RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2017, 7, 2475

Ligand- and copper-free Sonogashira and Heck couplings of (Het)aryl chlorides and bromides catalyzed by palladium nanoparticles supported on *in situ* generated $Al(OH)_3$†

Xing Li,* Xiaolei Gong, Zhipeng Li, Honghong Chang, Wenchao Gao and Wenlong Wei*

Received 18th October 2016
Accepted 26th November 2016

DOI: 10.1039/c6ra25416k

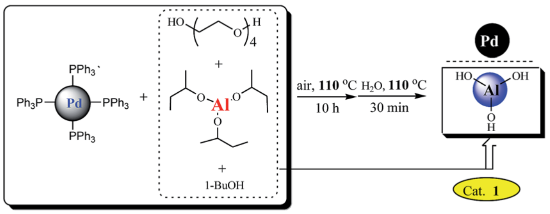
www.rsc.org/advances

The ligand- and copper-free Sonogashira reaction of (Het)aryl halides (Br and Cl) with various terminal alkynes and the Heck coupling of (Het)aryl halides (Br and Cl) with a series of olefins, catalyzed by palladium nanoparticles supported on newly generated $Al(OH)_3$, were developed. The catalyst can be readily recovered and reused 6 times without significant loss of activity and palladium leaching.

The efficiency of heterogeneous catalysis in organic synthesis can be improved by employing nanosized catalysts because of their extremely small size and large surface-to-volume ratio.[1] Recently, it has been demonstrated that palladium nanoparticles (PdNPs) as catalysts offer significant potential for a wide range of applications in organic synthesis.[2] The surface properties of these PdNPs and their catalytic activity are mainly decided by the nature of catalyst supports and the methods for their preparation. PdNPs are usually prepared by chemical vapor deposition from Pd precursors in the presence of hydrogen gas or by classical methods like impregnation or co-precipitation. To improve their catalytic activity, however, some improved methods for their preparation are required.

Palladium-catalyzed cross-coupling reactions have become one of the most prominent and powerful methods for the formation of carbon–carbon bonds.[3] Among them, the Sonogashira[4] and Heck[5] reactions have been found useful in the synthesis of a variety of target compounds with applications ranging from natural products and pharmaceuticals to organic functional materials. Significant progress has been achieved by using palladium salts[6,7] or homogeneous palladium complexes[8,9] as catalysts in the absence of copper co-catalysts. However, these two reactions still suffer from some limitations about the environmental and economical sustainability. In most cases, catalysts failed to be recycled and reused, and phosphorus ligands were also employed. To address these challenges, intense research efforts have been devoted to find suitable heterogeneous Pd catalysts of broad scope, capable of allowing the elimination of copper and phosphorus ligands, as well as affording recovery and reuse of costly palladium catalyst. Although several notable examples of truly green conditions for the Sonogashira[10] and Heck[11] reactions were reported, the substrate scope is still limited and successful examples for heteroaryl halides remain rare because the corresponding reactions of heteroaryl bromides proved to be more challenging.[12,13] From the viewpoint of synthetic cost, developing a generally applicable catalytic system with broader substrate scope has received considerable attention and is highly desirable. Herein, we will report the application of such a palladium nanoparticles catalyst[14] supported on $Al(OH)_3$ which was *in situ* formed (see Scheme 1) in ligand- and copper-free Sonogashira and Heck cross-coupling reactions of (Het)aryl bromides and chlorides. The catalyst has exhibited obviously higher catalytic activity than that prepared by co-precipitation, which demonstrate that the preparation methods of the catalyst exerted an important impact.[14d]

We first investigated the Sonogashira reaction between 4-methoxybromobenzene (**1o**) with phenylacetylene (**2a**) to optimize reaction conditions (Table 1). Screening of common solvents showed that DMSO was the best choice over DMF, and H_2O (entry 2 *vs.* 1 and 3). Bases have a strong effect on the yield, and NaOAc was the best among the bases screened, including K_2CO_3, K_3PO_4 and KOAc (entries 7 *vs.* 2, 4, 5). The reaction did

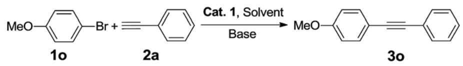


Scheme 1 Preparation of Pd nanoparticles catalyst **1**.

