

# One-pot synthesis of oligomeric aryl-substituted PPV analogs with extended $\pi$ -conjugation

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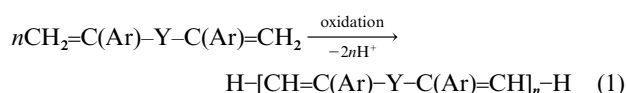
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A conceptually novel approach for a stepwise one-pot synthesis of oligomeric poly(phenylvinylene) (PPV,  $-\text{[C}_6\text{H}_4\text{-CH=CH]}-$ ) analogs with extended  $\pi$ -conjugation of the type  $\text{H-[CH=C(Ar)-C}_6\text{H}_4\text{-C(Ar)=CH]}_n\text{-H}$  ( $n = 2, 4$ ), 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  $\text{H-[CH=C(Ar)-C}_6\text{H}_4\text{-C(Ar)=CH]}_n\text{-HgCO}_2\text{CF}_3$  ( $n = 1, 2$ ) and its coupling in the presence of  $\text{PdCl}_2$ . 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.<sup>1a</sup> 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.<sup>1</sup> An effective and versatile approach for converting an  $n$ -mer to the corresponding  $(n + 2)$ -mer, is the McMurry reaction.<sup>1b</sup> It has been successfully applied to the preparation of cyclic sulfur-bridged annulenes<sup>1c</sup> and related compounds.<sup>1d</sup> 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  $\text{CH}_2=\text{C(Ar)-Y-C(Ar)=CH}_2$  [eqn. (1)].

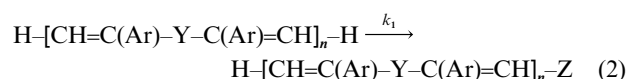


Thus, oligomers of the general structure  $\text{H-[CH=C(Ar)-Y-C(Ar)=CH]}_n\text{-H}$  ( $n = 2, 4, 8 \dots$ ), to be prepared by a one-pot sequential synthesis of the  $n\text{M} \rightarrow (\text{M})_n$ -type, were the target oligomers of the research reported here.

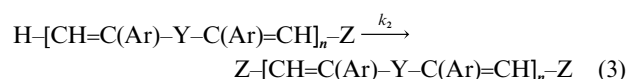
An oxidative-coupling-type oligomerization based on the above mentioned polymerization used for these monomers [eqn. (1)] could in fact be considered as a one-pot reaction. However, it would have resulted in a mixture of various  $n$ -mers, that would need to be separated from each other. A recently

reported relevant example, is that of the preparation of a mixture of oligotriacetylenes, and its separation into its pure oligomeric constituents.<sup>3</sup>

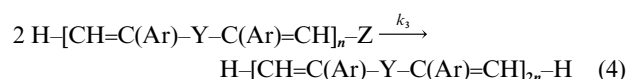
A novel general strategy for a one-pot sequential synthesis of mono-dispersed oligomers from bifunctional monomers is presented here. The synthesis of the above mentioned target oligomers is to be regarded as a specific example of this general approach. According to this approach, transformation of each  $n$ -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



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

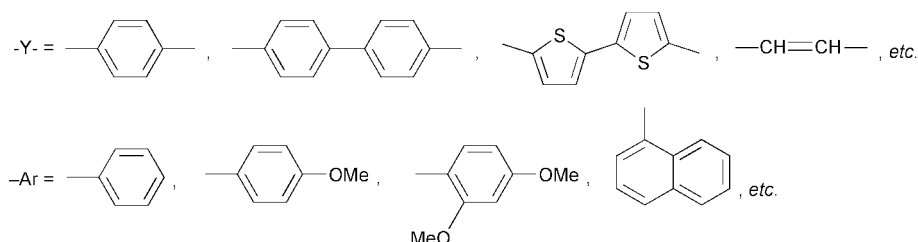


$k_1 \gg k_2$ , ( $n = 1, 2, 4, \dots$ ). The second step is an *in situ* coupling reaction,  $k_3$ , of two such monofunctionalized  $n$ -mer molecules to yield the corresponding  $2n$ -mer [eqn. (4)]. It is obvious that in



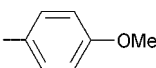
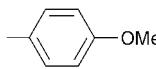
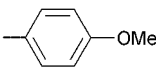
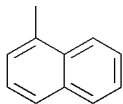
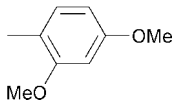

order for this approach to be applicable, each of these two consecutive reactions has to take place in a very high yield.

