A Highly Active and Reusable Self-Assembled Poly(Imidazole/ Palladium) Catalyst: Allylic Arylation/Alkenylation**

Shaheen M. Sarkar, Yasuhiro Uozumi,* and Yoichi M. A. Yamada*

Metalloproteins, supramolecular composites of polymeric peptides and metal species, are essential organic transformation systems for maintaining vital activity to promote highly efficient enzymatic reactions.^[1] For example, the metalloprotein catalase provides extremely high turnover efficiencies of 40000000 sec⁻¹. However, metalloproteins are easily disassimilated and exhibit substrate specificity. Therefore, the development of a metalloprotein-inspired polymeric metal catalyst is an important objective for organic, organometallic, and supramolecular chemistry, as well as sustainable and industrial process chemistry.^[2] These catalysts are expected to provide highly active and selective organic transformation systems with high reusability, safety, cleanness, ease of use, and substrate tolerance. In metalloproteins, the basic imidazole unit within histidine plays an important role for binding with metal species, thus forming catalytic sites within a supramolecular structure; therefore imidazole ligands are widely utilized as the building blocks of artificial metalorganic self-assembled supramolecules for functional materials including catalysts.^[3] We believe that some insoluble selfassembled complexes of amphiphilic polymeric imidazoles and metal species could offer catalytic activities as high as that of metalloproteins, but with much greater reusability.

We recently reported the preparation of highly active, reusable, heterogeneous polymeric metal catalysts for organic transformations, also known as molecular convolution, where a soluble linear polymer having multiple ligand groups is convoluted (noncovalently cross-linked) with transition metals through coordinative or ionic complexation.^[4] We envisioned applying this concept to the preparation of metalloprotein-inspired polymeric imidazole metal catalysts to produce highly active, reusable, heterogeneous, selfassembled catalysts. Herein we report the development of a novel polymeric imidazole/acrylamide palladium catalyst that

[*] Dr. S. M. Sarkar, Dr. Y. M. A. Yamada RIKEN Advanced Science Institute, Hirosawa Wako, Saitama 351-0198 (Japan) E-mail: ymayamada@riken.jp Prof. Dr. Y. Uozumi Institute for Molecular Science and The Graduate School for Advanced Studies, Myodaiji, Okazaki, Aichi 444-8787 (Japan) E-mail: uo@ims.ac.jp was utilized for the allylic arylation/alkenylation of allylic esters with aryl/alkenylboronic acids and tetraaryl borates. Even 0.8–40 ppm of the catalyst efficiently promoted the allylic arylation/alkenylation in alcohol or water with a catalytic turnover number (TON) of 20000–1250000, and the catalyst was reusable without loss of catalytic activity. We found that our molecular convolution methodology provided the globular-aggregated, self-assembled structure of the catalyst.

The metalloprotein-inspired polymeric imidazole/palladium catalyst **3** (MPPI-Pd) was readily prepared as follows. When the coordinative convolution of $[(NH_4)_2PdCl_4]$ (**2**; 1 mol equiv Pd) and poly[(N-vinylimidazole)-co-(N-isopropylacrylamide)₅]^[5] (**1**; 2 mol equiv imidazole) was carried out in a methanol/water (1:1) solution at 80 °C for 30 minutes, the resulting compound **3** (brown powder) was precipitated out (Scheme 1). The precipitates were hardly soluble in water, methanol, DMF, EtOAc, CH₂Cl₂, or *n*-hexane. As shown in the top left panel of Figure 1, scanning electron microscopy



Scheme 1. Preparation of a metalloprotein-inspired polymeric imidazole palladium catalyst (MPPI-Pd; **3**).

