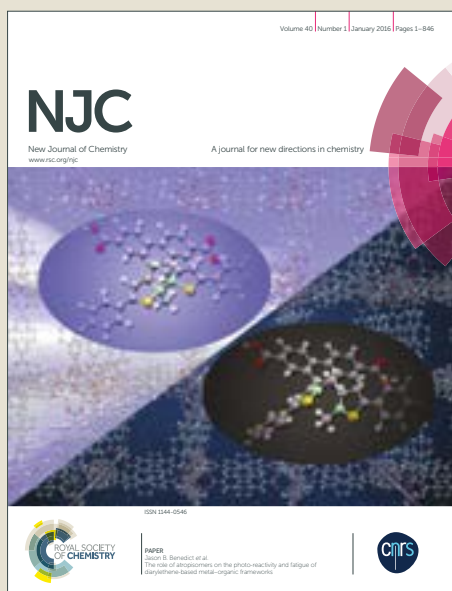


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ARTICLE

## Aqueous protocol for allylic arylation of cinnamyl acetates with sodium tetraphenylborate using Bedford-type palladacycle catalyst

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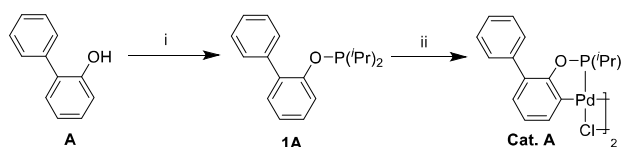
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Allylic arylation of cinnamyl acetates with sodium tetraphenylborate using 0.002 mol % of Bedford-type palladacycle catalyst is described. The developed methodology is applicable for wide range of cinnamyl acetates furnishing excellent yields up to 93%. Notably all reactions proceed smoothly under mild reaction conditions in water under air atmosphere.

### Introduction

The palladium catalyzed allylic nucleophilic substitution reactions popularly known as Tsuji–Trost reactions,<sup>1</sup> have wide applications in the synthesis of agrochemicals, natural products and pharmaceuticals.<sup>2</sup> Depending on the type of nucleophiles involved in the Tsuji–Trost reaction they are categorized as allylic amination,<sup>3</sup> allylic alkylation,<sup>4</sup> allylic arylation,<sup>5</sup> *O*-allylation<sup>6</sup> etc. Therefore, Tsuji–Trost reactions are versatile tool to introduce internal alkene into industrially important compounds with various functionalities. Notably 1,3-Diarylpropene derivatives are integral part of many natural products and biologically active compounds such as obtusastylene and obtustylene.<sup>5b</sup> Previously synthesis of 1,3-Diarylpropene derivatives was reported using Heck-type allylic C–H arylation with arylboronic acids which resulted in the mixture of the double-bond-migrated isomers.<sup>7</sup> Instead 1,3-Diarylpropene derivatives are easily synthesized using palladium-catalyzed Tsuji–Trost type allylic arylation in single step. Therefore, there is growing interest in palladium catalyzed allylic arylation reactions using aryl boron reagents because of their wide applications.<sup>8</sup> In most of the reports sodium tetraphenylborate (NaBPh<sub>4</sub>) and its derivatives are reagents of choice<sup>9</sup> due to their high reactivity as compared to the corresponding aryl boronic acid derivatives<sup>10</sup>. In this regard Uozumi *et al.* recently reported several effective catalysts at parts per million to parts per billion levels catalyst loading such as self-assembled poly(imidazole–palladium)

composite and palladium NNC-pincer complex for allylic arylation of allylic acetates with sodium tetraarylborates.<sup>11</sup> However, despite of impressive improvement the use of toxic organic solvent methanol or isopropanol, longer reaction time, and requirement of inert conditions are major drawbacks. Nevertheless, the reported methods leave room for further development to more effective and greener protocols. Ideally allylic arylation using lower catalyst loading, mild reaction conditions under air atmosphere and water as solvent is the more demanding approach in respect to industrial applications.<sup>12</sup> It is noteworthy to mention that water is the solvent of choice for many industrial applications, not only because it is an environmentally benign solvent but also because water is safe to handle, readily available and an inexpensive universal solvent. In this regard, we believe that Bedford type catalysts have good potential for developing an effective aqueous protocol for allylic arylation.<sup>13</sup> Recently our group has developed a new Bedford-type palladacycle catalyst (Scheme 1) and explored for aqueous Suzuki coupling as well as for borylation reactions.<sup>14</sup> Therefore, in continuation with our longtime interest in developing catalytic protocols for wide applications,<sup>15</sup> herein we report our studies on the application of our Bedford-type palladacycle catalyst (**Cat. A**, Scheme 1) for aqueous Tsuji–Trost type allylic arylation of cinnamyl acetates with sodium tetraphenylborates as an arylating agent.



