)[5a] of 1,6-dibromohexa-1,3,5-triene and various organozinc reagents **5**, using stereoselective monopalladium- and dipalladium-catalysed cross-coupling reactions.

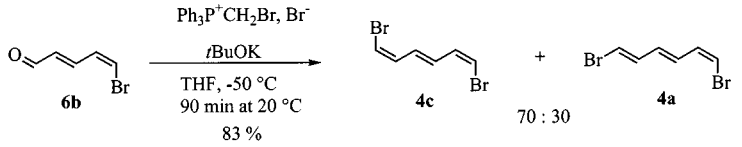
Results and Discussion

The 1*E*,3*E*,5*Z* (**4a**) and 1*E*,3*E*,5*E* (**4b**) isomers of 1,6-dibromohexa-1,3,5-triene have previously been prepared by us,[6] exploiting a Wittig reaction with (2*E*,4*E*)-5-bromopenta-2,4-dienal (**6a**), also synthesised by our group.[6,7] They have been used in palladium-catalysed cross-coupling reactions.[7b]

We have now synthesised the 1*Z*,3*E*,5*Z* isomer of 1,6-dibromohexa-1,3,5-triene (**4c**) for the first time, performing the Wittig reaction with (2*E*,4*Z*)-5-bromopenta-2,4-dienal (**6b**).[6,7] We obtained a mixture of isomers **4a** and **4c** (**4a**/**4c** = 30:70), in an overall yield of 83% (Scheme 1). These two isomers could be separated by flash chromatography and fractional crystallisation. All three isomers **4a**, **4b** and **4c** have been used, separately and in their pure states, in palladium-catalysed cross-coupling reactions.

Single Coupling Reaction

Numerous authors have shown that it is possible to control the coupling centre by means of the nature or the position of the leaving groups on the double bond.[8−12] This discrimination can be explained with different examples. When the starting molecule contains two different leaving groups, the single coupling product may be obtained selectively by chemical discrimination.[8] If the leaving groups are



Scheme 1

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identical, the presence of a heteroatom[9] or of an electroattractor group,[10] or of hindering steric effects,[11] tilt the cross-coupling reaction towards formation of the single coupling product. The use of prostereogenic catalysts allows enantioselective single coupling reactions.[12] We were particularly interested in cases in which the two leaving groups are identical. In such a case, for a symmetrical starting molecule, the difficulty in controlling the selective formation of a single coupling product without production of a double coupling product[13] can be overcome by using the organometallic reagent in a lesser quantity relative to the dihalogenated compound.[14] The configuration (*E* or *Z*) of the double bond in vinylic halo compounds produces a great difference in reactivities, however.[15]

We have performed a new and general synthesis of single coupling compounds **1** from the pure 1*E*,3*E*,5*Z* (**4a**)[5,6] and 1*E*,3*E*,5*E* (**4b**)[5a,6] isomers and the pure new 1*Z*,3*E*,5*Z* isomer (**4c**)[5a] of 1,6-dibromohexa-1,3,5-triene, by means of palladium-catalysed cross-coupling reactions with various organozinc reagents **5**.

The organozinc reagents **5** were prepared by transmetallation reactions, from organomagnesium (commercially available or prepared under Grignard conditions, Mg/Zn, Table 1) or organolithium (prepared by action of *n*-butyllithium, Li/Zn, Table 1) reagents and zinc dibromide, or by direct insertion of zinc metal into a carbon−halogen bond, using zinc dust activated successively by 1,2-dibromoethane and chlorotrimethylsilane[16] (Zn*, Table 1).

α) From (1*E*,3*E*,5*Z*)-1,6-Dibromohexa-1,3,5-triene (4a)

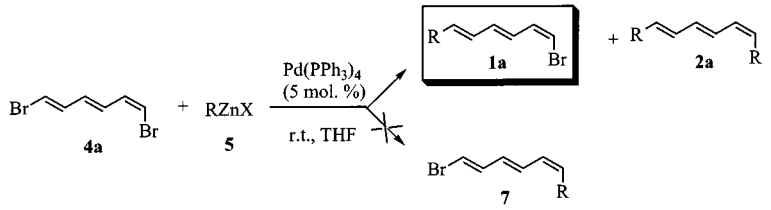
Firstly, we carried out the palladium-catalysed cross-coupling reactions on the 1*E*,3*E*,5*Z* stereoisomer **4a**. To optimise the single coupling reaction and limit the formation of double coupling product **2**, the dibromide reagent should be always in excess with respect to the organozinc reagent **5**.[5] Accordingly, we carried out the reaction by slow and steady addition (with a syringe pump) of the organozinc reagent **5** in solution in tetrahydrofuran (THF) to a solution of **4a** and a catalytic amount (around 5 mol %) of palladium complex in THF, at room temperature, until complete consumption of **4a** (Scheme 2). Results are summarised in Table 1.

Whatever the case, we never observed a single coupling reaction on the *Z* double bond (i.e. **7**) (Scheme 2). With aromatic, heteroaromatic, benzylic, aliphatic, functionalised aliphatic and vinylic organozinc reagents **5a** to **5j**, the reaction occurred regioselectively on the *E* double bond, and the single coupling products were obtained in moderate to good yields (47 to 66%) (Table 1, entries 1 to 10). Traces of double coupling products **2** were observed by TLC in some cases, but these were not isolated (Table 1, entries 1, 2 and

Table 1. Single coupling reaction results from **4a**

Entry	Organozinc reagent R	Organozinc reagent preparation	X	Single coupling product yield [%]	Double coupling product yield [%]
1	**5a:** phenyl	Mg/Zn	Br	**1aa:** 66	**2aa:** traces
2	**5b:** *p*-MeO−C_6H_4	Mg/Zn	Br	**1ab:** 63	**2ab:** traces
3	**5c:** 2-pyridyl	Li/Zn	Br	**1ac:** 50	-
4	**5d:** 2-thienyl	Li/Zn	Br	**1ad:** 62	-
5	**5e:** 2-furyl	Li/Zn	Br	**1ae:** 63	**2ae:** traces
6	**5f:** benzyl	Zn*[a]	Br	**1af:** 65	-
7	**5g:** *n*-pentyl	Mg/Zn	Br	**1ag:** 55	-
8	**5h:** AcO−$(CH_2)_3$−CH_2	Zn*	I	**1ah:** 61	-
9	**5i:** Cl-$(CH_2)_3$−CH_2	Zn*	I	**1ai:** 47	-
10	**5j:** $(EtO)_2CHCH_2$−$(CH=CH)_2$	Li/Zn	Br	**1aj:** 47	-
11	**5k:** $MeOOCCH_2$	Zn*	Br	**1ak:** 22	-
12	**5l:** C_5H_{11}−C≡C	Li/Zn	Br	**1al:** 62	**2al:** 7
13	**5m:** Me_3Si−C≡C	Li/Zn	Br	**1am:** 22	**2am:** 57

[a] Zn* : zinc dust activated successively by 1,2-dibromoethane and chlorotrimethylsilane.[16]



1aa, 2aa R = phenyl ; **1ab, 2ab** R = *p*-MeO-C_6H_4 ; **1ac** R = 2-pyridyl ; **1ad** R = 2-thienyl ; **1ae, 2ae** R = 2-furyl ; **1af** R = benzyl ; **1ag** R = *n*-pentyl ; **1ah** R = AcO-$(CH_2)_3$-CH_2 ; **1ai** R = Cl-$(CH_2)_3$-CH_2 ; **1aj** R = $(EtO)_2CHCH_2$-$(CH=CH)_2$; **1ak** R = $MeOOCCH_2$; **1al, 2al** R = C_5H_{11}-C≡C ; **1am, 2am** R = Me_3SiC≡C

Scheme 2

5). The weak reactivity of the Reformatsky reagent **5k**, due to a 1−3 equilibrium migration of the zinc atom from carbon to oxygen (enolate character),[17] might explain the poor yield observed for the formation of the single coupling product **1ak** (Table 1, entry 11).

The cross-coupling reaction with the acetal dienic zinc reagent **5j**, giving the single coupling product **1aj** (Table 1, entry 10), is an alternative method for preparation of the hexavinylogation reagent **8** (Scheme 3), previously synthesised in our laboratory.[18]

The cross-coupling reaction with acetylenic zinc reagents **5l** and **5m** (Table 1, entries 12 and 13) resulted in mixtures of single coupling products **1al** and **1am** and non-negligible quantities of double coupling products **2al** and **2am**; this last could be the major product (Table 1, entry 13). A similar lack of selectivity in cross-coupling reactions with acetylenic zinc reagent **5m** has previously been observed in the literature.[15,19]

To limit the formation of double coupling product **2am**, we carried out the cross-coupling reaction at −15 °C. However, at this temperature, the reaction is slowed down greatly, and after two hours we had only observed traces of single coupling product **1am** and double coupling product **2am**. We also changed the steric parameter of the palladium ligands to prevent the oxidative insertion of the *Z* double bond on the palladium. The steric parameter was determined by the ligand cone angle θ.[20] The steric effect of the catalyst was studied by performing the single coupling reaction between (1*E*,3*E*,5*Z*)-1,6-dibromohexa-1,3,5-triene (**4a**) and the trimethysilylacetylenic zinc bromide **5m** with palladium catalysts possessing different phosphane ligands. The reaction was performed, as described previously, by slow and steady addition (with a syringe pump) at room temperature of the organozinc reagent **5m** to a solution of dibromide reagent **4a** and catalyst PdL_n (Scheme 4). Results are summarised in Table 2.

Accordingly, using 1,3-(diphenylphosphanyl)propane as a ligand with a small cone angle θ, we obtained a similar result (Table 2, entry 1) to that obtained with triphenylphosphane as ligand (Table 2, entry 2), with the double coupling product **2am** as the major one. With tri(*o*-tolyl)phosphane, with a greater cone angle θ, as ligand the reaction was considerably slowed down, and we recovered some dibromide reagent **4a** (Table 2, entry 3). Increasing the reaction time did not improve the yield of single coupling product **1am**, but partial consumption of the dibromide reagent **4a** led to an increase in the yield of the double coupling product **2am** (Table 2, entry 4).

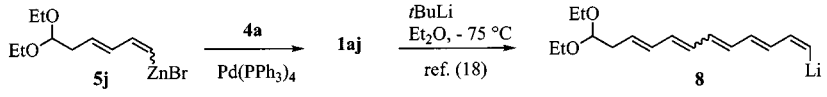
Hence, for stereoisomer **4a**, we had demonstrated that it was generally possible to access the single coupling products **1a** selectively, by slow and steady addition of the organozinc reagents **5**. Moreover, the single coupling reaction was regioselective and stereospecific; the coupling reaction occurring preferentially on the *E* double bond.

β) From (1*E*,3*E*,5*E*)-1,6-Dibromohexa-1,3,5-triene (4b)

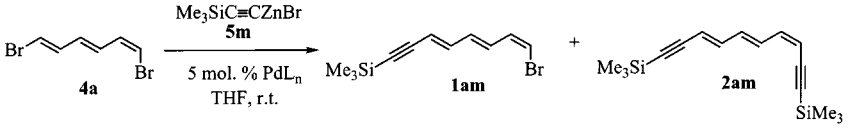
Our results for the stereoisomer **4a** permitted us to carry out some single coupling reactions on (1*E*,3*E*,5*E*)-1,6-dibromohexa-1,3,5-triene (**4b**) under similar conditions (Scheme 5). Results are summarised in Table 3. The yields of single coupling products **1b** were perceptibly lower than for the single coupling products **1a** obtained from **4a**; this could be explained by the formation of double coupling products **2b** (Table 3, entries 1 and 3). Incidentally, we were unable to isolate the double coupling product **2bb** (Table 3, entry 2), because of its great insolubility.

γ) From (1*Z*,3*E*,5*Z*)-1,6-Dibromohexa-1,3,5-triene (4c)

Carrying out the cross-coupling reaction, under the same reaction conditions, with the 1*Z*,3*E*,5*Z* stereoisomer **4c**, we obtained the single coupling products **1c** with yields close to those obtained from **4a** for single coupling compounds



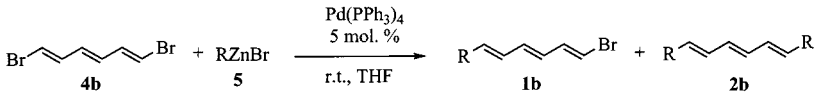
Scheme 3



Scheme 4

Table 2. Influence of the steric effect of palladium ligands in single coupling reactions with trimethylsilylacetyleniczinc bromide **5m**

Entry	L_n	θ	Reaction time	Single coupling product **1am**: yield [%]	Double coupling product **2am**: yield [%]	Dibromide **4a** recovered: yield [%]
1	$(Ph_2P-(CH_2)_3-PPh_2)_2$	127°	1 h 45	29	45	-
2	$(PPh_3)_4$	145°	1 h 45	22	57	-
3	$(P(o\text{-}Tol)_3)_4$	194°	1 h 45	43	14	34
4	$(P(o\text{-}Tol)_3)_4$	194°	2 h 30	46	32	16

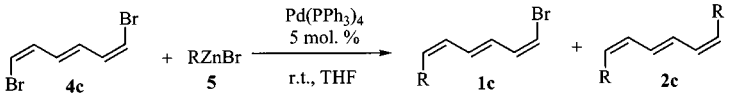


1ba, **2ba** R = phenyl ; **1bb**, **2bb** R = *p*-MeO-C_6H_4 ; **1bg**, **2bg** R = *n*-pentyl ; **1bn**, **2bn** R = *n*-hexyl

Scheme 5

Table 3. Single coupling reaction results from **4b**

Entry	Organozinc reagent R	Single coupling product yield [%]	Double coupling product yield [%]
1	**5a:** phenyl	**1ba:** 46	**2ba:** 12
2	**5b:** *p*-MeO−C_6H_4	**1bb:** 54	**2bb:** not isolated
3	**5g:** *n*-pentyl	**1bg:** 40	**2bg:** 7
4	**5n:** *n*-hexyl	**1bn:** 46	**2bn:** 9



1ca R = phenyl ; **1cb** R = *p*-MeO-C_6H_4 ; **1cg** R = *n*-pentyl

Scheme 6

Table 4. Single coupling reaction results from **4c**

Organozinc reagent R	Single coupling product yield [%]
5a: phenyl	**1ca:** 61
5b: *p*-MeO−C_6H_4	**1cb:** 63
5g: *n*-pentyl	**1cg:** 58

Table 5. Double coupling reaction results from **4a**

Organozinc reagent R	Organozinc reagent preparation	Double coupling product yield [%]
5a: phenyl	Mg/Zn	**2aa:** 89
5b: *p*-MeO−C_6H_4	Mg/Zn	**2ab:** 94
5c: 2-pyridyl	Li/Zn	**2ac:** 59
5g: *n*-pentyl	Mg/Zn	**2ag:** 58
5o: 3-furyl	Li/Zn	**2ao:** 75

1a, and with no trace of double coupling products **2c** (Scheme 6, Table 4).

