One-pot synthesis of oligomeric aryl-substituted PPV analogs with extended π-conjugation

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A conceptually novel approach for a stepwise one-pot synthesis of oligomeric poly(phenylvinylene) (PPV, –[C_6H_4–CH=CH]–) analogs with extended π-conjugation of the type H–[CH=C(Ar)–C_6H_4–C(Ar)=CH]$_n$–H (n = 2, 4), from the corresponding dienic monomers (n = 1), has been studied. The oligomerizations were performed in high yields by repeating the sequential preparation of the mercuric trifluoroacetate derivative H–[CH=C(Ar)–C_6H_4–C(Ar)=CH]$_n$–$HgCO_2CF_3$ (n = 1, 2) and its coupling in the presence of $PdCl_2$. The feasibility of this approach was demonstrated by a one-pot preparation of several tetramers, directly from the corresponding monomers.

Existing methodologies for the construction of mono-dispersed oligomers consist of a variety of approaches of repetitive multi-step synthesis.[1a] All of these approaches involve isolation and purification of each n-mer obtained (and in many cases, of intermediate products as well), prior to subjecting it to the sequence of reactions necessary to convert it to the (n + 1)-mer or to the (n + 2)-mer.[1] An effective and versatile approach for converting an n-mer to the corresponding (n + 2)-mer, is the McMurry reaction.[1b] It has been successfully applied to the preparation of cyclic sulfur-bridged annulenes[1c] and related compounds.[1d] A one-pot stepwise sequential synthesis of a mono-dispersed n-mer directly from the monomer, avoiding the need to isolate each of the intermediate n-mers in a pure form, has not yet been reported. The advantages and significance of such an approach are obvious.

It was our aim to develop a conceptually novel approach to a fully controlled one-pot sequential synthesis of conjugated oligomers, directly from the corresponding monomers. Ongoing research in our laboratory involves the synthesis and oxidative-coupling-type polymerization of a new class of conjugated dienic monomers of the general type CH_2=C(Ar)–Y–C(Ar)=CH_2 [2] [eqn. (1)].

$$n\mathrm{CH_2{=}C(Ar){-}Y{-}C(Ar){=}CH_2} \xrightarrow[-2n\mathrm{H^+}]{\text{oxidation}} \mathrm{H{-}[CH{=}C(Ar){-}Y{-}C(Ar){=}CH]_{\mathit{n}}{-}H} \quad (1)$$

Thus, oligomers of the general structure H–[CH=C(Ar)–Y–C(Ar)=CH]$_n$–H (n = 2, 4, 8 . . .), to be prepared by a one-pot sequential synthesis of the nM→(M)$_n$-type, were the target oligomers of the research reported here.

An oxidative-coupling-type oligomerization based on the above mentioned polymerization used for these monomers [eqn. (1)] could in fact be considered as a one-pot reaction. However, it would have resulted in a mixture of various n-mers, that would need to be separated from each other. A recently reported relevant example, is that of the preparation of a mixture of oligotriacetylenes, and its separation into its pure oligomeric constituents.[3]

A novel general strategy for a one-pot sequential synthesis of mono-dispersed oligomers from bifunctional monomers is presented here. The synthesis of the above mentioned target oligomers is to be regarded as a specific example of this general approach. According to this approach, transformation of each n-mer (starting always with n = 1) to the (n + 2)-mer consists of two reactions, carried out consecutively and repeatedly (in one pot). The first step consists of a monofunctionalization reaction of the non-reactive bifunctional n-mer. The rate constant (k_1) of the reaction yielding this product [eqn. (2)] has to be

$$\mathrm{H{-}[CH{=}C(Ar){-}Y{-}C(Ar){=}CH]_{\mathit{n}}{-}H} \xrightarrow{k_1} \mathrm{H{-}[CH{=}C(Ar){-}Y{-}C(Ar){=}CH]_{\mathit{n}}{-}Z} \quad (2)$$

much larger than the rate constant (k_2) of the reaction of its conversion to the bifunctional derivative [eqn. (3)], namely—

$$\mathrm{H{-}[CH{=}C(Ar){-}Y{-}C(Ar){=}CH]_{\mathit{n}}{-}Z} \xrightarrow{k_2} \mathrm{Z{-}[CH{=}C(Ar){-}Y{-}C(Ar){=}CH]_{\mathit{n}}{-}Z} \quad (3)$$

$k_1 \gg k_2$, (n = 1, 2, 4, . . .). The second step is an *in situ* coupling reaction, k_3, of two such monofunctionalized n-mer molecules to yield the corresponding 2n-mer [eqn. (4)]. It is obvious that in

$$2\ \mathrm{H{-}[CH{=}C(Ar){-}Y{-}C(Ar){=}CH]_{\mathit{n}}{-}Z} \xrightarrow{k_3} \mathrm{H{-}[CH{=}C(Ar){-}Y{-}C(Ar){=}CH]_{2\mathit{n}}{-}H} \quad (4)$$

order for this approach to be applicable, each of these two consecutive reactions has to take place in a very high yield.

