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Cross-Coupling

Dehydrative Cross-Coupling Reactions of Allylic Alcohols with Olefins

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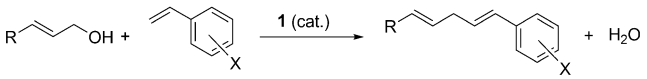
Abstract: The direct dehydrative activation of allylic alcohols and subsequent cross-coupling with alkenes by using palladium catalyst containing a phosphoramidite ligand is described. The activation of the allyl alcohol does not require stoichiometric additives, thus allowing clean, waste-free reactions. The scope is demonstrated by application of the protocol to a series allylic alcohols and vinyl arenes, leading to variety of 1,4-diene products. Based on kinetic studies, a mechanism is proposed that involves a palladium hydride species that activates the allyl alcohol to form the allyl intermediate.

Palladium-catalyzed cross-coupling reactions are commonly applied in the synthesis of natural products and complex biologically active compounds.[1] These catalytic processes are powerful methods to generate various synthetic building blocks in an efficient and selective manner, and as such, find wide application in the fine chemical and pharmaceutical industries.[2] Among the latest developments are cross-coupling reactions involving non-activated (and preferably abundant) substrates, leading to low-waste processes with high atom economy.[3] To this end, allylic alcohols, which are abundant structural motifs in renewables, are attractive substrates for direct use in allylic alkylation reactions, producing only water as a side product.[4] However, the C–O bonds of allyl alcohols are rather difficult to activate, and consequently, activators are typically used in (super)stoichiometric amounts for the in situ activation of the substrates. The use of activators obviously leads to waste production, dodging any potential benefits of the direct use of allyl alcohols.[5] Recently, our research group[6] and those of others[7] reported catalyst systems that allow the direct activation of allylic alcohols in alkylation and amination reactions without the need for stoichiometric activators. Coupling of several aliphatic and aromatic allylic alcohols with a variety of different nucleophiles has been reported. However, thus far, cross-coupling of allylic alcohols with olefins is limited to the use of at least one (pre- or in situ) stoichiometrically activated reagent.[8] For instance, nickel-catalyzed coupling of ethylene and allylic ethers produces the corresponding 1,4-dienes only in the presence of triethylsilyltrifluoromethanesulfonate (Et_3SiOTf) and triethylamine.[9] An iridium-catalyzed coupling protocol was reported that used potassium trifluoroborate substituted alkenes that were coupled to secondary allylic alcohols, nBu$_4$NHSO$_4$ being used as an activator.[10] Herein, we report the first example of a Pd-catalyzed dehydrative alkene–allyl cross-coupling reaction between non-activated allylic alcohols and vinyl arenes, in the absence of any stoichiometric activators (Scheme 1). The catalyst is a simple Pd catalyst, **1**, based on an accessible and scalable ligand, making this a versatile and clean cross-coupling reaction.



Scheme 1. Direct dehydrative cross-coupling of allylic alcohols with vinyl arenes using a simple, accessible catalyst.

Catalyst **1** (Figure 1) was developed previously in our group for C–C and C–N bond-forming reactions by using allylic alcohols, affording linear alkylated and aminated products in high yields and selectivity.[6] Notably, the activity of **1** was higher in the presence of 1,3-diethylurea (3 mol%), the high activity being attributed to the hydrogen bond assisted activation of the allylic alcohol to form the π-allyl Pd complex. This was the starting point of the current study.

Initial experiments were focused on the cross-coupling of cinnamyl alcohol (**2**) with styrene (**3a**), with solvent, ligand, and temperature being varied (Table 1). Under the standard reaction conditions, previously optimized for allylic alkylation reactions (toluene, 80 °C, 3 mol% 1,3-diethylurea), we were delighted to find the coupled product being formed in 31% yield

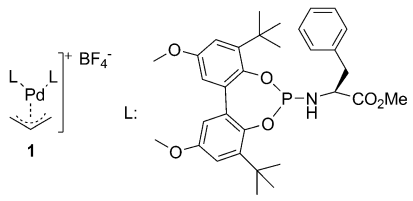


Figure 1. Schematic representation of catalyst **1** and the phosphoramidite ligand, L, used in this study.