Department of Chemistry and Chemical Engineering, Taiyuan University of Technology, 79 West Yingze Street, Taiyuan 030024, People's Republic of China. E-mail: lixing@tyut.edu.cn; weiwenlong@tyut.edu.cn

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ra25416k

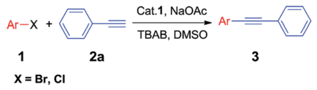
Table 1 Optimization of reaction conditions for the Sonogashira reaction[a]

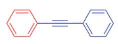


Entry	Solvent	Base	Yield[b] (%)
1	DMF	K_2CO_3	21
2	DMSO	K_2CO_3	36
3	H_2O	K_2CO_3	Trace
4	DMSO	K_3PO_4	13
5	DMSO	KOAc	37
6	DMSO	KOH	N.D.[c]
7	DMSO	NaOAc	62
8[d]	DMSO	NaOAc	91

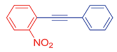
[a] Reactions were performed with 4-methoxybromobenzene (0.2 mmol) under N_2 atmosphere at 120 °C for 40 h. [b] Isolated yield. [c] N.D. = Not detected. [d] Reaction conditions: 4-methoxybromobenzene (0.2 mmol), phenylacetylene (1.5 equiv.), Pd catalyst **1** (8.8 mg, 0.2 mol%), NaOAc (1.5 equiv.), TBAB (0.5 equiv.), DMSO (1.0 mL), N_2, 120 °C.

Table 2 The scope of aryl halides with phenylacetylene[a,b]



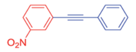


3a 93% (40 h)



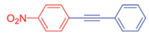
3b X = Br[c], 93% (35 h)

X = Cl, 68% (45 h)



3c X = Br[d], 96% (30 h)

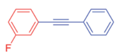
X = Cl, 75% (45 h)



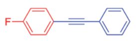
3d X = Br[d], 96% (30 h)

X = Cl, 81% (45 h)

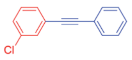
3e[c] 89% (35 h)



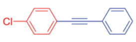
3f[c] 94% (35 h)



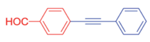
3g[c] 95% (35 h)



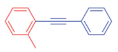
3h 93% (35 h)



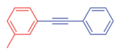
3i 98% (35 h)



3j[d] 92% (30 h)



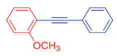
3k 81% (40 h)



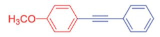
3l 86% (40 h)

3m X = Br, 92% (40 h)

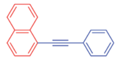
X = Cl, 41% (50 h)



3n[c] 81% (45 h)

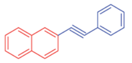


3o 91% (40 h)

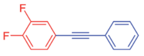


3p X = Br, 83% (45 h)

X = Cl, 53% (50 h)



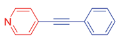
3q 86% (45 h)



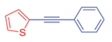
3r 98% (42 h)

3s 70% (45 h)

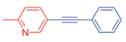
3t 83% (45 h)



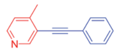
3u 91% (45 h)



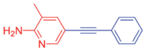
3v 75% (45 h)



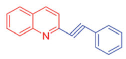
3w 72% (45 h)



3x 69% (50 h)



3y 73% (45 h)



3z 71% (50 h)

3za 81% (45 h)

3zb 93% (45 h)

[a] Reaction conditions: (hetero)aryl halide (0.2 mmol), phenylacetylene (34 μL, 1.5 equiv.), Pd catalyst **1** (8.8 mg, 0.2 mol%), NaOAc (24.5 mg, 1.5 equiv.), TBAB (32.3 mg, 0.5 equiv.), DMSO (1.0 mL), N_2, 120 °C. [b] Isolated yield. [c] 110 °C was used. [d] 90 °C was used in the absence of TBAB.

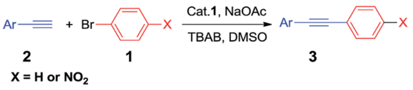
not give **3o** at all when KOH was used (entry 6). It was noteworthy that the addition of TBAB improved the result further, providing **3o** in 91% yield (entry 8).