**Scheme 1** Reaction Conditions: (i) NEt<sub>3</sub>, ClP(Pr)<sub>2</sub>, toluene, reflux, 16 h. (ii) PdCl<sub>2</sub>, toluene, reflux, 16 h.<sup>14</sup>

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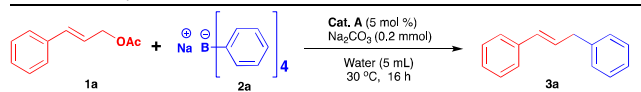
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## Result and Discussion

First, we investigated the reaction of cinnamyl acetate (**1a**) with sodium tetraphenylborate (**2a**) in the presence of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) with our Bedford-type palladacycle catalyst (Cat. A) in water and under inert conditions.

**Table 1.** Test Experiments<sup>a</sup>



Entry	Cat. A	$\text{Na}_2\text{CO}_3$	Argon	<b>3a</b> yield <sup>b</sup> [%]
1	+	+	+	98
2	-	+	+	0
3	+	-	+	98
4	+	-	-	98

<sup>a</sup> Reaction Conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), **Cat. A** (5 mol %),  $\text{Na}_2\text{CO}_3$  (0.20 mmol), Water, (5 mL), 30 °C, 16 h. <sup>b</sup> GC Yield

Interestingly, in our first attempt almost 98% yield of **3a** were obtained (Table 1, entry 1). Encouraged by this result a set of test reactions were carried out, to check the role of catalyst, base and inert conditions (Table 1). It was observed that in the absence of **Cat. A**, the reaction did not proceed, which confirms the important role of **Cat. A** (Table 1, entry 2). However, in the absence of base still 98% product **3a** was obtained and proves that base has no influence on the reaction outcome (Table 1, entry 3). Succeeding, we carried out reaction in air atmosphere; interestingly almost 98% of **3a** were obtained (Table 1, entry 4), therefore, all the next experiments were performed in air atmosphere. Additionally,

**Table 2** Screening of Metal Precursors<sup>a</sup>

Entry	Catalyst	<b>3a</b> yield <sup>b</sup> [%]
1	<b>Cat. A</b>	98
2	$\text{PdCl}_2$	98
3	$\text{Pd}(\text{OAc})_2$	98
4	$\text{Pd}(\text{PPh}_3)_4$	98
5	$\text{Pd/C}$	64
6	$\text{NiCl}_2$	37
7	$\text{Ni}(\text{OH})_2$	34
8	Nickel(III)(acac) <sub>2</sub>	17
9	$\text{Ni}(\text{NO}_2)_2$	13
10	$\text{NiI}_2$	16
11	$(\text{Ni}(\text{CH}_3\text{COO})_2) \cdot 4\text{H}_2\text{O}$	7
12	$[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NiCl}_2$	2
13	$\text{Cu}_2\text{O}$	3
14	$\text{Cu}_2\text{Br}$	1
15	$\text{CuBr}_2$	0
16	$\text{Cu}(\text{CH}_3\text{COO})_2$	0
17	$\text{Cu}(\text{NO}_2)_2$	0
18	$\text{CuSO}_4$	0
19	$\text{CuI}$	1
20	$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	0
21	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	0

<sup>a</sup> Reaction Conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), catalyst (5 mol %), water (2 mL), 30 °C, 16 h. <sup>b</sup> GC yield.