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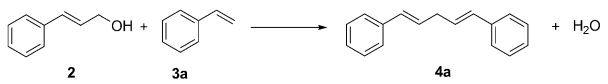
Table 1. Pd-catalyzed cross-coupling of cinnamyl alcohol (**2**) and styrene (**3a**): optimization of the reaction conditions and catalyst.[a]



2 3a 4a

Entry	Solvent	Temp [°C]	Time [h]	Ligand	Yield[b] [%]
1	toluene	80	60	L + 1,3-diethylurea	31
2	heptane	80	60	L + 1,3-diethylurea	10
3	1,4-dioxane	80	60	L + 1,3-diethylurea	73
4	DMF	80	60	L + 1,3-diethylurea	0
5	$ClCH_2CH_2Cl$	80	60	L + 1,3-diethylurea	0
6	MeCN	80	60	L + 1,3-diethylurea	0
7	1,4-dioxane	90	14	L + 1,3-diethylurea	41
8	1,4-dioxane	100	14	L + 1,3-diethylurea	36
9	1,4-dioxane	120	14	L + 1,3-diethylurea	100
10	1,4-dioxane	120	3	L	71
11	1,4-dioxane	120	3	L + 1,3-diethylurea[c]	56
12	1,4-dioxane	120	3	L + 1,3-diethylurea[d]	47
13	1,4-dioxane	120	3	L + 1,3-diethylurea[e]	33
14[f]	1,4-dioxane	120	5	L	100
15	1,4-dioxane	100	14	monophos	trace
16	1,4-dioxane	120	14	monophos	trace
17	1,4-dioxane	100	14	xanthphos	0
18	1,4-dioxane	120	18	PPh_3	13
19	1,4-dioxane	120	18	$P(OtBu)_3$	46

[a] Reaction conditions: cinnamyl alcohol (0.1 mmol), styrene (0.3 mmol), 3 mol% $[(\eta^3\text{-allyl})Pd(cod)]BF_4$, 3 mol% 1,3-diethylurea (entries 1–9), 6 mol% ligand, 0.2 M. [b] Yields are determined by ^1H NMR spectroscopy relative to the substrate and reaction intermediates. [c] 3 mol%. [d] 6 mol%. [e] 10 mol%. [f] 0.12 mmol styrene added.

(Table 1, entry 1). The solvent has a large influence on the yield of the reaction: by using *N*,*N*-dimethylformamide (DMF), 1,2-dichloroethane, CH_3CN, toluene, and heptane, a low yield was obtained; the highest yield (73% after 60 h) was obtained when 1,4-dioxane was used (Table 1, entries 1–6). Further improvement of the reaction yield (100% after 14 h) was achieved by raising the reaction temperature to 120 °C (Table 1, entries 7–9). For the alkylation reaction, we previously found an increase in reaction rate with increasing concentration of urea additives. Interestingly, increasing the amount of 1,3-diethylurea for the dehydrative cross-coupling reaction lowered the yield significantly (from 71% (no urea) to 33% (10 mol% urea) after 3 h; Table 1, entries 10–14). This negative effect suggests that the activation of the allyl alcohol may be different for this reaction compared to the previous reactions reported.[6] Urea most likely competes for coordination with the alkene substrate, thus perhaps leading to the inhibition of the catalyst.

Next, we explored some common phosphoramidite and phosphine ligands that were used in combination with the same Pd precursor, $[(\eta^3\text{-allyl})Pd(cod)]BF_4$ (cod = 1,5-cyclooctadiene). The reaction with the monophos-based complex produced the expected product only in trace amounts, both at 100 and 120 °C (Table 1, entries 15–16). The complex based on bidentate ligand xanthphos did not show any formation of the product (Table 1, entry 17). Some product formation was observed by using triphenylphosphine (13%) or tri(*tert*-butyl)-phosphite (46%), but the yields obtained after 18 h were much lower compared to the use of ligand L (see Figure 1 for the structure of L; 100% after only 5 h; see Table 1, entries 14, 18, and 19).

