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An efficient synthesis of functional stilbenes in Hiyama coupling reaction catalysed by H-spirophosphorane palladium complex

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ABSTRACT

An efficient Hiyama cross-coupling reaction of functionalised styrylsilanes with iodo- and bromobenzene has been performed using complex [$PdCl_2P(OCH_2CMe_2NH)$ $OCH_2CMe_2NH_2$] as precatalyst. The styrylsilanes underwent cross-coupling reactions with excellent selectivity and yield, up to 99%, of the corresponding *E*-stilbenes. When (*E*)-[1-(4-bromophenyl)-2-(1,1,3,3,3-pentamethyldisiloxy)]ethene was used as a source of the silane, a homocoupling reaction took place and polymeric compound containing 0.77% of palladium in the form of Pd(0) nanoparticles was obtained. This material used as a catalyst made it possible to obtain 40% and 38% of the Hiyama cross-coupling product in two subsequent runs.

1. Introduction

Stilbenes (1,2-diphenylethylenes) and their hydroxylated stilbenoid derivatives, with π-electron conjugated systems, constitute a class of compounds that have found an application in different areas: chemistry, biology and physics [1]. Stilbene moieties are recognised to exhibit anticancer, antibacterial, and fungistatic activities [2–4]. Due to the extended π-system, they have found an application in the manufacture of optoelectric and electronic devices: dye lasers, solar cells, fluorescent sensors, light-emitting diodes, scintillators, and others [5,6]. Some bioactive stilbene derivatives (Resveratrol, Combretastatin A-4) might be naturally obtainable through extraction from plant species; some need to be synthetically obtained. Among several synthetic routes providing substituted stilbenes, one must consider palladium-catalysed Heck reaction of aryl halide (or triflate) with styrene [7]. The Hiyama coupling presents an encouraging alternative route for the synthesis of *E*-stilbenes (Scheme 1) [8], which can be considered environmentally friendly taking into account the low toxicity of the silicon derivatives used as substrates [9–13].

During the course of our studies on the catalytic activity of palladium complexes with H-spirophosphorane ligands, we have developed a new efficient catalytic system for stereoselective synthesis of substituted *E*-stilbenes *via* Heck cross-coupling reaction [14]. In order to compare both procedures, namely Heck and Hiyama cross-coupling, we selected easily obtained complex [$PdCl_2P(OCH_2CMe_2NH)OCH_2CMe_2NH_2$] [15] as a precatalyst. Here we present an even more effective and stereoselective method of synthesis of unsymmetrical *E*-stilbenes through the Hiyama coupling (HC) of relevant styrylsilanes with iodo- and bromobenzene.

2. Experimental

2.1. Materials

^{1}H NMR (500 or 400 MHz, 298 K), ^{13}C NMR (126 or 100 MHz, 298 K) and ^{29}Si NMR (75 MHz, 298 K) spectra were recorded on a Bruker Avance 500 MHz or Varian XL 300 MHz spectrometer in $CDCl_3$ solution. Chemical shifts are reported as δ (in ppm) relative to the residual solvent ($CDCl_3$) peak for ^{1}H, ^{13}C and relative to TMS for ^{29}Si. Analytical gas chromatographic (GC) analyses for silylative coupling products were performed on a Varian Star 3400CX with a DB-5 fused silica capillary column (30 m × 0.15 mm) and TCD. Mass spectra of styrylsilanes were obtained by GC–MS analysis (Varian Saturn 2100T, equipped with a BD-5 capillary column (30 m) and an ion trap detector. High-resolution mass spectroscopic (HRMS) analyses were performed on an AMD-402 mass spectrometer. Thin-layer chromatography (TLC) was done on plates coated with 250 μm layer of silica gel (Aldrich and Merck), and column chromatography was conducted with silica gel 60 (70–230 mesh,

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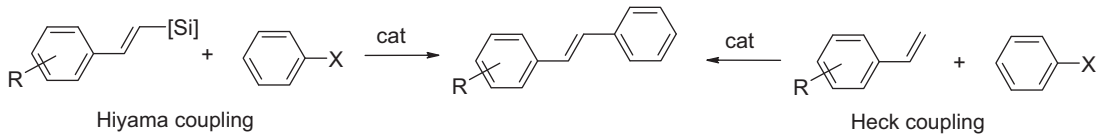


Scheme 1.

Fluka). Analytical gas chromatographic (GC) analyses for Hiyama coupling products were performed on Hewlett Packard 5890 fitted with a FID detector. Conversion of the substrates was calculated using internal standard method. MS spectra were measured on an ESI Finnigan Mat TSQ 700 instrument.

The chemicals were obtained from the following sources: toluene, styrene, 4-methylstyrene, 4-methoxystyrene, 3-methylstyrene, 4-chlorostyrene, 2-chlorostyrene, silica gel, celite®, and copper (I) chloride were bought from Aldrich, $CDCl_3$ from Dr Glaser A.G. Basel, vinylpentamethyldisiloxane from Gelest. The complexes: $[RuHCl(CO)(PPh_3)_3]$ and $[PdCl_2P(OCH_2CMe_2NH)OCH_2CMe_2NH_2]$ were prepared according to the procedure described in the literature [15,16].

2.2. General procedure for synthesis of styrylsilanes

The syntheses *via* silylative cross-coupling were performed under argon using $[RuHCl(CO)(PPh_3)_2]$ as a catalyst. The reagents and the solvent were distilled, dried and deoxygenated. The details are presented below. The substrates were synthesised in a manner similar to that reported previously [11a–b,17] with modifications that made it possible to achieve a significant improvement in the yield of the synthesis reaction. A toluene solution (25.4 mL, 1M) of two reagents: vinylpentamethyldisiloxane (2.54×10^{-2} mol) and styrene (3.05×10^{-2} mol) – ([ViSi]:[olefin] = 1:1.2) was placed in a 100 mL two-neck glass reactor with a magnetic stirring bar and a condenser connected to a bubbler. Then, the reaction mixture was stirred and heated to 110 °C under an argon flow. After 10 min, the ruthenium complex (1 mol%) was added. The solution colour changed from yellow to green and to yellow again. Next, more than 5 min later, copper (I) chloride was added ([CuCl]:[Ru] = 3:1), and substantial ethylene emission was observed. The synthesis process was carried out for the next 8–14 h. Then, the solvent excess was evaporated under vacuum. The crude product was separated from the reaction mixture using 'flash column' system (glass filter G3, silica gel, celite and membrane pomp) to remove residues of ruthenium complex and copper. Finally, the pure compound was obtained using the fraction distillation technique (yield 75–92%). The degree of conversion was calculated by GC and GC–MS analyses.