(SEM) images revealed that the precipitates formed a globular-aggregated, self-assembled structure similar to the quaternary structure of proteins. The globules ranged from 100 to 1000 nm in diameter, and aggregated to construct a mesoporous suprastructure. X-ray photoelectron spectroscopy (XPS) of the palladium showed a major peak at 336 eV and a minor peak at 334 eV, which were assigned as Pd^{II} and Pd⁰, respectively (Figure 1; bottom left). Transmission electron microscopy (TEM) observation revealed the formation of palladium nanoparticles having a diameter of (4.9 ± 2.5) nm (Figure 1; center left); these nanoparticles were obtained by reduction with MeOH. These results suggested that the

^[**] We thank the RIKEN ASI Advanced Technology Support Division and the Chemical Analysis Team for TEM, XPS, and ICP analyses, respectively. We gratefully acknowledge financial support from the JSPS (Grant-in-Aid for Scientific Research no. 20655035; Grant-in-Aid for Scientific Research on Innovative Area no. 2105) and RIKEN ASI (Fund for Seeds of Collaborative Research).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201103799.

Communications



Figure 1. SEM images of **3** before use (top left) and after the 5th reuse (top right). TEM images of the **3** before use (center left) and after the 5th reuse (center right). XPS images of the **3** before use (bottom left) and after 5th reuse (bottom right).

catalyst was a composite of the polymeric imidazole 1, palladium complexes, and palladium nanoparticles. In the composite, the palladium complexes should act as cross-linkers of 1 through palladium-imidazole coordination, and the imidazole units in 1 could serve to stabilize the palladium nanoparticles. Elementary analysis and ICP-AES analysis of the palladium supported the structure shown in Scheme 1.

The catalytic activity and reusability of the novel catalyst **3** were examined for allylic arylation/alkenylation of allylic esters with tetraaryl borates and arylboronic acids. Although there are numerous reports on aryl–aryl coupling with aryl boron reagents (Suzuki–Miyaura coupling), little attention has been paid to allyl–aryl coupling, which often requires a relatively high reaction temperature with a large amount (1–10 mol%) of catalyst.^[6] We previously reported the allylic arylation of allylic esters and tetraaryl borates using a microchannel reactor with poly(acrylamide triarylphosphine palladium) catalytic membrane.^[7] However, both the reactivity and substrate generality were insufficient. The results led us to the idea that newly developed catalysts could be applied to the allylic arylation to provide high catalytic activity and reusability as well as high substrate tolerance.

When the allylic arylation was examined using cinnamyl acetate (4a) and sodium tetraphenylborate (5a) in *i*PrOH/

 H_2O (1:1) with 40 ppm palladium (0.004 mol% Pd) using 3, the reaction proceeded smoothly to give 1,3-diphenylpropene (6a) quantitatively after 4 hours (Table 1, entry 1). In the reaction, the turnover number and frequency were 25000 and 6250 h^{-1} , respectively, which are the highest numbers for allylic arylation to date. Moreover, 3 was reused five times without any loss of catalytic activity to give **6a** quantitatively. The coupling reaction with the reused (5th) catalyst did not show evidence of leaching of the palladium species into the reaction mixture (ICP-AES analysis; entry 6). SEM and TEM observations,^[8] and XPS analysis of **3** and reused **3** indicated that the catalyst was undamaged and unchanged under the reaction conditions (Figure 1; top, center, and bottom right panels). The reaction in water without the use of any organic solvents also proceeded smoothly to give 6a in 98% yield (entry 7). The phenyl vinyl carbinol ester 4b gave 6a with a yield of 96% (entry 8). Electron-donating and electronwithdrawing substituents on the cinnamyl esters 4c-4g reacted with substituted tetraaryl borates 5a-d and were efficiently converted into the corresponding products 6b-i with yields in the range of 93–98% (entries 9–16).