Next, we briefly explored if Pd nanoparticles, possibly formed under catalytic conditions, may be the active species. For this purpose, a variety of commercially available Pd nanoparticles were used, as well as a series of Pd^0 and Pd^{II} precursors known to produce Pd nanoparticles under typical reaction conditions (Table 2). Catalysis with the commercial BASF and Lindlar's nanoparticles did not show any formation of the 1,4-diene product (Table 2, entries 1 and 2). The use of $Pd(OAc)_2$

Table 2. Pd-catalyzed cross-coupling of cinnamyl alcohol (**2**) and styrene (**3a**): control experiments with various Pd complexes and nanoparticles.[a]

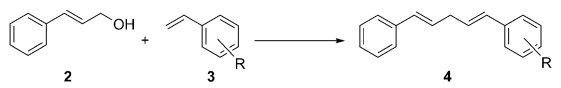
Entry	Temp [°C]	Time [h]	Catalyst	Yield [%][b]
1	120	18	Pd-np-BASF (0.5% Pd)	0
2	120	18	Lindlar's cat. (5% Pd)	0
3	80	26	$Pd(OAc)_2$	0
4	120	18	$Pd(OAc)_2$	0
5	120	18	$Pd(OAc)_2/nBu_4NCl$	0
6	120	14	$[Pd(dba)_2]$	0
7	120	14	$[Pd_2(dba)_3]$	0
8	120	14	$[(\eta^3\text{-allyl})Pd(cod)]BF_4$	44

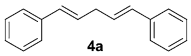
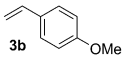
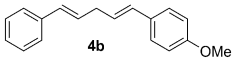
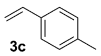
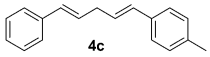
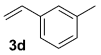
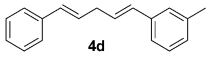
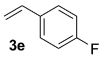
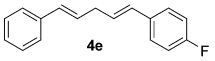
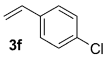
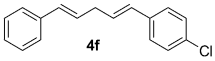
[a] Reaction conditions: Cinnamyl alcohol (0.1 mmol), styrene (0.3 mmol), 3 mol% Pd precursor or nanoparticle as catalyst, 1,4-dioxane, 0.2 M. [b] Yields are determined by ^1H NMR spectroscopy relative to the substrate and reaction intermediates.

failed to generate the desired product, even in the presence of a nanoparticle stabilizer, nBu_4NCl, and at elevated temperatures (Table 2, entries 3–5). Also the use of a Pd^0 complex as a precursor, $[Pd(dba)_2]$ and $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone), did not lead to formation of the diene product (Table 2, entries 6 and 7). Only the use of $[(\eta^3\text{-allyl})Pd(cod)]BF_4$ as a catalyst resulted in the formation of the product in 44% yield, thus suggesting that the allyl fragment at the Pd center plays a crucial role. To further rule out the role of nanoparticles, we performed selective poisoning experiments, which are commonly applied to discriminate homogeneous and heterogeneous catalyst species.[11] The addition of polyvinylpyridine (PVP; after 3 h), which is a selective poison for homogeneous catalysts,[12] directly terminated the reaction. These experiments together strongly indicate that Pd particles do not play a role in the current reaction (see the Supporting Information for details). On the basis of the combined results, we concluded that the cross-coupling reaction proceeds via well-defined homogeneous Pd complexes, a conclusion that is also in line with the kinetic studies (see below).