(E)-[1-(phenyl)-2-(1,1,3,3,3-pentamethyldisiloxane)]ethene (**1a**). bp 78–81 °C/1 mmHg, colourless liquid, yield 92%, purity >99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.12 (s, 9H, $-Si(CH_3)_3$), 0.23 (s, 6H, $-Si(CH_3)_2-$), 6.44 (d, 1H, J_{HH} = 19.2 Hz, Si–CH=CH–C_6H_5), 6.92 (d, 1H, J_{HH} = 19.2 Hz, Si–HC=CH–C_6H_5), 7.23–7.33 (m, 3H, 3,4-C_6H_5), 7.55 (d, 2H, J_{HH} = 2.1 Hz, 2-C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.9, 2.2, 127.0, 127.7, 128.4, 138.6, 139.6, 146.4; ^{29}Si NMR (79 MHz, $CDCl_3$) δ −2.80, 8.82; HRMS (EI) m/z calcd for $C_{13}H_{22}OSi_2$: 250.12092; found 250.12089.

(E)-[1-(4-chlorophenyl)-2-(triethoxysilyl)]ethene (**1b**). bp 106–110 °C/1 mmHg, less-yellow liquid, yield 75%, purity 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, 9H, $-Si(OCH_2CH_3)_3$), 3.88 (q, 9H, $-Si(OCH_2CH_3)_3$), 6.14 (d, 1H, J_{HH} = 19.5 Hz, Si–HC=CH–C_6H_4–Cl), 7.15 (d, 1H, J_{HH} = 19.5 Hz, Si–HC=CH–C_6H_4–Cl), 7.30 (d, 2H, J_{HH} = 8.4 Hz, $-C_6H_4$–Cl), 7.40 (d, 2H, J_{HH} = 8.4 Hz, $-C_6H_4$–Cl); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.2, 58.6, 118.6, 127.9, 128.7, 134.4, 136.1, 147.6; ^{29}Si NMR (79 MHz, $CDCl_3$) δ −56.32; HRMS (EI) m/z calcd for $C_{14}H_{21}ClO_3Si$: 300.09485; found 300.09271.

(E)-[1-(2-chlorophenyl)-2-(1,1,3,3,3-pentamethyldisiloxy)]ethene (**1c**). bp 85–88 °C/0.7 mmHg, less-yellow liquid, yield 86%, purity 96.5%; ^{1}H NMR(400 MHz, $CDCl_3$) δ 0.17 (s, 9H, $-Si(CH_3)_3$), 0.28 (s, 6H, $-Si(CH_3)_2-$), 6.46 (d, 1H, J_{HH} = 19.2 Hz, Si–HC=CH–C_6H_4–Cl), 7.22 (t, 2H, $-C_6H_4$–Cl), 7.28 (d, 1H, J_{HH} = 1.2 Hz, $-C_6H_4$–Cl), 7.39 (s, 1H, $-C_6H_4$–Cl), 7.40 (d, 1H, J_{HH} = 19.6 Hz, Si–HC=CH–C_6H_4–Cl), 7.64 (d, 1H, J_{HH} = 1.2 Hz, $-C_6H_4$–Cl). ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.8, 2.0, 116.5, 126.7, 128.9, 129.7, 132.2, 133.3, 136.2, 139.9. ^{29}Si NMR (79 MHz, $CDCl_3$) δ −3.30, 8.71; HRMS (EI) m/z calcd for $C_{13}H_{21}ClOSi_2$: 284.08195; found 284.08190.

(E)-[1-(4-bromophenyl)-2-(1,1,3,3,3-pentamethyldisiloxy)]ethene (**1d**). bp 104–108 °C/1 mmHg, colourless liquid, yield 88%, purity >99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.12 (s, 9H, $-Si(CH_3)_3$, 0.23 (s, 6H, $-Si(CH_3)_2-$), 6.41 (d, 1H, J_{HH} = 19.5 Hz, Si–HC=CH–C_6H_4–Br), 6.85 (d, 1H, J_{HH} = 19.2 Hz, Si–HC=CH–C_6H_4–Br), 7.31 (d, 2H, J_{HH} = 8.7 Hz, $-C_6H_4$–Br), 7.46 (d, 2H, J_{HH} = 8.4 Hz, $-C_6H_4$–Br); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.9, 2.1, 121.9, 127.9, 129.7, 131.5, 137.0, 142.6; ^{29}Si NMR (79 MHz, $CDCl_3$) δ −2.53, 9.29; HRMS (EI) m/z calcd for $C_{13}H_{21}BrOSi_2$: 328.03143; found 328.03138.

(E)-[1-(4-methylphenyl)-2-(1,1,3,3,3-pentamethyldisiloxy)]ethene (**1e**). bp 98–101 °C/1 mmHg, colourless liquid, yield 90%, purity 98%; ^{1}H NMR(400 MHz, $CDCl_3$) δ 0.16 (s, 9H, $-Si(CH_3)_3$), 0.25 (s, 6H, $-Si(CH_3)_2-$), 2.35 (s, 3H, $-CH_3$), 6.51 (d, 1H, J_{HH} = 19.2 Hz, Si–HC=CH–C_6H_4–CH_3), 6.94 (d, 1H, J_{HH} = 19.2 Hz Si–HC=CH–C_6H_4–CH_3), 7.23 (s, 2H, $-C_6H_4$–CH_3), 7.25 (s, 2H, $-C_6H_4$–CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.8, 2.2, 21.5, 123.8, 127.2, 128.4, 128.9, 138.2, 144.2; ^{29}Si NMR (79 MHz, $CDCl_3$) δ −3.07, 8.36; HRMS (EI) m/z calcd for $C_{14}H_{24}OSi_2$: 264.13657; found 264.13652.

