# One-Pot Suzuki/Heck Sequence for the Synthesis of (*E*)-Stilbenes Featuring a Recyclable Silica-Supported Palladium Catalyst *via* a Multi-Component Reaction in 1,3-Propanediol

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**Abstract:** The synthesis of (*E*)-stilbenes was performed following a one-pot Suzuki/Heck sequence through the use of potassium vinyltrifluoroborate. The combination of heterogeneous palladium/silica (Pd/SiO<sub>2</sub>) catalyst with potassium phosphate monohydrate ( $K_3PO_4$ ·H<sub>2</sub>O) as base resulted in useful to good isolated yields regardless of the *ortho-*, *meta-* or *para-*substitution of the aryl halides employed. In a sustainable approach, we found that bio-sourced 1,3propanediol could advantageously replace *N*-methylpyrrolidone (NMP) as similar yields were obtained.

## Introduction

During the last decade, the inherent property of heterogeneous catalysts to achieve successive chemical transformations in a single pot has emerged as a powerful tool for organic chemists. Indeed, such catalysts display numerous advantages toward their homogeneous analogues: removal of the catalyst by simple filtration, recyclability over several cycles, metal-free reaction media (dissolution-redeposition mechanism<sup>[1,2]</sup>), easy-to-handle (mainly air and moisture tolerant), providing therefore economically beneficial and environmentally friendly processes. Particularly, multifunctional heterogeneous Pd catalysts<sup>[3,4]</sup> have attracted much attention due to their ability to achieve the most relevant chemical transformations like C-C couplings (Heck, Hiyama, Suzuki,...), heteroannulation or hydrogenation. Following this approach, tandem one-pot multi-step sequences have been the subject of recent contributions toward the synthesis of biological relevant compounds. In 2000, Genêt et al. described the first tandem Heck/hydrogenation procedure<sup>[5]</sup> using a "Lindlar-type" Pd(0)/CaCO<sub>3</sub> catalyst for the synthesis of useful Wadsworth-Emmons reMoreover, the reactivity gap between aryl iodides and bromides resulting from the use of 1,3-propanediol allowed an efficient multi-component approach toward the synthesis of (E)-stilbenes. Furthermore, this heterogeneous catalyst was found to be extremely robust despite the use of aerobic conditions and was successfully re-used over several cycles.

**Keywords:** cross-coupling reactions; heterogeneous palladium catalysts; multi-component reaction; one-pot synthesis; stilbenes; Suzuki/Heck sequence

agents. In a similar fashion, Djakovitch and co-workers reported the one-pot preparation of bibenzyls<sup>[6,7]</sup> using common Pd(0)/C or Pd(II)/C catalysts while Corma et al. achieved the synthesis of a fragrance with raspberry scent<sup>[8]</sup> by exploiting the dual reactivity of an original and recyclable Pd(0)/TiO<sub>2</sub> catalyst. In 2008, Felpin and co-workers reported the first application of Pd(0)/BaCO<sub>3</sub> in a Suzuki/hydrogenation sequence<sup>[9]</sup> allowing a shortened protocol toward the synthesis of bifenazate; however, in situ decomposition of the support limits to date its potential applications. Recently, the same authors provided new insights toward heterogeneous one-pot protocol via a Heck/reduction/cyclisation procedure affording either 2-quinolones<sup>[10]</sup> or oxindoles.<sup>[11,12]</sup> Previous sequences involving successive Heck/Suzuki (Djakovitch et al.)<sup>[6]</sup> or Suzuki/Suzuki (Felpin et al.)<sup>[13]</sup> couplings have been reported for the preparation of, respectively, 4styrylbiphenyl and terphenyl derivatives through either I/Br (i.e., Heck) or Br/N<sub>2</sub>BF<sub>4</sub> (i.e., Suzuki) selective C–C couplings.