It is interesting to note that the alkyl vinyl carbinol esters **4h–j** underwent palladium-catalyzed (40 ppm) allyl–aryl coupling to yield the corresponding coupling products **6j–l** quantitatively (Table 1, entries 17–20). The reaction of alkyl vinyl carbinol esters must proceed via the corresponding π -allylpalladium intermediate bearing the β hydride on the sp³-carbon center, a species that often suffers from the β -hydride elimination under palladium-catalyzed conditions to give undesirable 1,3-dienes.^[9,10] However, no trace of 1,3-dienes was observed in the reactions. The palladium-catalyzed (40 ppm) reaction of **4i** was also performed in water to give **6k** quantitatively (entry 19).

Furthermore, the coupling of aliphatic 2-alkenyl acetates is more challenging than that of cinnamyl acetates in terms of reactivity. However, geranyl acetate (**4k**), neryl acetate (**4l**), prenyl acetate (**4m**), and 2-hexenyl acetate (**4n**) efficiently led to the corresponding phenylated compounds **6m–p** with yields in the range of 96–99% (Table 1, entries 21–25). Isomerization was not observed in the reactions, and water was used as a reaction solvent (entry 23). Alicyclic acetates **4o** and **4p** were readily converted into the corresponding products **6q** and **6r** with yield of 96% (entries 26 and 27); the reaction of *cis*-**4p** proceeded through net inversion to give *trans*-5-methoxycarbonyl-3-phenyl-1-cyclohexene (**6r**) as a single diastereomer (entry 27).

The heterogeneous catalyst **3** (40 ppm) also promoted allylic substitution with aryl/alkenylboronic acids, which are versatile and readily available boron reagents (Table 2). Thus, the reaction of **4a** with phenylboronic acid (**7a**) and methanolic or aqueous KF at 70 °C yielded **6a** quantitatively (entries 1 and 2). The substituted arylboronic acids **7b–d** readily underwent carbon–carbon bond formation under similar conditions to give **6h**, **6s**, and **6t** with a yield of 98% (entries 3–5). The alkyl vinyl carbinol esters **4i–j**, neryl acetate (**4l**), and cyclohexenyl acetate (**4o**) were converted into the corresponding alkenes **6k**, **6l**, **6n**, and **6q** with yields in the range of 97–99% (entries 6–9). Allylic alkenylation, the allyl–alkenyl coupling reaction, of allylic acetates with Table 1: Allylic arylation of allylic acetates with tetraarylborates.^[a]

	R ²		(40 p	om) R ²		
	R ¹ OAc	-	iPrOH/H ₂ C) or $H_2O^{-}R^{1}$		
	4	5	50 °C,	,4h 6		
Entry	Allylic ester 4		5 (R ³)	Product 6		Yield
Linuy	Allylic ester 4		J (iv)			[%]
	~ ^					[/]
1	Ph' V OAc	4a	5a (Ph)	Ph ² Ph	6a	99
2		4a	5a 5-	6a (3: 1st reuse)		99
3 1		4a 4a	5a 5a	6a (3: 2nd reuse)		99
4 5		4a 4a	5a 5a	6a (3: 4th reuse)		99
6		4a	5 a	6a (3 : 5th reuse)		99 ^[b]
7 ^[c]		4a	5 a	6a		98
0	OAc	46	F.a.	6.		06
ð	Ph	4 D	за	6a		96
•	OAc		-	Ph	~ 1	07
9	H ₃ C	4c	5 a	H ₃ C	6 D	97
10		4d	5 a		6c	93
				0 ₂ N ~		
11	OAc	4e	5a	Ph	6d	96
	CI			CI		
12	OAc	٨£	5.0	Ph	6.0	08
12	F	41	Ja	F	0e	90
	OAc			Ph		
13	Haco	4 g	5 a	H-CO	6 f	98
			EL //			
14		4a	У (4- МеС.Н.)		6g	98
15		4a	5C (4-		6h	96
			$CC_6 \Pi_4$	⇒ ^ Cl		
16		4a	5d (4-	Ph V	6i	98
	011		FC_6H_4)	F		
17		4h	5a	CH₃	6 i	98
	Ph OAc			Ph >> >Ph	-,	
18	$C_2 \Pi_5$	4i	5 a	\downarrow	6k	99
7 0 [c]	Ph' V OAc		-	Ph ^r 💙 Ph	~ 1	
19 ¹⁰	C ₆ H ₁₃	41	5a	C ₆ H ₁₃	6 K	99
20		4j	5 a	Ph	61	97
21	OAc	4 k	5 a	Ph	6 m	96
22		41	5 a		6 n	97
	OAc			⊂ _{Ph}		
23 ^[d]		41	5 a		6 n	99
24		4m	5a		60	98
			-	> Ph		
25	✓ ✓ ╰́OAc	4n	5 a	✓ ✓ Y YPh	6p	9/
26		4o	5 a		6a	96
		-		∼ `Ph		
27		4 p	5 a		6 r	96
	OAc			"''Ph		