Coupling reactions of symmetrically conjugated dienes of the type  $\text{CH}_2=\text{C(Ar)-Y-C(Ar)=CH}_2$  have not been reported,





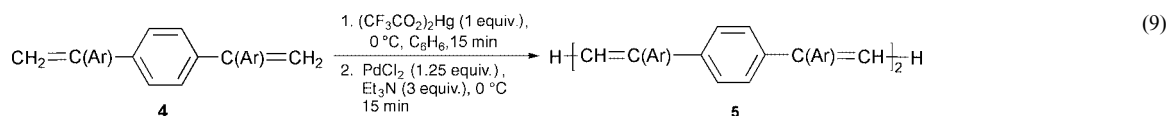
**Table 2** The preparation of the dimers  $[\text{Ar}^1(\text{Ar}^2)\text{C}=\text{CH}]_2$  **3** by coupling of **2**—experimental conditions and results<sup>a</sup>

Ar <sup>1</sup>	Ar <sup>2</sup>	<b>2</b> /mmol	PdCl <sub>2</sub> /mmol	Reaction time/h	Product <b>3</b> , yield (%)	Mp <sup>b</sup> / °C (lit., mp/ °C)
-Ph	-Ph	0.34	0.34	18	<b>3a</b> , 62	207
-Ph		0.36	0.36	4	<b>3b</b> , 56	215 (215) <sup>9</sup>
		2.8	2.8	4	<b>3c</b> , 62	157 <sup>c</sup> (158) <sup>10</sup>
-Ph		1.1	1.1	18	<b>3d</b> , 51	215
-Ph		0.45	0.45	18	<b>3e</b> , 60	102–105 <sup>c</sup>
-Ph	$\text{CH}_2=\text{C}(\text{Ph})-\text{C}_6\text{H}_4-$ 	0.48	0.48	18	<b>5a</b> <sup>d,e,f</sup> 38	135