Pursuing our efforts devoted to the application of heterogeneous Pd catalysts<sup>[14-21]</sup> in one-pot procedures,<sup>[7,22-25]</sup> we have recently disclosed the vinylation



Scheme 1. Overview of stilbene syntheses through one-pot tandem processes.

of aryl halides through the use of commercially available Pd/C.<sup>[26,27]</sup> Such compounds are useful intermediates for the synthesis of stilbenes, an important class of biologically relevant molecules including the wellknown resveratrol and combretastatin A-4. [28,29] Over the past few years, three reports dealing with homogenous Pd-based one-pot strategies, through either Hiyama/Heck<sup>[30]</sup> or double Heck<sup>[31,32]</sup> couplings, have emerged from the literature as valuable improvements toward the synthesis of stilbenes. Nevertheless, these methodologies display numerous practical limitations such as addition of catalyst, base, ligand or even solvent to achieve the second step (i.e., Heck coupling), large excess of vinyl source, use of ligands and Pd(0) stabilising additives (quaternary ammonium salt, PEG), highly toxic compounds (t-BuNH<sub>2</sub>, KF, DMF) and non-recyclable homogeneous catalysts as principal drawbacks (Scheme 1).

In order to solve the main disadvantages of the previously reported methods, we describe in this contribution an attractive one-pot Suzuki/Heck sequence with emphasis on the combination of heterogeneous Pd catalysts, bio-sourced solvent and ideally a multicomponent approach (MCR).

## **Results and Discussion**

Optimization of the Suzuki/Heck sequence was initially realised in a tandem manner (Scheme 2a) involving the vinylation of 3-bromoquinoline using previously optimised conditions  $[K_3PO_4, H_2O_3, G_3, H_2O_3]$ Pd/C (0.1 mol%), NMP, 100°C].<sup>[26,27]</sup> Complete conversion of 3-bromoquinoline was observed after 16 h and 3-vinylquinoline was directly subjected to Heck coupling. Addition of 3-chloroiodobenzene in excess (i.e., 2.0 equiv.) in the second step was essential as the remaining amount of potassium vinyltrifluoroborate (at least 0.5 equiv.) lead to the formation of the symmetrical stilbene 2 (see Table 1). While no conversion was observed at 100 °C for the desired Heck coupling reaction, addition of 0.9 mol% Pd/C and working at 140 °C allowed a full consumption of the in situ generated 3-vinylquinoline within 24 h. Interestingly, the Heck coupling did not require any addition of base and the corresponding stilbene 1 was isolated in a fair 50% yield. Nevertheless, under such conditions, severe limitations occurred with ortho aryl halides regardless of the electron-donating (OMe) or electronwithdrawing (Ac, NO<sub>2</sub>) nature of the ortho substituent, yielding the corresponding stilbenes in low yields (ca. 20%). Moreover, when 4-iodoanisole was subjected to the Heck coupling, a 2/1 mixture (ratio refers to GC area of each compound) of mono- and di-arylated compounds was observed (Scheme 2b).

In light of these observations, we switched the aryl halide in the vinylation step starting with a stoichiometric amount of 3-chloroiodobenzene and working initially with 1 mol% Pd/C (Table 1). Using such a tandem procedure, the corresponding stilbene was isolated in a moderate 43% yield due to the formation of a large amount of the symmetrical 3,3'-



Scheme 2. (a) Tandem Suzuki/Heck sequence for the synthesis of stilbene 1 via the vinylation of 3-bromoquinoline. (b) Selectivity observed with 4-iodoanisole.

dichlorostilbene 2 (Table 1, entry 1). When 3-bromoquinoline was engaged as the limiting reactant, an encouraging 58% yield was obtained, slightly improved to 64% when the reaction time was increased to 40 h in order to achieve complete conversion of the latter (Table 1, entry 2).