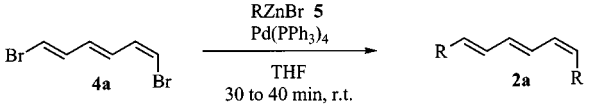
Double Coupling Reaction, Leading to Symmetrical Compounds 2

The disubstituted conjugated 1,3,5-hexatrienes **2** (with identical groups) were easily obtained from the three 1,6-dibromohexa-1,3,5-triene isomers **4a** (1*E*,3*E*,5*Z*), **4b** (1*E*,3*E*,5*E*) and **4c** (1*Z*,3*E*,5*Z*) and various organozinc reagents **5,** by a dipalladium-catalysed cross-coupling reaction in a one-step procedure.

Firstly, we carried out palladium-catalysed cross-coupling reactions on the 1*E*,3*E*,5*Z* stereoisomer **4a**, using aliphatic, aromatic and heteroaromatic organozinc reagents **5a−e**. The double coupling reaction occurred at room temperature, by rapid addition of a solution of organozinc reagent **5** to a solution of **4a** and catalyst $Pd(PPh_3)_4$ (5 to 10 mol %) in THF (Scheme 7). After conventional treatment and purification by silica gel column chromatography, the double coupling products **2a** were recovered in good to excellent yields (Table 5).

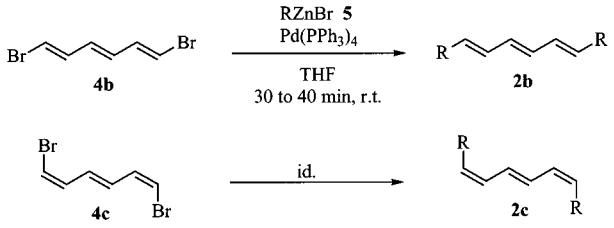
The stereochemistry of the double bonds in double coupling products **2a** (determined by ^{1}H NMR from the coupling constant values of the vinylic protons of each double bond) are identical to those of the corresponding double bonds in the starting dibromide compound **4a**. This double coupling reaction is hence stereoselective.

The double coupling reaction was applied to the 1*E*,3*E*,5*E* (**4b**) and 1*Z*,3*E*,5*Z* (**4c**) isomers, under the same reaction conditions and with the same organozinc reagents **5** (Scheme 8). The double coupling products **2b** and **2c** were obtained in yields similar to those of double coupling products **2a** from **4a** (Table 6 and 7). These double coupling reactions are also stereoselective (^{1}H NMR analysis).



2aa R = phenyl ; **2ab** R = *p*-MeO-C_6H_4 ; **2ac** R = 2-pyridyl ; **2ag** R = *n*-pentyl ; **1ao** R = 3-furyl

Scheme 7



2ba, **2ca** R = phenyl ; **2bb**, **2cb** R = *p*-MeO-C_6H_4 ; **2bg**, **2cg** R = *n*-pentyl ; **2bo**, **2co** R = 3-furyl

Scheme 8

Table 6. Double coupling reaction results from **4b**

Organozinc reagent R	Organozinc reagent preparation	Double coupling product yield [%]
5a: phenyl	Mg/Zn	**2ba:** 87
5b: *p*-MeO−C_6H_4	Mg/Zn	**2bb:** 70
5g: *n*-pentyl	Mg/Zn	**2bg:** 60
5o: 3-furyl	Li/Zn	**2bo:** 97

Table 7. Double coupling reaction results from **4c**

Organozinc reagent R	Organozinc reagent preparation	Double coupling product yield [%]
5a: phenyl	Mg/Zn	**2ca:** 65
5b: *p*-MeO−C_6H_4	Mg/Zn	**2cb:** 90
5g: *n*-pentyl	Mg/Zn	**2cg:** 61
5o: 3-furyl	Li/Zn	**2co:** 86

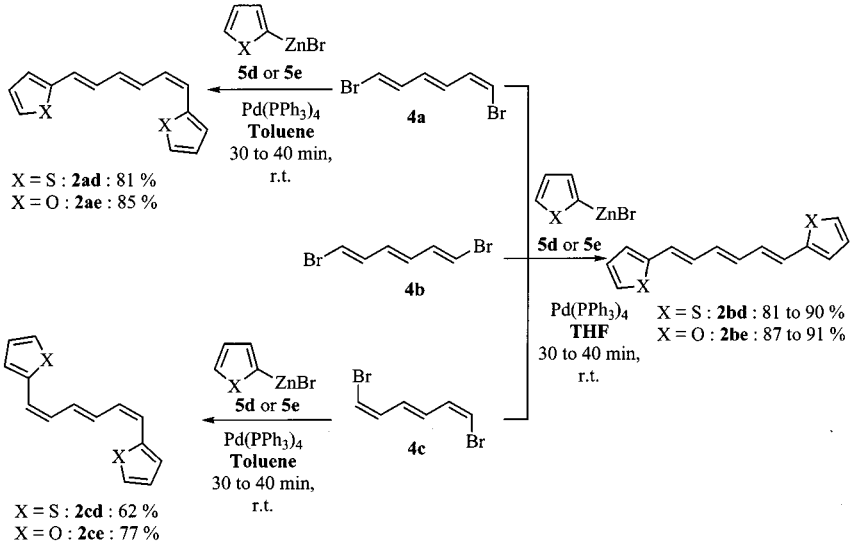
Numerous syntheses of 1,6-diphenylhexa-1,3,5-triene have previously been described in the literature. We can note, for example, the stereoselective syntheses of the 1*E*,3*E*,5*Z* (**2aa**), 1*E*,3*E*,5*E* (**2ba**) and 1*Z*,3*E*,5*Z* (**2ca**) isomers by Cao et al.[22] (6*E*,8*E*,10*E*)-Hexadeca-6,8,10-triene (**2bg**) was synthesised by Whiting et al.,[23] but never isolated, and a synthesis of (1*E*,3*E*,5*E*)-1,6-bis(4-methoxyphenyl)hexa-1,3,5-triene (**2bb**) was described by Spangler et al.[24] All other double coupling compounds were novel and gave satisfactory structural analyses.

Surprisingly, when the double coupling reaction was carried out in THF with 2-thienylzinc bromide (**5d**) and with 2-furylzinc bromide (**5e**), we exclusively obtained the 1*E*,3*E*,5*E* double coupling products **2bd** and **2be**, respectively, in excellent yields, regardless of the starting dibromide compound **4a**, **4b** or **4c** (Scheme 9). However, by carrying out the reaction in anhydrous toluene and using solutions of organozinc reagents **5d** and **5e** in toluene, we were able to suppress the isomerisation process and prepare the 1*E*,3*E*,5*Z* (**2ad** and **2ae**) or 1*Z*,3*E*,5*Z* (**2cd** and **2ce**) dicoupling products from **4a** or **4c**, respectively, (Scheme 9) with complete stereoselectivity.

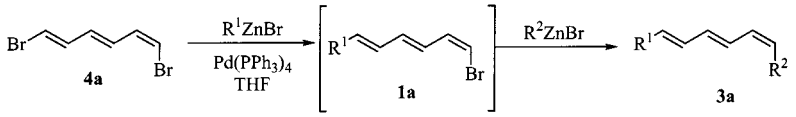
To the best of our knowledge, the *E*,*E*,*Z* and *Z*,*E*,*Z* disubstituted hexatrienes with 2-thienyl or 2-furyl substituents (**2ad**, **2cd**, **2ae**, **2ce**) have never been described, although the syntheses of (1*E*,3*E*,5*E*)-1,6-bis(2-thienyl)hexa-1,3,5-triene (**2bd**) and (1*E*,3*E*,5*E*)-1,6-bis(2-furyl)hexa-1,3,5-triene (**2be**) from a few stereospecific Wittig[25] or MacMurry[26] reactions have been reported. Recently, Märkl et al.[27] have demonstrated the easy isomerisation of some associated derivatives.

Double Coupling Reaction, Leading to Unsymmetrical Compounds 3

The results described previously in this paper have illustrated the great selectivity of formation of the single coup-



Scheme 9



3aa R^1 = phenyl, R^2 = *n*-pentyl ; **3ad** R^1 = 2-thienyl, R^2 = C_5H_{11}-C≡C ; **3ag** R^1 = *n*-pentyl, R^2 = phenyl ; **3an** R^1 = *n*-hexyl, R^2 = Me_3SiC≡C

Scheme 10

ling compounds **1** or of the double coupling compounds **2**, on the basis of good control over the speed of addition of the organozinc reagents **5**. Therefore, it was very important to exploit this selectivity, by the synthesis of double coupling compounds **3** possessing two different groups. These compounds **3** were obtained from the two isomers **4a** (1*E*,3*E*,5*Z*) and **4b** (1*E*,3*E*,5*E*) of 1,6-dibromohexa-1,3,5-triene in one-step or two-step procedures.

From the isomer **4a**, the single coupling reaction was first performed with an organozinc reagent R^1ZnBr, resulting in the (nonisolated) single coupling derivative **1a**. A second organozinc reagent R^2ZnBr was then added to this reaction mixture, and the second coupling reaction took place to give the intended compounds **3a** (Scheme 10).

These two successive single coupling reactions were regio- and stereoselective; the configurations of the double bonds, determined by ^1H NMR from the coupling constants, were identical with those of the starting dibromide compound **4a**. All these compounds **3a** are novel, and were obtained in a one-step procedure from the precursor **4a** in medium yields. Results are summarised in Table 8.

As well as this, the double coupling compounds **3b** were obtained from isomer **4b** in one-step or two-step procedures (Scheme 11).

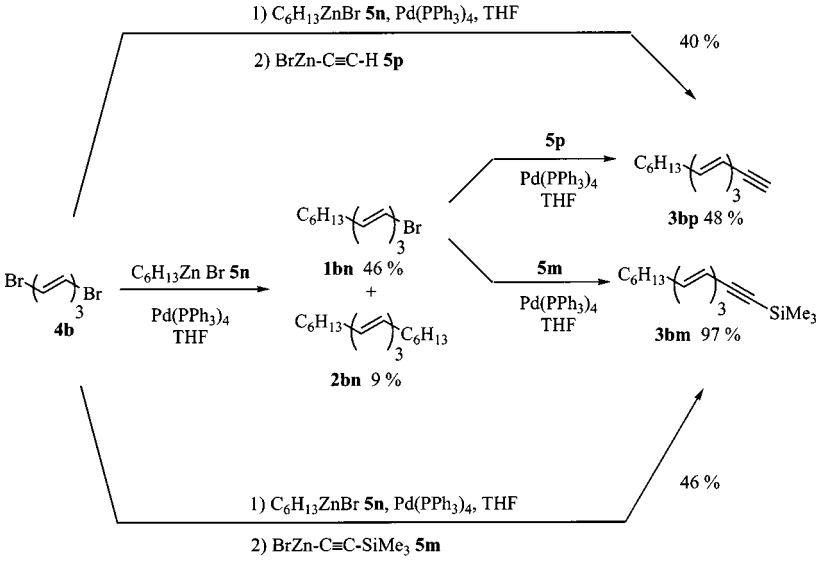
When the syntheses of **3bm** and **3bp** were executed in a two-step procedure, the intermediate **1bn** was purified by flash chromatography and used pure (i.e., without the double coupling compound **2bn**) for the second coupling reaction. When this process was used, the compounds **3bm** and **3bp** were obtained in overall yields of 45% and 22% respectively, against 46% and 40% for the one-step procedure. As in the case of the formation of compounds **3a**, these coupling reactions are regio- and stereoselective. The compounds **3bm** and **3bp** are novel and gave satisfactory structural analyses.

Conclusion

Firstly, we have obtained many single coupling products **1a**, **1b** and **1c** − in particular, some functionalised bromotrienes **1** − starting from the three isomers, **4a**, **4b** and **4c**,

Table 8. Double coupling reaction results from **4a**, leading to unsymmetrical compounds **3a**

Organozinc reagent R^1	Organozinc reagent R^1 preparation	Organozinc reagent R^2	Organozinc reagent R^2 preparation	Double coupling product yield [%]
5a: phenyl	Mg/Zn	**5g:** *n*-pentyl	Mg/Zn	**3aa:** 35
5d: 2-thienyl	Li/Zn	**5l:** $C_5H_{11}-C \equiv C$	Li/Zn	**3ad:** 51
5g: *n*-pentyl	Mg/Zn	**5a:** phenyl	Mg/Zn	**3ag:** 35
5n: *n*-hexyl	Mg/Zn	**5m:** $Me_3Si-C \equiv C$	Li/Zn	**3an:** 58



Scheme 11

respectively, of 1,6-dibromohexa-1,3,5-triene. All these products **1** are novel, and gave satisfactory structural analyses. The single coupling reaction is stereoselective; there is retention of the configuration of the double bond of the starting product **4**. Moreover, this reaction is regioselective, since, when performed on the 1*E*,3*E*,5*Z* isomer **4a**, the single coupling reaction occurs specifically on the *E* double bond.

Secondly, we have selectively synthesised various symmetrical double coupling products **2**, possessing *E,E,Z*, *E,E,E* and *Z,E,Z* configurations, in one step and in good yields, starting from the three isomers, **4a**, **4b** and **4c**, of 1,6-dibromohexa-1,3,5-triene. A great number of these products **2** are novel, and gave satisfactory structural analyses. The double coupling reaction, carried out in THF, is stereospecific. There is total retention of the configuration of the double bonds of the dibromide starting material, except in those cases in which 2-thienyl- and 2-furylzinc bromides **5d** and **5e** were used; in these there was a total *E,E,E* isomerisation. However, when this reaction was carried out in toluene, no isomerisation of the double coupling products was observed. These very interesting results then prompted us to synthesize some unsymmetrical double coupling compounds **3**. These were obtained in one-step or two-step procedures from the two 1,6-dibromohexa-1,3,5-triene isomers **4a** and **4b,** with complete regio- and stereoselectivity.

We have demonstrated an easy means of access to single and double coupling compounds **1**−**3** and the synthetic utility of the 1,6-dibromohexa-1,3,5-triene precursor. Application of these regio- and stereocontrolled reactions to access to biological active compounds is currently under investigation in our laboratory.