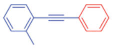
With the optimized protocol in hand, the scope of this catalytic system was next explored. Aryl halides in reaction with **2a** were investigated first (Table 2). The reaction worked very well for a range of aryl bromides with various substituents at the phenyl ring, and the products were isolated in good to excellent yields. Aryl bromides with electron-withdrawing substituents at the phenyl ring afforded the desired 1,3-diynes in high yields (**3b–3j**), whereas aryl bromides bearing electron-donating substituents provided the desired 1,3-diynes in 81–91% yields (**3k–3o**). The experimental results indicated that α-, and β-bromide substituted naphthalene afforded similarly good yields (**3p** and **3q**). Sterically hindered 1-bromo-3,4-difluorobenzene was also suitable for this transformation (**3r**). Moreover, the arene ring is not limited to benzene rings. Heteroaryl bromides derived from pyridines, thiophenes, quinolines, and pyrimidines could be converted to the corresponding cross-coupled products in modest to high yields (**3s–3zb**). NO_2-substituted aryl chlorides were also deemed to be suitable cross-coupling partners (**3b–3d**). Unfortunately, 1-chloronaphthalene and 4-methylchlorobenzene gave only 53% and 41% yields, respectively (**3p** and **3m**).

Consequently, the scope of the arylacetylenes was examined in the coupling with bromobenzene. Phenylacetylene bearing electron-donating and electron-withdrawing groups in the benzene ring furnished the products in good to excellent yields, respectively (Table 3, **3e–3m**, **3zc**). The reactions of 4-ethynyltoluene and 1-ethynyl-4-fluorobenzene with 4-nitrobromobenzene were smoothly carried out to furnish the desired products (Table 3, **3zd** and **3ze**). In addition, 2-ethynylpyridine and 3-ethynylthiophene, heteroaryl alkynes, were also viable partners, providing 74% and 31% yields, respectively (Table 3, **3s** and **3zf**).

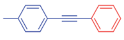
To test the effect of this nano-Pd catalyst in the Heck coupling reaction, the coupling of bromobenzene **1a** and butyl acrylate **4a** was chosen for initial study. Different solvents were explored in an effort to optimize the yield of **5a**. As shown in Table 4, TBAB gave **5a** in the highest yield and only poor to moderate yields were obtained with other solvents like dioxane, DMF, NMP, and acetonitrile (Table 4, entry 5 *vs.* 1–4). Among the bases evaluated, K_3PO_4 was found to be optimal. Lower yields were provided with K_2CO_3, TBAA, Et_3N and NaOAc (Table 4, entry 5 *vs.* 6–9). Further optimization clearly indicated

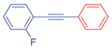
Table 3 The scope of (hetero)arylacetylenes with bromobenzene[a,b]

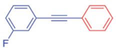


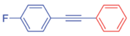

3k 82% (42 h)

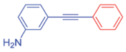

3l 89% (40 h)


3m 92% (40 h)

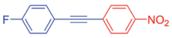

3e 80% (42 h)


3f 83% (42 h)

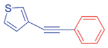

3g 88% (42 h)


3zc 81% (45 h)


3zd 86% (40 h)

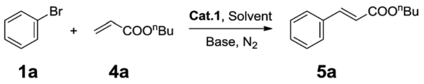

3ze 82% (40 h)


3s 74% (45 h)


3zf 31% (45 h)

[a] Reaction conditions: bromobenzene or 4-nitrobromobenzene (0.2 mmol), (hetero)aryl acetylene (1.5 equiv.), Pd catalyst **1** (0.2 mol% Pd), NaOAc (1.5 equiv.), TBAB (0.5 equiv.), DMSO (1.0 mL), N_2, 120 °C. [b] Isolated yield.

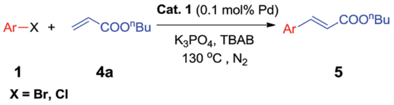
Table 4 Optimization of reaction conditions for the Heck reaction of bromobenzene with butyl acrylate[a]