Next, the influence of the base and nature of the heterogeneous catalyst was evaluated. Although AcOK and K<sub>2</sub>CO<sub>3</sub> allowed full conversions for the vinylation step, these latter led to only poor conversions  $(\sim 5-15\%)$  for the Heck coupling (Table 1, entries 3) and 4), even after prolonged reaction time (i.e., 96 h) or when a large excess of the base (up to 9 equiv.) was employed. Unexpectedly, only K<sub>3</sub>PO<sub>4</sub>·H<sub>2</sub>O exhibited a superior behaviour to perform both Suzuki and Heck couplings. Then, two heterogeneous catalysts freshly prepared in our laboratory were evaluated for this tandem procedure. While the well-known  $[Pd(NH_3)_4]/NaY^{[33]}$  (Table 1, entry 6) allowed a moderate conversion for the Heck coupling in 24 h (ca. 70%), higher reactivity was observed with Pd/SiO<sub>2</sub><sup>[34]</sup> (Table 1, entry 7). Indeed, 3-bromoquinoline was fully converted within 20 h and stilbene 1 was isolated with an improved 80% yield. However, the use of NMP is not compatible with a sustainable approach as this solvent has been recently prohibited in most chemical industries due to its toxicity. In order to fulfill this approach, 1,3-propanediol (1,3-PDO) was chosen as a solvent for this procedure. Indeed, 1,3-PDO can be regarded as a bio-sourced solvent since it is directly produced from corn syrup or by glycerol hydrogenolysis; moreover, this diol has a low vapour pressure and is not toxic thus affording a safe and environmentally benign procedure. This solvent proved its efficiency in the vinvlation step when aryl iodides were employed; indeed, activated aryl bromides like 3-bromoquinoline or 4-bromoacetophenone led to only moderate conversions (<40%). To our delight, despite a longer reaction time for the Heck coupling (i.e., 48 h), replacing NMP by 1,3-PDO resulted in good yields (*ca.* 60%) regardless of the heterogeneous catalyst employed (Table 1, entries 5 and 9 with, respectively, Pd/C and Pd/SiO<sub>2</sub>).

Taking advantage of the reactivity gap between aryl iodides and bromides when using 1,3-PDO as the solvent, a multi-component approach has been envisioned for such a one-pot synthesis. Remarkably, this new protocol afforded **1** in a similar yield (Table 1, entries 9/10) whereas a noteworthy decrease (i.e., -17%) occurred when NMP was used as solvent (Table 1, entries 7/8). As expected after the vinylation step, only a small amount of 3-vinylquinoline was detected by GC/MS in 1,3-PDO while the use of NMP afforded a 1/1 mixture of 3-vinylchlorobenzene and 3vinylquinoline. This observation can explain to some extent the lower product yield observed when using NMP in the coupling reaction involving the 3-chloroiodobenzene A and 3-bromoquinoline C in such MCR procedure (Table 1, entries 7/8).

Finally, the use of a stoichiometric amount of 3chloroiodobenzene **A** in 1,3-PDO afforded a useful 56% yield together with allowing us to decrease the amount of potassium vinyltrifluoroborate **B** engaged in the reaction (Table 1, entry 10).

Following these optimised reaction conditions, several aryl iodides were engaged in this one-pot procedure (Figure 1). Remarkably, this protocol proved to be helpful for the synthesis of stilbene **3**, isolated in a useful 56% yield (53% in 1,3-PDO), resulting from a full selectivity toward **3** (i.e., the di-arylated by-product is not observed thanks to this procedure). It is noteworthy that 1,3-PDO allowed an improved 62% yield – vs- 48% in NMP – when 4-iodoacetophenone was employed. Surprisingly, regardless of the tandem Table 1. Optimization of the one-pot Suzuki/Heck sequence.<sup>[a]</sup>



MCR

MCR

Tandem

Tandem

*Reaction conditions: tandem* 3-chloroiodobenzene (3 mmol), potassium vinyltrifluoroborate, K<sub>3</sub>PO<sub>4</sub>·H<sub>2</sub>O, Pd catalyst 1 mol%/A) (i.e., Pd/C: 64.0 mg; Pd/SiO<sub>2</sub>: 36.0 mg; [Pd]/NaY: 89 mg), solvent (3.0 mL), 100 °C, 4 h then addition of 3-bromoquinoline (2.0 mmol), 140 °C, 24 h. *MCR* all the reactants were mixed in NMP or 1,3-PDO (3.0 mL) in presence of

Isolated yields after flash column chromatography on silica. Values in parenthesis refer to conversion based on unreacted

1.5/1.65/1.0

1.5/1.65/1.0

1.5/1.65/1.0

1.0/1.1/1.5

<sup>[c]</sup> 40 h at 140 °C.