(E)-[1-(3-methylphenyl)-2-(1,1,3,3,3-pentamethyldisiloxy)]ethene (**1f**). bp 82–84 °C/0.7 mmHg, colourless liquid, yield 91%, purity 98.5%; ^{1}H NMR(400 MHz, $CDCl_3$) δ 0.15 (s, 9H, $-Si(CH_3)_3$), 0.26 (s, 6H, $-Si(CH_3)_2-$), 2.39 (s, 3H, $-CH_3$), 6.43 (d, 1H, J_{HH} = 19.2 Hz, Si–HC=CH–C_6H_4–CH_3), 6.94 (d, 1H, J_{HH} = 19.2 Hz, Si–HC=CH–C_6H_4–CH_3), 7.11 (d, 1H, J_{HH} = 7.2 Hz, $-C_6H_4$–CH_3), 7.24 (s, 1H, *o*-C_6H_4–CH_3), 7.28 (s, 1H, $-C_6H_4$–CH_3), 7.31 (s, 1H, $-C_6H_4$–CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.8, 2.0, 22.7, 123.6, 127.2, 128.4, 128.4, 128.9, 138.0, 138.2, 144.2; ^{29}Si NMR (79 MHz, $CDCl_3$) δ −3.09, 8.38; HRMS (EI) m/z calcd for $C_{14}H_{24}OSi_2$: 264.13657; found 264.13654.

(E)-[1-(4-methoxyphenyl)-2-(1,1,3,3,3-pentamethyldisiloxy)]ethene (**1g**). bp 102–105 °C/1 mmHg, colourless liquid, yield 89%, purity >99%; ^{1}H NMR(400 MHz, $CDCl_3$) δ 0.15 (s, 9H, $-Si(CH_3)_3$), 0.25 (s, 6H, $-Si(CH_3)_2-$), 3.87 (s, 3H, $-OCH_3$), 6.50 (d, 1H, J_{HH} = 19.2 Hz, Si–HC=CH–C_6H_4–OCH_3), 6.97 (d, 1H, J_{HH} = 19.2 Hz Si–HC=CH–C_6H_4–OCH_3), 6.93 (d, 2H, J_{HH} = 8.7 Hz, $-C_6H_4$–OCH_3), 7.48 (d, 2H, J_{HH} = 9.3 Hz, $-C_6H_4$–OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.9, 2.2, 55.3, 113.9, 127.8, 128.8, 132.2, 138.9, 144.9; ^{29}Si NMR (79 MHz, $CDCl_3$) δ −3.03, 8.35; HRMS (EI) m/z calcd for $C_{14}H_{24}O_2Si_2$: 280.13148; founded 280.13145.

2.3. Hiyama reaction procedure

The Hiyama reactions were carried out in a 50 mL Schlenk tube equipped with a magnetic stirrer under nitrogen atmosphere. In a typical experiment, the flask was charged with the reagents: catalyst (1.31×10^{-5} mol), iodo- or bromobenzene PhX (X = I, Br)

(1.31×10^{-3} mol), ArCH=CH[Si] 1.44×10^{-3} mol in THF or DMF as a solvent (2 mL) containing mesitylene as an internal standard. An activator, [^{n}Bu$_4$N]F (2.14×10^{-3} mol) was used as an additive. The mixture was heated and stirred at 60 °C for 12 h (THF) or at 140 °C for 4 h (DMF). After that time, the reaction mixture was cooled and the organic products were separated by extraction with diethyl ether (3 times with 7 mL), washed with water, dried over $MgSO_4$, and analysed by GC–MS. The structures of the synthesised (*E*)-stilbenes were confirmed by GC–MS and NMR spectroscopy, matching data reported in the literature [18].

(E)-stilbene (**2a**). mp 119–120 °C (lit. 121 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (s, 1H), 7.38 (t, J = 7.55 Hz, 1H), 7.48 (t, J = 8.42 Hz, 2H), 7.64 (d, J = 7.84 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 126.5, 127.6, 128.6, 128.7, 137.3; GC–MS: m/z (%) 180 (100), 179 (97), 178 (60), 165 (47), 152 (11), 89 (73), 76 (51).

(E)-4-chlorostilbene (**2b**). mp 128–129 °C (lit. 128–129 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (d, J = 4.35 Hz, 2H), 7.19 (t, J = 7.31 Hz, 1H), 7.24 (s, 1H), 7.25 (s, 1H), 7.29 (t, J = 7.87 Hz, 2H), 7.35 (d, J = 8.52 Hz, 2H), 7.43 (d, J = 7.26 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 126.6, 127.4, 127.7, 127.9, 128.7, 128.9, 129.3, 133.2, 135.9, 137.0; GC–MS: m/z (%) 214 (89), 180 (17), 179 (98), 178 (100), 89 (58), 76 (51).

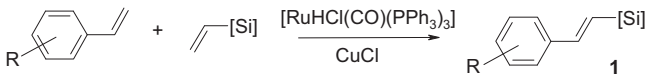
(E)-2-chlorostilbene (**2c**). mp 38–39 °C (lit. 39–40 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (d, J = 16.3 Hz, 1H), 7.08 (td, J = 5.90 Hz, 1H), 7.15 (td, J = 6.98 Hz, 1H), 7.21 (tt, J = 7.39 Hz, 1H), 7.27–7.35 (m, 3H), 7.47–7.49 (m, 3H), 7.57 (dd, J = 6.19 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 124.6, 126.4, 126.7, 126.8, 127.9, 128.4, 128.6, 129.7, 131.2, 133.3, 135.3, 136.9; GC–MS: m/z (%) 214 (43), 180(16), 179 (100), 178 (81), 89 (47), 76 (52).

(E)-4-bromostilbene (**2d**). mp 136–138 °C (lit. 136–137 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94 (d, J = 16.3 Hz, 1H), 7.02 (d, J = 16.3 Hz, 1H), 7.17–7.30 (m, 5H), 7.39 (d, J = 8.49 Hz, 2H), 7.42 (d, J = 7.39 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 121.3, 126.5, 127.4, 127.8, 127.9, 128.7, 129.4, 131.8, 136.3, 136.9; GC–MS: m/z (%) 260 (57), 258 (56), 179 (58), 178 (100), 89 (32), 76 (25).

