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Rhodium-Catalyzed C(sp^2)–H Addition of Arylboronic Acids to Alkynes Using a Boron-Based, Convertible *ortho*-Directing Group

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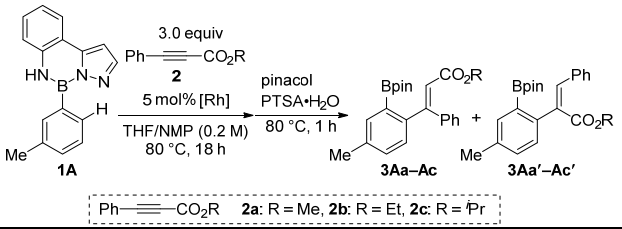
Temporary modification of a boronyl group with pyrazorylaniline allowed insertion of arylpropiolates and diphenylacetylenes into the *o*-C–H bond of arylboronic acids in the presence of rhodium catalysts, giving 3,3-diarylacrylates and triarylethene containing aryl groups bearing an *o*-boryl group stereoselectively. The boronyl group in the 3,3-diarylacrylates was converted into various functional groups, including chlorine, hydrogen, hydroxy, and aromatic groups.

Directed or nondirected addition of an aromatic C–H bond across carbon–carbon multiple bonds is recognized as one of the most efficient synthetic methods for arylethene and styrene derivatives.[1] In particular, directed C–H alkenylation has attracted much attention because it allows the highly regioselective introduction of organic groups into the *o*-position of the directing group. Since the establishment of Murai's Ru-catalyzed, carbonyl-directed alkenylation,[2] a variety of directing groups in combination with various transition metals, including Ru,[3] Rh,[4] Ir,[5] and Pd[6] have been developed for *o*-C–H alkenylation. However, this strategy significantly limits the substrate scope, when the directing group is not removable or convertible. To overcome this limitation, much attention has been focused on the development of convertible or traceless directing groups,[7] such as triazene[4f] and carboxylic acid[3o] groups. However, those convertible directing groups often lack high versatility in the subsequent transformations. Therefore, it is highly desirable to establish directing groups that can be converted into a variety of functional groups.

We have established pyrazorylaniline (PZA)[8] and anthranilamide (AAM)[9] as easily attachable and detachable directing groups for directed C–H functionalization reactions. In these studies, the PZA-modified boronyl group (Bpza) served as an *o*-directing group, which could be utilized for further transformations by the versatile reactivity of the boronyl group. However, the use of PZA has so far been limited to Ru-catalyzed *o*-C–H silylation[8a] and Ir-catalyzed *o*-C–H borylation.[8c] Our current focus is on the utilization of temporary directing groups such as PZA and AAM in *o*-C–H addition to carbon–carbon multiple bonds. In this work, we demonstrate the addition of *o*-C–H bonds of arylboronic acids to arylpropiolates, which provides 3,3-diarylacrylates bearing two different aryl groups, one of which has an *o*-boryl group. Unsymmetrical 3,3-diarylacrylates are utilized as key starting materials for asymmetric reactions for the synthesis of enantioenriched 3,3-diarylpropanoates.[10] Although stereoselective synthesis of unsymmetrical 3,3-diarylacrylates has been accomplished through several reactions,[11] such as Mizoroki–Heck-type reactions of cinnamate[12] and the Cu-catalyzed conjugate addition of arylboronic acid to alkynoate,[13] only a few examples of regioselective synthesis of *o*-functionalized 3,3-diarylpropanoate have been reported. Herein, we report Rh-catalyzed *o*-C–H alkenylation of PZA-modified arylboronic acids with arylpropiolate and diarylacetylenes. The boronyl group serving as a directing group in the alkenylation was subsequently converted into various functional groups.