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

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

Compound	Spectral data
<b>2a</b>	$\delta_{\text{H}}$ 6.33 (1H, s), 6.95–7.33 (10H, m); $m/z$ (EI) 415.9 ( $\text{M}^+$ , 20%), 178.9 ( $[(\text{Ph}_2)\text{C}=\text{CH}]^+$ , 100%)
<b>2b</b>	$\delta_{\text{H}}$ 3.82 (3H, s, OCH <sub>3</sub> ), 6.24 (1H, s), 6.62–7.39 (9H, m); $m/z$ (EI) 445.9 ( $\text{M}^+$ , 20%), 209 ( $[(\text{Ph})(4\text{-anisyl})\text{C}=\text{CH}]^+$ , 100%)
<b>2c</b>	$\delta_{\text{H}}$ 3.84 (6H, s, OCH <sub>3</sub> ), 6.22 (1H, s), 6.81–7.61 (8H, m); $m/z$ (EI) 239 ( $[(4\text{-anisyl})_2\text{C}=\text{CH}]^+$ , 100%)
<b>2d</b>	$\delta_{\text{H}}$ 6.41 (1H, s), 6.45 (1H, s), 7.29–7.95 (24H, m); $m/z$ (EI) 466 ( $\text{M}^+$ , 20%), 229 ( $[(\text{Ph})(\alpha\text{-naphthyl})\text{C}=\text{CH}]^+$ , 100%)
<b>2e</b>	$\delta_{\text{H}}$ 3.66 (3H, s, OCH <sub>3</sub> ), 3.86 (3H, s, OCH <sub>3</sub> ), 6.50 (1H, s), 7.26–7.31 (8H, m); $m/z$ (EI) 239 ( $[(\text{Ph})(2,4\text{-dimethoxyphenyl})\text{C}=\text{CH}]^+$ , 100%)
<b>2k</b>	$\delta_{\text{H}}$ 3.84 (3H, s, OCH <sub>3</sub> ), 5.46 (1H, d, $J$ 4), 5.48 (1H, d, $J$ 4), 6.45 (1H, s), 7.2–7.4 (14H, m); $\delta_{\text{C}}$ 114.6 (C=CH <sub>2</sub> ), 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 ( $\text{M}^+$ , 100%)
<b>3a</b>	$\delta_{\text{H}}$ 6.75 (2H, s), 7.23–7.45 (20H, m); $\delta_{\text{C}}$ 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 ( $\text{M}^+$ , 100%)
<b>3b</b>	$\delta_{\text{H}}$ 3.86 (6H, s, OMe), 6.67–7.41 (20H, m, Ar + vinyl H); $\delta_{\text{C}}$ 55.2 (4C, OMe), 113.5 (2C, =CH <sub>2</sub> ), 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 ( $\text{M}^+$ , 28%)
<b>3c</b>	$\delta_{\text{H}}$ 3.77 (12H, s, OMe), 6.64–7.50 (18H, m, Ar-H + vinyl H); $\delta_{\text{C}}$ 55.2 (OMe), 113.5 (=CH <sub>2</sub> ), 127.1 (4C, CH), 131.2, 141.11, 156.1, (C-C, Ar); $m/z$ (EI) 478.4 ( $\text{M}^+$ , 47%) 252.2 ( $[(4\text{-anisyl})_2\text{C}=\text{CH}]^+$ , 100%)
<b>3d</b>	$\delta_{\text{H}}$ 6.91–7.91 (m, Ar + vinyl H); $\delta_{\text{C}}$ 114.7 (C=CH <sub>2</sub> ), 149.9, 148.1, 140.8, 138.8 (5C, C-C), 126.3–136.6 (12C, Ar-CH); $m/z$ (EI) 458.2 ( $\text{M}^+$ , 100%)
<b>3e</b>	$\delta_{\text{H}}$ 3.63 (6H, s, OMe), 3.81 (6H, s, OMe), 6.49 (2H, s, vinyl H), 7.26–7.28 (16H, m, Ar-H); $\delta_{\text{C}}$ 55.5 (C-OMe), 115.5 (C=CH <sub>2</sub> ), 130.05, 132.10, 134.22, 140.07, 143.10 (5C, C-C), 124.66–128.00 (8C, CH-Ar); $m/z$ (EI) 478 ( $\text{M}^+$ , 5%)
<b>3i</b>	$\delta_{\text{H}}$ 3.83 (6H, s, OMe), 3.90 (6H, s, OMe), 6.69–7.38 (18H, m, Ar + vinyl H); $\delta_{\text{C}}$ 55.9 (OMe), 113.1 (C=CH <sub>2</sub> ), 125.8–129.8 (8C, Ar-CH), 149.7, 148.8, 148.5, 141.5, 134.3 (5C, C-C); $m/z$ (EI) 239 ( $[(3,4\text{-dimethoxyphenyl})(\text{Ph})\text{C}=\text{CH}]^+$ , 100%)
<b>3j</b>	$\delta_{\text{H}}$ 6.66 (2H, s, vinyl H), 7.25–7.60 (28H, m, Ar-H); $\delta_{\text{C}}$ 115.9 (=CH <sub>2</sub> ), 126.9–128.8 (8C, Ar-CH), 143.5, 140.3, 138.9, 137.4, 129.8 (5C, C-C); $m/z$ (EI) 268 ( $[(\text{biphenyl-4-yl})(\text{phenyl})\text{C}=\text{CH-CH}]^+$ , 100%)