(E)-4-methylstilbene (**2e**). mp 118–119 °C (lit. 119–120 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.36 (s, 3H), 6.98 (s, 1H), 6.99 (s, 1H), 7.07 (d, J = 7.55 Hz, 2H), 7.16 (t, J = 7.09 Hz, 1H), 7.26 (t, J = 7.30 Hz, 2H), 7.32 (d, J = 7.36 Hz, 2H), 7.41 (d, J = 7.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.28, 126.4, 126.5, 127.4, 127.8, 128.7, 129.4, 134.6, 137.5; GC–MS: m/z (%) 194 (100), 193 (45), 179 (99), 76 (6).

(E)-3-methylstilbene (**2f**). mp 46–47 °C (lit. 48.6–49.2 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.28 (s, 3H), 6.97–6.99 (m, 3H), 7.15 (t, J = 7.59 Hz, 2H), 7.21–7.27 (m, 4H), 7.41 (d, J = 7.80 Hz, 2H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 21.5, 123.7, 126.5, 127.2, 127.6, 128.4, 128.5, 128.6, 128.7, 128.9, 137.2, 137.4, 138.2; GC–MS: m/z (%) 194 (97), 193 (26), 179 (100), 178 (82), 76 (6).

(E)-4-methoxystilbene (**2g**). mp 134–135 °C (lit. 135–137 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.74 (s, 3H), 6.81 (d, J = 8.78 Hz, 2H), 6.93 (m, 2H), 7.16 (t, J = 5.6 Hz, 1H), 7.26 (t, J = 7.51 Hz, 2H), 7.37 (d, J = 8.75 Hz, 2H), 7.39 (d, J = 7.32 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.3, 114.1, 126.2, 126.6, 127.2, 127.7, 128.2, 128.6, 130.1, 137.6, 159.3; GC–MS: m/z (%) 210 (100), 209 (14), 195 (15), 179 (10), 76 (4).



[Si] = $SiMe_2OSiMe_3$ or $Si(OEt)_3$
R = H, Cl, Br, Me, OMe

Scheme 2.

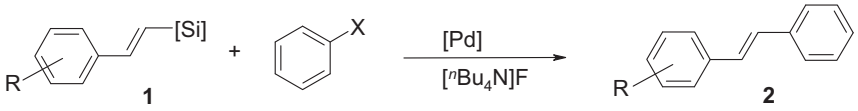
3. Results and discussion

3.1. Synthesis of styrylsilanes

In order to prepare the styrylsilanes to serve as substrates for the Hiyama cross-coupling, silylative coupling of vinylsilanes with substituted styrenes was used [11a,19]. Since an efficient protocol for this reaction had been reported by some of us previously, we utilised this route with slight modifications improving the yield of the products. The reaction was carried out in the presence of the ruthenium complex [$RuHCl(CO)(PPh_3)_3$] as a catalyst and CuCl as a co-catalyst. The amount of olefin was reduced from three- or five-fold molar excess to a nearly equimolar amount. The modified protocol allowed us to suppress the undesired homocoupling of vinylsilanes and resulted in improved yield of styrylsilanes. As seen from Scheme 2, the procedure was applicable to styrylsilanes bearing both electron-deficient as well as electron-rich substituents on phenyl ring. Application of this catalytic system effectively gives new useful reagents for Hiyama coupling: (*E*)-[1-(2-chlorophenyl)-2-(1,1,3,3,3-pentamethyldisiloxy)]ethene (**1c**) and (*E*)-[1-(3-methylphenyl)-2-(1,1,3,3,3-pentamethyldisiloxy)] ethene (**1f**), which have, to our knowledge, not been reported in the literature till now. The almost exclusive formation of E-styrylsilanes was corroborated by means of NMR and HRMS spectroscopic methods (see Section 2).

3.2. Hiyama cross-coupling reaction

At the outset of our studies, we probed the Hiyama coupling (HC) of styrylsilanes with iodobenzene under anaerobic conditions in THF at 60 °C and [^{n}Bu$_4$N]F as additive (Scheme 3). The cross-coupling of 1-aryl-2-silylethenes with iodobenzene led to the selective formation of corresponding stilbenes (Table 1). The reactions proceeded with almost exclusive ipso substitution, in a highly stereospecific manner, to afford mainly coupling products with an E configuration in good yields. The homocoupling product of iodobenzene, i.e. biaryl, was not observed. When the same conditions were applied to the Hiyama coupling with less reactive bromobenzene, no satisfactory results were obtained. These outcomes prompted us to undertake the coupling in more severe reaction conditions. In order to define the proper reaction conditions, we initially studied the C–C coupling of (*E*)-1-(4-chlorophenyl)-2-(triethoxysilyl)ethene as a model substrate. Preliminary experiments were carried out at 120 °C over 4 h in the



[Si] = $SiMe_2OSiMe_3$ or $Si(OEt)_3$ [Pd] = [$PdCl_2P(OCH_2CMe_2NH)OCH_2CMe_2NH_2$]
R = H, Cl, Br, Me, OMe X = I, Br

Scheme 3.

Table 1
Product distribution in Hiyama coupling reactions of halobenzene and substituted styrylsilanes $RC_6H_4CH{=}CH[Si]$.