We initially utilized PZA as a modifier of the boronyl group, which serves as an effective directing group for *o*-C–H silylation[8a] and borylation[8c] of arylboronic acids. Condensation of 3-methylphenylboronic acid with PZA afforded PZA-modified *m*-tolylboronic acid **1A** quantitatively. In the presence of rhodium and iridium complexes, **1A** was subjected to reaction with 3 equiv of methyl phenylpropiolate (**2a**) in *N*-methylpyrrolidone (NMP) at 80 °C for 18 h (Table 1). The resultant reaction mixture was treated with pinacol for detection and quantification of the product in the form of pinacol ester **3**. Although $[RhCl(cod)]_2$ failed to catalyze C–H alkenylation (entry 1), $[RhCl(coe)_2]_2$ afforded alkenylated product **3Aa** and regioisomeric **3Aa′** in 29% yield with 84:16 ratio (entry 2). **3Aa** was obtained as a mixture of *E*- and *Z*-isomers in 94:6 ratio. Although $[RhCl(C_2H_4)_2]_2$ exhibited comparable catalytic activity (entry 3), $[RhCl(PPh_3)_3]$, $[Rh(cod)_2]BF_4$, and $[Cp^*RhCl_2]_2$ showed no catalytic activity for *o*-C–H alkenylation (entries 4–6). No product was formed in the presence of $[IrCl(coe)_2]_2$, which is known to catalyze hydroxy-directed C–H alkenylation (entry 7).[14] The addition of monodentate or bidentate phosphine ligand suppressed the reaction (entries 8–10). Use of THF or toluene instead of NMP decreased the yield with improved *E*/*Z* ratio (entries 11 and 12). Polar solvents such as DMA and DMF were not suitable for this reaction (entries 13 and 14). Use of a 1:1 mixture of NMP and THF improved the yield to 48% (entry 15). We finally obtained a mixture of **3Aa** and **3Aa′** (88:12) in 68% isolated yield (*E*:*Z* = 94:6) using 5 mol% of $[RhCl(coe)_2]_2$ in NMP/THF (entry 16). It is notable that dialkenylated product was not observed under these reaction conditions. Ethyl phenylpropiolate (**2b**) and isopropyl phenylpropiolate (**2c**) gave almost the same results as **2a** (entries 17 and 18).

Table 1. Optimization of Reaction Conditions[a]

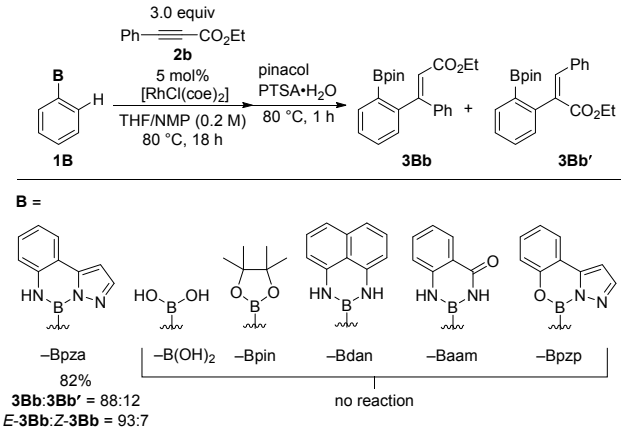


entry	2	Cat.	solvent	additive	3	% yield[b] (3:3′)[c]	E:Z of 3[c]
1	**2a**	$[RhCl(cod)_2]_2$	NMP	–	**3Aa**	0	–
2	**2a**	$[RhCl(coe)_2]_2$	NMP	–	**3Aa**	29 (84:16)	94:6
3	**2a**	$[RhCl(C_2H_4)_2]_2$	NMP	–	**3Aa**	27 (85:16)	94:6
4	**2a**	$[RhCl(PPh_3)_3]$	NMP	–	**3Aa**	0	–
5	**2a**	$[Rh(cod)_2]BF_4$	NMP	–	**3Aa**	0	–
6	**2a**	$[Cp^*RhCl_2]_2$	NMP	–	**3Aa**	0	–
7	**2a**	$[IrCl(coe)_2]_2$	NMP	–	**3Aa**	0	–
8	**2a**	$[RhCl(coe)_2]_2$	NMP	BINAP	**3Aa**	0	–
9	**2a**	$[RhCl(coe)_2]_2$	NMP	DPPE	**3Aa**	11	–
10	**2a**	$[RhCl(coe)_2]_2$	NMP	PCy_3	**3Aa**	0	–
11	**2a**	$[RhCl(coe)_2]_2$	THF	–	**3Aa**	13 (97:3)	–
12	**2a**	$[RhCl(coe)_2]_2$	toluene	–	**3Aa**	11 (91:9)	–
13	**2a**	$[RhCl(coe)_2]_2$	DMA	–	**3Aa**	3	–
14	**2a**	$[RhCl(coe)_2]_2$	DMF	–	**3Aa**	0	–
15	**2a**	$[RhCl(coe)_2]_2$	NMP/THF	–	**3Aa**	48 (88:12)	94:6
16[d]	**2a**	$[RhCl(coe)_2]_2$	NMP/THF	–	**3Aa**	68[e] (88:12)	94:6
17[d]	**2b**	$[RhCl(coe)_2]_2$	NMP/THF	–	**3Ab**	74[e] (86:14)[f]	93:7
18[d]	**2c**	$[RhCl(coe)_2]_2$	NMP/THF	–	**3Ac**	69[e] (85:15)[f]	95:5

[a]**1A** (0.2 mmol), **2** (0.6 mmol), and $[RhCl(coe)_2]_2$ (5 μmol) were stirred in solvent (1.0 mL) at 80 °C for 18 h. [b]GC yield. [c]Determined by GC analysis. [d]10 mol% Rh. [f]Isolated yield. [e]Determined by NMR analysis.