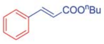


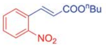
Entry	Solvent	Base	Cat. 1 (mol% Pd)	*T* (°C)	Yield[b] (%)
1	DMF (0.5 mL)	K_3PO_4	0.1	130	78
2	NMP (0.5 mL)	K_3PO_4	0.1	130	74
3	CH_3CN (0.5 mL)	K_3PO_4	0.1	130	61
4	Dioxane (0.5 mL)	K_3PO_4	0.1	130	Trace
5	TBAB (0.3 g)	K_3PO_4	0.1	130	99
6	TBAB (0.3 g)	K_2CO_3	0.1	130	48
7	TBAB (0.3 g)	TBAA	0.1	130	86
8	TBAB (0.3 g)	Et_3N	0.1	130	61
9	TBAB (0.3 g)	NaOAc	0.1	130	79
10	TBAB (0.3 g)	K_3PO_4	0.07	130	82
11	TBAB (0.3 g)	K_3PO_4	0.1	120	89

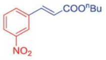
[a] Reaction conditions: bromobenzene (0.2 mmol), butyl acrylate (0.26 mmol, 1.3 equiv.), catalyst 1, base (0.2 mmol), solvent, N_2 for 19 h. [b] Isolated yield.

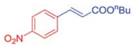
Table 5 Substrate scope of (hetero)aryl halides for the Heck coupling[a,b]

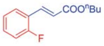


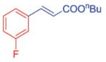

5a 99% (19 h)

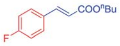

5b X = Br, 91% (19 h)
X = Cl[c], 93% (38 h)

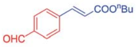

5c X = Br, 90% (23 h)
X = Cl[c], 85% (42 h)

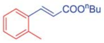

5d X = Br, 85% (23 h)
X = Cl[c], 76% (48 h)

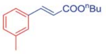

5e 92% (19 h)

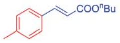

5f 89% (23 h)

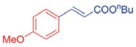

5g 82% (23 h)

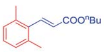

5h 85% (23 h)

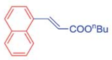

5i X = Br, 87% (23 h)
X = Cl[c], 72% (48 h)


5j X = Br, 84% (26 h)
X = Cl[c], 58% (54 h)

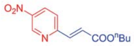

5k X = Br, 80% (26 h)
X = Cl[c], 41% (54 h)

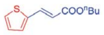

5l 72% (26 h)

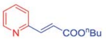

5m 57% (30 h)

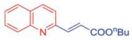

5n 86% (19 h)


5o 81% (19 h)


5p 76% (24 h)


5q 82% (19 h)


5r 43% (32 h)


5s 75% (30 h)

[a] Reaction conditions: (hetero)aryl bromide (0.2 mmol), butyl acrylate (0.26 mmol), catalyst **1** (0.1 mol% Pd), K_3PO_4 (0.2 mmol), TBAB (0.3 g), N_2, 130 °C. [b] Isolated yield. [c] Reaction conditions: aryl chloride (0.2 mmol), butyl acrylate (0.26 mmol), catalyst **1** (0.1 mol% Pd), K_3PO_4 (0.2 mmol), TBAB (0.3 g), DMF (0.2 mL), N_2, 130 °C.

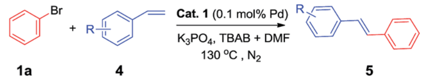
that lower catalyst loading and temperature resulted in bad results (Table 4, entries 10–11 *vs.* 5).

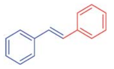
To demonstrate the generality of this nanoparticles pd catalyst **1**, our attention was next focused on investigating the substrate scope for Heck cross-coupling using a variety of aryl halides.[15] In all of our cases, both electron-rich and electron-poor groups and some heteroaryl rings substituted aryl bromides reacted with butyl acrylate to give the desired products in moderate to high yields, exhibiting a good efficiency (Table 5, **5a–5s**). It was found that moderate to good yields could also be obtained when NO_2- and Me-substituted chlorobenzenes were used as substrates with longer reaction time and more catalyst loading (Table 5, **5b–5d** and **5i–5k**). Furthermore, a series of functional groups, including Me-, F-, and diMe-substituted styrenes could smoothly couple with bromobenzene to provide good results (Table 6, **5t–5za**).

We further turned our attention to the recovery and reuse of the nano-Pd catalyst **1** through the Sonogashira reaction between 4-methoxybromobenzene (**1o**) with phenylacetylene (**2a**) and the results are shown in Table 7. The catalyst could be recovered through membrane filtration and reused in the next reaction. The experimental results showed that the catalytic activity and reaction yield did not obviously decrease after the sixth consecutive cycles. Moreover, the palladium leaching during the recovery process was not obviously observed which was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Table 7, runs 1–6 *vs.* 0).