Entry	$RC_6H_4CH{=}CH[Si]$	PhX	Conversion of PhX (%)	Yield (%) of *E*-stilbenes
1	**1a** $C_6H_5CH{=}CHSiMe_2OSiMe_3$	PhI[a]	100	**2a** 98
2	**1a** $C_6H_5CH{=}CHSiMe_2OSiMe_3$	PhBr[b]	98	**2a** 95
3	**1b** 4-$ClC_6H_4CH{=}CHSi(OEt)_3$	PhI[a]	91	**2b** 90
4	**1b** 4-$ClC_6H_4CH{=}CHSi(OEt)_3$	PhBr[b]	93	**2b** 91
5	**1c** 2-$ClC_6H_4CH{=}CHSiMe_2OSiMe_3$	PhI[a]	99	**2c** 97
6	**1c** 2-$ClC_6H_4CH{=}CHSiMe_2OSiMe_3$	PhBr[b]	97	**2c** 92
7	**1d** 4-$BrC_6H_4CH{=}CHSiMe_2OSiMe_3$	PhI[a]	100	**2d** 99
8	**1d** 4-$BrC_6H_4CH{=}CHSiMe_2OSiMe_3$	PhBr[b]	10	–
9	**1e** 4-$MeC_6H_4CH{=}CHSiMe_2OSiMe_3$	PhI[a]	96	**2e** 95
10	**1e** 4-$MeC_6H_4CH{=}CHSiMe_2OSiMe_3$	PhBr[b]	95	**2e** 92
11	**1f** 3-$MeC_6H_4CH{=}CHSiMe_2OSiMe_3$	PhI[a]	99	**2f** 98
12	**1f** 3-$MeC_6H_4CH{=}CHSiMe_2OSiMe_3$	PhBr[b]	95	**2f** 91
13	**1g** 4-$OMeC_6H_4CH{=}CHSiMe_2OSiMe_3$	PhI[a]	99	**2g** 97
14	**1g** 4-$OMeC_6H_4CH{=}CHSiMe_2OSiMe_3$	PhBr[b]	95	**2g** 93
15	**1b** 4-$ClC_6H_4CH{=}CHSi(OEt)_3$ [*]	PhI[a]	90	**2b** 88
16	**1b** 4-$ClC_6H_4CH{=}CHSi(OEt)_3$ [**]	PhI[a]	88	**2b** 87
17	**1b** 4-$ClC_6H_4CH{=}CHSi(OEt)_3$	PhBr[c]	5	**2b** 5
18	**1b** 4-$ClC_6H_4CH{=}CHSi(OEt)_3$	PhBr[d]	7	**2b** 7

[Pd catalyst] 1.31×10^{-5} mol; [^{n}Bu$_4$N]F 2.14×10^{-3} mol; PhX (1.31×10^{-3} mol); $RC_6H_4CH{=}CH[Si]$ 1.44×10^{-3} mol; mesitylene as internal standard. The yields of compounds are an average of at least two runs.
Entries 1–14, [Pd catalyst] = $[PdCl_2P(OCH_2CMe_2NH)OCH_2CMe_2NH_2]$.
[*] Entry 15 [Pd catalyst] = $PdCl_2$.
[**] Entry 16 [Pd catalyst] = $Pd(OAc)_2$.
[a] THF, 60 °C, 12 h.
[b] DMF, 140 °C, 4 h.
[c] Cs_2CO_3 as a base, DMF, 120 °C, 4 h.
[d] NaOH as a base, DMF, 120 °C, 4 h.

Table 2
Product distribution in Hiyama coupling reactions of 4-$OMeC_6H_4CH{=}CH$ $SiMe_2OSiMe_3$ and halosubstituted methoxybenzenes.

Entry	$RC_6H_4CH{=}CH[Si]$	PhX	Yield (%) of *E*-stilbenes[*]
1	4-$OMeC_6H_4CH{=}CHSiMe_2OSiMe_3$	2-Iodoanisole[a]	26
2	4-$OMeC_6H_4CH{=}CHSiMe_2OSiMe_3$	4-Iodoanisole[a]	15
3	4-$OMeC_6H_4CH{=}CHSiMe_2OSiMe_3$	2-Bromoanisole[b]	91
4	4-$OMeC_6H_4CH{=}CHSiMe_2OSiMe_3$	3-Bromoanisole[b]	82
5	4-$OMeC_6H_4CH{=}CHSiMe_2OSiMe_3$	4-Bromoanisole[b]	17

[*] Yield of isolated product.
[a] THF, 60 °C, 12 h.
[b] DMF, 140 °C, 4 h.

presence of the [^{n}Bu$_4$N]F, Cs_2CO_3 or NaOH. Tetrabutylammonium fluoride appeared to be the most effective activator compared with the two remaining bases. The yield of the reaction for cesium carbonate or sodium hydroxide was very low (5–7%). Having optimised the HC procedure, we were able to get almost exclusively the E-isomer of 4-chlorostilbene with satisfactory yield. Other palladium sources, such as $PdCl_2$ and $Pd(OAc)_2$, were less effective than complex $[PdCl_2P(OCH_2CMe_2NH)OCH_2CMe_2NH_2]$ (entries 15 and 16 respectively). Subsequently, the Hiyama coupling (HC) of styrylsilanes with bromobenzene (Scheme 3) was performed in DMF under anaerobic conditions at 140 °C. To evaluate the effectiveness of the catalytic system, substituted styrylsilanes incorporating electron-withdrawing or electron-donating groups were tested.

It should be noted that the kind of substituent within the aromatic ring had no impact on the yield or the stereochemistry of the stilbenes formed. The reactions of styrylsilanes having either an electron-donating group in a *para*-position, i.e. (Me, OMe) (entries 9, 10 and 13, 14) or an electron withdrawing group, (Cl) (entries 3, 4), proceeded smoothly, with an excellent yield of the products, exceeded 90%. Similarly, no steric effect was observed. Both small and sterically hindered styrylsilanes coupled effectively to give substituted stilbenes. To extend the scope of the protocol, we applied the optimum conditions to screen methoxy substituted halobenzenes. It was found that the catalytic system based on bromosubstituted anisoles is more effective than iodosubstituted one (Table 2).