Once catalyst **1** was identified as an effective catalyst and the reaction conditions were optimized, we explored the substrate scope for the dehydrative cross-coupling reaction (Table 3). The coupling of cinnamyl alcohol with styrene, which was used as the model reaction, gave full conversion and afforded the product **4a** in 90% yield upon isolation (Table 3, entry 1). Substituted styrene derivatives, either with electron-donating or electron-withdrawing groups, were also efficiently

Table 3. Cross-coupling of cinnamyl alcohol with styrene derivatives[a]



Entry	Alkene	Product	Yield [%][b]
1			90
2			58
3			65
4			70
5			55
6			66

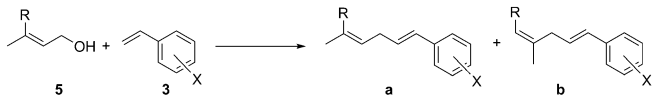
[a] Reaction conditions: cinnamyl alcohol (0.1 mmol), styrene derivative (0.12 mmol), 3 mol% catalyst **1**, 1,4-dioxane, 0.2 M, 120 °C, 14 h. [b] Yield of isolated product.

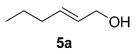
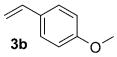
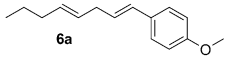
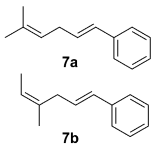
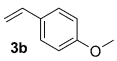
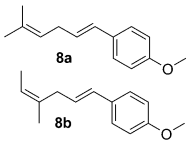
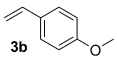
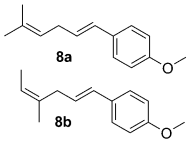
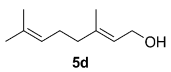
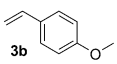
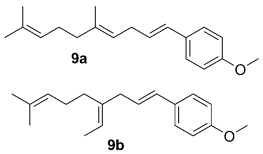
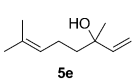
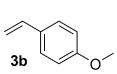
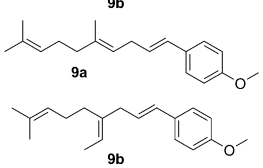
coupled to cinnamyl alcohol, generating the corresponding 1,4-dienes as the only products with full conversions. The yields upon isolation were only moderate for these products owing to losses during purification.[13] The use of electron-rich *p*-methoxy and *p*-methylstyrene afforded the products **4b** and **4c** in 58% and 65% yields upon isolation, respectively, (Table 3, entries 2 and 3); *m*-methylstyrene resulted in product **4d** being isolated in 70% yield (Table 3, entry 4). The electron-deficient substrates, *p*-fluoro and *p*-chlorostyrene, led to the corresponding products being isolated in 55% (**4e**) and 66% (**4f**) yield, respectively (Table 3, entries 5 and 6).

The cross-coupling reaction was further extended to aliphatic allylic alcohols, which are generally more challenging to activate than cinnamyl alcohol. Also, for these substrates, the reaction with styrene derivatives resulted in the formation of the corresponding 1,4-diene products, significantly broadening the scope of this reaction (Table 4). The catalytic reaction of 2-hexen-ol (**5a**) and *p*-methoxystyrene (**3b**) afforded product **6a** in 47% yield upon isolation as a single product (Table 4, entry 1). Application of methyl-substituted allylic alcohols (either at the 1- or the 3-position) generated two regioisomers. These two products can be explained by an isomerization of the π-allyl intermediate involving β-hydrogen elimination (see below). The coupling reaction of styrene with prenol, **5b**, produced products **7a** and **7b** in a 10:23 isomeric ratio and 30% yield upon isolation (Table 4, entry 2). Importantly, the coupling of *p*-methoxystyrene, **3b**, with **5b** resulted in a reaction yield and product distribution that was similar to that found with the coupling with styrene (**8a** and **8b**; Table 4, entry 3). The coupling of **3b** with **5c**, which is an isomer of **5b**, led to the same products (**8a** and **8b**) but in a different product ratio (1:1 compared to 10:21; Table 4, entries 3 and 4). In line with this, the coupling of **3b** with the regioisomeric alcohols, geraniol, **5d**, and linalool, **5e**, resulted in products **9a** and **9b** in different ratios (10:8 and 10:2, Table 4, entries 5 and 6) and in moderate yields upon isolation. This clearly indicates that the regioselectivity of the reaction depends on the isomeric form of the starting alcohol.