Experimental Section

General Remarks: NMR spectra were recorded on a Bruker AC 200 MHz or Bruker AM 400 MHz with Aspect 3000 calculator. $CDCl_3$ or C_6D_6 was used as solvent. − Mass spectra were recorded on an ATI Unicam Automass, fitted (or not) with a GC-mass coupling (high resolution J&W column, 30 m, 0.25 mm ID, 0.25, rate: 1.2 mL/min). − IR spectra were recorded on a Perkin−Elmer 16 PC FT-IR (neat, cm^{-1}). − Microanalyses were carried out in IR-COF Microanalysis Laboratory of Rouen. Analytical TLC was performed on Kieselgel 60F-254−0.25 nm plates and developed with UV 250 nm or phosphomolybdic acid. All reactions were carried out under anhydrous conditions under inert atmosphere. THF was distilled from sodium and benzophenone, and toluene from calcium hydride. Products were purified by silica gel column chromatography (SDS Company, 230−400 mesh). − Melting points were measured on a Reichert−Jung microscope apparatus. Catalysts $Pd(PPh_3)_4$, $Pd[Ph_2P-(CH_2)_3-PPh_2]_2$ and Pd(*o*-tolyl)$_4$, were prepared following literature procedures.[21]

(1*Z*,3*E*,5*Z*)-1,6-Dibromohexa-1,3,5-triene (4c): At −50 °C and under argon atmosphere, potassium *tert*-butoxide (1.38 g, 12.3 mmol, 1.2 equiv.) in THF (20 mL) was added to a stirred solution of (bromomethyl)triphenylphosphonium bromide (5.36 g, 12.3 mmol, 1.2 equiv.) in THF (50 mL). The yellow solution obtained was stirred for 1 h at −50 °C; then (2*E*,4*Z*)-5-bromopenta-2,4-dienal (**6b**) (1.60 g, 9.9 mmol, 1.0 equiv.) in THF (10 mL) was added. After stirring for 2 h 30 at room temperature, the mixture was hydrolysed using aqueous $NaHCO_3$ (50 mL, 5%) and extracted with pentane (3 × 20 mL). The organic layers were combined, dried over $MgSO_4$ and evaporated. The brown residue was triturated with pentane (6 × 5 mL), to extract the 1,6-dibromohexa-1,3,5-triene from the triphenylphosphane oxide. After evaporation of the pentane, the yellow solid was purified by silica gel column chromatography (pentane/Et_2O, 95:5) to give 1.37 g of (1*Z*,3*E*,5*Z*)-1,6-dibromohexa-1,3,5-triene (**4c)** (58% yield, white solid) and 0.59 g of (1*E*,3*E*,5*Z*)-1,6-dibromohexa-1,3,5-triene (**4a)** (25% yield, white solid). Overall yield: 83%. − Analysis for (1*Z*,3*E*,5*Z*)-1,6-dibromohexa-1,3,5-triene (**4c)**: M.p. 63 °C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.26 (d, 2 H, H^1 and H^6, *J* = 5.6 Hz), 6.68 (m, 4 H, H^2, H^3, H^4 and H^5). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 110.52 (2 C, C^1 and C^6), 131.23 (2 C), 132.27 (2 C). − MS (EI, 70 eV); *m*/*z* (rel. int.): 240 (6%) [M$^+$·], 238 (13%) [M$^+$·], 236 (6%) [M$^+$·], 159 (30) [M − Br], 157 (30) [M − Br], 78 (100) [M − 2 Br]. − IR (KBr, neat): ṽ = 736, 1596 cm^{-1}. − $C_6H_6Br_2$ (237.92): calcd. C 30.29, H 2.54; found C 30.14, H 2.41.

Single Coupling Reactions: Syntheses of Single Coupling Compounds 1

General Procedure for the Palladium-Catalysed Cross-Coupling Reaction between 1,6-Dibromohexa-1,3,5-triene 4 and Organozinc Reagents 5: A solution of organozinc reagent **5** in THF was slowly added dropwise, using a syringe pump, at room temperature and under argon, to a stirred solution of **4** and $Pd(PPh_3)_4$ in THF (5 mL). The reaction was monitored by TLC (SiO_2, pentane as eluent, UV and phosphomolybdic acid in EtOH for developing). When the reaction was complete, as indicated by the total consumption of **4**, the solution was hydrolysed using aqueous $NaHCO_3$ (5 mL, 5%) and extracted with pentane (3 × 15 mL). The organic layers were combined, dried over $MgSO_4$ and evaporated. The residue was purified by silica gel column chromatography.

(1*Z*,3*E*,5*E*)-1-Bromo-6-phenylhexa-1,3,5-triene (1aa): This compound (60 mg, yellow solid) was obtained from **4a** (92 mg, 0.39 mmol, 1.00 equiv.), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol, 0.08 equiv.), and organozinc reagent **5a** (0.5 M in THF, 1.2 mL, 0.60 mmol, 1.54 equiv.). Yield 66%. − M.p. 64 °C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.14 (d, 1 H, H^1, *J* = 6.7 Hz), 6.52 (dd, 1 H, H^4, *J* = 14.2 and 10.2 Hz), 6.60 (dd, 1 H, H^3, *J* = 14.2 and 9.8 Hz), 6.61 (d, 1 H, H^6, *J* = 15.6 Hz), 6.67 (dd, 1 H, H^2, *J* = 9.8 and 6.7 Hz), 6.84 (dd, 1 H, H^5, *J* = 15.6 and 10.2 Hz), 7.16 to 7.39 (m, 5 H, phenyl). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 108.40 (C^1), 126.56 (2 C, phenyl), 127.94, 128.29, 128.58, 128.68 (2 C, phenyl), 132.60, 134.61, 136.52, 136.94 (phenyl). − MS (EI, 70 eV); *m*/*z* (rel. int.): 236 (15) [M$^+$·], 234 (15) [M$^+$·], 155 (100) [M − Br]. − IR (KBr, neat): ṽ = 688, 996, 1446, 1606, 1734, 1882, 1954, 3020−3072 cm^{-1}. − $C_{12}H_{11}Br$ (235.12): calcd. C 61.30, H 4.72; found C 61.36, H 4.84.

(1*Z*,3*E*,5*E*)-1-Bromo-6-(4-methoxyphenyl)hexa-1,3,5-triene (1ab): This compound (166 mg, yellow solid) was obtained from **4a** (238 mg, 1.00 mmol, 1.00 equiv.), $Pd(PPh_3)_4$ (60 mg, 0.05 mmol, 0.05 equiv.), and organozinc reagent **5b** (0.15 M in THF, 10.0 mL, 1.50 mmol, 1.50 equiv.). Yield 63%. − M.p. 72 °C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.76 (s, 3 H, OC*H*$_3$), 6.10 (d, 1 H, H^1, *J* = 7.0 Hz), 6.49 (dd, 1 H, H^4, *J* = 14.7 and 10.0 Hz), 6.55 (dd, 1 H, H^3, *J* = 14.7 and 9.7 Hz), 6.56 (d, 1 H, H^6, *J* = 15.5 Hz), 6.65 (dd, 1 H, H^2, *J* = 9.7 and 7.0 Hz), 6.72 (dd, 1 H, H^5, *J* = 15.5 and 10.0 Hz), 6.81 (d, 2 H, phenyl, *J* = 8.7 Hz), 7.31 (d, 2 H, phenyl, *J* = 8.7 Hz). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.28 (O*C*H$_3$), 107.65 (C^1), 114.20 (2 C, phenyl), 126.58, 127.20, 127.90 (2 C, phenyl), 129.81 (phenyl), 132.77, 134.32, 136.92, 159.59 (phenyl).

− MS (EI, 70 eV); *m/z* (rel. int.): 266 (30) [M^{+}·], 264 (30) [M^{+}·], 185 (100) [M − Br]. − IR (KBr, neat): $\tilde{\nu}$ = 684, 706, 994, 1254, 1594, 2836−3078 cm^{-1}. − $C_{13}H_{13}BrO$ (265.15): calcd. C 58.89, H 4.94; found C 58.73, H 4.86.

(1*Z*,3*E*,5*E*)-1-Bromo-6-(2-pyridyl)hexa-1,3,5-triene (1ac): This compound (74 mg, yellow solid) was obtained from **4a** (149 mg, 0.63 mmol, 1.00 equiv.), $Pd(PPh_3)_4$ (50 mg, 0.04 mmol, 0.06 equiv.), and organozinc reagent **5c** (0.4 M in THF, 2.0 mL, 0.80 mmol, 1.27 equiv.). Yield 50%. − M.p. 52 °C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.22 (d, 1 H, H^1, *J* = 6.4 Hz), 6.57 (dd, 1 H, H^3, *J* = 14.6 and 10.2 Hz), 6.68 (d, 1 H, H^6, *J* = 15.4 Hz), 6.69 to 6.82 (m, 2 H, H^2 and H^4), 7.08 (ddd, 1 H, pyridyl, *J* = 7.5, 6.0 and 1.1 Hz), 7.27 (dd, 1 H, pyridyl, *J* = 7.8 and 1.1 Hz), 7.33 (dd, 1 H, H^5, *J* = 15.4 and 10.5 Hz), 7.56 (td, 1 H, pyridyl, *J* = 7.5 and 1.8 Hz), 8.54 (dd, 1 H, pyridyl, *J* = 6.0 and 1.8 Hz). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 109.47 (C^1), 121.92, 122.01, 130.46, 132.29, 132.37, 133.41, 135.49, 136.28, 149.58 (pyridyl), 155.11 (pyridyl). − MS (EI, 70 eV); *m/z* (rel. int.): 237 (6) [M^{+}·], 235 (6) [M^{+}·], 156 (75) [M − Br], 130 (100). − IR (KBr, neat): $\tilde{\nu}$ = 774, 998, 1300,1580, 3002−3078 cm^{-1}.

(1*Z*,3*E*,5*E*)-1-Bromo-6-(2-thienyl)hexa-1,3,5-triene (1ad): This compound (164 mg, yellow solid) was obtained from **4a** (261 mg, 1.10 mmol, 1.00 equiv.), $Pd(PPh_3)_4$ (60 mg, 0.05 mmol, 0.05 equiv.), and organozinc reagent **5d** (0.5 M in THF, 3.0 mL, 1.50 mmol, 1.36 equiv.). Yield 62%. − M.p. 76 °C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.14 (d, 1 H, H^1, *J* = 6.8 Hz), 6.45 (dd, 1 H, H^4, *J* = 14.4 and 10.1 Hz), 6.57 (dd, 1 H, H^3, *J* = 14.4 and 10.2 Hz), 6.65 (dd, 1 H, H^2, *J* = 10.2 and 6.8 Hz), 6.65 (dd, 1 H, H^5, *J* = 15.4 and 10.1 Hz), 6.74 (d, 1 H, H^6, *J* = 15.4 Hz), 6.93 (dd, 1 H, thienyl, *J* = 5.0 and 3.4 Hz), 6.97 (d, 1 H, thienyl, *J* = 3.4 Hz), 7.15 (d, 1 H, thienyl, *J* = 5.0 Hz). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 108.34 (C^1), 125.08 (thienyl), 126.53 (thienyl), 127.23 (C^6), 127.68 (thienyl), 128.06 (C^3), 128.29 (C^5), 132.49 (C^2), 135.87 (C^4), 142.48 (thienyl) (carbon attributed by 2D ^{1}H/^{13}C NMR). − MS (EI, 70 eV) *m/z* (rel. int.): 242 (20) [M^{+}·], 240 (20) [M^{+}·], 161 (90) [M − Br], 128 (100). − IR (KBr, neat): $\tilde{\nu}$ = 700, 810−852, 982, 1286, 1600, 3020−3076 cm^{-1}. − $C_{10}H_9BrS$ (241.15): calcd. C 49.81, H 3.76, S 13.29; found C 50.12, H 3.68, S 13.28.

(1*Z*,3*E*,5*E*)-1-Bromo-6-(2-furyl)hexa-1,3,5-triene (1ae): This compound (90 mg, very unstable brown oil, which polymerised rapidly) was obtained from **4a** (151 mg, 0.63 mmol, 1.00 equiv.), $Pd(PPh_3)_4$ (45 mg, 0.04 mmol, 0.06 equiv.), and organozinc reagent **5e** (0.5 M in THF, 2.0 mL, 1.00 mmol, 1.59 equiv.). Yield 63%. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.13 (d, 1 H, H^1, *J* = 6.7 Hz), 6.27 (d, 1 H, furyl, *J* = 3.3 Hz), 6.35 (dd, 1 H, furyl, *J* = 3.3 and 1.8 Hz), 6.39 (d, 1 H, H^6, *J* = 15.5 Hz), 6.45 (dd, 1 H, H^4, *J* = 14.3 and 11.0 Hz), 6.58 (dd, 1 H, H^3, *J* = 14.3 and 10.4 Hz), 6.65 (dd, 1 H, H^2, *J* = 10.4 and 6.7 Hz), 6.74 (dd, 1 H, H^5, *J* = 15.5 and 11.0 Hz), 7.34 (d, 1 H, furyl, *J* = 1.8 Hz). − MS (EI, 70 eV); *m/z* (rel. int.): 226 (20) [M^{+}·], 224 (20) [M^{+}·], 145 (40) [M − Br], 115 (100).

(1*Z*,3*E*,5*E*)-1-Bromo-7-phenylhepta-1,3,5-triene (1af): This compound (107 mg, yellow oil) was obtained from **4a** (158 mg, 0.66 mmol, 1.00 equiv.), $Pd(PPh_3)_4$ (45 mg, 0.04 mmol, 0.06 equiv.), and organozinc reagent **5f** (0.5 M in THF, 2.5 mL, 1.25 mmol, 1.89 equiv.). Yield 65%. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.42 (d, 2 H, H^7, *J* = 7.0 Hz), 5.95 (dt, 1 H, H^6, *J* = 15.0 and 7.1 Hz), 6.09 (d, 1 H, H^1, *J* = 7.0 Hz), 6.17 (dd, 1 H, H^5, *J* = 15.0 and 9.9 Hz), 6.37 (dd, 1 H, H^4, *J* = 14.8 and 9.9 Hz), 6.44 (dd, 1 H, H^3, *J* = 14.8 and 9.7 Hz), 6.60 (dd, 1 H, H^2, *J* = 9.7 and 7.0 Hz), 7.14 to 7.29 (m, 5 H, phenyl). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.20 (C^7), 126.21, 126.66, 128.30 (2 C, phenyl), 128.48 (2 C, phenyl), 130.28, 131.25, 132.55, 135.80, 136.23, 139.63 (phenyl). − MS (EI, 70 eV); *m/z* (rel. int.): 226 (5) [M^{+}·], 224 (5) [M^{+}·], 91 (100) [$C_6H_5-CH_2$]. − IR (NaCl, neat): $\tilde{\nu}$ = 698, 748, 990, 1452−1494, 1602, 2922, 3024 cm^{-1}.