In conclusion, we have developed efficient, practical and general copper-free Sonogashira and Heck cross-coupling reactions using a nanoparticles pd catalyst supported on *in*

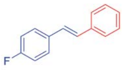
Table 6 The scope of Heck coupling of aryl olefin with bromobenzene[a,b]

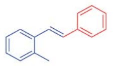


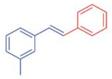

5t 85% (19 h)

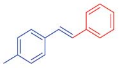

5u 89% (19 h)

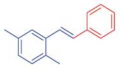

5v 87% (19 h)


5w 85% (19 h)


5x 82% (24 h)

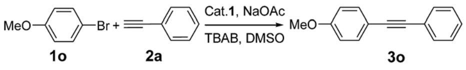

5y 84% (24 h)


5z 88% (24 h)


5za 80% (24 h)

[a] Reaction conditions: bromobenzene (0.2 mmol), aryl olefin (1.3 equiv.), catalyst **1** (0.1 mol% Pd), base (K_3PO_4, 1.0 equiv.), TBAB (0.3 g), DMF (0.2 mL), temperature (130 °C), N_2. [b] Isolated yield.

Table 7 Recycling test of the Pd catalyst **1**[a]



Run	Time (h)	Yield[b] (%)	Pd content[c] (wt%)
0	40	91	0.48
1	40	91	0.48
2	41	90	0.47
3	42	90	0.46
4	42	90	0.46
5	43	90	0.46
6	45	89	0.45

[a] Reaction conditions: **1o** (1.0 equiv.), **2a** (1.5 equiv.), Pd catalyst **1** (0.2 mol% Pd), NaOAc (1.5 equiv.), TBAB (0.5 equiv.), DMSO (1.0 mL), N_2, 120 °C. [b] Isolated yield. [c] The Pd content of the recovered catalyst **1**.

situ generated $Al(OH)_3$. Broad substrate scope, high levels of functional group compatibility especially with heteraryl compounds, and modest to high yields of products are the notable features of the present reactions.

Acknowledgements

We appreciate gratefully the Natural Science Foundation of Shanxi Province (No. 201601D011028 and 20130110094) for financial support.

Notes and references

1 (*a*) V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara and J.-M. Basset, *Chem. Rev.*, 2011, **111**, 3036; (*b*) D. Wang and D. Astruc, *Chem. Rev.*, 2014, **114**, 6949.

2 (*a*) C. Deraedt and D. Astruc, *Acc. Chem. Res.*, 2014, **47**, 494; (*b*) A. Bej, K. Ghosh, A. Sarkar and D. W. Knight, *RSC Adv.*, 2016, **6**, 11446; (*c*) A. Fihri, M. Bouhrara, B. Nekoueishahraki, J.-M. Basset and V. Polshettiwar, *Chem. Soc. Rev.*, 2011, **40**, 5181.

3 (*a*) See ref. 2*a*; (*b*) A. Balanta, C. Godard and C. Claver, *Chem. Soc. Rev.*, 2011, **40**, 4973; (*c*) L. Yin and J. Liebscher, *Chem. Rev.*, 2007, **107**, 133; (*d*) Á. Molnár, *Chem. Rev.*, 2011, **111**, 2251; (*e*) J. C. C. C. Seechurn, M. O. Kitching, T. J. Colacot and V. Snieckus, *Angew. Chem., Int. Ed.*, 2012, **51**, 5062; (*f*) C. Torborg and M. Beller, *Adv. Synth. Catal.*, 2009, **351**, 3027.

4 (*a*) R. Chinchilla and C. Nájera, *Chem. Rev.*, 2007, **107**, 874; (*b*) T. Ren, *Chem. Rev.*, 2008, **108**, 4185; (*c*) R. Chinchilla and C. Nájera, *Chem. Soc. Rev.*, 2011, **40**, 5084; (*d*) H. Doucet and J.-C. Hierso, *Angew. Chem., Int. Ed.*, 2007, **46**, 834; (*e*) C. A. Fleckenstein and H. Plenio, *Chem. Soc. Rev.*, 2010, **39**, 694; (*f*) N. M. Jenny, M. Mayor and T. R. Eaton, *Eur. J. Org. Chem.*, 2011, 4965.