To get insight in the reaction mechanism for these dehydrative cross-coupling reactions, we

Table 4. Cross coupling of aliphatic allyl alcohols with styrene derivatives.[a]

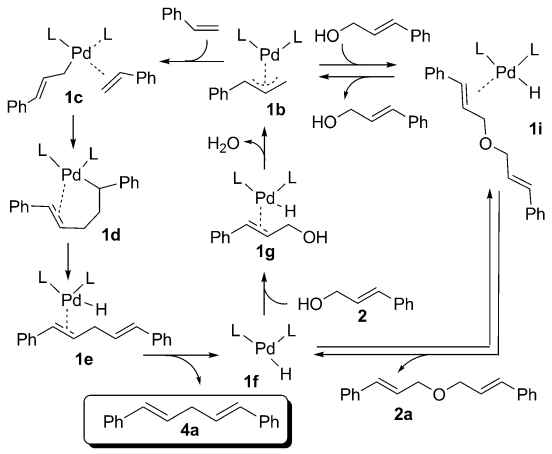


Entry	Alcohol	Alkene	Product	Yield [%][b]
1				47
2				30 (19:23)
3				32 (10:21)
4				38 (1:1)
5				40 (10:8)
6				42 (10:2)

[a] Reaction conditions: cinnamyl alcohol (0.1 mmol), styrene derivative (0.12 mmol), 3 mol% catalyst **1**, 1,4-dioxane, 0.2 M, 120 °C, 14 h. [b] Yield of isolated product.

performed kinetic studies (with cinnamyl alcohol and styrene as model substrates) by monitoring the reaction progress in time with ^{1}H NMR spectroscopy. These experiments show a zero order reaction rate dependence on the cinnamyl alcohol concentration and a positive order dependence in [styrene] (see the Supporting Information for details). Moreover, we observed bis(cinnamyl)ether (**2a**) as a reaction intermediate, which was consumed during the course of the reaction. In a separate experiment, **2a** was directly used as substrate for the cross-coupling reaction with styrene. The reaction rate in this experiment was identical to that of the coupling reaction with cinnamyl alcohol, suggesting that under catalytic conditions there is a fast equilibrium between cinnamyl alcohol and the bis(cinnamyl)ether.

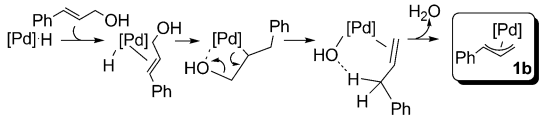
Based on these kinetic data, we propose the mechanism for the dehydrative cross-coupling reactions shown in Scheme 2. Starting from the π-allyl complex **1b**, coordination and the subsequent insertion of styrene gives intermediate **1c** and **1d**, respectively. Subsequent β-hydride elimination and decoordination gives product **4a** and reactive Pd hydride intermediate **1f**. After coordination of the substrate to this species, the π-allyl complex resting state **1b** can form. From π-allyl complex **1b**, allyl ether **2a** can be formed after nucleophilic attack of the cinnamyl alcohol. This reaction is likely slow compared to the product-forming pathway (as formation of the ether is minor compared to product formation, and the ether in turn serves also as substrate), and as such it does not appear in the rate equation.



Scheme 2. Proposed mechanism for the cross-coupling reactions of cinnamyl alcohol with vinyl arenes. For clarity, we have neither indicated the charge of the Pd center (cationic throughout the cycle), nor included the counterion (BF_4^-).

Most likely, according to kinetic experiments (zero order in [allylic alcohol] and a positive order in [styrene]), the rate-determining step involves either coordination of styrene to the catalyst, **1b**, or the subsequent migration to the allyl fragment. Notably, the oxidation state of the Pd center remains the same (+II) throughout the entire catalytic cycle.