8

9

10

11

[a]

[b]

<sup>[d]</sup> 48 h at 140 °C.

procedure or the solvent used, close yields (*ca.* 60–65%) were obtained with 4-iodonitrobenzene. The most interesting feature of these methodologies comes from the similar yields achieved in an MCR fashion, highlighting the "MCR in 1,3-PDO" methodology as a protocol of choice toward efficient and greener chemistry.

Pd/SiO<sub>2</sub> (36.0 mg, 1 mol%/A), 100 °C, 4 h then 140 °C, 48 h.

3-bromoquinoline determined by GC/MS.

NMP

1,3-PDO

1,3-PDO

1,3-PDO

On the other hand, a special behaviour was observed with *ortho* aryl iodides due to their lower reactivity in Heck coupling. The use of NMP afforded only low yields (26-34%) whatever the conditions used (excess of aryl iodides or 3-bromoquinoline). Indeed, the symmetrical (*E*)-1,2-bis-(3-quinolyl)-ethene **6** was the main product as observed by GC/MS (Scheme 3 a). This was attributed to the high reac-

tivity of activated aryl bromides toward Suzuki and Heck couplings in NMP. Thus, the use of 1,3-PDO appeared to be of particular interest in order to dramatically decrease the reactivity of aryl bromides towards Suzuki coupling. To our delight, such a solvent (Scheme 3b) was successfully applied to the synthesis of stilbene **7**, isolated in a satisfactory 44% yield according to a limited conversion (*ca.* 70%). Noticeably, in the case of 2-iodonitrobenzene the corresponding stilbene **9** was isolated in an excellent 76% yield, these kinds of substrate (i.e., 2-vinylnitrobenzene) affording valuable intermediates toward the synthesis of indoles.<sup>[35]</sup> This procedure demonstrated its usefulness as illustrated by overall good isolated yields (44–76%, Scheme 3) with a range of either electron-donating or

K<sub>3</sub>PO<sub>4</sub>(H<sub>2</sub>O

K<sub>3</sub>PO<sub>4</sub>(H<sub>2</sub>O

K<sub>3</sub>PO<sub>4</sub>(H<sub>2</sub>O

K<sub>3</sub>PO<sub>4</sub>(H<sub>2</sub>O

63

61<sup>[d]</sup>

59<sup>[d]</sup>

56<sup>[d]</sup>



**Figure 1.** "Tandem *vs.* MCR' and "NMP *vs.* 1,3-PDO" behaviour for the one-pot Suzuki/Heck sequence. (n.p. = not performed). *Reaction conditions: tandem* 3-chloroiodobenzene (3.0 mmol), potassium vinyltrifluoroborate (3.3 mmol),  $K_3PO_4$ ·H<sub>2</sub>O (9.0 mmol), Pd/SiO<sub>2</sub> (36.0 mg, 1 mol%/A), NMP or 1,3-PDO (3.0 mL), 100°C, 4 h then addition of 3-bromoquinoline (2.0 mmol), 140°C, 24 h. *MCR* all the reactants were mixed in NMP or 1,3-PDO (3.0 mL) in presence of Pd/SiO<sub>2</sub> (36.0 mg, 1 mol%/A), 100°C, 4 h then 140°C, 48 h.

(a)



Scheme 3. "NMP vs. 1,3-PDO" behaviour observed for the one-pot Suzuki/Heck sequence with *ortho* aryl iodides. (n.p. = not performed).

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electron-withdrawing functional groups (Ac, Cl,  $NO_2$ ,  $NH_2$ , Me). As expected, close isolated yields were achieved in an MCR fashion.