Coupling reactions of symmetrically conjugated dienes of the type CH_2=C(Ar)–Y–C(Ar)=CH_2 have not been reported,

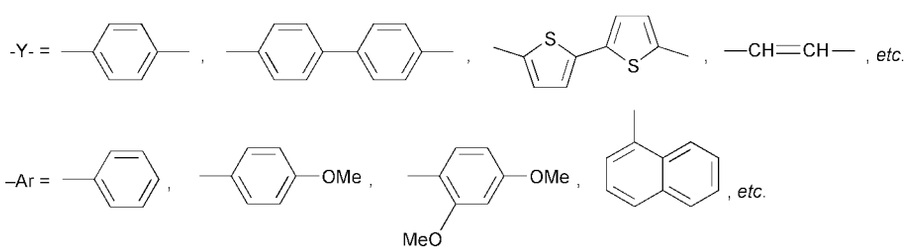

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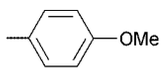
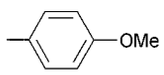
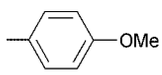
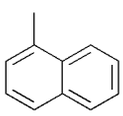
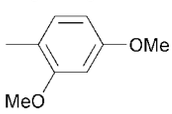
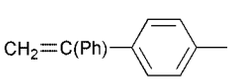
Table 1 Preparation of $Ar^1(Ar^2)C{=}CH{-}HgCl$ **2** from $Ar^1(Ar^2)C{=}CH_2$ **1**—experimental conditions and results[a]

Ar^1	Ar^2	**1**/mmol	$Hg(CO_2CF_3)_2$/ mmol	Product **2**, yield (%)	Mp[b]/ °C (lit., mp/ °C)
–Ph	–Ph	8.6	8.6	**2a**, 58	142 (143)[c]
–Ph		8.6	8.6	**2b**, 67	133
		4.0	4.0	**2c**, 60	146 (146.5)[c]
–Ph		5.7	5.7	**2d**, 56	125
–Ph		2.4	2.4	**2e**, 60	165[d]
–Ph		3.5	3.5	**2k**, 65	138

[a] The products were prepared according to the general procedure detailed in the Experimental section. [b] The products were crystallized from benzene. [c] See ref. 8. [d] The product **2e** was crystallized from a mixture of petroleum ether–ethyl acetate.

except for the above mentioned case of their oxidative-coupling-type stepwise polymerization.[2] However, several reports are available on the coupling of ArCH=CH–Z type compounds, which could be used for our synthesis [eqn. (5)].

$$2\ PhCH{=}CH{-}Z \xrightarrow{PdX_2} PhCH{=}CH{-}CH{=}CHPh + 2\ ZX_2 + Pd(0) \quad (5)$$

(Z = –HgCl,[5] –B(OH),[5] $-SiMe_3$,[6] *etc.*)

Results and discussion

1,1-Diarylethylenes (**1**) were used as model compounds for the monofunctionalization of the dienic *n*-mers (*n* = 1, 2, 4), and for the subsequent coupling of the product of this reaction. The two corresponding reactions applied in this case were the chloromercuration of 1,1-diarylethylenes to give the derived $Ar^1(Ar^2)C{=}CH{-}HgCl$ **2**,[4] followed by $PdCl_2$-induced coupling reaction[7] of **2** to yield the corresponding 1,1,4,4-tetraarylbuta-1,3-diene **3** [eqns. (6) and (7)].

$$\underset{\mathbf{1}}{Ar^1(Ar^2)C{=}CH_2} \xrightarrow[2.\ NaCl]{1.\ HgX_2} \underset{\mathbf{2}}{Ar^1(Ar^2)C{=}CH{-}HgX} \quad (6)$$

$$\underset{\mathbf{2}}{Ar^1(Ar^2)C{=}CH{-}HgX} \xrightarrow{PdCl_2} \underset{\mathbf{3}}{Ar^1(Ar^2)C{=}CH{-}CH{=}C(Ar^1)(Ar^2)} \quad (7)$$