[a] Reaction conditions: **4** (0.5 mmol), **5** (1 mmol), **3** (20 nmol), *i*PrOH/H₂O

(0.75 mL each) or H_2O (1.5 mL), 50 °C, 4 h. [b] Palladium species were not detected in the reaction mixture (ICP-AES). [c] The reaction was carried out in water for 8 h. [d] The reaction was carried out in water for 24 h. alkenylboronic acids is more challenging in terms of reactivity as well as isomerization of olefins compared to allylic arylation.^[11] However, the reaction of **4a** with (*E*)-1-pentenylboronic acid (**7e**) proceeded smoothly with 40 ppm of **3** under similar reaction conditions to give (1*E*, 4*E*)-1-phenyloctadiene (**6u**) in a 98% yield, wherein no isomerization occurred (entry 10). Neryl acetate (**41**) was also coupled with alkenylboronic acid **7e** to give the triene **6v** in a 98% yield (entry 11). Furthermore, the allylic vinylation efficiently proceeded under similar conditions. Thus, the allylic vinylation of **4a** and **4h** with dibutyl vinylboronate (**7f**) yielded the corresponding *exo*dienes **6w** and **6x** in 95% yield without the formation of isomers (entries 12 and 13).

Since 3 promoted efficient allylic arylations and alkenylations, 0.8 ppm of 3 was used for the reaction of 4a and 5a under similar reaction conditions (Scheme 2). We were pleased to find that the desired product 6a was obtained quantitatively, wherein the TON and TOF were more than one million (1250000) and 104000 h⁻¹, respectively. To the best of our knowledge, this is the highest TON and TOF for allylic arylation.

In conclusion, the novel globular-aggregated, self-assembled supramolecular composite **3** of a polymeric imidazole and a palladium species was developed. Catalyst **3** (0.8–40 ppm Pd) efficiently catalyzed the allylic arylation/alkenylation in alcohol or water under mild reaction conditions. The catalyst **3** provided the highest TON and TOF for allylic arylation/alkenylation, and was reused five times without loss of catalytic activity.

Experimental Section

Preparation of MPPI-Pd (**3**): An aqueous solution of $[(NH_4)_2PdCl_4]$ (**2**; 108 mg, 0.379 mmol; 5 mL) was slowly added to a solution of the imidazole polymer **1** (500 mg, 0.758 mmol) in methanol (5 mL) at 25 °C. The resulting brown suspension was heated at 80 °C for 45 min before the precipitates were filtered off through a glass filter. The precipitates were washed with H₂O and MeOH, successively, at 80 °C for 30 min in a flask. The precipitates were filtered off, washed with MeOH on the glass filter, and dried under reduced pressure to give **3** (583 mg, 92 %). Anal. Calcd for C₇₀H₁₂₂N₁₄O₁₀Cl₂Pd·5H₂O: C, 52.97; H, 8.38; N, 12.35; Cl, 4.47; Pd, 6.70. Found: C, 53.07; H, 8.30; N, 12.82; Cl, 4.64; Pd, 6.96. IR (KBr): 3285, 2972, 2875, 1658, 1530, 1453, 1386, 1236, 1172, 928, 834, 728, 655 cm⁻¹.