(1*Z*,3*E*,5*E*)-1-Bromoundeca-1,3,5-triene (1ag): This compound (127 mg, yellow oil) was obtained from **4a** (240 mg, 1.00 mmol, 1.00 equiv.), $Pd(PPh_3)_4$ (70 mg, 0.06 mmol, 0.06 equiv.), and organozinc reagent **5g** (0.4 M in THF, 3.5 mL, 1.40 mmol, 1.40 equiv.). Yield 55%. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83 (t, 3 H, H^{11}, *J* = 6.9 Hz), 1.18 to 1.39 (m, 6 H, H^8, H^9 and H^{10}), 2.05 (dt, 2 H, H^7, *J* = 7.2 and 7.1 Hz), 5.78 (dt, 1 H, H^6, *J* = 15.0 and 7.2 Hz), 6.04 (d, 1 H, H^1, *J* = 7.1 Hz), 6.10 (dd, 1 H, H^5, *J* = 15.0 and 9.8 Hz), 6.32 (dd, 1 H, H^4, *J* = 15.0 and 9.8 Hz), 6.37 (dd, 1 H, H^3, *J* = 15.0 and 9.4 Hz), 6.57 (dd, 1 H, H^2, *J* = 9.4 and 7.1 Hz). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.88 (C^{11}), 22.44, 28.67, 31.32, 32.80, 112.21 (C^1), 125.62, 130.28, 132.66, 136.79, 138.17. − MS (EI, 70 eV); *m/z* (rel. int.): 230 (5) [M^{+}·], 228 (5) [M^{+}·], 160−158 (5), 91 (60), 79 (100). − IR (NaCl, neat): $\tilde{\nu}$ = 694, 988, 1322, 1462, 1684, 2858−2928 cm^{-1}.

(5*E*,7*E*,9*Z*)-10-Bromodeca-5,7,9-trienyl Acetate (1ah): This compound (61 mg, yellow oil) was obtained from **4a** (88 mg, 0.37 mmol, 1.00 equiv.), $Pd(PPh_3)_4$ (21 mg, 0.02 mmol, 0.05 equiv.), and organozinc reagent **5h** (0.35 M in THF, 3.1 mL, 1.10 mmol, 2.97 equiv.). Yield 61%. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42 (m, 2 H, H^3), 1.58 (m, 2 H, H^2), 1.98 (s, 3 H, C*H*$_3$), 2.09 (q, 2 H, H^4, *J* = 7.0 Hz), 4.00 (t, 2 H, H^1, *J* = 6.6 Hz), 5.75 (dt, 1 H, H^5, *J* = 15.1 and 7.0 Hz), 6.06 (d, 1 H, H^{10}, *J* = 7.1 Hz), 6.10 (dd, 1 H, H^6, *J* = 15.1 and 10.0 Hz), 6.31 (dd, 1 H, H^7, *J* = 15.0 and 10.0 Hz), 6.38 (dd, 1 H, H^8, *J* = 15.0 and 9.6 Hz), 6.57 (dd, 1 H, H^9, *J* = 9.6 and 7.1 Hz). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.92 (*C*H$_3$), 25.26, 27.99, 30.26, 64.23 (C^1), 107.35 (C^{10}), 126.00, 130.59, 132.53, 136.43, 136.96, 171.11 (CH$_3$*C*OO). − MS (EI, 70 eV); *m/z* (rel. int.): 274 (5) [M^{+}·], 272 (5) [M^{+}·], 186 (10) [M − H_3C-COO], 184 (10) [M − H_3C-COO], 105 (80), 91 (100). − IR (NaCl, neat): $\tilde{\nu}$ = 690, 992, 1046, 1240, 1366, 1738, 2934 cm^{-1}. − $C_{12}H_{17}BrO_2$ (273.17): calcd. C 52.76, H 6.27; found C 52.72, H 6.25.

(1*Z*,3*E*,5*E*)-1-Bromo-10-chlorodeca-1,3,5-triene (1ai): This compound (106 mg, yellow oil) was obtained from **4a** (215 mg, 0.90 mmol, 1.00 equiv.), $Pd(PPh_3)_4$ (52 mg 0.04 mmol, 0.08 equiv.), and organozinc reagent **5i** (0.5 M in THF, 9.0 mL, 4.50 mmol, 5.00 equiv.). Yield 47%. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.51 (m, 2 H, H^9), 1.73 (m, 2 H, H^8), 2.10 (td, 2 H, H^7, *J* = 7.3 and 7.1 Hz), 3.48 (t, 2 H, H^{10}, *J* = 6.7 Hz), 5.75 (dt, 1 H, H^6, *J* = 15.2 and 7.1 Hz), 6.07 (d, 1 H, H^1, *J* = 7.1 Hz), 6.11 (dd, 1 H, H^5, *J* = 15.2 and 9.8 Hz), 6.31 (dd, 1 H, H^4, *J* = 15.0 and 9.8 Hz), 6.38 (dd, 1 H, H^3, *J* = 15.0 and 9.5 Hz), 6.57 (dd, H^2, *J* = 9.5 and 7.1 Hz). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.15, 31.91, 31.98, 44.80, 107.42, 126.08, 130.70, 132.55, 136.42, 136.81. − MS (EI, 70 eV); *m/z* (rel. int.): 250(5) [M^{+}·], 248 (5) [M^{+}·], 91 (100). − IR (NaCl, neat): $\tilde{\nu}$ = 690, 990, 1318, 2934−2860 cm^{-1}.

12-Bromo-1,1-diethoxidodeca-3,5,7,9,11-pentaene (1aj): This compound was obtained (229 mg, red oil) as a mixture of 3*E*,5*E*,7*E*,9*E*,11*E* and 3*E*,5*Z*,7*E*,9*E*,11*E* isomers, from **4a** (357 mg, 1.50 mmol, 1.00 equiv.), $Pd(PPh_3)_4$ (87 mg, 0.08 mmol, 0.05 equiv.), and organozinc reagent **5j** (0.15 M in THF, 13.0 mL, 1.95 mmol, 1.30 equiv.). Yield 47%. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (t, 6 H, OCH_2CH_3, *J* = 7.0 Hz); 2.41 to 2.48 (m, 2 H, H^2); 3.46 to 3.52 (m, 2 H, OCH_2CH_3); 3.61 to 3.70 (m, 2 H, OCH_2CH_3); 4.50 (t, 1 H, H^1, *J* = 5.7 Hz); 5.68 to 5.82 (m, 1 H, H^3); 5.92 à 6.79 (m, 8 H, H^4, H^5, H^6, H^7, H^8, H^9, H^{10} and H^{12}); 6.66 (dd, 1 H, H^{11}, *J* = 9.6 and 7.2 Hz). − MS (EI, 70 eV); *m/z* (rel. int.): 282 (2) [M − EtOH], 280 (2) [M − EtOH], 103 (100), 75 (50).

(3*E*,5*E*,7*Z*)-Methyl-8-bromoocta-3,5,7-trienoate (1ak): This compound (26 mg, yellow oil) was obtained from **4a** (120 mg, 0.50 mmol, 1.00 equiv.), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol, 0.06 equiv.), and organozinc reagent **5k** (1.6 M in THF, 1.0 mL, 1.60 mmol, 3.20 equiv.). Yield 22%. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.10 (d, 2 H, H^2, J = 7.4 Hz), 3.62 (s, 3 H, CH_3), 5.94 (dt, 1 H, H^3, J = 15.0 and 7.4 Hz), 6.11 (d, 1 H, H^8, J = 7.1 Hz), 6.19 (dd, 1 H, H^4, J = 15.0 and 10.2 Hz), 6.34 (dd, 1 H, H^5, J = 14.9 and 10.2 Hz), 6.44 (dd, 1 H, H^6, J = 14.9 and 10.0 Hz), 6.58 (dd, 1 H, H^7, J = 10.0 and 7.1 Hz). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 37.92 (CH_3), 51.88 (C^2), 108.43 (C^8), 127.48, 127.70, 132.31, 133.47, 135.40, 173.25 (C^1). − MS (EI, 70 eV); *m*/*z* (rel. int.): 232 (5) [$M^{+\cdot}$], 230 (5) [$M^{+\cdot}$], 173 (2) [M − $COOCH_3$], 171 (2) [M − $COOCH_3$], 91 (100), 59 (15) [$COOCH_3$]. − IR (NaCl, neat): $\tilde{\nu}$ = 692, 990, 1260, 1740, 2920 cm^{-1}.

(1*Z*,3*E*,5*E*)-1-Bromotrideca-1,3,5-trien-7-yne (1al): This compound (115 mg, colourless oil) was obtained from **4a** (175 mg, 0.74 mmol, 1.00 equiv.), $Pd(PPh_3)_4$ (42 mg, 0.04 mmol, 0.05 equiv.), and organozinc reagent **5l** (0.4 M in THF, 3.75 mL, 1.50 mmol, 2.03 equiv.). Yield 62%. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, 3 H, H^{13}, J = 7.1 Hz), 1.19 to 1.37 (m, 4 H, H^{12} and H^{11}), 1.49 (tt, 2 H, H^{10}, J = 7.4 and 7.1 Hz), 2.28 (dt, 2 H, H^9, J = 7.1 and 2.3 Hz), 5.66 (dt, 1 H, H^6, J = 15.3 and 2.3 Hz), 6.16 (d, 1 H, H^1, J = 7.0 Hz), 6.35 (dd, 1 H, H^4, J = 14.6 and 11.0 Hz), 6.49 (dd, 1 H, H^3, J = 10.3 and 14.6 Hz), 6.54 (dd, 1 H, H^5, J = 15.2 and 11.0 Hz), 6.59 (dd, 1 H, H^2, J = 10.3 and 7.0 Hz). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.93 (C^{13}), 19.68, 22.16, 28.32, 31.03, 79.97 (C^8), 95.54 (C^7), 109.31 (C^1), 114.21 (C^6), 128.84, 132.25, 135.40, 139.78. − MS (EI, 70 eV); *m*/*z* (rel. int.): 254 (35) [$M^{+\cdot}$], 252 (35) [$M^{+\cdot}$], 115 (100). − IR (NaCl, neat): $\tilde{\nu}$ = 684−702, 984, 1334, 1604, 2206, 2930−2858 cm^{-1}.

(1*Z*,3*E*,5*E*)-1-Bromo-8-(trimethylsilyl)-octa-1,3,5-trien-7-yne (1am): This compound (34 mg, colourless oil) was obtained from **4a** (146 mg, 0.61 mmol, 1.00 equiv.), $Pd(PPh_3)_4$ (44 mg, 0.04 mmol, 0.07 equiv.), and organozinc reagent **5m** (0.4 M in THF, 3.4 mL, 1.36 mmol, 2.22 equiv.). Yield 22%. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.14 (s, 9 H, CH_3), 5.66 (d, 1 H, H^6, J = 15.5 Hz), 6.21 (d, 1 H, H^1, J = 6.4 Hz), 6.36 (dd, 1 H, H^4, J = 13.8 and 11.1 Hz), 6.54 (dd, 1 H, H^3, J = 13.8 and 10.4 Hz), 6.60 (dd, 1 H, H^2, J = 10.4 and 6.4 Hz), 6.66 (dd, 1 H, H^5, J = 15.5 and 11.1 Hz). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = −0.21 (3 C, CH_3), 99.29 (C^7 or C^8), 104.29 (C^8 or C^7), 110.29 (C^1), 113.02 (C^6), 130.25, 132.08, 134.93, 142.07. − MS (EI, 70 eV); *m*/*z* (rel. int.): 256 (75) [$M^{+\cdot}$], 254 (75) [$M^{+\cdot}$], 241 (70) [M − CH_3], 239 (70) [M − CH_3], 175 (95) [M − Br], 159 (95), 73 (100) [$Si(CH_3)_3$]. − IR (NaCl, neat): $\tilde{\nu}$ = 694, 844, 984, 1250, 2130, 2958 cm^{-1}.

(1*E*,3*E*,5*E*)-1-Bromo-6-phenylhexa-1,3,5-triene (1ba): This compound (81 mg, yellow solid) was obtained from **4b** (178 mg, 0.75 mmol, 1.00 equiv.), $Pd(PPh_3)_4$ (60 mg, 0.05 mmol, 0.07 equiv.), and organozinc reagent **5a** (0.5 M in THF, 3.0 mL, 1.50 mmol, 2.00 equiv.). Yield 46%. − M.p. 99 °C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.18 (dd, 1 H, H^3, J = 14.9 and 11.0 Hz), 6.30 (d, 1 H, H^1, J = 13.8 Hz), 6.35 (dd, 1 H, H^4, J = 14.9 and 10.5 Hz), 6.57 (d, 1 H, H^6, J = 15.5 Hz), 6.72 (dd, 1 H, H^5, J = 15.5 and 10.5 Hz), 6.74 (dd, 1 H, H^2, J = 13.8 and 11.0 Hz), 7.16 to 7.38 (m, 5 H, phenyl). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 108.79 (C^1), 126.46 (2 C, phenyl), 127.79, 128.18, 128.64 (2 C, phenyl), 129.84, 133.81, 134.01, 137.54, 139.35 (phenyl). − MS (EI, 70 eV); *m*/*z* (rel. int.): 236 (15) [$M^{+\cdot}$], 234 (15) [$M^{+\cdot}$], 155 (100) [M − Br]. − IR (KBr, neat): $\tilde{\nu}$ = 692, 740, 992, 1446, 1448, 1560, 1614, 1728, 1876, 1954, 3066 cm^{-1}. − $C_{12}H_{11}Br$ (235.12): calcd. C 61.30, H 4.72; found C 61.23, H 4.82.

(1*E*,3*E*,5*E*)-1-Bromo-6-(4-methoxyphenyl)hexa-1,3,5-triene (1bb): This compound (77 mg, yellow solid) was obtained from **4b** (127 mg, 0.53 mmol, 1.00 equiv.), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol, 0.06 equiv.), and organozinc reagent **5b** (0.4 M in THF, 2.5 mL, 1.00 mmol, 1.89 equiv.). Yield 54%. − M.p. 133 °C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.76 (s, 3 H, OCH_3), 6.13 (dd, 1 H, H^3, J = 14.9 and 11.0 Hz), 6.26 (d, 1 H, H^1, J = 13.5 Hz), 6.33 (dd, 1 H, H^4, J = 14.9 and 9.8 Hz), 6.52 (d, 1 H, H^6, J = 15.5 Hz), 6.59 (dd, 1 H, H^5, J = 15.5 and 9.8 Hz), 6.73 (dd, 1 H, H^2, J = 13.5 and 11.0 Hz), 6.80 (d, 2 H, phenyl, J = 8.7 Hz), 7.28 (d, 2 H, phenyl, J = 8.7 Hz). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.25 (OCH_3), 108.10 (C^1), 114.13 (2 C, phenyl), 126.21, 127.68 (2 C, phenyl), 128.75, 129.87 (phenyl), 133.67, 134.16, 137.68, 159.45 (phenyl). − MS (EI, 70 eV); *m*/*z* (rel. int.): 266 (15) [$M^{+\cdot}$], 264 (15) [$M^{+\cdot}$], 185 (100) [M − Br]. − IR (KBr, neat): $\tilde{\nu}$ = 740, 760, 996, 1258, 1596, 2840−3062 cm^{-1}. − $C_{13}H_{13}BrO$ (265.15): calcd. C 58.89, H 4.94; found C 58.93, H 5.12.