The chloromercurations were carried out at room temperature in benzene. Mercuric trifluoroacetate $Hg(TFA)_2$ was more efficient than $Hg(NO_3)_2$ as a mercurating agent. Equimolar amounts of $Hg(TFA)_2$ had to be used, since an excess could result in the formation of by-products of the type $Ar^1(Ar^2)C{=}C(HgX)_2$.[4] The monohalomercury derivative of the monomeric diene, $CH_2{=}C(Ph){-}C_6H_4{-}C(Ph){=}CH{-}HgCl$, and several $Ar^1(Ar^2)C{=}CH{-}HgCl$ type compounds, were prepared from the corresponding diene and 1,1-diarylethylenes, respectively. The experimental conditions and the results obtained are summarized in Table 1.

The coupling of **2** [eqn. (7)] was carried out in benzene in the presence of stoichiometric amounts of $PdCl_2$, to give the corresponding 1,1,4,4-tetraarylbuta-1,3-dienes **3** in moderate yields. The experimental conditions and the results obtained are summarized in Table 2. It should be noted that **2k**, derived from a conjugated dienic monomer, was significantly less reactive compared to the substrates **2a**–**2e**.

The structures of the coupling products, 1,1,4,4-tetraarylbuta-1,3-dienes **3a**–**3e**, were determined based on their ^{1}H-NMR, ^{13}C-NMR and MS spectral data which are detailed in Table 3.

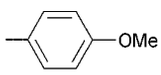
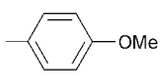
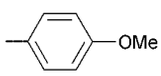
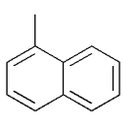
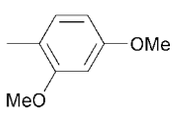
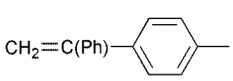
The relatively low solubility of the $Ar^1(Ar^2)C{=}CH{-}HgCl$ type compounds **2** and their high stability, suggested that higher yields of **3** could have been obtained using its *in situ* formed precursor, $Ar^1(Ar^2)C{=}CH(HgCO_2CF_3)$, which is soluble and more reactive compared to **2**. It was found that a two-step one-pot synthesis of **3** directly from **1**, bypassing the preparation and isolation of $Ar^1(Ar^2)C{=}CH{-}HgCl$, could be carried out. Several variations of experimental conditions for this one-pot reaction [eqn. (8)] were studied. The optimal experimental conditions found and the results obtained are given in the Table 4.

$$\underset{\mathbf{1}}{2\ Ar^1(Ar^2)C{=}CH_2} \longrightarrow \underset{\mathbf{3}}{[Ar^1(Ar^2)C{=}CH]_2} \quad (8)$$

The yields of the coupling products **3** obtained in this one-pot synthesis were much higher than the corresponding ones obtained by the coupling of $Ar^1(Ar^2)C{=}CH{-}HgCl$.

The exclusive formation of the monochloromercury derivative $CH_2{=}C(Ph){-}C_6H_4{-}C(Ph){=}CH{-}HgCl$ **2k**, as opposed to the corresponding dichloromercury derivative, indicates that $k_1 \gg k_2$ [eqns. (2) and (3)] for the oligomers $H{-}[CH{=}C(Ar){-}C_6H_4C(Ar){=}CH]_n{-}H$, at least for *n* = 1. Based on this observation and on the encouraging results obtained for the one-pot dimerization of $Ar^1(Ar^2)C{=}CH_2$ **1** [eqn. (8), Table 3], a direct consecutive two-step one-pot dimerization of the monomer $CH_2{=}C(Ar){-}C_6H_4{-}C(Ar){=}CH_2$ **4** to give the dimeric product $H{-}[CH{=}C(Ar){-}C_6H_4{-}C(Ar){=}CH]_2{-}H$ **5**, was carried out. Optimization of the experimental conditions [eqn. (9)] led to a relatively short reaction time (15 min) for each of the two reactions, namely the *in situ* formation of the monomercuric trifluoroacetate derivative of **4** and its coupling to the dimeric product **5**. Very high yields (92–100%) of the dimers **5** were obtained within an overall reaction period of 30 min. The experimental conditions and results are summarized in Table 5. The structures of the dimers