the effects of solvent volume confirm that 2 mL of water is sufficient to achieve higher yield of **3a** (See SI, Table 1). In order to compare the catalyst activity of **Cat. A** with other catalysts, we screened various commercially available transition metal salts and complexes of palladium, nickel, copper and iron (Table 2). It was observed that most of the palladium salts and complexes are good catalyst for allylic arylation and almost 98% of **3a** were obtained (Table 2, entries 1–5). Interestingly, with  $\text{NiCl}_2$  and  $\text{Ni}(\text{OH})_2$  as catalyst moderate yields of **3a** up to 37% and 34% respectively were obtained (Table 2, entries 6 and 7) while use of other nickel salts and complexes resulted in lower yield of product **3a** (Table 2, entries 8–12). In addition, reactions performed with copper and iron catalysts were not successful (Table 2, entries 13–21). Therefore, among the screened catalysts, palladium catalysts were identified to be the best catalysts for allylic arylation under aqueous conditions. Subsequently among the screened catalysts it is important to select the best palladium catalyst having high catalytic activity at lower catalyst loading. Thus, we checked the lowest possible catalyst loading of our Bedford-type palladacycle catalyst (**Cat. A**). This study is done by systematic decreasing of **Cat. A** loading from 5 mol % to 0.0002 mol % and its effect on the yield of **3a** were studied (Table 3). To select the lowest effective catalyst loading for achieving higher yields reactions were stopped after 8 hours. It was observed that with use of up to 0.008 mol % of **Cat. A** there is no significant decrease in yield of **3a** and almost 98% yield was obtained (Table 3, entries 1–9), while lowering the catalyst loading further results in decrease in the yield of **3a** (Table 3, entries 10–14).

**Table 3** Catalyst Screening and Effect of Catalyst Loading<sup>a</sup>

Entry	Catalyst	Catalyst (mol %)	<b>3a</b> yield <sup>b</sup> [%]
1	<b>Cat. A</b>	2	98
2	<b>Cat. A</b>	1	98
3	<b>Cat. A</b>	0.5	98
4	<b>Cat. A</b>	0.25	98
5	<b>Cat. A</b>	0.13	98
6	<b>Cat. A</b>	0.063	98
7	<b>Cat. A</b>	0.031	98
8	<b>Cat. A</b>	0.016	98
9	<b>Cat. A</b>	0.008	98
10	<b>Cat. A</b>	0.004	76
11	<b>Cat. A</b>	0.002	57
12	<b>Cat. A</b>	0.001	37
13	<b>Cat. A</b>	0.0005	32
14	<b>Cat. A</b>	0.0002	9
15	$\text{PdCl}_2$	0.008	49
16	$\text{Pd}(\text{OAc})_2$	0.008	20
17	$\text{PdCl}_2(\text{PPh}_3)_2$	0.008	15
18	$\text{Pd}(\text{PPh}_3)_4$	0.008	3

<sup>a</sup> Reaction Conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), Pd-catalyst, water (2 mL), 30 °C, 8 h. <sup>b</sup> GC yield.

Table 4 Optimization of the Reaction Conditions<sup>a</sup>

Entry	Cat. A (mol %)	NaB(Ph) <sub>4</sub> (mmol)	T (°C)	Time (h)	3a yield <sup>b</sup> [%]
<b>Effect of time</b>					
1	0.008	0.40	30	2	61
2	0.008	0.40	30	4	78
3	0.008	0.40	30	6	86
4	0.008	0.40	30	8	98
5	0.008	0.40	30	10	98
<b>Effect of NaBPh<sub>4</sub> stoichiometry</b>					
6	0.008	0.40	30	8	98
7	0.008	0.30	30	8	89
8	0.008	0.20	30	8	76
9	0.008	0.10	30	8	68
10	0.008	0.05	30	8	43
<b>Effect of temperature</b>					
11	0.008	0.40	40	8	98
12	0.004	0.40	40	8	98
13	0.002	0.40	40	8	84
14	0.001	0.40	40	8	58
15	0.0005	0.40	40	8	52
16	0.008	0.40	50	8	98
17	0.004	0.40	50	8	98
18	0.002	0.40	50	8	97
19	0.001	0.40	50	8	80
20	0.0005	0.40	50	8	68
21	0.0005	0.40	50	16	93

<sup>a</sup> Reaction Conditions: **1a** (0.20 mmol), **2a**, Cat. A, water (2 mL). <sup>b</sup> GC yield.