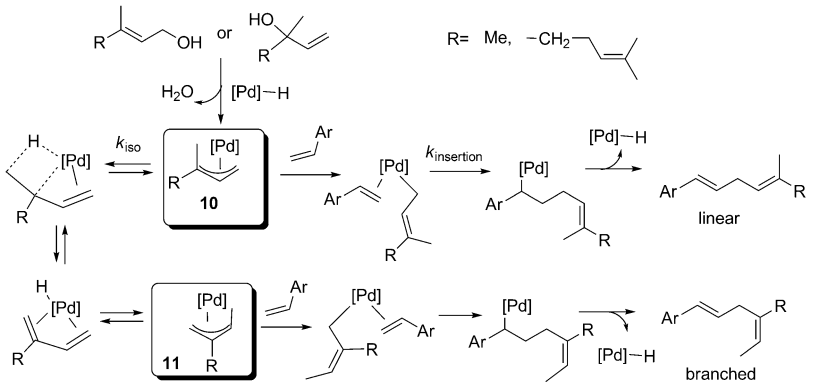
Activation of the allyl alcohol by hydride species $[(L)_2PdH]$ to form allyl intermediate **1b**, which is the key step of the proposed catalytic cycle, likely proceeds via the steps shown in Scheme 3. Coordination and insertion of the C=C bond of the substrate leads to a β-hydroxy-alkyl intermediate. Subsequent β-hydroxy elimination[14] and intramolecular deprotonation of the acidic allylic C–H bond[15] by the hydroxo ligand then leads to formation of **1b** with elimination of water.



Scheme 3. Proposed allylic alcohol activation steps involving a Pd hydride species. For clarity, we have neither indicated the charge of the Pd center (cationic throughout the cycle), nor included the counterion (BF_4^-).

Other allyl alcohols most likely react in a similar manner as the cinnamyl alcohol. The formation of two isomers when methyl-substituted allyl alcohols are used is easily explained by an isomerization process of the allyl moiety from allyl intermediate **10** to allyl intermediate **11**, involving β-hydride elimination at the methyl substituent (Scheme 4). This process is likely preceded by formation of a σ-allyl intermediate. Both the linear and branched products derive from insertion of the vinyl arene into the Pd–C bond of the allyl moiety at the least hindered position. The linear product arises directly from **10**, while the branched product arises from isomerized allyl intermediate **11**. β-Hydride elimination following the vinyl arene insertion step generates the observed products and regenerates the Pd hydride intermediate.

As noted, the linear to branched ratios depend on the isomeric form of the starting alcohol. The branched aliphatic alco-



Scheme 4. Proposed isomerization mechanism for the linear and branched products. For clarity, we have neither indicated the charge of the Pd center (cationic throughout the cycle), nor included the counterion (BF_4^-).

hols, **5c** and **5e**, afforded respective linear products, **8a** and **9a**, in higher relative ratios than with the linear alcohols, **5b** and **5d**, and vice versa (Table 4, entries 3–6). This observation is less easy to explain mechanistically, but may be related to the formation of diastereomers/regioisomers of intermediate **10** (see Figure S6 in the Supporting Information) in different ratios, depending on the allyl alcohol substrate. Such isomers are expected to have dissimilar insertion and isomerization rates (Scheme 4), thus leading to different product ratios.

In conclusion, we present here the first examples of Pd-catalyzed direct dehydrative cross-coupling reactions with allylic alcohols and styrene derivatives. Pd catalyst **1** is active in the absence of additional activators, and is based on a simple scalable phosphoramidite ligand. Based on kinetic studies, we propose a mechanism in which the allyl alcohol is activated by a Pd hydride complex, explaining why additional activators are not needed. The catalyst shows activity towards both aromatic and aliphatic allylic alcohols that can be coupled with various substituted styrene derivatives. With high activities and a wide substrate scope, this is an interesting, broadly applicable, new protocol for the formation of 1,4-dienes.

Experimental Section

Preparation of catalyst 1

Catalyst **1** was prepared by mixing phosphoramidite ligand, L, (0.2 mmol) and [(η^3-allyl)Pd(cod)]BF_4 precursor (0.1 mmol) in 5 mL dry dichloromethane. After stirring the mixture for 15 min at room temperature, the solvent was evaporated under vacuum. Co-evaporation with dry toluene afforded catalyst **1** quantitatively.