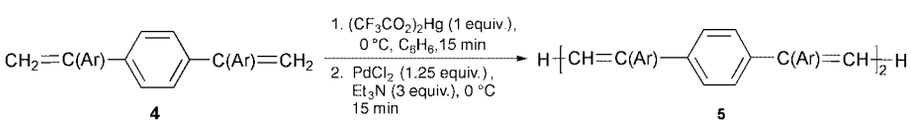
Table 2 The preparation of the dimers $[Ar^1(Ar^2)C{=}CH]_2$ **3** by coupling of **2**—experimental conditions and results[a]

Ar^1	Ar^2	**2**/mmol	$PdCl_2$/ mmol	Reaction time/h	Product **3**, yield (%)	Mp[b]/ °C (lit., mp/ °C)
–Ph	–Ph	0.34	0.34	18	**3a**, 62	207
–Ph		0.36	0.36	4	**3b**, 56	215 (215)[9]
		2.8	2.8	4	**3c**, 62	157[c] (158)[10]
–Ph		1.1	1.1	18	**3d**, 51	215
–Ph		0.45	0.45	18	**3e**, 60	102–105[c]
–Ph		0.48	0.48	18	**5a**[d,e,f] 38	135

[a] The products were prepared according to the general procedure detailed in the Experimental section. [b] The products were crystallized from ethanol. [c] The products were crystallized from benzene. [d] A mixture of THF and HMPA (4 equiv.) was used instead of benzene. [e] The spectral data of **5a** are given in Table 6. [f] The yield of **5a** after a reaction time of 48 hours was 40%.

Table 3 Spectral data of $Ar^1(Ar^2)C{=}CH{-}HgCl$ **2** and $[Ar^1(Ar^2)C{=}CH]_2$ **3**

Compound	Spectral data
2a	δ_H 6.33 (1H, s), 6.95–7.33 (10H, m); *m/z* (EI) 415.9 (M^+, 20%), 178.9 ($[(Ph_2)C{=}CH]^+$, 100%)
2b	δ_H 3.82 (3H, s, OCH_3), 6.24 (1H, s), 6.62–7.39 (9H, m); *m/z* (EI) 445.9 (M^+, 20%), 209 ($[(Ph)(4\text{-anisyl})C{=}CH]^+$, 100%)
2c	δ_H 3.84 (6H, s, OCH_3), 6.22 (1H, s), 6.81–7.61 (8H, m); *m/z* (EI) 239 ($[(4\text{-anisyl})_2C{=}CH]^+$, 100%)
2d	δ_H 6.41 (1H, s), 6.45 (1H, s), 7.29–7.95 (24H, m); *m/z* (EI) 466 (M^+, 20%), 229 ($[(Ph)(\alpha\text{-naphthyl})C{=}CH]^+$, 100%)
2e	δ_H 3.66 (3H, s, OCH_3), 3.86 (3H, s, OCH_3), 6.50 (1H, s), 7.26–7.31 (8H, m); *m/z* (EI) 239 ($[(Ph)(2,4\text{-dimethoxyphenyl})C{=}CH]^+$, 100%)
2k	δ_H 3.84 (3H, s, OCH_3), 5.46 (1H, d, *J* 4), 5.48 (1H, d, *J* 4), 6.45 (1H, s), 7.2–7.4 (14H, m); δ_C 114.6 ($C{=}CH_2$), 127.9–129.6 (14C, Ar-CH), 136.4 (2C, C-C), 141.1 (C-C), 141.6 (C-C), 145.0 (C-C), 149.3 (C-C), 158.0 (C-Hg); *m/z* (EI) 518 (M^+, 100%)
3a	δ_H 6.75 (2H, s), 7.23–7.45 (20H, m); δ_C 126.03 (2C, =CH-), 127.34–128.25 (18C, Ar-CH), 130.7 (4C, C-C), 140.01 (2C, C-C), 142.53 (2C, C-C), 144.08 (2C, C-C); *m/z* (EI) 358 (M^+, 100%)
3b	δ_H 3.86 (6H, s, OMe), 6.67–7.41 (20H, m, Ar + vinyl H); δ_C 55.2 (4C, OMe), 113.5 (2C, $=CH_2$), 127.05, 127.15, 127.3, 127.8, 127.84 (5C, Ar–CH), 130.6, 131.9, 138.9, 172.4, (4C, C-C, Ar); *m/z* (EI) 418 (M^+, 28%)
3c	δ_H 3.77 (12H, s, OMe), 6.64–7.50 (18H, m, Ar-H + vinyl H); δ_C 55.2 (OMe), 113.5 ($=CH_2$), 127.1 (4C, CH), 131.2, 141.11, 156.1, (C-C, Ar); *m/z* (EI) 478.4 (M^+, 47%) 252.2 ($[(4\text{-anisyl})_2C{=}CH]^+$, 100%)
3d	δ_H 6.91–7.91 (m, Ar + vinyl H); δ_C 114.7 ($C{=}CH_2$), 149.9, 148.1, 140.8, 138.8 (5C, C-C), 126.3–136.6 (12C, Ar-CH); *m/z* (EI) 458.2 (M^+, 100%)
3e	δ_H 3.63 (6H, s, OMe), 3.81 (6H, s, OMe), 6.49 (2H, s, vinyl H), 7.26–7.28 (16H, m, Ar-H); δ_C 55.5 (C-OMe), 115.5 ($C{=}CH_2$), 130.05, 132.10, 134.22, 140.07, 143.10 (5C, C-C), 124.66–128.00 (8C, CH-Ar); *m/z* (EI) 478 (M^+, 5%)
3i	δ_H 3.83 (6H, s, OMe), 3.90 (6H, s, OMe), 6.69–7.38 (18H, m, Ar + vinyl H); δ_C 55.9 (OMe), 113.1 ($C{=}CH_2$), 125.8–129.8 (8C, Ar-CH), 149.7, 148.8, 148.5, 141.5, 134.3 (5C, C-C); *m/z* (EI 239 ($[(3,4\text{-dimethoxyphenyl})(Ph)C{=}CH]^+$, 100%)])
3j	δ_H 6.66 (2H, s, vinyl H), 7.25–7.60 (28H, m, Ar-H); δ_C 115.9 ($=CH_2$), 126.9–128.8 (8C, Ar-CH), 143.5, 140.3, 138.9, 137.4, 129.8 (5C, C-C); *m/z* (EI) 268 ($[(biphenyl\text{-}4\text{-}yl)(phenyl)C{=}CH\text{-}CH]^+$, 100%)