5 For general reviews of Heck coupling, see: (*a*) I. P. Beletskaya and A. V. Cheprakov, *Chem. Rev.*, 2000, **100**, 3009; (*b*) D. M. Cartney and P. J. Guiry, *Chem. Soc. Rev.*, 2011, **40**, 5122; (*c*) N. T. S. Phan, M. Van Der Sluys and C. W. Jones, *Adv. Synth. Catal.*, 2006, **348**, 609; (*d*) C. I. M. Santos, J. F. B. Barata, M. Amparo, F. Faustino, C. Lodeiro and M. G. P. M. S. Neves, *RSC Adv.*, 2013, **3**, 19219.

6 (*a*) E. Negishi and L. Anastasia, *Chem. Rev.*, 2003, **103**, 1979; (*b*) T. Fukuyama, M. Shinmen, S. Nishitani, M. Sato and I. Ryu, *Org. Lett.*, 2002, **4**, 1691; (*c*) B. Liang, M. Dai, J. Chen and Z. Yang, *J. Org. Chem.*, 2005, **70**, 391; (*d*) Y. Liang, Y. X. Xie and J. H. Li, *J. Org. Chem.*, 2006, **71**, 379.

7 (*a*) K. Hirotaki and T. Hanamoto, *J. Org. Chem.*, 2011, **76**, 8564; (*b*) S. Li, Y. Lin, H. Xie, S. Zhang and J. Xu, *Org. Lett.*, 2006, **8**, 391; (*c*) P. Cyr, S. T. Deng, J. M. Hawkins and K. E. Price, *Org. Lett.*, 2013, **15**, 4342; (*d*) H. L. Parker, J. Sherwood, A. J. Hunt and J. H. Clark, *ACS Sustainable Chem. Eng.*, 2014, **2**, 1739.

8 (*a*) B. de Carné-Carnavalet, A. Archambeau, C. Meyer, J. Cossy, B. Folléas, J.-L. Brayer and J.-P. Demoute, *Org. Lett.*, 2011, **13**, 956; (*b*) H. Hu, F. Yang and Y. Wu, *J. Org. Chem.*, 2013, **78**, 10506; (*c*) P. Ehlers, A. Neubauer, S. Lochbrunner, A. Villinger and P. Langer, *Org. Lett.*, 2011, **13**, 1618; (*d*) D. Mery, K. Heuze and D. Astruc, *Chem. Commun.*, 2003, 1934; (*e*) J. Cheng, Y. Sun, F. Wang, M. Guo, J. H. Xu, Y. Pan and Z. Zhang, *J. Org. Chem.*, 2004, **69**, 5428; (*f*) D. Lee, Y. Kwon and M. Jin, *Adv. Synth. Catal.*, 2011, **353**, 3090; (*g*) K. W. Anderson and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2005, **44**, 6173.

9 (*a*) C. Wu and J. Zhou, *J. Am. Chem. Soc.*, 2014, **136**, 650; (*b*) C. Zhang, C. B. Santiago, J. M. Crawford and M. S. Sigman, *J. Am. Chem. Soc.*, 2015, **137**, 15668; (*c*) M. G. Lauer, M. K. Thompson and K. H. Shaughnessy, *J. Org. Chem.*, 2014, **79**, 10837; (*d*) M. L. Kantam, P. Srinivas, J. Yadav, P. R. Likhar and S. Bhargava, *J. Org. Chem.*, 2009, **74**, 4882; (*e*) D.-H. Lee, A. Taher, S. Hossain and M.-J. Jin, *Org. Lett.*, 2011, **13**, 5540; (*f*) L. Qin, H. Hirao and J. Zhou, *Chem. Commun.*, 2013, **49**, 10236; (*g*) M. Oberholzer and C. M. Frech, *Green Chem.*, 2013, **15**, 1678; (*h*) G. R. Rosa and D. S. Rosa, *RSC Adv.*, 2012, **2**, 5080; (*i*) J. Mo, L. Xu and J. Xiao, *J. Am. Chem. Soc.*, 2005, **127**, 751.