Therefore, the catalyst activity of all palladium catalysts was again compared under the same reaction conditions at 0.008 mol % catalyst loading to select the best palladium catalyst (Table 3, entries 9, 15–18). It was observed that among all the screened palladium catalysts, **Cat. A** gave the highest yield of **3a** up to 98% (Table 3, entry 9) while only moderate yields up to 49% were obtained with PdCl<sub>2</sub> (Table 3, entry 15). Interestingly with PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and Pd(OAc)<sub>2</sub> lower yields 20% and 15% respectively of **3a** were obtained (Table 3, entries 16 and 17) and with Pd(PPh<sub>3</sub>)<sub>4</sub> the lowest yield 9% of **3a** was obtained (Table 3, entry 18). Therefore, our catalyst screening study confirms the superiority of **Cat. A** over the screened catalysts. Subsequently a detailed optimization study was done for **Cat. A** catalyzing allylic arylation of cinnamyl acetate with sodium tetraphenylborate under aqueous conditions. For optimization of our protocol we firstly performed a time study (Table 4, entries 1–5) and it was observed that after 8 hours 98% yield of product **3a** was obtained (Table 4, entry 4). Then we checked the influence of stoichiometric ratio of sodium tetraphenylborate on yield of **3a** (Table 4, entries 6–10) and we observed that 98% yield of **3a** was obtained with two equivalence of sodium tetraphenylborate (Table 4, entry 6). However, further lowering the amount of sodium tetraphenylborate results in lower yield of **3a** (Table 4, entries 7–10). Finally, the influence of temperature was checked and reactions were carried out at 40 °C (Table 4, entries 11–15) and 50 °C (Table 4, entries 16–21) by varying catalyst loadings of

Table 5 Substrate Scope Study<sup>a</sup>

Entry	Product	Yield <sup>b</sup> [%]
1	<b>3a</b>	93
2	<b>3b</b>	89
3	<b>3c</b>	91
4	<b>3d</b>	78
5	<b>3e</b>	74
6	<b>3f</b>	72
7	<b>3g</b>	49
8	<b>3h</b>	84
9	<b>3i</b>	89
10	<b>3j</b>	69
11	<b>3k</b>	64
12	<b>3l</b>	80

<sup>a</sup> Reaction Conditions: **1** (0.20 mmol), **2a** (0.40 mmol), **Cat. A** (0.002 mol %), water (2 mL), 50 °C, 8 h. <sup>b</sup> NMR Yield.

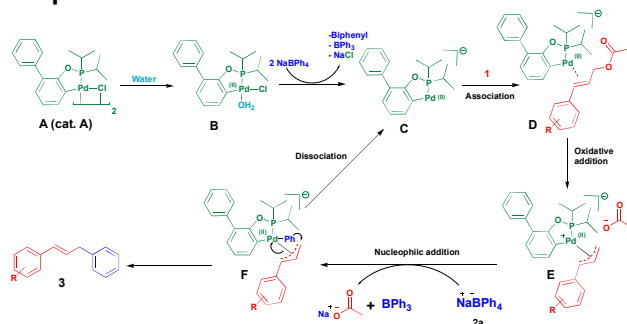
**Cat. A** from 0.008 mol % to 0.0005 mol %. Interestingly with increasing temperature up to 50 °C higher yields up to 97% of **3a** were obtained, notably with lower catalyst loading of 0.002 mol % of **Cat. A** (Table 4, entry 18). Remarkably 68% yield of **3a** was obtained with 0.0005 mol % of **Cat. A** within 8 hours (Table 4, entry 20) which is further improved to 93% by extending reaction time to 16 hours (Table 4, entry 21). Our study confirms that either by increasing the reaction temperature or by extending the reaction time further lowering of catalyst loading is possible to still achieve high yields of **3a**. However, considering the time as limiting factor to achieve higher yields in short time the next substrate scope study was explored at 50 °C with 0.002 mol % of **Cat. A**.