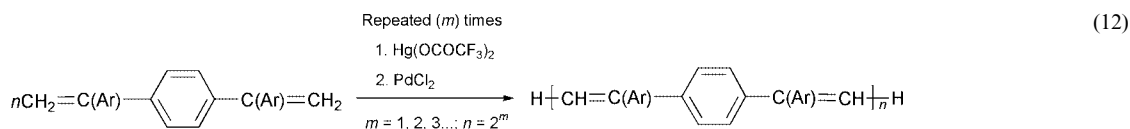
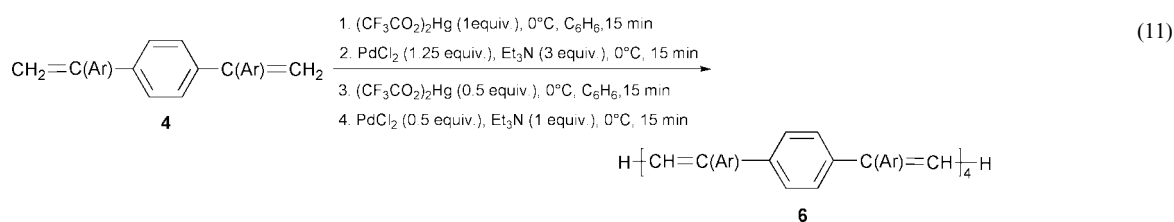
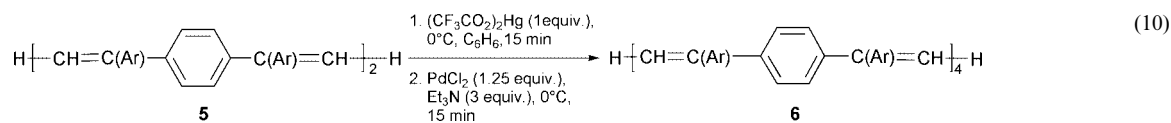
**5** were determined based on their <sup>1</sup>H-NMR, and mass spectral data, which are detailed in Table 6.

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 <sup>1</sup>H-NMR and mass spectral data, which are detailed in Table 6.

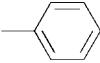

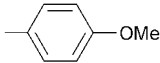

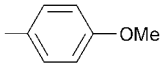
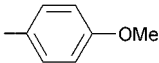
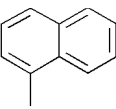

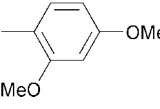

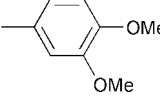

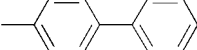

The possibility of performing the novel approach for construction of mono-dispersed *n*-mers (*n* = 2, 4) directly from the

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  $\text{H}-[\text{CH}=\text{C}(\text{Ar})-\text{C}_6\text{H}_4-\text{C}(\text{Ar})=\text{CH}]_n-\text{H}$  (*n* = 2, 4) were prepared directly from the corresponding



**Table 4** Preparation of  $[\text{Ar}^1(\text{Ar}^2)\text{C}=\text{CH}]_n$  (**3**) from  $\text{Ar}^1(\text{Ar}^2)\text{C}=\text{CH}_2$  (**1**) in a one-pot reaction—experimental conditions and results<sup>a</sup>

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

<sup>a</sup> Experimental conditions for the coupling reaction of **1** to yield **3**: 1) benzene, 0 °C, **1** (1 equiv.), Hg(CO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> (1 equiv.), 15 min; 2) PdCl<sub>2</sub> (1 equiv.), Et<sub>3</sub>N (3 equiv.), 15 min at 0 °C. <sup>b</sup> The products were crystallized from ethanol. <sup>c</sup> 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

<sup>1</sup>H (200 MHz) and <sup>13</sup>C (200 MHz) NMR spectra were obtained in CDCl<sub>3</sub> with SiMe<sub>4</sub> 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<sub>2</sub>O<sub>5</sub> before use. HMPA (AR) was dried by LiAlH<sub>4</sub> and

distilled from its mixture with LiAlH<sub>4</sub> into the reaction flask. Triethylamine was kept over sodium hydroxide and was distilled from this mixture before use. PdCl<sub>2</sub> (Merck, 99%) was used as purchased. Mercuric trifluoroacetate was prepared according to a known procedure<sup>11</sup> and dried in a vacuum for 12 hours before use. The 1,1-diarylethylenes<sup>12</sup> and the  $\alpha,\alpha'$ -diaryl-*p*-divinylbenzene type compounds CH<sub>2</sub>=C(Ar)-C<sub>6</sub>H<sub>4</sub>-C(Ar)=CH<sub>2</sub> were prepared by a previously described methods<sup>2,13</sup> 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<sup>1</sup>(Ar<sup>2</sup>)C=CH-HgCl (**2**)


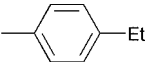
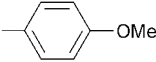
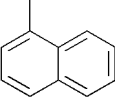
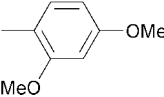
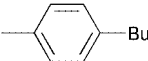
A modification of a reported procedure<sup>8</sup> was used.