10 (*a*) B. M. Choudary, S. Madhi, N. S. Chowdari, M. L. Kantam and B. Sreedhar, *J. Am. Chem. Soc.*, 2002, **124**, 14127; (*b*) A. Ohtaka, T. Teratani, R. Fujii, K. Ikeshita, T. Kawashima, K. Tatsumi, O. Shimomura and R. Nomura, *J. Org. Chem.*, 2011, **76**, 4052; (*c*) R. Ciriminna, V. Pandarus, G. Gingras, F. Béland, P. D. Carà and M. Pagliaro, *ACS Sustainable Chem. Eng.*, 2013, **1**, 57; (*d*) L.-M. Tan, Z.-Y. Sem, W.-Y. Chong, X. Liu, W. L. Kwan and C.-L. K. Lee, *Org. Lett.*, 2013, **15**, 65; (*e*) P. D. Stevens, G. Li, J. Fan, M. Yen and Y. Gao, *Chem. Commun.*, 2005, 4435; (*f*) A. Komáromi and Z. Novák, *Chem. Commun.*, 2008, 4968; (*g*) M. Jin and D. Lee, *Angew. Chem., Int. Ed.*, 2010, **49**, 1119.

11 (*a*) L. K. Yeung and R. M. Crooks, *Nano Lett.*, 2001, **1**, 14; (*b*) E. H. Rahim, F. S. Kamounah, J. Frederiksen and J. B. Christensen, *Nano Lett.*, 2001, **1**, 499; (*c*) B. H. Lipshutz and B. R. Taft, *Org. Lett.*, 2008, **10**, 1329; (*d*) R. Bernini, S. Cacchi, G. Fabrizi, G. Forte, F. Petrucci, A. Prastaro, S. Niembro, A. Shafir and A. Vallribera, *Green Chem.*, 2010, **12**, 150; (*e*) R. Bernini, S. Cacchi, G. Fabrizi, G. Forte, S. Niembro, F. Petrucci, R. Pleixats, A. Prastaro, R. M. Sebastián, R. Soler, M. Tristany and A. Vallribera, *Org. Lett.*, 2008, **10**, 561; (*f*) A. R. Siamaki, A. E. R. S. Khder, V. Abdelsayed, M. S. El-Shall and B. F. Gupton, *J. Catal.*, 2011, **279**, 1.

12 (*a*) C. Torborg, J. Huang, T. Schulz, B. Schäffner, A. Zapf, A. Spannenberg, A. Börner and M. Beller, *Chem.–Eur. J.*, 2009, **15**, 1329; (*b*) X. Pu, H. Li and T. J. Colacot, *J. Org. Chem.*, 2013, **78**, 568; (*c*) J. Pschierer and H. Plenio, *Org. Lett.*, 2009, **11**, 2551; (*d*) H. Remmele, A. Kollhofer and H. Plenio, *Organometallics*, 2003, **22**, 4098.

13 (*a*) D. W. Tay, H. Jong, Y. H. Lim, W. Wu, X. Chew, E. G. Robins and C. W. Johannes, *J. Org. Chem.*, 2015, **80**, 4054; (*b*) W. Pei, J. Mo and J. Xiao, *J. Organomet. Chem.*, 2005, **690**, 3546.

14 (*a*) X. Li, X. Y. Yan, H. H. Chang, L. C. Wang, Y. Zhang, W. W. Chen, Y. W. Li and W. L. Wei, *Org. Biomol. Chem.*, 2012, **10**, 495; (*b*) X. Li, L. C. Wang, H. H. Chang, C. X. Zhang and W. L. Wei, *Appl. Catal., A*, 2013, **462**, 15; (*c*) X. Li, W. W. Chen, H. H. Chang, Z. Q. Shao and W. L. Wei, *Synthesis*, 2014, **46**, 1593; (*d*) X. Li, T. Zhu, Z. Shao, Y. Li, H. Chang, W. Gao, Y. Zhang and W. Wei, *Tetrahedron*, 2016, **72**, 69.

15 Extensive screening showed that the optimized reaction conditions were 0.2 mmol (hetero)aryl bromide, 1.3 equiv. of butyl acrylate, catalyst **1** (4.4 mg, 0.1 mol% Pd), 1 equiv. of K_3PO_4 and TBAB (0.3 g) under N_2 atmosphere at 130 °C.