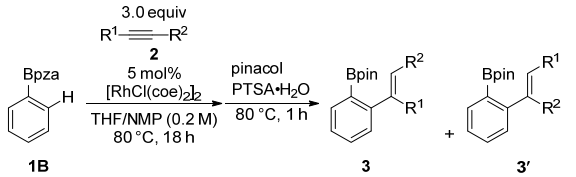
Other modifiers on the boronyl group were also tested under the optimized reaction conditions for **1A** (Scheme 1). PZA-modified phenylboronic acid **1B** afforded a mixture of **3Bb** and **3Bb′** in 82% yield in 88:12 ratio. On the other hand, the reaction of phenylboronic acid and its pinacol ester did not give any desired products. Phenylboronic acid modified with 1,8-diaminonaphthalene (Bdan), which serves as a protecting group in Suzuki–Miyaura cross-coupling,[15] showed no reactivity. Anthranilamide-modified phenylboronic acid (Baam), which serves as an efficient directing group in Ru-catalyzed *o*-C–H silylation gave no product either. The pyrazorylphenol-modified boronyl group (Bpzp), which forms a dimeric structure even in solution (^{11}B NMR signal at 3.3 ppm in benzene-d_6), also exhibited no directing ability.[8b] These results indicate that PZA is an essential directing group to promote the C–H alkenylation.

Scheme 1. Scope of Substrate



The scope of the reaction was assessed by varying alkynes under the optimized reaction conditions (Table 2). Among a series of aryl propiolates having a monosubstituted aromatic ring (entries 1–5), 4-methyl-substituted **2d** afforded **3Bd** and **3Bd′** in 75% yield with 91:9 *E*/*Z* ratio. 4-Methoxy-substituted **2e** afforded **3Be** with higher stereoselectivity for the *Z*-isomer (entry 2). In contrast, **2f** bearing an electron-withdrawing 4-trifluoromethyl group afforded *E*-**3Bf** with high selectivity (entry 3). A 2-methyl group on the aromatic ring gave **3Bh** with lower regioselectivity but with higher *E*/*Z* ratio (entry 5). 2-Naphthyl- and 1-naphthyl-substituted propiolates (**2i** and **2j**) also gave the corresponding products (entries 6 and 7). While acetylenedicarboxylate **2k** resulted in no reaction (entry 8), diphenylacetylene (**2l**) underwent C–H insertion at 135 °C with moderate yield with high stereoselectivity (entry 9). Although diphenylacetylene **2m** bearing an electron-donating 4-methoxyphenyl group showed no reactivity even at 135 °C (entry 10), the reaction of **2n** bearing 4-trifluoromethylphenyl groups proceeded at 110 °C, giving the hydroalkenylation product in 72% yield (entry 11).

Table 2. Scope of Alkyne



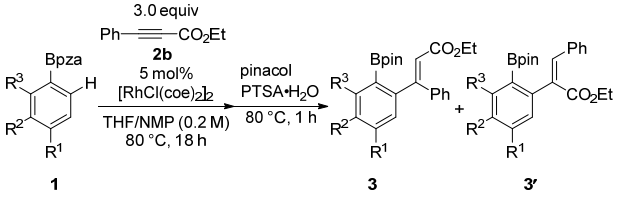
entry	2	R^1	R^2	product	% yield[b] (3:3′)[c]	E:Z of 3[c]
1	**2d**	4-MeC_6H_4	CO_2Et	**3Bd**	75 (89:11)	91:9
2	**2e**	4-$MeOC_6H_4$	CO_2Et	**3Be**	67 (93:7)	71:29
3	**2f**	4-$CF_3C_6H_4$	CO_2Et	**3Bf**	52 (91:9)	99:1
4	**2g**	3-MeC_6H_4	CO_2Et	**3Bg**	69 (87:13)	94:6
5	**2h**	2-MeC_6H_4	CO_2Et	**3Bh**	59 (74:26)	99:1
6	**2i**	2-naphthyl	CO_2Et	**3Bi**	84 (89:11)	92:8
7[d]	**2j**	1-naphthyl	CO_2Et	**3Bj**	51 (80:20)	89:11
8	**2k**	CO_2Et	CO_2Et	**3Bk**	0	–
9	**2l**	Ph	Ph	**3Bl**	47	>99:1

10	**2m**	4-$MeOC_6H_4$	4-$MeOC_6H_4$	**3Bm**	0	–
11	**2n**	4-$CF_3C_6H_4$	4-$CF_3C_6H_4$	**3Bn**	73	>99:1

[a]**1B** (0.2 mmol), **2** (0.6 mmol), and $[RhCl(coe)_2]_2$ (0.01 mmol) were stirred in solvent (1.0 mL) at 80 °C for 18 h. [b]Isolated yield. [c]Determined by NMR analysis. [d]110 °C.