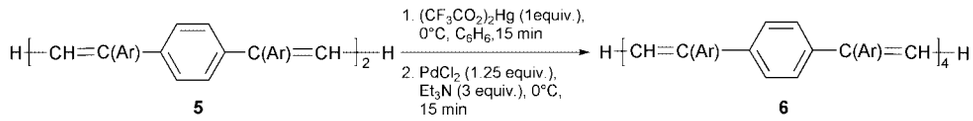
4 5 (9)

5 were determined based on their ^{1}H-NMR, and mass spectral data, which are detailed in Table 6.

Several of the dimers **5** prepared by the one-pot synthesis approach, were isolated and further dimerized to the corresponding tetramers **6** in a two-step one-pot synthesis, applying the same experimental conditions used for preparing these dimers [eqn. (10)]. The results are summarized in Table 7. The structure of the tetramers **6** obtained were determined based on their ^{1}H-NMR and mass spectral data, which are detailed in Table 6.

The possibility of performing the novel approach for construction of mono-dispersed *n*-mers ($n = 2, 4$) directly from the corresponding monomers described in this report, has been verified and demonstrated quite impressively. This was done by carrying out a one-pot synthesis of the same tetramers **6**, directly from the corresponding monomers **4**, in four consecutive steps [eqn. (11)]. The tetramers were obtained in high yields (86–90%) within an overall reaction time of one hour! The results are summarized in Table 6.

In conclusion, the feasibility of applying a novel approach to a consecutive stepwise one-pot synthesis of conjugated oligomers [eqns. (2)–(4)], has been demonstrated. Conjugated oligomers of the type $H{-}[CH{=}C(Ar){-}C_6H_4{-}C(Ar){=}CH]_n{-}H$ ($n = 2, 4$) were prepared directly from the corresponding



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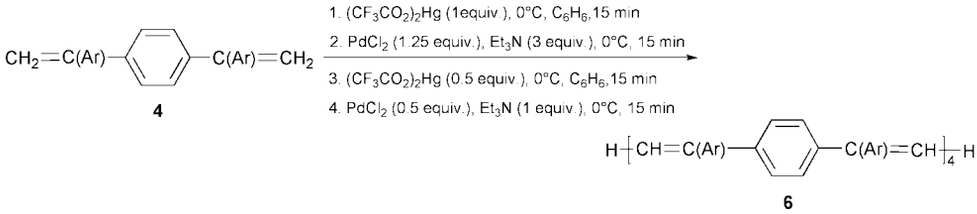