General procedure for allylic arylation catalyzed by MPPI-Pd (3):

Reaction of cinnamyl acetate (4a) with sodium tetraphenylborate (5a): A 2.5 mL glass vessel was charged with sodium tetraphenylborate (5a; 342 mg, 1 mmol), 3 (0.03 mg, 40 ppm) in 2-propanol and water (1:1; 0.75 mL each). Cinnamyl acetate (4a; 88 mg, 0.5 mmol) was added to the reaction mixture, and the reaction vessel was then shaken using a PetiSyzer (HiPep Laboratories, Japan) at 50 °C for 4 h. The reaction mixture was filtered, and the recovered 3 was washed with Et₂O (4×3 mL). The combined filtrate was dried over MgSO₄ and concentrated

Communications

Table 2: Allylic arylation/alkenylation of allylic acetates with arylboronic/ alkenylboronic acids.^[a]

	R'	4 7	MeOH or H ₂ O 70 °C, 3 h 6		
Entry	Allylic ester	7 (R ³)	Product		Yielc [%]
1 2 ^[b]	4a 4a	7a (Ph) 7a	Ph	6a 6a	97 99
3	4a	7b (4-ClC ₆ H ₄)	Ph	6h	98
4	4a	7c (4-MeOC ₆ H ₄)	Ph OCH3	6 s	98
5	4a	7d (3,4- (MeO) ₂ C ₆ H ₃)	Ph OCH3 OCH3	6t	98
6	4i	7a	Ph Ph	6 k	99
7	4j	7a	Ph Ph	61	99
8	41	7a	Ph	6 n	98
9	40	7a	Ph	6q	97
10	4a	7e ((E)- ////)	Ph	6 u	98
11	41	7e		6 v	98
12	4a	7 f [CH₂≕CHB(O- <i>n</i> Bu)₂]	Ph	6 w	95
13	4h	7 f	Ph	6x	95



[a] Reaction conditions: **4** (0.5 mmol), **7** (0.6 mmol), **3** (20 nmol), MeOH (1.5 mL), 70°C, 3 h. [b] The reaction was carried out in water for 60 h.



Scheme 2. Allylic arylation of 4a with 5a catalyzed by 0.8 ppm of 3.

under reduced pressure. The residue was chromatographed on silica gel (*n*-hexane/ethyl acetate 9:1) to give **6a** in 99% yield.

Reaction of cinnamyl acetate (4a) with phenylboronic acid (7a): A 2.5 mL glass vessel was charged with phenylboronic acid (7a; 73.1 mg, 0.6 mmol), potassium fluoride (72.5 mg, 1.25 mmol), 3 (0.03 mg, 40 ppm), and MeOH (1.5 mL). Cinnamyl acetate (4a; 0.5 mmol) was added to the mixture, and the reaction mixture was then shaken using a PetiSyzer (HiPep Laboratories, Japan) at 70 °C for 3 h. The reaction mixture was filtered, and the recovered 3 was washed four times with Et₂O on the filter (4×3 mL). The combined filtrate was dried over MgSO₄ and then concentrated under reduced pressure. The residue was chromatographed on silica gel (*n*-hexane/ ethyl acetate 9:1) to give (E)-1,3-diphenylpropene (**6a**) in 97% yield.