(1*E*,3*E*,5*E*)-1-Bromoundeca-1,3,5-triene (1bg): This compound (85 mg, yellow oil) was obtained from **4b** (220 mg, 0.92 mmol, 1.00 equiv.), $Pd(PPh_3)_4$ (53 mg, 0.05 mmol, 0.05 equiv.), and organozinc reagent **5g** (0.5 M in THF, 4.5 mL, 2.25 mmol, 2.45 equiv.). Yield 40%. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.86 (t, 3 H, H^{11}, J = 6.6 Hz), 1.20 to 1.41 (m, 6 H, H^8, H^9 and H^{10}), 2.06 (q, 2 H, H^7, J = 6.8 Hz), 5.78 (dt, 1 H, H^6, J = 15.1 and 6.8 Hz), 5.99 (dd, 1 H, H^5, J = 15.1 and 10.4 Hz), 6.01 (dd, 1 H, H^3, J = 14.7 and 10.9 Hz), 6.20 (dd, 1 H, H^4, J = 14.7 and 10.4 Hz), 6.22 (d, 1 H, H^1, J = 13.4 Hz), 6.69 (dd, 1 H, H^2, J = 13.4 and 10.9 Hz). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.89 (C^{11}), 22.36, 28.88, 31.28, 32.73, 107.19 (C^1), 127.09, 129.59, 134.02, 137.39, 137.54. − MS (EI, 70 eV); *m*/*z* (rel. int.): 230 (5) [$M^{+\cdot}$], 228 (5) [$M^{+\cdot}$], 160−158 (5), 91 (60), 79 (100). − IR (NaCl, neat): $\tilde{\nu}$ = 734, 990, 1378, 1462, 1686, 2856−2926 cm^{-1}.

(1*E*,3*E*,5*E*)-1-Bromododeca-1,3,5-triene (1bn): This compound (49 mg, yellow oil) was obtained from **4b** (104 mg, 0.44 mmol, 1.00 equiv.), $Pd(PPh_3)_4$ (38 mg, 0.03 mmol, 0.07 equiv.), and organozinc reagent **5n** (0.5 M in THF, 2.0 mL, 1.00 mmol, 2.30 equiv.). Yield 46%. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.87 (t, 3 H, H^{12}, J = 6.8 Hz), 1.16 to 1.42 (m, 8 H, H^8, H^9, H^{10} and H^{11}), 2.07 (q, 2 H, H^7, J = 6.8 Hz), 5.78 (dt, 1 H, H^6, J = 15.2 and 6.8 Hz), 5.99 (dd, 1 H, H^5, J = 14.9 and 10.7 Hz), 6.01 (dd, 1 H, H^3, J = 14.9 and 10.8 Hz), 6.20 (dd, 1 H, H^4, J = 14.9 and 10.7 Hz), 6.23 (d, 1 H, H^1, J = 13.5 Hz), 6.70 (dd, 1 H, H^2, J = 13.5 and 10.8 Hz). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.01 (C^{12}), 21.51, 28.79, 28.99, 31.61, 32.75, 107.25 (C^1), 127.12, 129.59, 134.10, 137.49, 137.63. − MS (EI, 70 eV); *m*/*z* (rel. int.): 244 (20) [$M^{+\cdot}$], 242 (20) [$M^{+\cdot}$], 160−158 (20), 91 (95), 79 (100). − IR (NaCl, neat): $\tilde{\nu}$ = 692, 986, 1316, 1460, 2854−2926−2956 cm^{-1}.

(1*Z*,3*E*,5*Z*)-1-Bromo-6-phenylhexa-1,3,5-triene (1ca): This compound (146 mg, yellow oil) was obtained from **4c** (241 mg, 1.01 mmol, 1.00 equiv.), $Pd(PPh_3)_4$ (60 mg, 0.05 mmol, 0.05 equiv.), and organozinc reagent **5a** (0.5 M in THF, 4.0 mL, 2.00 mmol, 1.98 equiv.). Yield 61%. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.21 (d, 1 H, H^1, J = 5.3 Hz), 6.38 (dd, 1 H, H^5, J = 11.3 and 11.2 Hz), 6.61 (d, 1 H, H^6, J = 11.3 Hz), 6.65 to 6.79 (m, 2 H, H^2 and H^3), 6.98 (dd, 1 H, H^4, J = 14.5 and 11.2 Hz), 7.24 to 7.51 (m, 5 H, phenyl). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 109.60 (C^1), 128.11, 129.17 (2 C, phenyl), 129.81(2 C, phenyl), 130.60, 131.09, 133.04, 133.30, 133.47, 138.12 (phenyl). − MS (EI, 70 eV) *m*/*z* (rel. int.): 236 ($M^{+\cdot}$, 15%), 234 ($M^{+\cdot}$, 15%), 155 (M − Br, 100%). − IR (NaCl, neat): $\tilde{\nu}$ = 700, 992, 1322, 1410, 1444, 1490, 1598, 3022−3078 cm^{-1}.

(1*Z*,3*E*,5*Z*)-1-Bromo-6-(4-methoxyphenyl)hexa-1,3,5-triene (1cb): This compound (85 mg, red oil) was obtained from **4c** (121 mg,

0.51 mmol, 1.00 equiv.), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol, 0.06 equiv.), and organozinc reagent **5b** (0.4 M in THF, 3.0 mL, 1.20 mmol, 2.35 equiv.). Yield 63%. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.77 (s, 3 H, OCH_3), 6.13 (d, 1 H, H^1, *J* = 6.5 Hz), 6.22 (dd, 1 H, H^5, *J* = 12.0 and 11.4 Hz), 6.46 (d, 1 H, H^6, *J* = 11.4 Hz), 6.60 (dd, 1 H, H^3, *J* = 12.8 and 10.2 Hz), 6.64 (dd, 1 H, H^2, *J* = 10.2 and 6.5 Hz), 6.81 (d, 2 H, phenyl, *J* = 8.7 Hz), 6.90 (dd, 1 H, H^4, *J* = 12.8 and 12.0 Hz), 7.31 (d, 2 H, phenyl, *J* = 8.7 Hz). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.25 (O*C*H$_3$), 108.39 (C^1), 113.80 (2 C, phenyl), 128.28, 129.60, 129.95 (phenyl), 130.29 (2 C, phenyl), 131.81, 132.70 (2 C), 158.93 (phenyl). − MS (EI, 70 eV); *m*/*z* (rel. int.): 266 (15) [M$^+$·], 264 (15) [M$^+$·], 185 (100) [M − Br], 100). − IR (KBr, neat): $\tilde{\nu}$ = 700, 996, 1252, 1508, 1600, 2836−3082 cm^{-1}.

(1*Z*,3*E*,5*Z*)-1-Bromoundeca-1,3,5-triene (1cg): This compound (68 mg, yellow oil) was obtained from **4c** (122 mg, 0.51 mmol, 1.00 equiv.), $Pd(PPh_3)_4$ (50 mg, 0.04 mmol, 0.08 equiv.), and organozinc reagent **5g** (0.4 M in THF, 1.3 mL, 0.52 mmol, 1.02 equiv.). Yield 58%. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.87 (t, 3 H, H^{11}, *J* = 6.7 Hz), 1.23 to 1.54 (m, 6 H, H^8, H^9 and H^{10}), 2.18 (dt, 2 H, H^7, *J* = 7.7 and 6.8 Hz), 5.59 (dt, 1 H, H^6, *J* = 10.7 and 7.7 Hz), 6.09 (dd, 1 H, H^5, *J* = 10.8 and 10.0 Hz), 6.13 (d, 1 H, H^1, *J* = 7.4 Hz), 6.47 (dd, 1 H, H^4, *J* = 15.0 and 10.0 Hz), 6.68 (dd, 1 H, H^2, *J* = 9.9 and 7.4 Hz), 6.69 (dd, 1 H, H^3, *J* = 15.0 and 9.9 Hz). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.04 (C^{11}), 22.57, 28.06, 29.28, 31.54, 108.32 (C^1), 128.22, 128.98, 132.49, 133.54, 136.32. − MS (EI, 70 eV); *m*/*z* (rel. int.): 230 (5) [M$^+$·], 228 (5) [M$^+$·], 160−158 (5), 91 (60), 79 (100). − IR (NaCl, neat): $\tilde{\nu}$ = 700, 986, 1316, 1460, 1610, 2854−2924 cm^{-1}.

Double Coupling Reactions: Syntheses of Symmetrical Double Coupling Compounds 2

General Procedure for the Palladium-Catalysed Cross-Coupling Reaction between 1,6-Dibromohexa-1,3,5-triene 4 and Organozinc Reagents 5: At room temperature and under argon, an excess of a solution of organozinc reagent **5** was added to a stirred solution of 1,6-dibromohexa-1,3,5-triene **4** and $Pd(PPh_3)_4$ in THF (5 mL) or toluene (5 mL; for compounds 2ad, 2ae, 2cd and 2ce). After 20 min, the mixture was hydrolysed using aqueous $NaHCO_3$ (20 mL, 5%) and extracted with pentane (3 × 15 mL). The organic layers were combined, dried over $MgSO_4$ and evaporated. The residue was purified by silica gel column chromatography.

General Procedure for Organozinc Reagents 5d and 5e in Toluene: Organozinc reagents **5d** and **5e** (0.5 M) were first prepared in THF, from thiophene and furan, by metallation with *n*-butyllithium followed by transmetallation with zinc dibromide.[16] Then, toluene was added in volume equivalent to that of THF, and the THF was evaporated off by vacuum pump, with stirring. The volume of organozinc solution was made up with toluene to obtain a 0.5 M solution.

(1*E*,3*E*,5*Z*)-1,6-Diphenylhexa-1,3,5-triene (2aa): This compound (210 mg, yellow solid) was obtained from **4a** (241 mg, 1.01 mmol, 1.0 equiv.) and $Pd(PPh_3)_4$ (120 mg, 0.10 mmol, 0.1 equiv.) in THF (5 mL), and organozinc reagent **5a** (0.35 M in THF, 8.0 mL, 2.80 mmol, 2.8 equiv.). Yield 89%. − M.p. 194 °C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.29 (dd, 1 H, H^5, *J* = 11.6 and 11.3 Hz), 6.42 (d, 1 H, H^6, *J* = 11.6 Hz), 6.49 (dd, 1 H, H^3, *J* = 14.8 and 10.7 Hz), 6.55 (d, 1 H, H^1, *J* = 15.8 Hz), 6.81 (dd, 1 H, H^2, *J* = 15.8 and 10.7 Hz), 6.86 (dd, 1 H, H^4, *J* = 14.8 Hz; *J* = 11.3 Hz), 7.13 to 7.38 (m, 10 H, phenyl). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.55 (2 C), 127.14, 127.70, 128.43 (2 C), 128.73 (2 C), 129.13 (2 C), 129.24, 129.66, 130.29, 130.39, 133.26, 135.76, 137.40 (phenyl); 137.78 (phenyl). MS (EI, 70 eV); *m*/*z* (rel. int.): 232 (55) [M$^+$·], 215 (10), 141 (45), 128 (35), 115 (40), 91 (100). − IR (KBr, neat): $\tilde{\nu}$ = 692, 750, 998, 1446, 1490, 1752, 1824, 1890, 1948, 3012 cm^{-1}.

(1*E*,3*E*,5*Z*)-1,6-Bis(4-methoxyphenyl)hexa-1,3,5-triene (2ab): This compound (280 mg, yellow solid) was obtained from **4a** (242 mg, 1.02 mmol, 1.00 equiv.) and $Pd(PPh_3)_4$ (100 mg, 0.09 mmol, 0.09 equiv.) in THF (5 mL), and organozinc reagent **5b** (0.5 M in THF, 5.0 mL, 4.00 mmol, 3.92 equiv.). Yield 94%. − M.p. 86 °C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.80 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 6.23 (dd, 1 H, H^5, *J* = 11.3 and 11.1 Hz), 6.36 (d, 1 H, H^6, *J* = 11.3 Hz), 6.48 (dd, 1 H, H^3, *J* = 15.4 and 9.5 Hz), 6.52 (d, 1 H, H^1, *J* = 15.5 Hz), 6.74 (dd, 1 H, H^2, *J* = 15.5 and 9.3 Hz), 6.84 (d, 2 H, phenyl, *J* = 8.8 Hz), 6.86 (dd, 1 H, H^4, *J* = 15.4 and 11.1 Hz), 6.89 (d, 2 H, phenyl, *J* = 8.9 Hz), 7.30 (d, 2 H, phenyl, *J* = 8.8 Hz), 7.33 (d, 2 H, phenyl, *J* = 8.9 Hz). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.26 (2 C, O*C*H$_3$), 113.69 (2 C, phenyl), 114.05 (2 C, phenyl), 127.20, 127.55 (2 C, phenyl), 128.64, 128.87, 129.09, 130.15 (phenyl), 130.18 (2 C, phenyl), 130.41 (phenyl), 132.28, 135.23, 157.55 (phenyl), 158.55 (phenyl). MS (EI, 70 eV); *m*/*z* (rel. int.): 292 (26) [M$^+$·], 121 (100). − IR (KBr, neat): $\tilde{\nu}$ = 774, 838, 1032, 1252, 1440, 1506, 1602, 1734, 1890, 2056, 2838−3006 cm^{-1}.

(1*E*,3*E*,5*Z*)-1,6-Bis(2-pyridyl)hexa-1,3,5-triene (2ac): This compound (114 mg, yellow solid) was obtained from **4a** (194 mg, 0.82 mmol, 1.00 equiv.) and $Pd(PPh_3)_4$ (55 mg, 0.05 mmol, 0.06 equiv.) in THF (5 mL), and organozinc reagent **5c** (0.35 M in THF, 8.0 mL, 2.80 mmol, 3.41 equiv.). Yield 59%. − M.p. 72 °C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.34 (d, 1 H, H^6, *J* = 11.6 Hz), 6.44 (dd, 1 H, H^5, *J* = 11.6 and 10.3 Hz), 6.58 (dd, 1 H, H^3, *J* = 14.9 and 11.2 Hz), 6.64 (d, 1 H, H^1, *J* = 15.3 Hz), 7.00 to 7.08 (m, 2 H, pyridyl), 7.17 and 7.23 (2 d, 2 H, pyridyl, *J* = 7.9 Hz), 7.42 (dd, 1 H, H^2, *J* = 15.3 and 11.2 Hz), 7.50 à 7.61 (m, 2 H, pyridyl), 7.95 (dd, 1 H, H^4, *J* = 14.9 and 10.3 Hz), 8.51 and 8.59 (2 d, 2 H, pyridyl, *J* = 4.8 Hz). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 121.30, 121.85, 122.04, 124.62, 128.73, 132.61, 133.19, 133.31 (2 C), 135.99, 136.31, 136.60, 149.35 (pyridyl), 149.62 (pyridyl), 155.49 (pyridyl), 156.47 (pyridyl). − MS (EI, 70 eV); *m*/*z* (rel. int.): 234 (60) [M$^+$·], 233 (100) [M − H], 156 (50) [M − C_5H_4N], 154 (85), 130 (55), 117 (65), 78 (10) [C_5H_4N]. − IR (KBr, neat): $\tilde{\nu}$ = 812, 1004, 1428, 1468, 1582, 3000 cm^{-1}. − $C_{16}H_{14}N_2$ (234.30): calcd.C 82.02, H 6.02, N 11.96; found C 81.54, H 5.94, N 11.92.