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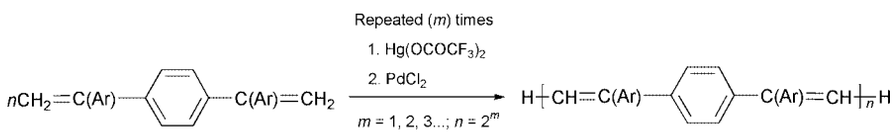


(12)

Table 4 Preparation of $[Ar^1(Ar^2)C{=}CH]_2$– **3** from $Ar^1(Ar^2)C{=}CH_2$ **1** in a one-pot reaction—experimental conditions and results[a]

Product **3**, yield (%)	mp[b]/°C lit., mp/°C	Ar^2	Ar^1
3a, 88	207		
3b, 85	215 (215)[9]	OMe	
3c, 89	157[c] (158)[10]	OMe	OMe
3d, 91	215		
3e, 92	102–105[c]	OMe, MeO	
3i, 64	140	OMe, OMe	
3j, 59	80		

[a] Experimental conditions for the coupling reaction of **1** to yield **3**: 1) benzene, 0 °C, **1** (1 equiv.), $Hg(CO_2CF_3)(2)$, (1 equiv.), 15 min; 2) $PdCl_2$ (1 equiv.), Et_3N (3 equiv.), 15 min at 0 °C. [b] The products were crystallized from ethanol. [c] The products were crystallized from benzene.

monomers ($n = 1$) by carrying out a one-pot synthesis according to the following general sequence of reactions [eqn. (12)].

Experimental

General

^1H (200 MHz) and ^{13}C (200 MHz) NMR spectra were obtained in $CDCl_3$ with $SiMe_4$ as standard; J values are given in Hz. Benzene (AR) was dried over sodium wire, tetrahydrofuran (AR) was distilled before use from a colored THF solution of sodium benzophenone ketyl. Acetonitrile (AR) was distilled over P_2O_5 before use. HMPA (AR) was dried by $LiAlH_4$ and distilled from its mixture with $LiAlH_4$ into the reaction flask. Triethylamine was kept over sodium hydroxide and was distilled from this mixture before use. $PdCl_2$ (Merck, 99%) was used as purchased. Mercuric trifluoroacetate was prepared according to a known procedure[11] and dried in a vacuum for 12 hours before use. The 1,1-diarylethylenes[12] and the α,α′-diaryl-*p*-divinylbenzene type compounds $CH_2{=}C(Ar){-}C_6H_4{-}C(Ar){=}CH_2$ were prepared by a previously described methods[2,13] and were dried in a vacuum before use.

All reactions were carried out in a 100 ml three-neck flask. The reaction setup consisted of a three-neck flask (100 ml) fitted with a self-sealing rubber septum, equipped with magnetic stirring and a dry nitrogen inlet. Liquid materials were introduced into the reaction flask using a syringe. All glass parts, syringes and needles were thoroughly dried at 130 °C and assembled while warm. All the reactions for the synthesis of the oligomers were carried out under nitrogen in anhydrous conditions.

A general procedure for the preparation of $Ar^1(Ar^2)C{=}CH{-}HgCl$ (2)

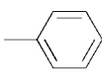
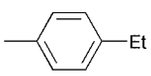
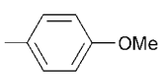
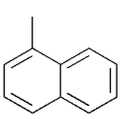
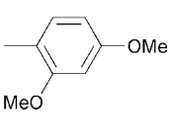
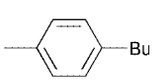
A modification of a reported procedure[8] was used.

A solution of $Ar^1(Ar^2)C{=}CH_2$ (3.5–8.6 mmol) and an equivalent amount of mercuric trifluoroacetate in benzene (8–15 ml), or acetonitrile (8–15 ml), was stirred for 45 min at room temperature. An aqueous solution (2 M) of sodium chloride (40 ml) was then added and the mixture was further stirred for 1 h. The solvents were removed and the white solid residue was washed several times with water and then with hexane. The solid was extracted with chloroform and filtered. The solvent was removed from the filtrate. The residue was the practically pure product $Ar^1(Ar^2)C{=}CH{-}HgCl$ **2**, which was used without further purification. This general procedure was used for the preparation of compounds **2a**–**2e**.