General procedure for dehydrative cross-coupling reactions

Cinnamyl alcohol, **2**, (0.1 mmol), styrene, **3a**, (0.12 mmol) and catalyst **1** were added to a flame-dried Schlenk flask. The Schlenk flask was flushed with argon before the solvent (1,4-dioxane, 0.5 mL) was added and then placed into the preheated oil bath (80–120 °C). After the reaction was stopped the product was isolated in pure form by column chromatography.

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Keywords: alkenes · allylic alcohols · cross-coupling · palladium · phosphoramidite

[1] a) K. C. Nicolaou, P. G. Bulger, D. Sarlah, *Angew. Chem.* **2005**, *117*, 4516–4563; *Angew. Chem. Int. Ed.* **2005**, *44*, 4442–4489; b) A. Suzuki, *Angew. Chem.* **2011**, *123*, 6854–6869; *Angew. Chem. Int. Ed.* **2011**, *50*, 6722–6737.

[2] a) H. U. Blaser, C. Malan, B. Pugin, F. Spindler, H. Steiner, M. Studer, *Adv. Synth. Catal.* **2003**, *345*, 103–151; b) A. Schmid, J. S. Dordick, B. Hauer, A. Kiener, M. Wubbolts, B. Witholt, *Nature* **2001**, *409*, 258–268; c) P. Gallezot, *Catal. Today* **2007**, *121*, 76–91.

[3] a) I. T. Horváth, P. T. Anastas, *Chem. Rev.* **2007**, *107*, 2169–2173; b) B. Trost, *Acc. Chem. Res.* **2002**, *35*, 695–705.

[4] a) M. Bandini, G. Cera, M. Chiarucci, *Synthesis* **2012**, 504–512; b) M. Bandini, M. Tragni, *Org. Biomol. Chem.* **2009**, *7*, 1501–1507; c) E. Emer, R. Sinisi, M. G. Capdevila, D. Petruzziello, F. De Vincentiis, P. G. Cozzi, *Eur. J. Org. Chem.* **2011**, 647–666; d) Y. Tamaru, *Eur. J. Org. Chem.* **2005**, 2647–2656.

[5] a) X. Lu, L. Lu, J. Sun, *J. Mol. Catal.* **1987**, *41*, 245–251; b) X. Lu, X. Jiang, X. Tao, *J. Organomet. Chem.* **1988**, *344*, 109–118; c) M. Kimura, T. Tomizawa, Y. Horino, S. Tanaka, Y. Tamaru, *Tetrahedron Lett.* **2000**, *41*, 3627–3629; d) M. Kimura, Y. Horino, R. Mukai, S. Tanaka, Y. Tamaru, *J. Am. Chem. Soc.* **2001**, *123*, 10401–10402; e) M. Kimura, M. Futamata, K. Shibata, Y. Tamaru, *Chem. Commun.* **2003**, 234–235; f) M. Kimura, M. Futamata, R. Mukai, Y. Tamaru, *J. Am. Chem. Soc.* **2005**, *127*, 4592–4593; g) B. M. Trost, J. Quancard, *J. Am. Chem. Soc.* **2006**, *128*, 6314–6315; h) I. Starý, I. G. Stara, P. Kocovsky, *Tetrahedron Lett.* **1993**, *34*, 179–182; i) I. Starý, I. G. Stara, P. Kocovsky, *Tetrahedron* **1994**, *50*, 529–537; j) Y. Masuyama, J. P. Takahara, Y. Kurusu, *J. Am. Chem. Soc.* **1988**, *110*, 4473–4474; k) K. Itoh, N. Hamaguchi, M. Miura, M. Nomura, *J. Chem. Soc. Perkin Trans. 1* **1992**, 2833–2835; l) T. Satoh, M. Ikeda, M. Miura, M. Nomura, *J. Org. Chem.* **1997**, *62*, 4877–4879; m) S. C. Yang, C. W. Hung, *J. Org. Chem.* **1999**, *64*, 5000–5001; n) S. C. Yang, Y. C. Tsai, Y. J. Shue, *Organometallics* **2001**, *20*, 5326–5330; o) Y. J. Shue, S. C. Yang, H. C. Lai, *Tetrahedron Lett.* **2003**, *44*, 1481–1485.