A solution of Ar<sup>1</sup>(Ar<sup>2</sup>)C=CH<sub>2</sub> (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<sup>1</sup>(Ar<sup>2</sup>)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<sup>1</sup>(Ar<sup>2</sup>)C=CH]<sub>2</sub> (**3**) by coupling of **2**

A modification of a reported procedure<sup>7</sup> for the coupling of Ar<sup>1</sup>(Ar<sup>2</sup>)C=CH-HgCl **2** was used. Dry benzene (5–20 ml), PdCl<sub>2</sub> (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<sub>6</sub>H<sub>4</sub>-C(Ar)=CH]<sub>2</sub>-H **5** from the corresponding monomers **4** in a one-pot synthesis—experimental conditions and results<sup>a</sup>

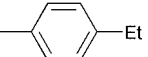
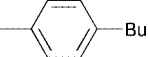
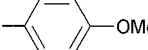
Ar	<b>4</b> /mmol	PdCl <sub>2</sub> /mmol	Hg(CO <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub> /mmol	Et <sub>3</sub> N/mmol	Product <b>5</b> , yield (%)
	0.9	0.9	0.9	2.7	<b>5a</b> , 92
	0.3	0.3	0.3	0.9	<b>5b</b> , 95
	0.9	0.9	0.9	0.27	<b>5c</b> , 96
	0.52	0.52	0.52	1.56	<b>5d</b> , 100
	0.5	0.5	0.5	1.5	<b>5e</b> , 98
	0.25	0.25	0.25	0.75	<b>5f</b> , 92

<sup>a</sup> 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<sub>6</sub>H<sub>4</sub>-C(Ar)=CH]<sub>2</sub>-H **5** and the tetramers H-[CH=C(Ar)-C<sub>6</sub>H<sub>4</sub>-C(Ar)=CH]<sub>4</sub>-H **6**