A general procedure for the preparation of the dimers $[Ar^1(Ar^2)C{=}CH]_2$ (3) by coupling of 2

A modification of a reported procedure[7] for the coupling of $Ar^1(Ar^2)C{=}CH{-}HgCl$ **2** was used. Dry benzene (5–20 ml), $PdCl_2$ (0.28–1.10 mmol) and a 3–4-fold excess of LiCl were introduced into a three-neck flask. The mixture was cooled to 0 °C and magnetically stirred under nitrogen. To an equivalent amount of organometallic the reactant **2** was then added, which caused an immediate color change to dark brown. Stirring was continued for 4–48 hours. Water, pentane and active carbon were added, the reaction mixture was shaken and filtered. The filtrate was extracted with pentane, the organic layer washed with water, dried over anhydrous magnesium

Table 5 The preparation of H–[CH=C(Ar)–C_6H_4–C(Ar)=$CH]_2$–H **5** from the corresponding monomers **4** in a one-pot synthesis—experimental conditions and results[a]

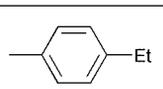
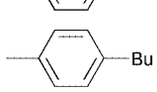
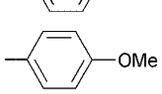
Ar	**4**/mmol	$PdCl_2$/ mmol	$Hg(CO_2CF_3)_2$/ mmol	Et_3N/ mmol	Product **5**, yield (%)
	0.9	0.9	0.9	2.7	**5a**, 92
	0.3	0.3	0.3	0.9	**5b**, 95
	0.9	0.9	0.9	0.27	**5c**, 96
	0.52	0.52	0.52	1.56	**5d**, 100
	0.5	0.5	0.5	1.5	**5e**, 98
	0.25	0.25	0.25	0.75	**5f**, 92

[a] The products were prepared according to the general procedure detailed in the Experimental section.

Table 6 Spectral data of the dimers H–[CH=C(Ar)–C_6H_4–C(Ar)=$CH]_2$–H **5** and the tetramers H–[CH=C(Ar)–C_6H_4–C(Ar)=$CH]_4$–H **6**

Compound	Spectral data
5a	δ_H 5.67 (2H, d, *J* 2), 5.71 (2H, d, *J* 2), 6.58 (2H, d, *J* 10), 7.48–7.67 (28H, m, Ar-H); *m/z* (EI) 562.2 (M^+, 100%)
5b	δ_H 1.62 (12H, t, *J* 4.1, CH_3), 2.68 (8H, q, *J* 4, CH_2), 5.29 (2H, d, *J* 2), 5.43 (2H, d, *J* 2), 6.32 (2H, d, *J* 13), 7.16–7.79 (24H, m, Ar-H); *m/z* (EI) 674.1 (M^+, 35%)
5c	δ_H 3.62 (12H, s, OMe), 5.38 (2H, d, *J* 2), 5.42 (2H, d, *J* 2), 6.25 (2H, d, *J* 9), 6.63–6.93, 7.21–7.37 (24H, m, Ar-H); *m/z* (EI) 682.3 (M^+, 80%)
5d	δ_H 5.59 (2H, d, *J* 2), 5.64 (2H, d, *J* 2), 6.48 (2H, d, *J* 10), 7.25–7.98 (38H, m, Ar-H); *m/z* (FAB) 763.212 ($[M + 1]^+$, 100%)
5e	δ_H 3.61 (12H, s, OMe), 3.84 (12H, s, OMe), 5.29 (2H, d, *J* 2), 5.66 (2H, d, *J* 2), 6.48–6.52, 7.13–7.36 (22H, m, Ar + vinyl H); *m/z* (FAB) 803 ($[M + 1]^+$, 10%)
5f	δ_H 1.16 (12H, t, *J* 4.1, CH_3), 1.63 (8H, m, CH_2), 1.82 (8H, m, CH_2), 2.62 (8H, t, *J* 4.3), 5.66 (2H, d, *J* 2), 5.68 (2H, d, *J* 2), 6.55 (2H, d, *J* 11), 7.35–7.56 (24H, m, Ar-H); *m/z* (FAB) 787.335 ($[M^+]^+$, 100%)
6b	δ_H 1.24 (24H, t, *J* 4, CH_3), 2.66 (16H, q, *J* 4.1, CH_2), 5.29 (2H, d, *J* 2), 5.43 (2H, d, *J* 2), 6.33 (6H, d, *J* 10), 7.19–7.43 (48H, m, Ar-H); *m/z* (FAB) 1347.578 ($[M + 1]^+$, 10%)
6c	δ_H 3.62 (24H, s, OMe), 5.38 (2H, d, *J* 2), 5.42 (2H, d, *J* 2), 6.23 (6H, d, *J* 11), 6.85–6.92, 7.18–7.43 (48H, m, Ar-H); *m/z* (EI) 684.2 (100%)
6f	δ_H 1.16 (24H, t, *J* 4, CH_3), 1.63 (16H, m, CH_2), 1.82 (16H, m, CH_2), 2.62 (16H, t, *J* 4.1, CH_2), 5.66 (2H, d, *J* 2), 5.68 (2H, d, *J* 2), 6.55 (6H, d, *J* 11), 7.35–7.56 (48H, m, Ar-H); *m/z* (EI) 1572.381 (M^+, 100%)