Received: June 4, 2011 Published online: August 30, 2011

Keywords: allylic compounds · boron · heterogeneous catalysis · metalloproteins · self-assembly

- D. Sadava, D. M. Hillis, H. C. Heller, M. R. Berenbaum, *Life: The Science of Biology: Evolution, Diversity, and Ecology*, Freeman, New York, 2009.
- [2] a) "Solid-Phase Palladium Catalysis for High-throughput Organic Synthesis": Y. Uozumi, T. Hayashi in Handbook of Combinatorial Chemistry (Eds.: K. C. Nicolaou, R. Hanko, W. Hartwig), Wiley-VCH, Weinheim, 2002, chap. 19; b) "Solid-Phase Bound Catalysts: Properties and Applications": T. Franzel, W. Solodenko, A. Kirschning in Polymeric Materials in Organic Synthesis and Catalysis (Ed.: M. R. Buchmeiser), Wiley-VCH, Weinheim, 2003, chap. 4; c) Y. Uozumi, Top. Curr. Chem. 2004, 242, 77; d) "Combinatorial Methods for the Discovery of Catalysts": H. Wennemers, in Highlights in Bioorganic Chemistry (Eds.: C. Schmuck, H. Wennemers), Wiley-VCH, Weinheim, 2004, p. 436; e) Z. Wang, G. Chen, K. Ding, Chem. Rev. 2009, 109, 322; f) J. Lu, P. H. Toy, Chem. Rev. 2009, 109, 815; g) K. Baer, M. Krausser, E. Burda, W. Hummel, A. Berkessel, H. Gröger, Angew. Chem. 2009, 121, 9519; Angew. Chem. Int. Ed. 2009, 48, 9355; h) Y. Uozumi, Y. M. A. Yamada, Chem. Rec. 2009, 9, 51; i) M. Lamblin, L. Nassar-Hardy, J.-C. Hierso, E. Fouquet, F.-X. Felpin, Adv. Synth. Catal. 2010, 352, 33; j) Y. M. A. Yamada, Y. Uozumi, J. Synth. Org. Chem. Jpn. 2011, 69, 542.
- [3] For reviews, see: a) R. J. P. Williams, Pure Appl. Chem. 1974, 38, 249; b) D. E. Benson, M. S. Wisz, H. W. Hellinga, Curr. Opin. Biotechnol. 1998, 9, 370; c) M. Tadokoro, K. Nakasuji, Coord. Chem. Rev. 2000, 198, 205; d) J. A. R. Navarroa, B. Lippert, Coord. Chem. Rev. 2001, 222, 219; e) D. N. Bolon, C. A. Voigt, S. L. Mayo, Curr. Opin. Chem. Biol. 2002, 6, 125; f) S. Kitagawa, R. Kitaura, S. Noro, Angew. Chem. 2004, 116, 2388; Angew. Chem. Int. Ed. 2004, 43, 2334; g) J. A. Branta, Y. Liua, D. F. Savaa, D. Beauchampa, M. Eddaoudi, J. Mol. Struct. 2006, 796, 160; h) W. Lin, W. J. Rieter, K. M. L. Taylor, Angew. Chem. 2009, 121, 660; Angew. Chem. Int. Ed. 2009, 48, 650; i) T. Ueno, Angew. Chem. 2010, 122, 3958; Angew. Chem. Int. Ed. 2010, 49, 3868; For recent examples, see: j) F. G. M. Niele, R. J. M. Nolte, J. Am. Chem. Soc. 1988, 110, 172; k) L. Dobrzanska, G. O. Lloyd, H. G. Raubenheimer, L. J. Barbour, J. Am. Chem. Soc. 2005, 127, 13134; l) Y.-S. Lo, W.-S. Chen, J.-Y. Yang, I. J. B. Lin, M.-H. Wu, M.-C. Shih, Thin Solid Films 2008, 516, 1175; m) I. Imaz, J. Hernando, D. Ruiz-Molina, D. Maspoch, Angew. Chem. 2009, 121, 2361; Angew. Chem. Int. Ed. 2009, 48, 2325; n) L. Yang, L. Luo, S. Zhang, X. Su, J. Lan, C.-T. Chenb, J. You, Chem. Commun. 2010, 46, 3938.
- [4] For a review, see: a) Y. M. A. Yamada, Chem. Pharm. Bull. 2005, 53, 723; recent examples, see: b) Y. M. A. Yamada, Y. Uozumi, Org. Lett. 2006, 8, 1375; c) Y. Uozumi, Y. M. A. Yamada, T. Beppu, N. Fukuyama, M. Ueno, T. Kitamori, J. Am. Chem. Soc. 2006, 128, 15994; d) Y. M. A. Yamada, Y. Maeda, Y. Uozumi, Org. Lett. 2006, 8, 4259; e) Y. M. A. Yamada, H. Guo, Y. Uozumi, Org. Lett. 2007, 9, 1501; f) Y. M. A. Yamada, Y. Uozumi, Tetrahedron 2007, 63, 8492; g) Y. M. A. Yamada, C. Jin, Y. Uozumi, Org. Lett. 2010, 12, 4540.
- [5] B. Mattiasson, A. Kumar, A. E. Ivanov, I. Y. Galaev, *Nat Protoc.* 2007, 2, 214, and references therein.
- [6] For recent achievements, see: a) H. Tsukamoto, M. Sato, Y. Kondo, Chem. Commun. 2004, 1200; b) C. Néjera, J. Gil-Moltó,