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Thereupon as results from our optimization study on allylic arylation, our final optimized reaction conditions are cinnamyl acetate (**1a**, 0.20 mmol), sodium tetraphenylborate (**2a**, 0.40 mmol), **Cat. A** (0.002 mol %) in water (2 mL) at 50 °C for 8 hours under air atmosphere. Using this optimized reaction conditions the substrate scope was checked for various cinnamyl acetate derivatives (Table 5). First cinnamyl acetates bearing electron-donating groups such as (*E*)-3-(*p*-tolyl)allyl acetate (**1b**) and (*E*)-3-(4-methoxyphenyl)allyl acetate (**1c**) were screened which resulted in excellent yield of corresponding arylated product **3b** and **3c** up to 89% and 91% respectively (Table 5, entries 2 and 3). Effects of electron withdrawing (*E*)-3-(4-nitrophenyl)allyl acetate (**1d**) were studied and moderate yield up to 78% of **3d** were obtained (Table 5, entry 4). It was observed that *p*-halo substituted cinnamyl acetates such as (*E*)-3-(4-chlorophenyl)allyl acetate (**1e**) and (*E*)-3-(4-fluorophenyl)allyl acetate (**1f**) also reacted smoothly and 74% yield of **3e** and 72% yield of **3f** were obtained (Table 5, entries 5 and 6). However, lower yield 49% of **3g** were obtained with (*E*)-3-(4-(trifluoromethyl)phenyl)allyl acetate (**1g**) (Table 5, entry 7). Next we checked the effect of sterically hindered *ortho* and *meta* disubstituted derivatives of cinnamyl acetates such as (*E*)-3-(2,4-dimethylphenyl)allyl acetate (**1h**) and (*E*)-3-(2,4-dimethoxyphenyl)allyl acetate (**1i**) interestingly higher yields of **3h** and **3i** up to 84% and 89% respectively were obtained (Table 5, entries 8 and 9). Moreover, *ortho* substituted cinnamyl acetates such as (*E*)-3-(2-fluorophenyl)allyl acetate (**1j**) and (*E*)-3-(2-chlorophenyl)allyl acetate (**1k**) also reacted efficiently and arylated products **3j** and **3k** obtained in 69% and 64% yield (Table 5, entries 10 and 11). Likewise with (*E*)-3-(3-fluorophenyl)allyl acetate (**1l**) up to 80% yield of **3l** were obtained (Table 5, entry 12). Therefore, overall substrate scope study confirms the wide applicability of our protocol. Its noteworthy to mention that in all cases traces of biphenyl side product formed.

## Proposed Mechanism:



Scheme 2 Proposed mechanism

The **Cat. A** is dimer (**A**) and as soon as water is added the **Cat. A** dimer breaks down and form Pd (II) intermediate (**B**) (Scheme 2). It should be noted that because of bulky isopropyl substituent the phosphorous center is rich in electron density and well shielded against cleavage by nucleophilic attack on

phosphorus favoring oxidative addition of the NaBPh<sub>4</sub> and a well-balanced steric bulk stabilizes the palladacyclic motive. Hence, we suggest that addition of NaBPh<sub>4</sub> induces first a double transmetalation of phenyl groups, followed by a reductive elimination of biphenyl resulting in an under-coordinated, palladacyclic anionic Pd(0) species (**C**). Our previous mechanistic study on Suzuki coupling<sup>14</sup> and in current study the formation of traces of biphenyl as side product support the formation of intermediate **B** and **C**. In next step the palladium coordinates to the alkene bond of **1**, forming a η<sup>2</sup> π-allyl-Pd(0) complex (**D**). Subsequently oxidative addition of palladium occurs in which the leaving group acetate is expelled result in forming intermediate a η<sup>3</sup> π-allyl-Pd(II) complex (**E**). In next step the phenyl nucleophile formed by transmetalation from NaBPh<sub>4</sub> adds to the allyl group (**F**) result in formation of product **3a**. After the completion of the reaction, the palladium detaches from the product **3a** and forming again Pd (0) intermediate (**C**) and catalytic cycle starts again.

## Conclusions

In conclusion, a greener aqueous protocol for allylic arylation of cinnamyl acetates with sodium tetraphenylborate using 0.002 mol % of Bedford-type palladacycle catalyst is reported. All reactions proceed efficiently at mild reaction conditions in water under air atmosphere within a short reaction time of 8 hours. All corresponding products are obtained in excellent yields up to 93%. In addition, we also confirmed that further lowering of catalyst loading under aqueous condition is possible by increasing temperature or time as with 0.0005 mol % of Bedford-type palladacycle catalyst almost 93% product was obtained.

## Conflicts of interest

There are no conflicts to declare.