[6] Y. Gumrukcu, B. de Bruin, J. N. H. Reek, *ChemSusChem* **2014**, *7*, 890–896.

[7] a) F. Ozawa, H. Okamoto, S. Kawagishi, S. Yamamoto, T. Minami, M. Yoshifuji, *J. Am. Chem. Soc.* **2002**, *124*, 10968–10969; b) D. Banerjee, R. V. Jagadeesh, K. Junge, H. Junge, M. Beller, *ChemSusChem* **2012**, *5*, 2039–2044; c) D. Banerjee, R. V. Jagadeesh, K. Junge, H. Junge, M. Beller, *Angew. Chem.* **2012**, *124*, 11724–11728; *Angew. Chem. Int. Ed.* **2012**, *51*, 11556–11560; d) R. Ghosh, A. Sarkar, *J. Org. Chem.* **2011**, *76*, 8508–8512; e) H. Kinoshita, H. Shinokubo, K. Oshima, *Org. Lett.* **2004**, *6*, 4085–4088; f) I. Usui, S. Schmidt, M. Keller, B. Breit, *Org. Lett.* **2008**, *10*, 1207–1210.

[8] a) J. Y. Hamilton, D. Sarlah, E. M. Carreira, *J. Am. Chem. Soc.* **2014**, *136*, 3006–3009; b) B. Sundararaju, M. Achard, C. Bruneau, *Chem. Soc. Rev.* **2012**, *41*, 4467–4483; c) R. Kumar, E. V. Van der Eycken, *Chem. Soc. Rev.* **2013**, *42*, 1121–1146 and references in there.

[9] R. Matsubara, T. F. Jamison, *J. Am. Chem. Soc.* **2010**, *132*, 6880–6881.

[10] J. Y. Hamilton, D. Sarlah, E. M. Carreira, *J. Am. Chem. Soc.* **2013**, *135*, 994–997.

[11] a) J. A. Widegren, R. G. Finke, *J. Mol. Catal. A* **2003**, *198*, 317–341; b) N. T. S. Phan, M. van der Sluys, C. W. Jones, *Adv. Synth. Catal.* **2006**, *348*, 609–679.

[12] a) K. Yu, W. Sommer, J. M. Richardson, M. Weck, C. W. Jones, *Adv. Synth. Catal.* **2005**, *347*, 161–171; b) S. Klingelhöfer, W. Heitz, A. Greiner, S. Oestreich, S. Forster, M. Antonietti, *J. Am. Chem. Soc.* **1997**, *119*, 10116–10120; c) R. Narayanan, M. A. El-Sayed, *J. Am. Chem. Soc.* **2003**, *125*, 8340–8347; d) K. Yu, W. Sommer, M. Weck, C. W. Jones, *J. Catal.* **2004**, *226*, 101–110.

[13] Styrene derivatives and their respective coupling products have similar polarities, thus entailing a separation problem for purification by column chromatography.

[14] A. J. C. Walters, O. Troeppner, I. Ivanović-Burmazović, C. Tejel, M. P. del Río, J. N. H. Reek, B. de Bruin, *Angew. Chem.* **2012**, *124*, 5247–5251; *Angew. Chem. Int. Ed.* **2012**, *51*, 5157–5161.

[15] a) B. de Bruin, J. A. Brands, J. J. J. M. Donners, M. P. J. Donners, R. de Gelder, J. M. M. Smits, A. W. Gal, A. L. Spek, *Chem. Eur. J.* **1999**, *5*, 2921–2936; b) B. de Bruin, M. J. Boerakker, J. J. J. M. Donners, B. E. C. Christiaans, P. P. J. Schlebos, R. de Gelder, J. M. M. Smits, A. L. Spek, A. W. Gal, *Angew. Chem.* **1997**, *109*, 2153–2157; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2064–2067; c) B. de Bruin, P. H. M. Budzelaar, A. W. Gal, *Angew. Chem.* **2004**, *116*, 4236–4251; *Angew. Chem. Int. Ed.* **2004**, *43*, 4142–4157.

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