The recyclability of the catalyst was addressed as follows: the first three runs were conducted with 3chloroiodobenzene using a tandem procedure in 1,3-PDO, followed by two runs with 2-iodonitrobenzene (see Supporting Information for detailed recycling procedure). As indicated in Table 2, similar yields towards the *chloro*-stilbene 1 were achieved during the three first runs outlining the good recyclability of the Pd/SiO<sub>2</sub> catalyst. Considering the potential industrial application of such procedures it is always interesting to demonstrate the versatility of heterogeneous catalysts to be used for different reaction sets by modifying at least one of the substrates. This allows us to address the possible contamination of solid material, that is, Pd/SiO<sub>2</sub> catalyst, by remaining organic material. With this intention, 3-chloroiodobenzene was replaced by 2-iodonitrobenzene in the vinylation step. Remarkably, no trace of *chloro*-stilbene 1, nor other compounds related to 3-chloroiodobenzene, was detected by GC after the 4<sup>th</sup> run, highlighting, therefore, the recycling protocol quality.<sup>[36]</sup> Thus, the desired nitro-stilbene 9 was obtained in excellent yields upon recycling, 70% and 68% for the 4<sup>th</sup> and 5<sup>th</sup> run, respectively. Interestingly, these yields are very close to the ones obtained with the fresh catalyst (i.e., 76%, see Scheme 3), showing that the catalyst exhibits high stability over these reaction conditions.

In summary, the  $Pd/SiO_2$  catalyst has demonstrated a very good recyclability, displaying a higher behaviour than homogeneous catalysts for potential applications in fine chemical industry.

Additionally to these recycling experiments, we conducted analyses of the fresh and used  $Pd/SiO_2$  catalysts using various spectroscopic methods. While XPS analysis of the freshly prepared  $Pd/SiO_2$  catalyst

exhibit clearly a peak at 336.7 eV attributed to Pd<sup>2+</sup> species (i.e., a signal at ca. 335.1 eV is expected for Pd(0) species as measured for the reduced sample, Supporting Information)<sup>[37–39]</sup> as amorphous see "PdO", that of the used catalyst indicates a strong modification of chemical nature of the material as the surface scanning of the sample showed mainly encapsulation of the catalytic material by potassium fluoride (see Supporting Information). These analyses were confirmed by TEM analyses of both samples. TEM of the fresh catalyst clearly shows particles with an average size of 6-10 nm (Figure 2a) the diffractogram of which (Figure 2b) exhibits lattice fringes at 2.56 Å and 2.53 Å which correspond respectively to (101) and (011) crystallographic planes of PdO. That of used catalyst (Figure 3) showed the formation of large particles (ca. 15-50 nm) corresponding to metallic palladium [i.e., Pd(0)-particles] as observed from the diffractogram (Figure 3b). In correlation with the results obtained from XPS, TEM at low magnification showed large areas without any palladium species (Figure 3a). TEM-EDX of the sample indicates a relatively high contamination of the material by salts, mainly potassium fluoride, a result confirmed by elemental analysis of the recycled material (ca.  $45\%_{wt}$ KF).

Additionally, DRX investigations of fresh and used catalysts were performed. While that of fresh catalyst confirms the presence of crystalline PdO particles with an average size of 6 nm, DRX analyses of reused material clearly match with the presence of a  $K_2SiF_6$  phase (see Supporting Information). In spite of this, the catalyst was proved to be highly recyclable.

In summary, all analyses indicate that chemical modification of the  $Pd/SiO_2$  catalyst occurred during the reaction. As expected, Pd(II) species (as PdO) were reduced *under the reaction conditions* to Pd(0) species forming large aggregates on the support upon

Table 2. Recyclability of the Pd/SiO<sub>2</sub> catalyst for the one-pot synthesis of stilbenes.

R +	$\begin{array}{c} & & & \\ & & & \\ \hline & & & \\ & & \\ \hline & & \\ &$	+ 3-bromoquinoline 1,3-PDO, 140 °C, 48 h	
			1 (R = <i>m</i> -Cl) 9 (R = <i>o</i> -NO <sub>2</sub> )
Run	Aryl iodide	Product	Yield [%] <sup>[a,b]</sup>
1 <sup>st</sup> 2 <sup>nd</sup> 3 <sup>rd</sup>	3-chloroiodobenzene	1	63 69 67
4 <sup>th</sup> 5 <sup>th</sup>	2-iodonitrobenzene	9	70 69

<sup>[a]</sup> In all cases, the conversion of 3-bromoquinoline was >98%.