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## Notes and references

- (a) J. Tsuji, H. Takahashi and M. Morikawa, *Tetrahedron Lett.*, 1965, **6**, 4387; (b) B. M. Trost, and M. L. Crawley, *Chem. Rev.*, 2003, **103**, 2921; (c) J. Muzart, *Tetrahedron*, 2005, **61**, 4179; (d) L. Milhau and P. Guiry, *J. Top. Organomet. Chem.*, 2011, **38**, 95; (e) N. A. Butt and W. Zhang, *Chem. Soc. Rev.*, 2015,

- 44, 7929; (f) R. K. Sharma, S. Sharma, S. Dutta, R. Zboril and M. B. Gwanade, *Green Chem.*, 2015, **17**, 3207; (g) A. K. Rathi, M. B. Gawande, R. Zboril and R. S. Varma, *Coord. Chem. Rev.*, 2015, **291**, 68.
- 2 (a) J. Tsuji, *Acc. Chem. Res.*, 1969, **2**, 144; (b) B. M. Trost, *Angew. Chem. Int. Ed.*, 1989, **28**, 1173; (c) Trost, B. M. *Acc. Chem. Res.*, 1996, **29**, 355; (d) B. Sundararaju, M. Achard and C. Bruneau, *Chem. Soc. Rev.*, 2012, **41**, 4467; (e) S. Oliver and P. A. Evans, *Synthesis*, 2013, 3179.
- 3 (a) J. Muzart, *Eur. J. Org. Chem.*, 2007, 3077; (b) A. M. Johns, Z. Liu and J. F. Hartwig, *Angew. Chem. Int. Ed.*, 2007, **46**, 7259; (c) Y. S. Wagh, P. J. Tambade, D. N. Sawant and B. M. Bhanage, *Eur. J. Org. Chem.*, 2010, **26**, 5071; (d) Y. S. Wagh, D. N. Sawant, P. J. Tambade, K. P. Dhake, and B. M. Bhanage, *Tetrahedron*, 2011, **67**, 2414; (e) Y. S. Wagh, D. N. Sawant, K. P. Dhake and B. M. Bhanage, *Catal. Sci. Technol.*, 2012, **2**, 835; (f) B. R. Vaddula, A. Saha, R. S. Varma, and J. Leazer, *Eur. J. Org. Chem.*, 2012, 6707; (g) M. Rueping, C. Vila and U. Uria, *Org. Lett.*, 2012, **14**, 768; (h) D. Krishnan, M. Wu, M. Chiang, Y. Li, P. -H. Leung and S. A. Pullarkat, *Organometallics*, 2013, **32**, 2389; (i) R. B. N. Baig, B. R. Vaddula, M. A. Gonzalez and R. S. Varma, *RSC Adv.*, 2014, **4**, 9103; (j) J. Jing, X. Huo, J. Shen, J. Fu, Q. Meng and W. Zhang, *Chem. Commun.*, 2017, **53**, 5151.
- 4 (a) C. Chevrin, J. Le Bras, F. Henin, J. Muzart, A. Pla-Quintana, A. Roglans and R. Pleixats, *Organometallics*, 2004, **23**, 4796; (b) M. Rueping, B. J. Nachtsheim and A. Kuenkel, *Org. Lett.*, 2007, **9**, 825; (c) B. M. Trost and M. L. Crawley, *Top. Organomet. Chem.*, 2012, **38**, 321; (d) Y. Hong and B. M. Stoltz, *Eur. J. Org. Chem.*, 2013, 2745; (e) B. M. Trost, *Tetrahedron*, 2015, **71**, 5708; (f) Q. Jinlong and J. Gaoxi, *Current Catalysis*, 2017, **6**, 25; (g) Y. -L. Lai and J. -M. Huang, *Org. Lett.* 2017, **19**, 2022.
- 5 (a) T. Mino, T. Kogure, T. Abe, T. Koizumi, T. Fujita and M. Sakamoto, *Eur. J. Org. Chem.*, 2013, 1501; (b) K. Watanabe, T. Mino, T. Abe, T. Kogure and M. Sakamoto, *J. Org. Chem.*, 2014, **79**, 6695; (c) Y. Lee, S. Shabbir, S. Lee, H. Ahn and H. Rhee, *Green Chem.*, 2015, **17**, 3579; (d) S. Y. Lee and J. F. Hartwig, *J. Am. Chem. Soc.*, 2016, **138**, 15278.