To obtain mechanistic information about the system, the yield of the product as a function of the time of the reaction of (*E*)-[1-(4-methylphenyl)-2-(1,1,3,3,3-pentamethyldisiloxy)]ethene (**1e**) with bromobenzene was studied. As shown in Fig. 1, the reaction

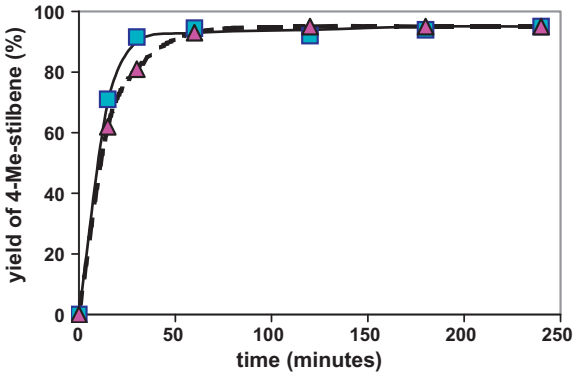


Fig. 1. Reaction profile study of the Hijama cross-coupling of (*E*)-[1-(4-methylphenyl)-2-(1,1,3,3,3-pentamethyldisiloxy)]ethene (**1e**) with bromobenzene (solid line), and a poisoning test (dotted line) with Hg(0) added before reaction starts (reaction conditions: DMF, 140 °C).

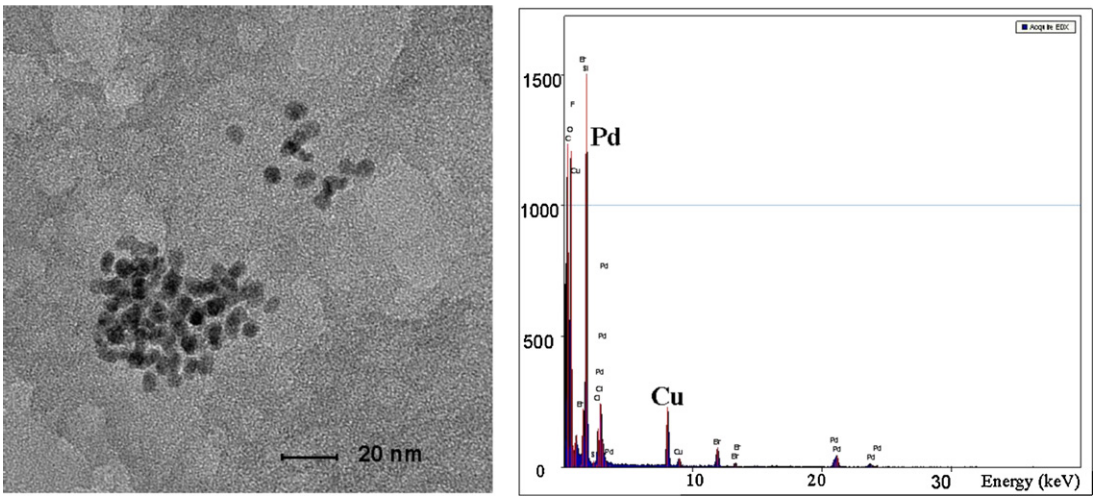
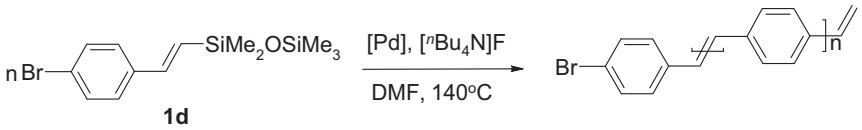


Fig. 2. TEM micrograph and energy dispersive X-ray spectrum (with the use of Cu grid) of post reaction solution between (*E*)-[1-(4-methylphenyl)-2-(1,1,3,3,3-pentamethyldisiloxy)] ethene (**1e**) and bromobenzene.



Scheme 4.

starts immediately, over 70% yield of the relevant stilbene is obtained within 15 min, and no induction period is observed. The lack of an induction period as well as sigmoidal kinetics points to the contribution of homogenous catalyst in catalytic process. This supposition was confirmed by mercury poisoning test [20], which was performed twice using 250 equivalents of mercury relative to palladium. In the first case, mercury was added together with the substrates, and in the second one, after 15 min of reaction. As can be seen in Fig. 1, no suppression of the reaction course was observed, as expected for the homogeneous catalyst.

Analysis of the post-reaction solution using TEM (transmission electron microscopy) and EDS (energy dispersive X-ray spectroscopy) (Fig. 2) showed the presence of Pd(0) nanoparticles with the mean size 6–7 nm. These nanoparticles were, most probably, formed in the final stage of the catalytic process, when practically all substrates had been used up.

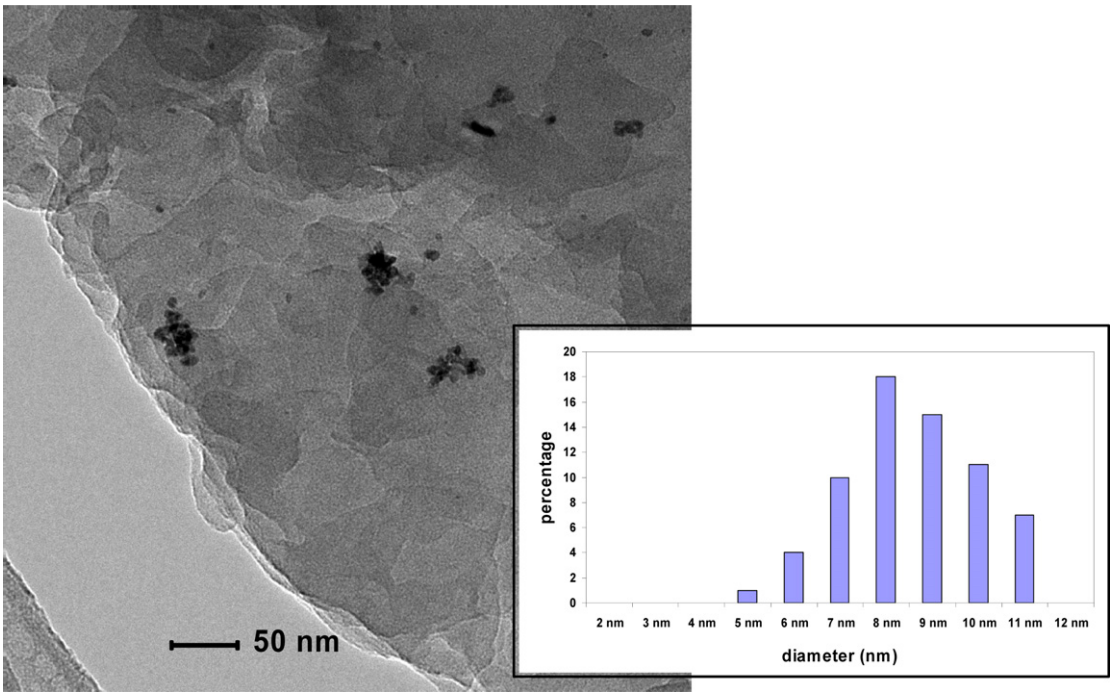


Fig. 3. TEM micrograph of polycondensation product of (*E*)-[1-(4-bromophenyl)-2-(1,1,3,3,3-pentamethyldisiloxy)]ethene (**1d**) and the corresponding size histogram of Pd(0) nanoparticles (70 Pd nanoparticles measured).