<sup>[b]</sup> Isolated yield after flash column chromatography over silica.

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Figure 2. TEM of the fresh Pd/SiO<sub>2</sub> catalyst.

cooling. Additionally, during the reaction set, the material is contaminated by salts resulting from a partial surface restructuring that probably precipitate onto the material upon cooling, mainly as potassium hexa-fluorosilicate and potassium fluoride. These salts might stabilise small palladium particles (i.e., colloids) in the bulk during such cross-coupling reaction and generate, very probably, *in situ* palladium species as  $PdL_2F^-$  known to be particularly active in Heck reactions.

# Conclusions

These studies focused on broadly applicable one-pot heterogeneous Suzuki/Heck sequence toward the syn-





Figure 3. TEM of the Pd/SiO<sub>2</sub> after 5 runs.

thesis of (E)-stilbenes, highlighting an easily homemade Pd/SiO<sub>2</sub> catalyst. Particularly, we found that NMP could be advantageously replaced by 1,3-PDO featuring an improved synthesis of *ortho* derivatives and an original multi-component reaction taking into account the reactivity gap between aryl iodides and bromides in both Suzuki and Heck couplings. Furthermore, this heterogeneous catalyst was found to be extremely robust despite the use of aerobic conditions and was successfully re-used over several cycles. We believe that the combination of recyclable heterogeneous Pd catalysts, 1,3-PDO as solvent and ideally a multi-component reaction represents an attractive protocol and a sensible approach toward greener chemistry.

## **Experimental Section**

The catalytic reactions were carried out in sealed pressure tubes under air. The qualitative and quantitative analysis of the reactants and the products was made by gas chromatography. Conversions and yields were determined by GC based on the relative area of GC signals referred to an internal standard (biphenyl) calibrated to the corresponding pure compound. Potassium vinyltrifluoroborate was purchased from Trigona OHG, Wiesbaden (DE). 1,3-Propanediol was purchased from Carlo Erba-SDS sold with the green solvent label. Pd/C [Pd/C 5%wt, 55% water, 36% Pd dispersion, only Pd(II)-species through TPR and XPS analyses] catalyst was obtained from Evonik. The [Pd(NH<sub>3</sub>)<sub>4</sub>]/NaY catalyst was prepared according the procedure previously reported.[33,40] The palladium content determinations of the heterogeneous catalyst were performed by ICP-AES spectroscopy from a solution obtained by treatment of the catalysts with a mixture of HBF<sub>4</sub>, HNO<sub>3</sub> and HCl in a Teflon reactor at 180°C. Transmission electron microscopy (TEM) was carried out on a JEOL 2010 microscope with an instrumental magnification of  $50,000 \times$  to  $100,000 \times$  and an acceleration voltage of 200 kV. The point-to-point resolution of the microscope was 0.19 nm and the resolution between lines was 0.14 nm. The microscope is equipped with an EDX link ISIS analyser from Oxford instruments. The powder samples were directly deposited on holey-carbon coated copper grid. XPS measurements were recorded on an Axis Ultra DLD from Kratos Analytical spectrometer equipped with a dual anode (Mg and Al Ka source) and a high power Al monochromator. The measurements of the binding energies were referred to the characteristic C1s peak of the carbon fixed at the generally accepted value of 285.0 eV. Liquid NMR spectra were recorded on a Bruker AC-250 spectrometer. All chemical shifts were measured relative to residual <sup>1</sup>H or <sup>13</sup>C NMR resonances in the deuterated solvents: CDCl<sub>3</sub>,  $\delta =$ 7.26 ppm for <sup>1</sup>H, 77.0 ppm for <sup>13</sup>C; DMSO,  $\delta = 2.50$  ppm for <sup>1</sup>H, 39.5 ppm for <sup>13</sup>C. Data are reported as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, q= quartet, m=multiplet, br=broad). Melting points were determined in open capillary tubes and are uncorrected. Flash chromatography was performed at a pressure slightly greater than atmospheric pressure using silica (Merck Silica Gel 60, 230-400 mesh). Thin layer chromatography was performed on Fluka Silica Gel 60 F254. GC analyses were performed on an HP 4890 chromatograph equipped with a FID detector, a HP 6890 autosampler and a HP-5 column (crosslinked 5% phenyl-methylsiloxane,  $30 \text{ m} \times 0.25 \text{ mm}$  i.d.× 0.25 µm film thickness). Nitrogen is used as carrier gas. The mass spectra were obtained on a Shimadzu GC-MS- QP2010S equipped with a Sulpelco SLB-5MS column (95% methylpolysiloxane +5% phenylpolysiloxane,  $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ µm}$ ) with He as carrier gas was used. The experimental error was estimated to be  $\Delta_{rel} = \pm 5\%$ .