- 6 (a) B. M. Trost and F. D. Toste, *J. Am. Chem. Soc.*, 1998, **120**, 815; (b) B. Schmidt and S. Nave, *Adv. Synth. Catal.*, 2006, **348**, 531; (c) S. F. Kirsch, L. E. Overman and N. S. White, *Org. Lett.*, 2007, **9**, 911; (d) Y. S. Wagh, D. N. Sawant, K. P. Dhake, K. M. Deshmukh and B. M. Bhanage, *Tetrahedron Lett.*, 2011, **52**, 5676; (e) A. Saha, J. Leazer and R. S. Varma, *Green Chem.*, 2012, **14**, 67; (f) R. B. N. Baig and R. S. Varma, *Ind. Eng. Chem. Res.*, 2014, **53**, 18625; (g) U. Uria, C. Vila, M. -Y. Lin and M. Rueping, *Chem. Eur. J.*, 2014, **20**, 13913; (h) M. Halder, M. M. Islam, S. Ahammed and S. M. Islam, *RSC Adv.*, 2016, **6**, 8282; (i) C. A. Discolo, A. G. Graves and D. R. Deardorff, *J. Org. Chem.*, 2017, **82**, 1034.
- 7 (a) Y. C. Jung, R. K. Mishra, C. H. Yoon and K. W. Jung, *Org. Lett.*, 2003, **5**, 2231; (b) F. M. A. Bar, M. A. Khanfar, A. Y. Elnagar, F. A. Badria, A. M. Zaghoul, K. F. Ahmad, P. W. Sylvester and K. A. El Sayed, *Bioorg. Med. Chem.*, 2010, **18**, 496.
- 8 (a) L. Botella and C. J. Najera, *Organomet. Chem.*, 2002, **663**, 46; (b) H. Ohmiya, Y. Makida, T. Tanaka and M. Sawamura, *J. Am. Chem. Soc.*, 2008, **130**, 17276; (c) Y. M. A. Yamada, T. Watanabe, K. Torii and Y. Uozumi, *Chem. Commun.*, 2009, 5594; (d) H. Ohmiya, Y. Makida, D. Li, M. Tanabe and M. Sawamura, *J. Am. Chem. Soc.*, 2010, **132**, 879; (e) F. C. Pigge, *Synthesis*, 2010, **11**, 1745; (f) D. Li, T. Tanaka, H. Ohmiya and M. Sawamura, *Org. Lett.*, 2010, **12**, 3344. (g) Y. Junga and I. Kim, *Org. Biomol. Chem.*, 2015, **13**, 4331.
- 9 (a) E. Blart, J. P. Genet, M. Safi, M. Savignac and D. Sinou, *Tetrahedron*, 1994, **50**, 505; (b) Z. Dong and Z. Ye, *Adv. Synth. Catal.*, 2014, **356**, 3401; (c) C. Najera, J. Gil-Molto, S. Karlströma, *Adv. Synth. Catal.*; 2004, **346**, 1798; (d) Z. Dong and Z. Ye, *Applied Catalysis, A: General*, 2015, **489**, 61; (e) Y. M. A. Yamada, *Chem. Pharm. Bull.*, 2017, **65**, 805.
- 10 (a) H. Tsukamoto, T. Uchiyama, T. Suzuki and Y. Kondo, *Org. Biomol. Chem.*, 2008, **6**, 3005; (b) H. Ohmiya, Y. Makida, D. Li, T. Tanaka and M. Sawamura, *J. Am. Chem. Soc.*, 2010, **132**, 879; (c) B. Yao, Y. Liu, M. -D. Wang, J. -H. Li, R. -Y. Tang, X. -G. Zhang and C. -L. Deng, *Adv. Synth. Catal.*, 2012, **354**, 1069; (d) C. Li, J. Xing, J. Zhao, P. Huynh, W. Zhang, P. Jiang and Y. J. Zhang, *Org. Lett.*, 2012, **14**, 390; (e) J. Zhao, J. Ye and Y. J. Zhang, *Adv. Synth. Catal.*, 2013, **355**, 491; (f) J. Ye, J. Zhao, J. Xu, Y. Mao and Y. J. Zhang, *Chem. Commun.*, 2013, **49**, 9761; (g) H. -B. Wu, X. -T. Ma and S. -K. Tian, *Chem. Commun.*, 2014, **50**, 219.