(1*E*,3*E*,5*Z*)-1,6-Bis(2-thienyl)hexa-1,3,5-triene (2ad): This compound (88 mg, orange solid) was obtained from **4a** (100 mg, 0.42 mmol, 1.00 equiv.) and $Pd(PPh_3)_4$ (24 mg, 0.02 mmol, 0.05 equiv.) in toluene (5 mL), and organozinc reagent **5d** (0.5 M in toluene, 3.0 mL, 1.50 mmol, 3.57 equiv.). Yield 85%. − M.p. 217 °C. − ^{1}H NMR (200 MHz, C_6D_6): δ = 6.06 (dd, 1 H, H^5, *J* = 11.5 and 10.8 Hz), 6.28 (dd, 1 H, H^3, *J* = 14.4 and 11.0 Hz), 6.36 (d, 1 H, H^6, *J* = 10.8 Hz), 6.49 (d, 1 H, H^1, *J* = 15.4), 6.64 to 6.86 (m, 5 H, H^2 and thienyl), 7.16 (m, 2 H, thienyl), 7.21 (dd, 1 H, H^4, *J* = 14.4 and 11.5 Hz). − ^{13}C NMR (50 MHz, C_6D_6): δ = 122.37, 124.99, 126.18, 126.50, 126.79, 127.21, 127.82, 128.18, 129.17, 129.29, 129.77, 135.91, 140.42 (thienyl), 141.08 (thienyl). − MS (EI, 70 eV); *m*/*z* (rel. int.): 244 (100) [M$^+$·], 147 (40), 97 (90). − IR (KBr, neat): $\tilde{\nu}$ = 700, 772, 994, 3012−3098 cm^{-1}. − $C_{14}H_{12}S_2$ (244.37): calcd. C 68.81, H 4.95, S 26.24; found C 68.78, H 4.96, S 26.14.

(1*E*,3*E*,5*Z*)-1,6-Bis(2-furyl)hexa-1,3,5-triene (2ae): This compound (128 mg, yellow solid) was obtained from **4a** (177 mg, 0.74 mmol, 1.00 equiv.) and $Pd(PPh_3)_4$ (40 mg, 0.03 mmol, 0.04 equiv.) in toluene (5 mL), and organozinc reagent **5e** (0.5 M in toluene, 5.0 mL, 2.50 mmol, 3.38 equiv.). Yield 81%. − M.p. 48 °C. − ^{1}H NMR

(200 MHz, C_6D_6): δ = 5.96 (d, 1 H, H^6, *J* = 11.3 Hz); 5.97 to 6.06 (m, 5 H, furyl); 6.22 (d, 1 H, H^1, *J* = 15.5 Hz); 6.28 (dd, 1 H, H^3, *J* = 14.6 and 11.1 Hz); 6.98 (dd, 1 H, H^2, *J* = 15.5 and 11.1 Hz); 7.02 (m, 1 H, furyl); 7.05 (m, 1 H, furyl); 7.54 (dd, 1 H, H^4, *J* = 14.6 and 9.6 Hz). − ^{13}C NMR (50 MHz, C_6D_6): δ = 109.06, 111.14, 111.67, 112.02, 116.61, 120.92, 127.45, 128.35, 131.50, 135.76, 142.54 (furyl), 142.71 (furyl), 153.85 (furyl), 154.38 (furyl). MS (EI, 70 eV); *m*/*z* (rel. int.): 212 (100) [M^+·]. − IR (KBr, neat): $\tilde{\nu}$ = 736, 994, 1482, 3038, 3146 cm^{-1}. − $C_{14}H_{12}O_2$ (212.25): calcd. C 79.23, H 5.70; found C 79.65, H 5.45.

(6*E*,8*E*,10*Z*)-Hexadeca-6,8,10-triene (2ag): This compound (128 mg, colourless oil) was obtained from **4a** (238 mg, 1.0 mmol, 1.0 equiv.) and $Pd(PPh_3)_4$ (120 mg, 0.1 mmol, 0.1 equiv.) in THF (5 mL), and organozinc reagent **5g** (0.5 M in THF, 5.0 mL, 2.5 mmol, 2.5 equiv.). Yield 58%. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83 (t, 6 H, H^1 and H^{16}, *J* = 6.8 Hz), 1.18 to 1.38 (m, 12 H, H^2, H^3, H^4, H^{13}, H^{14} and H^{15}), 2.03 (q, 2 H, H^5, *J* = 7.0 Hz), 2.12 (dt, 2 H, H^{12}, *J* = 7.7 and 7.0), 5.35 (dt, 1 H, H^{11}, *J* = 10.5 and 7.7 Hz), 5.69 (dt, 1 H, H^6, *J* = 14.3 and 7.0 Hz), 5.94 (dd, 1 H, H^{10}, *J* = 11.4 and 10.5 Hz), 6.05 (dd, 1 H, H^7, *J* = 14.3 and 10.7 Hz), 6.11 (dd, 1 H^8, *J* = 14.0 and 10.7 Hz), 6.33 (dd, 1 H, H^9, *J* = 14.0 and 11.4 Hz). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.96 (2 C, C^1 and C^{16}); 22.47 (2 C), 27.75, 28.93, 29.32, 31.34, 31.42, 32.72, 125.95, 128.57, 130.50, 131.94, 132.70, 135.12. − MS (EI, 70 eV); *m*/*z* (rel. int.): 220 (40) [M^+·], 93 (100). − IR (NaCl, neat): $\tilde{\nu}$ = 730, 990, 1466, 2926 cm^{-1}.

(8*E*,10*E*,12*Z*)-Eicosa-8,10,12-triene-6,14-diyne (2al): This compound (15 mg, colourless oil) was obtained from **4a** (175 mg, 0.74 mmol, 1.00 equiv.), $Pd(PPh_3)_4$ (42 mg, 0.04 mmol, 0.05 equiv.), and organozinc reagent **5l** (0.4 M in THF, 3.75 mL, 1.50 mmol, 2.03 equiv.). Yield 7%. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.89 and 0.90 (2t, 6 H, H^1 and H^{20}, *J* = 6.8 and 6.3 Hz), 1.19 to 1.37 (m, 8 H, H^2, H^3, H^{18} and H^{19}), 1.45 to 1.59 (m, 4 H, H^4 and H^{17}), 2.32 (dt, 1 H, H^5, *J* = 7.1 and 2.4 Hz), 2.38 (dt, 1 H, H^{16}, *J* = 7.0 and 2.4 Hz), 5.45 (dt, 1 H, H^{13}, *J* = 10.1 and 2.4 Hz), 5.64 (dt, 1 H, H^8, *J* = 15.4 and 2.4 Hz), 6.31 (dd, 1 H, H^{12}, *J* = 11.0 and 10.1 Hz), 6.31 (dd, 1 H, H^{11}, *J* = 14.8 and 11.0 Hz), 6.59 (dd, 1 H, H^9, *J* = 15.4 and 11.2 Hz), 6.74 (dd, 1 H, H^{10}, *J* = 14.8 and 11.2 Hz). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.93 (2 C, C^1 and C^{20}), 19.65, 19.71, 22.13 (2 C), 28.36, 28.40, 31.00, 31.03, 77.80 (C^6 or C^{15}), 80.12 (C^{15} or C^6), 95.14 (C^{14}), 98.60 (C^7), 110.93 (C^{13}), 113.20 (C^8), 130.97, 133.87, 138.13, 140.33. − MS (EI, 70 eV); *m*/*z* (rel. int.): 268 (70) [M^+·], 211 (30), 155 (100). − IR (NaCl, neat): $\tilde{\nu}$ = 726−752, 990, 1328, 1462, 2204, 2858−2956 cm^{-1}.

(3*E*,5*E*,7*Z*)-1,10-Bis(trimethylsilyl)-deca-3,5,7-triene-1,9-diyne (2am): This compound (96 mg, colourless oil) was obtained from **4a** (146 mg, 0.61 mmol, 1.00 equiv.), $Pd(PPh_3)_4$ (44 mg, 0.04 mmol, 0.07 equiv.), and organozinc reagent **5m** (0.4 M in THF, 3.4 mL, 1.36 mmol, 2.22 equiv.). Yield 57%. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.18 (s, 9 H, CH_3), 0.20 (s, 9 H, CH_3), 5.50 (d, 1 H, H^8, *J* = 10.6 Hz), 5.68 (d, 1 H, H^3, *J* = 15.4 Hz), 6.36 (dd, 1 H, H^6, *J* = 11.1 and 15.3 Hz), 6.40 (dd, 1 H, H^5, *J* = 11.2 and 11.1 Hz), 6.72 (dd, 1 H, H^4, *J* = 11.2 and 15.4 Hz), 6.79 (dd, 1 H, H^7, *J* = 15.3 and 10.6 Hz). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = −0.20 (6 C, *C*H_3), 99.32, 101.96, 102.99, 104.46, 110.76 (C^8), 112.90 (C^3), 132.11, 134.52, 140.13, 142.30. − MS (EI, 70 eV); *m*/*z* (rel. int.): 272 (100) [M^+·], 257 (50) [M − CH_3], 183 (100), 73 (100) [$Si(CH_3)_3$]. − IR (NaCl, neat): $\tilde{\nu}$ = 758, 844, 990, 1250, 2116, 2142, 2898, 2960, 3024 cm^{-1}.

(1*E*,3*E*,5*Z*)-1,6-Bis(3-furyl)hexa-1,3,5-triene (2ao): This compound (60 mg, yellow solid) was obtained from **4a** (90 mg, 0.38 mmol, 1.0 equiv.) and $Pd(PPh_3)_4$ (49 mg, 0.04 mmol, 0.1 equiv.) in THF (5 mL), and organozinc reagent **5o** (0.5 M in THF, 5.0 mL, 2.50 mmol, 6.5 equiv.). Yield 75%. − M.p. 81 °C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.13 (d, 1 H, H^6, *J* = 11.4 Hz), 6.19 (dd, 1 H, H^5, *J* = 11.4 and 11.0 Hz), 6.42 (dd, 1 H, H^3, *J* = 14.5 and 10.9 Hz), 6.45 (d, 1 H, H^1, *J* = 15.3 Hz), 6.55 (m, 2 H, furyl), 6.58 (dd, 1 H, H^2, *J* = 15.3 and 10.9 Hz), 6.78 (dd, 1 H, H^4, *J* = 14.5 and 11.0 Hz), 7.37 (s, 1 H, furyl), 7.41 (s, 1 H, furyl), 7.44 (s, 1 H, furyl), 7.51 (s, 1 H, furyl). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 107.25 (furyl), 110.78 (furyl), 119.18, 122.59, 122.79 (furyl); 124.62 (furyl); 128.61, 128.93, 129.11, 134.58, 140.83 (furyl), 141.45 (furyl), 143.04 (furyl), 143.66 (furyl). − MS (EI, 70 eV); *m*/*z* (rel. int.): 212 (100) [M^+·], 183 (50). − IR (KBr, neat): $\tilde{\nu}$ = 760, 804, 991, 1150, 1504, 3140 cm^{-1}.

(1*E*,3*E*,5*E*)-1,6-Diphenylhexa-1,3,5-triene (2ba): This compound (195 mg, yellow solid) was obtained from **4b** (230 mg, 0.97 mmol, 1.0 equiv.) and $Pd(PPh_3)_4$ (120 mg, 0.10 mmol, 0.1 equiv.) in THF (5 mL), and organozinc reagent **5a** (0.25 M in THF, 12.0 mL, 3.00 mmol, 3.0 equiv.). Yield 87%. − M.p. 202 °C (ref.[22]:203 ≈ 204 °C). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.47 (dd, 2 H, H^3 and H^4, *J* = 7.0 Hz; ^4J = 3.0 Hz), 6.55 (d, 2 H, H^1 and H^6, *J* = 15.4 Hz), 6.83 (ddd, 2 H, H^2 and H^5, *J* = 15.4 and 7.0 Hz; ^4J = 3.0 Hz), 7.14 to 7.38 (m, 10 H, phenyl). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.31 (4 C), 127.47 (2 C), 128.58 (4 C), 129.07 (2 C), 132.62 (2 C), 133.51 (2 C), 137.34 (2 C, phenyl). − MS (EI, 70 eV); *m*/*z* (rel. int.): 232 (70) [M^+·], 215 (14), 141 (55), 128 (55), 115 (55), 91 (100). − IR (KBr, neat): $\tilde{\nu}$ = 692, 996, 1448, 1490, 1824, 1890, 1948, 3012−3058 cm^{-1}.

(1*E*,3*E*,5*E*)-1,6-Bis(4-methoxyphenyl)hexa-1,3,5-triene (2bb): This compound (108 mg, orange solid) was obtained from **4b** (125 mg, 0.58 mmol, 1.00 equiv.) and $Pd(PPh_3)_4$ (57 mg, 0.05 mmol, 0.09 equiv.) in THF (5 mL), and organozinc reagent **5b** (0.5 M in THF, 2.5 mL, 1.25 mmol, 2.16 equiv.). The crude product was insoluble or only very slightly soluble in most of the common solvents. Hence, after hydrolysis with aqueous $NaHCO_3$ (5%), it was extracted with CH_2Cl_2 (3 × 175 mL), dried over $MgSO_4$ and evaporated. The impurities were eliminated by washing with Et_2O. Yield 70%. − M.p. 256 °C (ref.[24]:250 ≈ 251 °C). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.76 (s, 6 H, OCH_3), 6.40 (dd, 2 H, H^3 and H^4, *J* = 6.9 Hz; ^4J = 3.0 Hz), 6.47 (d, 2 H, H^1 and H^6, *J* = 15.5 Hz), 6.70 (ddd, 2 H, H^2 and H^5, *J* = 15.5 and 6.9 Hz; ^4J = 3.0 Hz), 6.80 (d, 4 H, phenyl, *J* = 8.7 Hz), 7.29 (d, 4 H, phenyl, *J* = 8.7 Hz). − MS (EI, 70 eV); *m*/*z* (rel. int.): 292 (36) [M^+·], 121 (100). − IR (KBr, neat): $\tilde{\nu}$ = 816, 996, 1252, 1440, 1510, 1602, 1722, 1894, 2050, 2838−3012 cm^{-1}.