Compound	Spectral data
<b>5a</b>	$\delta_{\text{H}}$ 5.67 (2H, d, <i>J</i> 2), 5.71 (2H, d, <i>J</i> 2), 6.58 (2H, d, <i>J</i> 10), 7.48–7.67 (28H, m, Ar-H); <i>m/z</i> (EI) 562.2 (M <sup>+</sup> , 100%)
<b>5b</b>	$\delta_{\text{H}}$ 1.62 (12H, t, <i>J</i> 4.1, CH <sub>3</sub> ), 2.68 (8H, q, <i>J</i> 4, CH <sub>2</sub> ), 5.29 (2H, d, <i>J</i> 2), 5.43 (2H, d, <i>J</i> 2), 6.32 (2H, d, <i>J</i> 13), 7.16–7.79 (24H, m, Ar-H); <i>m/z</i> (EI) 674.1 (M <sup>+</sup> , 35%)
<b>5c</b>	$\delta_{\text{H}}$ 3.62 (12H, s, OMe), 5.38 (2H, d, <i>J</i> 2), 5.42 (2H, d, <i>J</i> 2), 6.25 (2H, d, <i>J</i> 9), 6.63–6.93, 7.21–7.37 (24H, m, Ar-H); <i>m/z</i> (EI) 682.3 (M <sup>+</sup> , 80%)
<b>5d</b>	$\delta_{\text{H}}$ 5.59 (2H, d, <i>J</i> 2), 5.64 (2H, d, <i>J</i> 2), 6.48 (2H, d, <i>J</i> 10), 7.25–7.98 (38H, m, Ar-H); <i>m/z</i> (FAB) 763.212 ([M + 1] <sup>+</sup> , 100%)
<b>5e</b>	$\delta_{\text{H}}$ 3.61 (12H, s, OMe), 3.84 (12H, s, OMe), 5.29 (2H, d, <i>J</i> 2), 5.66 (2H, d, <i>J</i> 2), 6.48–6.52, 7.13–7.36 (22H, m, Ar + vinyl H); <i>m/z</i> (FAB) 803 ([M + 1] <sup>+</sup> , 10%)
<b>5f</b>	$\delta_{\text{H}}$ 1.16 (12H, t, <i>J</i> 4.1, CH <sub>3</sub> ), 1.63 (8H, m, CH <sub>2</sub> ), 1.82 (8H, m, CH <sub>2</sub> ), 2.62 (8H, t, <i>J</i> 4.3), 5.66 (2H, d, <i>J</i> 2), 5.68 (2H, d, <i>J</i> 2), 6.55 (2H, d, <i>J</i> 11), 7.35–7.56 (24H, m, Ar-H); <i>m/z</i> (FAB) 787.335 ([M] <sup>+</sup> , 100%)
<b>6b</b>	$\delta_{\text{H}}$ 1.24 (24H, t, <i>J</i> 4, CH <sub>3</sub> ), 2.66 (16H, q, <i>J</i> 4.1, CH <sub>2</sub> ), 5.29 (2H, d, <i>J</i> 2), 5.43 (2H, d, <i>J</i> 2), 6.33 (6H, d, <i>J</i> 10), 7.19–7.43 (48H, m, Ar-H); <i>m/z</i> (FAB) 1347.578 ([M + 1] <sup>+</sup> , 10%)
<b>6c</b>	$\delta_{\text{H}}$ 3.62 (24H, s, OMe), 5.38 (2H, d, <i>J</i> 2), 5.42 (2H, d, <i>J</i> 2), 6.23 (6H, d, <i>J</i> 11), 6.85–6.92, 7.18–7.43 (48H, m, Ar-H); <i>m/z</i> (EI) 684.2 (100%)
<b>6f</b>	$\delta_{\text{H}}$ 1.16 (24H, t, <i>J</i> 4, CH <sub>3</sub> ), 1.63 (16H, m, CH <sub>2</sub> ), 1.82 (16H, m, CH <sub>2</sub> ), 2.62 (16H, t, <i>J</i> 4.1, CH <sub>2</sub> ), 5.66 (2H, d, <i>J</i> 2), 5.68 (2H, d, <i>J</i> 2), 6.55 (6H, d, <i>J</i> 11), 7.35–7.56 (48H, m, Ar-H); <i>m/z</i> (EI) 1572.381 (M <sup>+</sup> , 100%)

**Table 7** Preparation of the tetramers H-[CH=C(Ar)-C<sub>6</sub>H<sub>4</sub>-C(Ar)=CH]<sub>4</sub>-H **6** from: a) from the dimers **5** in a one-pot synthesis; B) from the monomers **4** in a one-pot synthesis

Yield (%)		Product	Ar
A	B		
71	86	<b>6b</b>	
65	89	<b>6f</b>	
75	90	<b>6c<sup>a</sup></b>	

<sup>a</sup> 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 pro-

cedure was used for the preparation of the [Ar<sup>1</sup>(Ar<sup>2</sup>)C=CH]<sub>2</sub> type compounds **3a–3e**.

#### A general procedure for the preparation of the dimers [Ar<sup>1</sup>(Ar<sup>2</sup>)C=CH]<sub>2</sub> (**3**) from Ar<sup>1</sup>(Ar<sup>2</sup>)C=CH<sub>2</sub> (**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<sub>2</sub>, 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<sub>4</sub>. 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<sub>6</sub>H<sub>4</sub>-C(Ar)=CH]<sub>2</sub>-H (**5**) from the dienic monomers CH<sub>2</sub>=C(Ar)-C<sub>6</sub>H<sub>4</sub>-C(Ar)=CH<sub>2</sub> (**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<sup>1</sup>(Ar<sup>2</sup>)-C=CH<sub>2</sub> **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<sub>6</sub>H<sub>4</sub>-C(Ar)=CH]<sub>4</sub>-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<sub>2</sub> (0.150 g, 0.9 mmol) and Et<sub>3</sub>N (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<sub>3</sub>N (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<sub>3</sub>N (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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