- 11 (a) Y. Uozumi, H. Danjo and T. Hayashi, *J. Org. Chem.*, 1999, **64**, 3384; (b) S. M. Sarkar, Y. Uozumi and Y. M. A. Yamada, *Angew. Chem. Int. Ed.*, 2011, **50**, 9437; (c) Y. M. A. Yamada, S. M. Sarkar and Y. J. Uozumi, *Am. Chem. Soc.*, 2012, **134**, 3190; (d) G. Hamasaka, F. Sakurai and Y. Uozumi, *Chem. Comm.*, 2015, **51**, 3886; (e) G. Hamasaka, F. Sakurai and Y. Uozumi, *Tetrahedron*, 2015, **71**, 6437.
- 12 (a) A. Zapf and M. Beller, *Topics in Catalysis*, 2002, **19**, 101; (b) H. -S. Blaser, A. Indolese, F. Naud, U. Nettekoven and A. Schnyder, *Adv. Synth. Catal.*, 2004, **346**, 1583; (c) C. Torborg and M. Beller, *Adv. Synth. Catal.*, 2009, **351**, 3027.
- 13 (a) R. B. Bedford and S. L. Welch, *Chem. Commun.*, 2001, 129; (b) R. B. Bedford, S. L. Hazelwood and M. E. Limmert, *Chem. Commun.*, 2002, 2610; (c) R. B. Bedford, C. S. J. Cazin and S. L. Hazelwood, *Angew. Chem., Int. Ed.*, 2002, **41**, 4120; (d) R. B. Bedford, S. L. Hazelwood, P. N. Horton and M. B. Hursthouse, *Dalton Trans.*, 2003, 4164; (e) R. B. Bedford and M. E. Blake, *Adv. Synth. Catal.*, 2003, **345**, 1107; (f) R. B. Bedford, *Chem. Commun.*, 2003, 1787.
- 14 (a) A. N. Marziale, Stefan H. Faul, T. Reiner, S. Schneider and J. Eppinger, *Green Chem.*, 2010, **12**, 35; (b) A. N. Marziale, D. Jantke, S. H. Faul, T. Reiner, E. Herdtweck and J. Eppinger, *Green Chem.*, 2011, **13**, 169; (c) A. Zernickel, W. Du, S. A. Ghorpade, D. N. Sawant, A. Makki, N. Sekar and J. Eppinger, *J. Org. Chem.*, 2018, **83**, 1842.
- 15 (a) D. N. Sawant, Y. S. Wagh, K. D. Bhatte and B. M. Bhanage, *J. Org. Chem.*, 2011, **76**, 5489; (b) D. N. Sawant, Y. S. Wagh, P. J. Tambade, K. D. Bhatte and B. M. Bhanage, *Adv. Synth. Catal.*, 2011, **353**, 781; (c) V. S. Patil, V. S. Padalkar, A. S. Chaudhari and N. Sekar, *Catal. Sci. Technol.*, 2012, **2**, 1681; (d) A. S. Chaudhari, Y. S. Parab, V. Patil, N. Sekar and S. R. Shukla, *RSC Adv.*, 2012, **2**, 12112; (e) S. G. Ghorpade, D. N. Sawant, A. Makki, N. Sekar and J. Eppinger, *Green Chem.*, 2018, **20**, 425.

# Aqueous protocol for allylic arylation of cinnamyl acetates with sodium tetraphenylborate using Bedford-type palladacycle catalyst

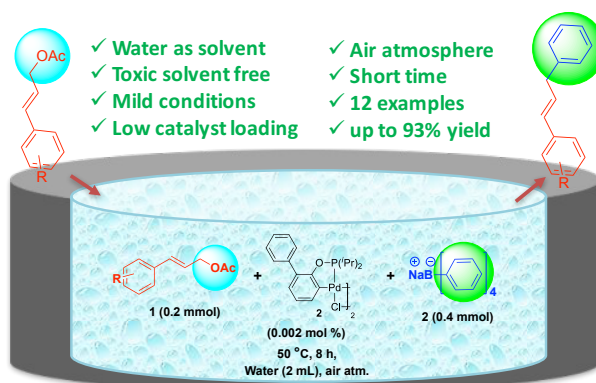
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## TOC



Allylic arylation using 0.002 mol % of Bedford-type palladacycle catalyst is described under mild reaction conditions.