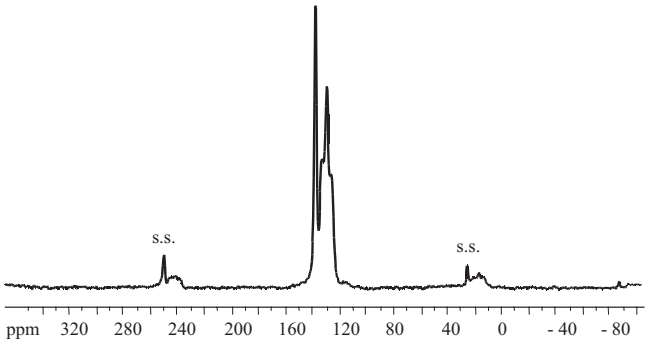


Fig. 4. CPMAS spectrum of polycondensation product of (*E*)-[1-(4-bromophenyl)-2-(1,1,3,3,3-pentamethyldisiloxy)]ethene made at r.t., s.s. denotes spinning sidebands.

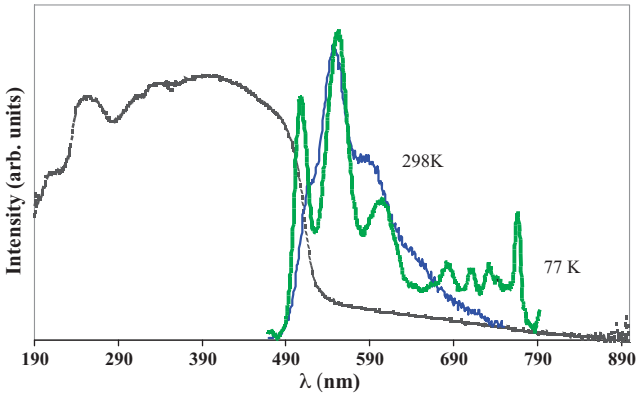


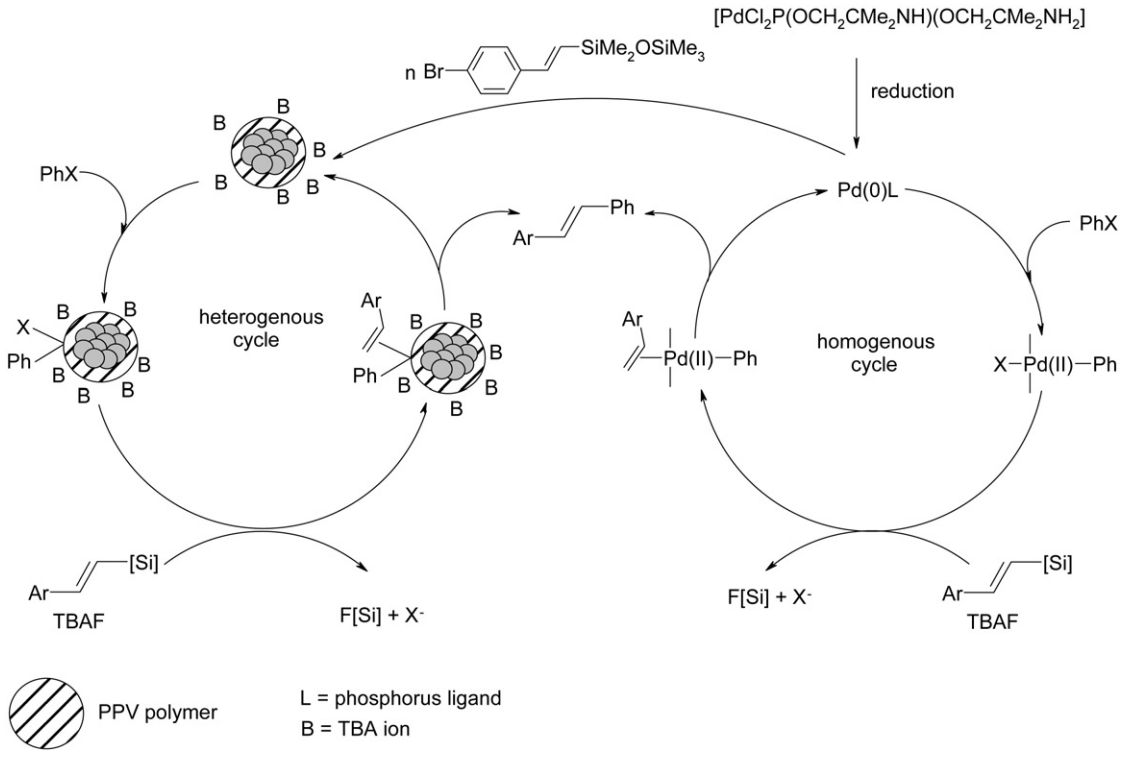
Fig. 5. Photoluminescence spectra of the polymer measured at 298 and 77 K. The excitation wavelength was 300 nm and 350 nm respectively. The emission peaks occur at: (298) 517, 548 and 590 nm; (77 K) 526, 567, 616 nm.