(1*E*,3*E*,5*E*)-1,6-Bis(2-thienyl)hexa-1,3,5-triene (2bd): This compound (139 mg, orange solid) was obtained from **4c** (or **4a** or **4b**) (151 mg, 0.63 mmol, 1.00 equiv.) and $Pd(PPh_3)_4$ (40 mg, 0.03 mmol, 0.05 equiv.) in THF (5 mL), and organozinc reagent **5d** (0.5 M in THF, 7.0 mL, 3.50 mmol, 5.55 equiv.). Yield 90%. − M.p. 199 °C (ref.:212 ≈ 213 °C[25,26]; 198 ≈ 199 °C[28]). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.36 (dd, 2 H, H^3 and H^4, *J* = 5.9 Hz; ^4J = 3.0 Hz), 6.61 (ddd, 2 H, H^2 and H^5, *J* = 15.0 and 5.9 Hz; ^4J = 3.0 Hz), 6.67 (d, 2 H, H^1 and H^6, *J* = 15.0 Hz), 6.92 (dd, 2 H, thienyl, *J* = 6.5 and 3.6 Hz), 6.93 (d, 2 H, thienyl, *J* = 3.6 Hz), 7.11 (d, 2 H, thienyl, *J* = 6.5 Hz). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 124.43 (2 C), 125.36 (2 C), 125.85 (2 C), 127.63 (2 C), 128.86 (2 C), 132.78 (2 C), 142.95 (2 C, thienyl). − MS (EI, 70 eV); *m*/*z* (rel. int.): 244 (60) [M^+·], 147 (40), 97 (100). − IR (KBr, neat): $\tilde{\nu}$ = 696, 856, 924, 994, 3050 cm^{-1}. − $C_{14}H_{12}S_2$ (244.37): calcd.C 68.81, H 4.95, S 26.24; found C 68.57, H 4.82, S 25.96.

(1*E*,3*E*,5*E*)-1,6-Bis(2-furyl)hexa-1,3,5-triene (2be): This compound (155 mg, yellow solid) was obtained from **4c** (or **4a** or **4b**) (191 mg, 0.80 mmol, 1.00 equiv.) and $Pd(PPh_3)_4$ (40 mg, 0.03 mmol, 0.04 equiv.) in THF (5 mL), and organozinc reagent **5e** (0.5 M in THF, 8.0 mL, 4.00 mmol, 5.00 equiv.). Yield 91%. − M.p. 147 °C (ref.[26]:149 °C). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.26 (d, 2 H, furyl, *J* = 3.3 Hz), 6.35 (d, 2 H, H^1 and H^6, *J* = 15.5 Hz), 6.38 (dd, 2 H, furyl, *J* = 3.3 and 1.7 Hz), 6.41 (dd, 2 H, H^3 and H^4, *J* = 7.2 Hz; ^4J = 3.1 Hz), 6.76 (ddd, 2 H, H^2 and H^5, *J* = 15.3 and 7.2 Hz; ^4J = 3.1 Hz), 7.35 (d, 2 H, furyl, *J* = 1.8 Hz). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 108.63 (2 C), 111.79 (2 C), 119.86 (2 C), 127.67 (2 C), 133.17 (2 C), 142.21 (2 C, furyl), 153.34 (2 C, furyl). − MS (EI, 70 eV); *m*/*z* (rel. int.): 212 (100) [M$^+$·]. − IR (KBr, neat): ṽ = 736, 994, 1484, 3008, 3118 cm^{-1}. − $C_{14}H_{12}O_2$ (212.25): calcd.C 79.23, H 5.70; found C 79.15, H 5.67.

(6*E*,8*E*,10*E*)-Hexadeca-6,8,10-triene (2bg): This compound (132 mg, colourless oil) was obtained from **4b** (238 mg, 1.00 mmol, 1.00 equiv.) and $Pd(PPh_3)_4$ (57 mg, 0.05 mmol, 0.05 equiv.) in THF (5 mL), and organozinc reagent **5g** (0.5 M in THF, 5.0 mL, 2.50 mmol, 2.50 equiv.). Yield 60%. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83 (t, 6 H, H^1 and H^{16}, *J* = 6.8 Hz), 1.13 to 1.39 (m, 12 H, H^2, H^3, H^4, H^{13}, H^{14} and H^{15}), 2.04 (dt, 4 H, H^5 and H^{12}, *J* = 7.3 and 7.2 Hz), 5.66 (dt, 2 H, H^6 and H^{11}, *J* = 14.7 and 7.3 Hz), 6.03 (dd, 2 H, H^7 and H^{10}, *J* = 14.7 and 9.5 Hz), 6.13 to 6.17 (m, 2 H, H^8 and H^9). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.98 (2 C, C^1 and C^{16}), 22.51 (2 C), 29.05 (2 C), 31.38 (2 C), 32.76 (2 C), 130.43 (2 C), 130.78 (2 C), 134.29 (2 C). − MS (EI, 70 eV); *m*/*z* (rel. int.): 220 (40) [M$^+$·], 93 (100). − IR (NaCl, neat): ṽ = 992, 1460, 2924 cm^{-1}.

(1*E*,3*E*,5*E*)-1,6-Bis(3-furyl)hexa-1,3,5-triene (2bo): This compound (81 mg, yellow solid) was obtained from **4b** (109 mg, 0.46 mmol, 1.00 equiv.) and $Pd(PPh_3)_4$ (48 mg, 0.04 mmol, 0.09 equiv.) in THF (5 mL), and organozinc reagent **5o** (0.5 M in THF, 5.0 mL, 2.50 mmol, 5.43 equiv.). Yield 97%. − M.p. decomposition from 88 °C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.36 (dd, 2 H, H^3 and H^4, *J* = 6.7 Hz; ^4J = 3.1 Hz), 6.41 (d, 2 H, H^1 and H^6, *J* = 15.4 Hz), 6.54 (ddd, 2 H, H^2 and H^5, *J* = 15.4 and 6.7 Hz; ^4J = 3.1 Hz), 6.54 (m, 2 H, furyl), 7.35 (m, 2 H, furyl), 7.43 (s, 2 H, furyl). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 107.28 (2 C, furyl), 121.76 (2 C), 124.66 (2 C, furyl), 127.72 (2 C), 128.99 (4 C), 132.36 (2 C). − MS (EI, 70 eV); *m*/*z* (rel. int.): 212 (100) [M$^+$·]. − IR (KBr, neat): ṽ = 774, 994, 1156, 1504, 3140 cm^{-1}.

(1*Z*,3*E*,5*Z*)-1,6-Diphenylhexa-1,3,5-triene (2ca): This compound (166 mg, yellow solid) was obtained from **4c** (263 mg, 1.10 mmol, 1.00 equiv.) and $Pd(PPh_3)_4$ (57 mg, 0.05 mmol, 0.05 equiv.) in THF (5 mL), and organozinc reagent **5a** (1 M in THF, 3.0 mL, 3.00 mmol, 2.73 equiv.). Yield 65%. − M.p. 100 °C (ref.[22]:110 °C). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.31 (ddd, 2 H, H^2 and H^5, *J* = 11.2 and = 7.4 Hz; ^4J = 3.1 Hz), 6.47 (d, 2 H, H^1 and H^6, *J* = 11.2 Hz), 6.93 (dd, 2 H, H^3 and H^4, *J* = 7.4 Hz; ^4J = 3.1 Hz), 7.20 to 7.40 (m, 10 H, phenyl). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 127.11 (2 C), 128.35 (4 C), 129.05 (4 C), 130.26 (2 C), 130.69 (2 C), 131.56 (2 C), 137.57 (2 C, phenyl). − MS (EI, 70 eV); *m*/*z* (rel. int.): 232 (70) [M$^+$·], 215 (14), 141 (55), 128 (55), 115 (55), 91 (100). − IR (KBr, neat): ṽ = 694, 786, 1448, 1492, 1758, 1824, 1884, 1948, 3020 cm^{-1}. − $C_{18}H_{16}$ (232.32): calcd. C 93.06, H 6.94; found C 92.78, H 6.99.

(1*Z*,3*E*,5*Z*)-1,6-Bis(4-methoxyphenyl)hexa-1,3,5-triene (2cb): This compound (264 mg, yellow solid) was obtained from **4c** (240 mg, 1.00 mmol, 1.00 equiv.) and $Pd(PPh_3)_4$ (60 mg, 0.05 mmol, 0.05 equiv.) in THF (5 mL), and organozinc reagent **5b** (0.4 M in THF, 6.0 mL, 2.40 mmol, 2.40 equiv.). Yield 90%. − M.p. 145 °C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.82 (s, 6 H, OCH_3), 6.22 (ddd, 2 H, H^2 and H^5, *J* = 11.3 and 7.3 Hz; ^4J = 3.1 Hz), 6.38 (d, 2 H, H^1 and H^6, *J* = 11.3 Hz), 6.90 (dd, 2 H, H^3 and H^4, *J* = 7.3 Hz; ^4J = 3.1 Hz), 6.89 (d, 4 H, phenyl, *J* = 8.7 Hz), 7.29 (d, 4 H, phenyl, *J* = 8.7 Hz). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.22 (2 C, OCH_3), 113.69 (4 C, phenyl), 128.81 (2 C), 129.81 (2 C), 130.23 (4 C, phenyl), 130.26 (2 C, phenyl), 131.06 (2 C), 158.63 (2 C, phenyl). − MS (EI, 70 eV); *m*/*z* (rel. int.): 292 (50) [M$^+$·], 121 (100). − IR (KBr, neat): ṽ = 774, 820, 850, 1028, 1254, 1636, 1506, 1602, 1734, 1904, 2048, 2838−3014 cm^{-1}.

(1*E*,3*E*,5*Z*)-1,6-Bis(2-thienyl)hexa-1,3,5-triene (2cd): This compound (76 mg, orange solid) was obtained from **4c** (120 mg, 0.50 mmol, 1.00 equiv.) and $Pd(PPh_3)_4$ (35 mg, 0.03 mmol, 0.06 equiv.) in toluene (5 mL), and organozinc reagent **5d** (0.5 M in toluene, 2.5 mL, 1.25 mmol, 2.50 equiv.). Yield 62%. − M.p. 155 °C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.27 (ddd, 2 H, H^2 and H^5, *J* = 11.3 and 8.0 Hz; ^4J = 2.9 Hz), 6.55 (d, 2 H, H^1 and H^6, *J* = 11.3 Hz), 7.04 (m, 4 H, thienyl), 7.17 (dd, 2 H, H^3 and H^4, *J* = 8.0 Hz; ^4J = 2.9 Hz), 7.29 to 7.32 (m, 2 H, thienyl). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 124.43 (2 C), 125.36 (2 C), 125.85 (2 C), 127.63 (2 C), 128.86 (2 C), 132.78 (2 C), 142.95 (2 C, thienyl). − MS (EI, 70 eV); *m*/*z* (rel. int.): 244 (85) [M$^+$·], 147 (50), 97 (100). − IR (KBr, neat): ṽ = 696, 856, 924, 994, 3050 cm^{-1}. − $C_{14}H_{12}S_2$ (244.37): calcd. C 68.81, H 4.95, S 26.24; found C 68.98, H 4.98, S 26.09.

(1*Z*,3*E*,5*Z*)-1,6-Bis(2-furyl)hexa-1,3,5-triene (2ce): This compound (138 mg, yellow solid) was obtained from **4c** (199 mg, 0.84 mmol, 1.00 equiv.) and $Pd(PPh_3)_4$ (40 mg, 0.03 mmol, 0.04 equiv.) in toluene (5 mL), and organozinc reagent **5e** (0.5 M in toluene, 5.0 mL, 2.50 mmol, 2.98 equiv.). Yield 77%. − M.p. 94 °C. − ^{1}H NMR (200 MHz, C_6D_6): δ = 5.93 (d, 2 H, H^1 and H^6, *J* = 11.4 Hz), 6.06 (m, 4 H, furyl), 6.13 (ddd, 2 H, H^2 and H^5, *J* = 11.4 and 7.8 Hz; ^4J = 3.1 Hz), 7.04 (m, 2 H, furyl), 7.63 (dd, 2 H, H^3 and H^4, *J* = 7.8 Hz; ^4J = 3.1 Hz). − ^{13}C NMR (50 MHz, C_6D_6): δ = 111.29 (2 C), 111.64 (2 C), 117.16 (2 C), 127.58 (2 C), 133.62 (2 C), 142.75 (2 C, furyl), 154.43 (2 C, furyl). − MS (EI, 70 eV); *m*/*z* (rel. int.): 212 (100) [M$^+$·]. − IR (KBr, neat): ṽ = 736, 816, 1398, 1484, 3054, 3144 cm^{-1}.

(6*Z*,8*E*,10*Z*)-Hexadeca-6,8,10-triene (2cg): This compound (104 mg, colourless oil) was obtained from **4c** (183 mg, 0.77 mmol, 1.00 equiv.) and $Pd(PPh_3)_4$ (44 mg, 0.04 mmol, 0.05 equiv.) in THF (5 mL), and organozinc reagent **5g** (0.5 M in THF, 4.0 mL, 2.00 mmol, 2.50 equiv.). Yield 61%. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, 6 H, H^1 and H^{16}, *J* = 6.6 Hz), 1.25 to 1.45 (m, 12 H, H^2, H^3, H^4, H^{13}, H^{14} and H^{15}), 2.18 (dt, 4 H, H^5 and H^{12}, *J* = 7.6 and 6.8 Hz), 5.44 (dt, 2 H, H^6 and H^{11}, *J* = 10.5 and 7.6 Hz), 6.05 (m, 2 H, H^7 and H^{10}), 6.46 (dd, 2 H, H^8 and H^9, *J* = 7.6 Hz; ^4J = 3.0 Hz). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.98 (2 C, C^1 and C^{16}), 22.50 (2 C), 27.79 (2 C), 29.32 (2 C), 31.43 (2 C), 127.79 (2 C), 128.76 (2 C), 132.60 (2 C, C8 and C9). − MS (EI, 70 eV); *m*/*z* (rel. int.): 220 (40) [M$^+$·], 93 (100). − IR (NaCl, neat): ṽ = 756, 988, 1466, 2926 cm^{-1}.