## Preparation of the Pd/SiO<sub>2</sub> Catalyst<sup>[41,42]</sup>

The catalyst was prepared by the wet impregnation method. To a suspension of agglomerated silica (10 g, Aerosil 200/ Degussa) in toluene (40 mL) was added Pd(acac)<sub>2</sub> (2.8 g). The mixture was then stirred for 2 h at room temperature under argon. Then toluene was removed by evaporation affording a slightly yellow material. The solid was calcined under air flow (80 mLmin<sup>-1</sup>) at 300 °C for 7 h giving a brown powder. AAS determination gave 8.9% wt Pd.

#### **General Procedure for the Catalytic Runs**

3-Chloroiodobenzene (714 mg, 3 mmol, 1.5 equiv.), potassium vinyltrifluoroborate (442 mg, 3.3 mmol, 1.65 equiv.), K<sub>3</sub>PO<sub>4</sub>·H<sub>2</sub>O (2070 mg, 9.0 mmol, 3.0 equiv./Ar-I), Pd/SiO<sub>2</sub> (36.0 mg, 1.0 mol% [Pd]/Ar-I) and NMP (3.0 mL, 1.0 M/ Ar-I) were introduced in a sealed tube under air. This latter was placed in a preheated oil bath at 100°C under vigorous stirring for 4 h. Then, 3-bromoquinoline (416 mg, 2 mmol, 1.0 equiv.) was added and the reaction mixture was stirred at 140 °C during 24 h. After cooling at room temperature, 15 mL of H<sub>2</sub>O and 15 mL of CH<sub>2</sub>Cl<sub>2</sub> or EtOAc were added and the solution was stirred at room temperature for 1 h. The organic layer was separated and the aqueous layer was extracted with 2×20 mL of CH<sub>2</sub>Cl<sub>2</sub> or EtOAc. The combined organic layers were dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography over silica with petroleum ether/AcOEt (8/2) to give stilbene 1 as a pale yellow solid; yield: 426 mg (80%).

#### **General Procedure for the Recycling Experiments**

At the end of the first run, the reaction mixture was cooled to room temperature and diluted with 15 mL of  $H_2O$  and 15 mL of  $CH_2Cl_2$ . The resulting solution was stirred at room temperature for 1 h and filtered under vacuum. The crude catalyst was successively washed with  $2 \times 10$  mL  $H_2O$ ,  $2 \times 10$  mL EtOH and  $2 \times 10$  mL  $Et_2O$ . The recycled catalyst was dried at room temperature under vacuum for 1 h and used in the next run.

#### **GLC Analysis**

An aliquot of the reaction mixture was sampled and quenched with 1 mL of water in a test tube. The mixture was extracted with 1 mL of  $CH_2Cl_2$  and the organic layer was filtered through an  $MgSO_4$  pad. The resulting dry organic layer was then analysed by GLC.

#### **Characterization of Organic Compounds**

All compounds were characterized through <sup>1</sup>H, <sup>13</sup>C NMR, and mas spectra obtained from GC-MS, elemental analysis and melting point (see Supporting Information).

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