S. Karlström, Adv. Synth. Catal. 2004, 346, 1798; c) K. Manabe,
K. Nakada, N. Aoyama, S. Kobayashi, Adv. Synth. Catal. 2005, 347, 1499; d) M. Monreno-Mañas, R. Pleixats, S. Villarroya, Organometallics 2001, 20, 4524; e) G. W. Kabalka, G. Dong, B. Venkataiah, Org. Lett. 2003, 5, 893; f) E. Paetzold, G. Oehme, J. Mol. Catal. A 2000, 152, 69; g) E. Blart, J. P. Genêt, M. Safl, M. Savignac, D. Sinou, Tetrahedron Lett. 1994, 50, 505; h) N. Miyaura, K. Yamada, H. Suginome, A. Suzuki, J. Am. Chem. Soc. 1985, 107, 972.

- [7] a) Y. M. A. Yamada, T. Watanabe, K. Torii, Y. Uozumi, *Chem. Commun.* 2009, 5594; b) Y. M. A. Yamada, T. Watanabe, K. Torii, T. Beppu, N. Fukuyama, Y. Uozumi, *Chem. Eur. J.* 2010, *16*, 11311.
- [8] The mean diameter of the palladium nanoparticles in the reused (5th) catalyst was (4.8 ± 2.4) nm.
- [9] For excellent palladium-catalyzed arylation of secondary allylic acetates possessing β -hydrides on sp²- or sp³-carbon centers, see:

a) H. Ohmiya, Y. Mikida, D. Li, T. Tanaka, M. Sawamura, *J. Am. Chem. Soc.* **2010**, *132*, 879; b) H. Ohmiya, Y. Mikida, T. Tanaka, M. Sawamura, *J. Am. Chem. Soc.* **2008**, *130*, 17276; c) G. Orar, *Tetrahedron Lett.* **2003**, *44*, 4311; d) D. Bouyssi, V. Gerusz, G. Balme, *Eur. J. Org. Chem.* **2002**, 2445; e) J.-Y. Legros, J.-C. Flaud, *Tetrahedron Lett.* **1990**, *31*, 7453.

- [10] For resin-supported palladium-catalyzed arylation of secondary allylic esters possessing β-hydrides on sp²- or sp³-carbon centers, see: Y. Uozumi, H. Danjo, T. Hayashi, J. Org. Chem. 1999, 64, 3384.
- [11] a) Y. Kobayashi, Y. Tokoro, K. Watatani, *Eur. J. Org. Chem.* 2000, 3825; b) Y. Kayaki, T. Koda, T. Ikariya, *Eur. J. Org. Chem.* 2004, 4989; c) G. W. Kabalka, M. Al-Masum, *Org. Lett.* 2006, *8*, 11; d) H. Tsukamoto, T. Uchiyama, T. Suzuki, Y. Kondo, *Org. Biomol. Chem.* 2008, *6*, 3005.