(1*Z*,3*E*,5*Z*)-1,6-Bis(3-furyl)hexa-1,3,5-triene (2co): This compound (141 mg, yellow solid) was obtained from **4c** (183 mg, 0.77 mmol, 1.00 equiv.) and $Pd(PPh_3)_4$ (48 mg, 0.04 mmol, 0.05 equiv.) in THF (5 mL), and organozinc reagent **5o** (0.5 M in THF, 5.0 mL, 2.50 mmol, 3.25 equiv.). Yield 86%. − M.p. decomposition from 110 °C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.18 (d, 2 H, H^1 and H^6, *J* = 11.2 Hz), 6.23 (ddd, 2 H, H^2 and H^5, *J* = 11.2 and 7.0 Hz; ^4J = 3.0 Hz), 6.54 (m, 2 H, furyl), 6.85 (dd, 2 H, H^3 and H^4, *J* =

7.0 Hz; ^4J = 3.0 Hz), 7.41 (m, 2 H, furyl), 7.51 (s, 2 H, furyl). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 110.81 (2 C, furyl), 120.08 (2 C), 122.71 (2 C, furyl), 129.10 (4 C), 130.79 (4 C). − MS (EI, 70 eV); *m*/*z* (rel. int.): 212 (100) [M^+·]. − IR (KBr, neat): $\tilde{\nu}$ = 736, 1000, 1584, 3120 cm^{-1}.

Double Coupling Reactions: Syntheses of Unsymmetrical Double Coupling Compounds 3

General Procedure for the Palladium-Catalysed Cross-Coupling Reaction between 1,6-Dibromohexa-1,3,5-triene 4 and Organozinc Reagents 5: a) By a One-Step Procedure: A solution of organozinc reagent **5** (R^1ZnBr) in THF was slowly added dropwise, using a syringe pump, at room temperature and under argon, to a stirred solution of **4** and $Pd(PPh_3)_4$ in THF (5 mL). The reaction was monitored by TLC (SiO_2, pentane as eluent, UV and phosphomolybdic acid in EtOH for developing). When the reaction was complete, as indicated by the total consumption of **4**, a second organozinc reagent **5** (R^2ZnBr) solution was quickly added to a stirred solution of 1,6-dibromohexa-1,3,5-triene **4** and $Pd(PPh_3)_4$ in THF (5 mL). After 20 min, the mixture was hydrolysed using aqueous $NaHCO_3$ (20 mL, 5%) and extracted with pentane (3 × 15 mL). The organic layers were combined, dried over $MgSO_4$ and evaporated. The residue was purified by silica gel column chromatography.

b) By a Two-Step Procedure: A solution of organozinc reagent **5n** in THF was slowly added dropwise, using a syringe pump, at room temperature and under argon, to a stirred solution of **4b** and $Pd(PPh_3)_4$ in THF (5 mL). The reaction was monitored by TLC (SiO_2, pentane as eluent, UV and phosphomolybdic acid in EtOH for developing). When the reaction was complete, as indicated by the total consumption of **4b**, the solution was hydrolysed using aqueous $NaHCO_3$ (5 mL, 5%) and extracted with pentane (3 × 15 mL). The organic layers were combined, dried over $MgSO_4$ and evaporated. The residue was purified by silica gel column chromatography. The intermediate single coupling compound **1bn**, isolated pure, was used for the second step of the synthesis. A solution of organozinc reagent **5m** or **5p** was quickly added to a stirred solution of single coupling compound **1bn** and $Pd(PPh_3)_4$ in THF. After 20 min, the mixture was hydrolysed using aqueous $NaHCO_3$ (20 mL, 5%) and extracted with pentane (3 × 15 mL). The organic layers were combined, dried over $MgSO_4$ and evaporated. The residue was purified by silica gel column chromatography.

(1*E*,3*E*,5*Z*)-1-Phenylundeca-1,3,5-triene (3aa): This compound (32 mg, colourless oil) was obtained from **4a** (120 mg, 0.50 mmol, 1.00 equiv.) and $Pd(PPh_3)_4$ (30 mg 0.02 mmol, 0.04 equiv.) in THF (5 mL), and organozinc reagent **5a** (0.1 M in THF, 6.0 mL, 0.60 mmol, 1.20 equiv.) and organozinc reagent **5g** (0.2 M in THF, 7.5 mL, 1.50 mmol, 3.00 equiv.). Yield 35%. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.02 (t, 3 H, H^{11}, J = 6.6 Hz), 1.28 to 1.59 (m, 6 H, H^8, H^9 and H^{10}), 2.34 (q, 2 H, H^7, J = 7.6 and 6.9 Hz), 5.61 (dt, 1 H, H^6, J = 10.4 and 7.6 Hz), 6.21 (dd, 1 H, H^5, J = 11.3 and 10.4 Hz), 6.46 (dd, 1 H, H^3, J = 14.5 and 10.6 Hz), 6.64 (d, 1 H, H^1, J = 15.4 Hz), 6.75 (dd, 1 H, H^4, J = 14.5 and 11.3 Hz), 6.99 (dd, 1 H, H^2, J = 15.4 and 10.6 Hz), 7.20 to 7.40 (m, 5 H, phenyl). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.30 (C^{11}), 22.79, 28.17, 29.12, 31.72, 126.49 (2 C), 127.44, 127.53, 128.77 (2 C), 129.08, 129.55, 132.25, 132.90, 133.57, 137.66. − MS (EI, 70 eV); *m*/*z* (rel. int.): 226 (20) [M^+·], 169 (6), 155 (45), 91 (100). − IR (NaCl, neat): $\tilde{\nu}$ = 700, 772, 992, 1344, 1480, 1570, 1598, 2826, 3032 cm^{-1}.

(1*E*,3*E*,5*Z*)-1-(2-Thienyl)trideca-1,3,5-trien-7-yne (3ad): This compound (140 mg, orange oil) was obtained from **4a** (253 mg, 1.06 mmol, 1.00 equiv.) and $Pd(PPh_3)_4$ (85 mg, 0.07 mmol, 0.07 equiv.) in THF (5 mL), and organozinc reagent **5d** (0.35 M in THF, 5.0 mL, 1.75 mmol, 1.60 equiv.) and organozinc reagent **5l** (0.35 M in THF, 10.0 mL, 3.50 mmol, 3.30 equiv.). Yield 51%. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.92 (t, 3 H, H^{13}, J = 6.9 Hz), 1.24 to 1.62 (m, 6 H, H^{10}, H^{11} and H^{12}), 2.41 (dt, 2 H, H^9, J = 6.9 Hz; ^5J = 2.3 Hz), 5.43 (dt, 1 H, H^6, J = 10.2 Hz; ^5J = 2.3 Hz), 6.37 (dd, 1 H, H^5, J = 11.0 and 10.2 Hz), 6.41 (dd, 1 H, H^4, J = 15.1 and 10.0 Hz), 6.72 (m, 1 H, H^3), 6.77 (dd, 1 H, H^2, J = 15.3 and 9.5 Hz), 6.85 (d, 1 H, H^1, J = 15.3 Hz), 6.93 to 7.01 (m, 2 H, thienyl), 7.17 (d, 1 H, thienyl, J = 4.1 Hz). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.99 (C^{13}), 19.77, 22.15, 28.47, 31.12, 78.02 (C^8), 98.35 (C^9), 109.93, 124.70, 126.15, 126.44, 127.65, 128.77, 130.26, 134.34, 138.45, 142.75. − MS (EI, 70 eV); *m*/*z* (rel. int.): 256 (95) [M^+·], 199 (50), 185 (70), 165 (65), 97 (100). − IR (NaCl, neat): $\tilde{\nu}$ = 698, 808, 854, 998, 2140, 2858−2928 cm^{-1}.

(1*Z*,3*E*,5*E*)-1-Phenylundeca-1,3,5-triene (3ag): This compound (40 mg, colourless oil) was obtained from **4a** (121 mg, 0.51 mmol, 1.00 equiv.) and $Pd(PPh_3)_4$ (35 mg, 0.03 mmol, 0.06 equiv.) in THF (5 mL), and organozinc reagent **5g** (0.15 M in THF, 5.0 mL, 0.75 mmol, 1.50 equiv.) and organozinc reagent **5a** (0.1 M in THF, 10.0 mL, 1.00 mmol, 2.00 equiv.). Yield 35%. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, 3 H, H^{11}, J = 6.7 Hz), 1.25 to 1.43 (m, 6 H, H^8, H^9 and H^{10}), 2.10 (dt, 2 H, H^7, J = 7.2 and 6.9 Hz), 5.77 (dt, 1 H, H^6, J = 14.7 and 7.2 Hz), 6.11 (dd, 1 H, H^5, J = 14.7 and 10.4 Hz), 6.24 (dd, 1 H, H^2, J = 11.2 and 11.0 Hz), 6.35 (dd, 1 H, H^4, J = 14.6 and 10.4 Hz), 6.38 (d, 1 H, H^1, J = 11.0 Hz), 6.69 (dd, 1 H, H^3, J = 14.6 and 11.2 Hz), 7.20 to 7.40 (m, 5 H, phenyl). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.98 (C^{11}), 24.47, 28.85, 31.34, 32.79, 126.61, 126.70, 128.15(2C), 128.85 (3 C), 130.37 (2C), 135.81, 136.55, 137.72. − MS (EI, 70 eV); *m*/*z* (rel. int.): 226 (26) [M^+·], 169 (6), 155 (45), 91 (100). − IR (NaCl, neat): $\tilde{\nu}$ = 700, 772, 994, 1446, 1598, 2854, 3016 cm^{-1}.

(3*Z*,5*E*,7*E*)-1-Trimethylsilyltetradeca-3,5,7-trien-1-yne (3an): This compound (195 mg, yellow oil) was obtained from **4a** (309 mg, 1.30 mmol, 1.00 equiv.) and $Pd(PPh_3)_4$ (90 mg, 0.08 mmol, 0.06 equiv.) in THF (5 mL), and organozinc reagent **5n** (0.45 M in THF, 8.0 mL, 3.60 mmol, 2.80 equiv.) and organozinc reagent **5m** (0.50 M in THF, 10.0 mL, 5.00 mmol, 3.80 equiv.). Yield 58%. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.20 (s, 9 H), 0.86 (t, 3 H, H^{14}, J = 6.6 Hz), 1.19 to 1.41 (m, 8 H, H^{10}, H^{11}, H^{12} and H^{13}), 2.11 (q, 2 H, H^9, J = 7.0 Hz), 5.37 (d, 1 H, H^3, J = 10.4 Hz), 5.80 (dt, 1 H, H^8, J = 14.7 and 7.0 Hz), 6.15 (dd, 1 H, H^7, J = 14.7 and 10.4 Hz), 6.34 (dd, 1 H, H^6, J = 14.4 and 10.4 Hz), 6.39 (dd, 1 H, H^4, J = 11.0 and 10.4 Hz), 6.62 (dd, 1 H, H^5, J = 14.4 and 11.0 Hz). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 0.12 (3C), 14.19 (C^{14}), 22.71, 28.99, 29.24, 31.81, 33.07, 101.36, 102.68, 107.85, 127.65, 130.44, 136.64, 138.48, 141.43. − MS (EI, 70 eV); *m*/*z* (rel. int.): 260 (15) [M^+·], 245 (5), 73 (100). − IR (NaCl, neat): $\tilde{\nu}$ = 758, 844, 992, 1250, 2140, 2854−2926−2956 cm^{-1}.

(3*E*,5*E*,7*E*)-1-Trimethylsilyltetradeca-3,5,7-trien-1-yne (3bm): This compound (71 mg, orange oil) was obtained from **4b** (141 mg, 0.59 mmol, 1.00 equiv.) and $Pd(PPh_3)_4$ (35 mg, 0.03 mmol, 0.05 equiv.) in THF (5 mL), and organozinc reagent **5n** (0.45 M in THF, 3.0 mL, 1.35 mmol, 2.30 equiv.) and organozinc reagent **5m** (0.50 M in THF, 6.0 mL, 1.25 mmol, 2.40 equiv.). Yield 46%. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.17 (s, 9 H), 0.86 (t, 3 H, H^{14}, J = 6.5 Hz), 1.15 to 1.41 (m, 8 H, H^{10}, H^{11}, H^{12} and H^{13}), 2.09 (q, 2 H, H^9, J = 6.7 Hz), 5.54 (d, 1 H, H^3, J = 15.5 Hz), 5.78 (dt, 1 H, H^8, J = 15.2 and 6.7 Hz),5.98 to 6.16 (m, 2 H, H^6, H^5), 6.26 (dd, 1 H, H^7, J = 14.7 and 10.0 Hz), 6.62 (dd, 1 H, H^4, J = 15.5 and 10.4 Hz). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = − 0.12 (3C), 14.01 (C^{14}), 22.51, 28.80, 29.03, 31.61, 32.87, 104.90, 109.64, 129.31, 129.96, 135.92,

138.11, 143.00. − MS (EI, 70 eV); *m/z* (rel. int.): 260 (20) [$M^{+}\cdot$], 245 (5), 73 (100). − IR (NaCl, neat): $\tilde{\nu}$ = 760, 844, 994, 1250, 2114, 2854−2926−2956 cm^{-1}.

(3*E*,5*E*,7*E*)-Tetradeca-3,5,7-trien-1-yne (3bp): This compound (22 mg, yellow oil) was obtained from **4b** (270 mg, 1.13 mmol, 1.00 equiv.) and $Pd(PPh_3)_4$ (55 mg, 0.05 mmol, 0.04 equiv.) in THF (5 mL), and organozinc reagent **5n** (0.50 M in THF, 6.5 mL, 3.25 mmol, 2.90 equiv.) and organozinc reagent **5p** (0.40 M in THF, 10.0 mL, 1.25 mmol, 2.40 equiv.). Yield 10%. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.86 (t, 3 H, H^{14}, *J* = 6.7 Hz), 1.16 to 1.41 (m, 8 H, H^{10}, H^{11}, H^{12} and H^{13}), 2.10 (q, 2 H, H^{9}, *J* = 6.7 Hz), 3.04 (d, 1 H, H^{1}, ^{5}J = 2.2 Hz), 5.51 (dd, 1 H, H^{3}, *J* = 15.4 and 2.2 Hz), 5.80 (dt, 1 H, H^{8}, *J* = 15.0 and 6.7 Hz), 6.05 (dd, 1 H, H^{6}, *J* = 14.6 and 10.0 Hz), 6.12 (dd, 1 H, H^{5}, *J* = 14.6 and 10.6 Hz), 6.28 (dd, 1 H, H^{7}, *J* = 15.0 and 10.0 Hz), 6.66 (dd, 1 H, H^{4}, *J* = 15.4 and 10.6 Hz). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.02 (C^{14}), 22.51, 28.79, 29.00, 31.61, 32.87, 79.59, 85.02, 108.49, 128.94, 129.81, 136.22, 138.43, 143.66. − MS (EI, 70 eV); *m/z* (rel. int.): 188 (25) [$M^{+}\cdot$], 117 (100), 104 (95), 91 (90), 78 (75). − IR (NaCl, neat): $\tilde{\nu}$ = 992, 1376, 1458, 2092, 2854−2926−3018, 3308 cm^{-1}.

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