Table 7 Preparation of the tetramers H–[CH=C(Ar)–C_6H_4–C(Ar)=$CH]_4$–H **6** from: a) from the dimers **5** in a one-pot synthesis; B) from the monomers **4** in a one-pot synthesis

Yield (%)			
A	B	Product	Ar
71	86	**6b**	
65	89	**6f**	
75	90	**6c**[a]	

[a] The terminal methylene groups of the tetramer **6c** underwent reduction in the column when purified by column chromatography on silica gel 60; **6c** in this reduced form was the product isolated.

sulfate and filtered. The residue recovered from the filtrate was purified by column chromatography on silica gel, using petroleum ether (bp 60–80 °C) as eluent. This general procedure was used for the preparation of the $[Ar^1(Ar^2)C{=}CH]_2$ type compounds **3a**–**3e**.

A general procedure for the preparation of the dimers $[Ar^1(Ar^2)C{=}CH]_2$ (3) from $Ar^1(Ar^2)C{=}CH_2$ (1) in a one-pot synthesis

Benzene (10–12 ml) was introduced into a three-neck flask and cooled to 0 °C. To it was added the 1,1-diarylethylene (0.8–1.2 mmol) followed by an equivalent amount of mercuric trifluoroacetate, $PdCl_2$, and three equivalents triethylamine. The reaction mixture was stirred for 15 min at 0 °C. Methylene chloride, carbon black and water were added to the reaction mixture, which was shaken and filtered. The aqueous layer was extracted with methylene chloride, the organic layers were combined and dried over anhydrous $MgSO_4$. Column chromatography on silica gel was applied to the residue after removing the solvent from the dried extract to yield the corresponding pure 1,1,4,4-tetraarylbuta-1,3-dienes **3a**–**3j**.

A general procedure for preparation of the dimers H–[CH=C(Ar)–C_6H_4–C(Ar)=$CH]_2$–H (5) from the dienic monomers $CH_2{=}C(Ar)–C_6H_4–C(Ar){=}CH_2$ (4)

The procedure used was the same as that described above under

the conditions used for the preparation of the 1,1,4,4-tetraarylbuta-1,3-dienes of type **3** from **1** in a one-pot synthesis, except for the use of diene **4** (0.9 mmol) instead of $Ar^1(Ar^2)$-C=CH_2 **1**. This general procedure was used for the preparation of the dimers **5a**–**5f**.

A general procedure for preparation of the tetramers H–[CH=C(Ar)–C_6H_4–C(Ar)=CH]$_4$–H (6)

Method A. Preparation of the tetramers **6** by a one-pot synthesis from the corresponding dimers **5**. Benzene (10 ml) was introduced into a three-neck flask and cooled to 0 °C. To it was added the dimer **5** (0.9 mmol) followed by mercuric trifluoroacetate (0.380 g, 0.9 mmol) and the reaction mixture stirred for 15 min at 0 °C. $PdCl_2$ (0.150 g, 0.9 mmol) and Et_3N (0.370 g, 2.7 mmol) were then added, and the reaction mixture was further stirred for 15 min at 0 °C. The work-up was the same as described above in the procedure for preparation of **3** *via* coupling for **2** except for the use of cyclohexane as eluent instead of petroleum ether.

Method B. Preparation of the tetramers **6** by a one-pot synthesis from the corresponding monomeric dienes **4**. The monomer **4** (0.18–0.58 mmol) was added to benzene (10 ml) in a three-neck flask and cooled to a temperature of 0 °C, which was maintained throughout the whole synthesis. One equivalent of mercuric trifluoroacetate was added to this solution and the mixture was stirred for 15 min. Palladium chloride (1.25 equiv.) and Et_3N (3 equiv.) were then added and stirring was continued for 15 min. A second portion of mercuric trifluoroacetate (0.5 equiv.) was added and the reaction mixture stirred for 15 min. Palladium chloride (0.58 equiv.) and Et_3N (1.5 equiv.) were then added and stirring continued for 15 min. Work-up of the reaction mixture was done as described for method A. The general procedures of methods A and B were used for the preparation of the tetramers **6b**, **6c** and **6f**.

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