3.3. Spectroscopic characterisation and catalytic activity of PPV derivative

Interestingly, when (*E*)-[1-(4-bromophenyl)-2-(1,1,3,3,3-pentamethyldisiloxy)]ethene (**1d**) was used as the substrate in DMF at 140 °C, a mere 10% yield of stilbene was observed in the process (Table 1, entry 8). Instead, a polymeric product insoluble in dimethylformamide was formed in the system quantitatively. According to ICP-MS analysis it contained 0.77% of palladium. Actually, TEM analysis (Fig. 3) of the polymer corroborated the presence of roughly spherical palladium nanoparticles, mainly arranged in the form of agglomerates, with an average size of 8 ± 1.4 nm. We were curious about the catalytic properties of the obtained polymer. The Hiyama cross coupling of (*E*)-[1-(4-methoxyphenyl)-2-(1,1,3,3,3-pentamethyldisiloxy)]ethene with bromobenzene catalysed by the obtained polymer Pd-PPV (the ratio [Pd]:[PhBr] = 0.005:1) gave 40% yield of (*E*)-4-methoxystilbene. The Pd-PPV polymer separated from the reaction mixture and used in the second run again produced 38% of stilbene. To identify the catalytically active species in the system operating with Pd-PPV, again the mercury poisoning test was performed. The addition of 250 equivalents of mercury relative to palladium together with substrates quenched the reaction; only a residual amount of (*E*)-4-methoxystilbene was obtained. These results suggest that most probably Pd(0) species in the form of PdNPs trapped in PPV polymer are involved in the catalytic process [21].

A Pd-PPV polymeric product, tentatively proposed as a mixture of linear and branched poly(phenylene-vinylene) PPV polymers, was also isolated in the absence of bromobenzene in the reaction system, as a yellow-green precipitate (Scheme 4).

The Hiyama homocoupling of (*E*)-[1-(4-bromophenyl)-2-(1,1,3,3,3-pentamethyldisiloxy)] ethene (**1d**) proceeded due to the presence of a labile bromine substituent on the phenyl ring. A similar homocoupling process giving a poly(phenylene-vinylene) derivative with high yield and stereoselectivity has been reported in the literature for 1,3-bis[(*E*)-4-bromostyryl]



Scheme 5. Possible mechanism of cross-coupling reactions.

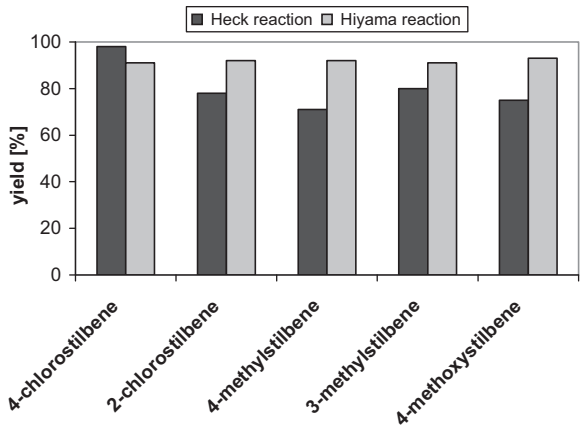


Fig. 6. Yield of selected stilbenes obtained in Hiyama and Heck [14] reactions in DMF at 140 °C.

tetramethyldisiloxane [22]. However, the authors did not mentioned the palladium species involved in polymer. The very low solubility of PPV in most available solvents (e.g. in DMF 3 mg/100 ml) makes the structure of the polymer difficult to establish unambiguously. Nevertheless, solid ^{13}C NMR and the IR spectra allowed us to propose the possible polymeric structure. The cross-polarisation magic-angle spinning (CPMAS) spectrum shown in Fig. 4 reveals signals attributed to the aromatic carbon atoms at 126.18, 129.48, 132.80, 137.72 ppm as anticipated for the structure of PPV [23].

The very strong absorptions in the IR spectrum at 837 and 966 cm^{-1} corresponding to phenylene and trans-vinylene C–H out-of-plane bands point to the presence of E-vinylene fragments, as does a weak band at 3021 cm^{-1} corresponding to trans-vinylene C–H stretch [24–26]. The solid state reflectance spectra (measured at room temperature over 190−890 nm range) and emission spectra are shown in Fig. 5. The features of reflectance spectrum are analogous to those published before [27]. When exposed on UV light, the polymer exhibits a green emission. In contrast to a spectrum measured at room temperature with bands at 517, 548 and 590 nm, the emission spectrum measured at 77 K reveals well resolved bands shifted to 526, 567, 616 nm [28,29].

4. Conclusions

We can conclude that a palladium complex with H-spirophosphorane $H(POCH_2CMe_2NH)_2$ ligand, $[PdCl_2P(OCH_2CMe_2NH)OCH_2CMe_2NH_2]$ appears to be an efficient and stereoselective precatalyst for the Hiyama cross-coupling reaction of iodo- and bromobenzene with substituted styrylsilanes, with conversion exceeding 90%. In competitive experiments, reported before [14], the yield of *E*-stilbenes in the Heck cross-coupling reaction was slightly lower than in the Hiyama cross-coupling, with the lowest value, 71%, for (*E*)-4-methylstilbene, although 98% of (*E*)-4-chlorostilbene was also formed (Fig. 6). The mechanistic investigations of Hiyama cross-coupling reactions indicate that the complex $[PdCl_2P(OCH_2CMe_2NH)OCH_2CMe_2NH_2]$ presumably acts as homogenous precatalyst in the commonly accepted mechanism initially proposed by Hiyama and Hatanaka (Scheme 5) [30]. In the first step the mechanism depends on oxidative addition of halobenzene to a reduced Pd(0) complex. In the second step, its transmetallation takes place with an appropriate styrylsilane, and finally *E*-stilbene is eliminated with simultaneous regeneration of Pd(0) catalyst. Under the defined reaction conditions, in the presence of (*E*)-[1-(4-bromophenyl)-2-(1,1,3,3,3-pentamethyldisiloxy)]ethane as a substrate, the same molecular precatalyst is responsible for generation of Pd(0) nanoparticles formed in situ in the system. Palladium nanoparticles are trapped in PPV polymeric product contemporaneously generated following the homocoupling reaction of bromosubstituted siloxane. The mercury test and TEM studies performed suggest that these Pd nanoparticles might be involved in the heterogenous catalytic process of the Hiyama cross-coupling. The obtained polymeric derivative of poly(phenylenevinylene) needs further examination, but at the same time the presented simple catalytic methodology open the window of opportunity to the application in e.g. LED devices.

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