A variety of PZA-modified arylboronic acids were then reacted with ethyl propiolate (**2b**) (Table 3). **1C** and **1D** bearing 4-methyl and 4-methoxyphenyl groups gave the corresponding products in 62% and 48% yields, respectively (entries 1 and 2). Although the reaction of **1E** bearing an electron-withdrawing 4-trifluoromethyl group was found to be inefficient, products were obtained in 30% yield in the presence of 8 mol% $[RhCl(coe)_2]_2$ (entry 3). In the screening of substituents at the 3-position, the reaction proceeded at the less hindered *o*-positions selectively, giving methyl-, methoxy-, trifluoromethyl-, and bromo-substituted **3** in 48–74% yields (entries 4–7). The reaction was also applicable to **1I** bearing the 2-methoxy group, giving **3Ib** selectively, albeit in low yield (entry 8). In these substrates, dialkenylated products were not observed.

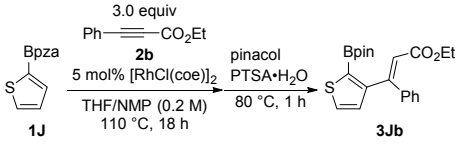
Table 3. Scope of PZA-Modified Arylboronic Acids



entry	**1**	R^1	R^2	R^3	**3**	% yield[b] (**3**:**3′**)[c]	*E*/*Z* of **3**[c]
1	**1C**	Me	H	H	**3Cb**	62 (87:13)	93:7
2	**1D**	MeO	H	H	**3Db**	48 (90:10)	94:6
3	**1E**	CF_3	H	H	**3Eb**	30 (87:13)	91:9
4	**1A**	H	Me	H	**3Ab**	74 (86:14)	93:7
5	**1F**	H	MeO	H	**3Fb**	48 (87:13)	97:3
6	**1G**	H	CF_3	H	**3Gb**	64 (87:13)	94:6
7	**1H**	H	Br	H	**3Hb**	60 (88:12)	94:6
8	**1I**	H	H	MeO	**3Ib**	28 (nd)	nd

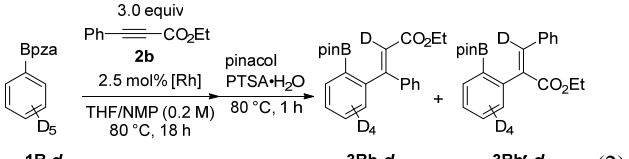
[a]**1** (0.2 mmol), **2b** (0.6 mmol), and $[RhCl(coe)_2]_2$ (0.01 mmol) were stirred in solvent (1.0 mL) at 80 °C for 18 h. [b]Isolated yield, [c]Determined by NMR analysis.

2-Thienylboronic acid derivative **1J** underwent C–H alkenylation at the 3-position selectively, giving **3Jb** in 56% yield with an *E*/*Z* ratio of 88:12 (eq. 1).

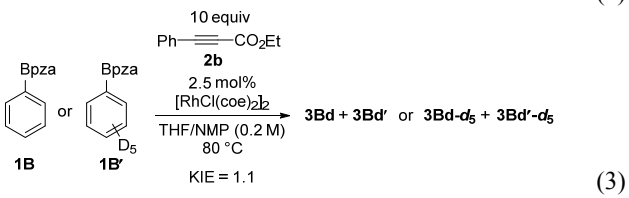


(1)

To gain insights into the reaction mechanism, deuterium-labeling experiments were carried out. The reaction of deuterium-labeled substrate **1Bb-*d*$_5$** and **2b** proceeded under the optimized conditions, giving **3Bb-*d*$_5$** and **3Bb′-*d*$_5$** in 66% combined yield (88:12) (eq. 2). Deuterium incorporation at the vinyl position of **3Bb-*d*$_5$** was 96%. We also measured the kinetic isotope effect (KIE) by carrying out separate reactions of **1B** and **1B-*d*$_5$**. In the presence of 10 equiv of **2b**, the KIE value in the initial stage of the reaction was determined to be 1.1 (eq. 3, see SI). This result suggests that C–H cleavage is not the rate-determining step.

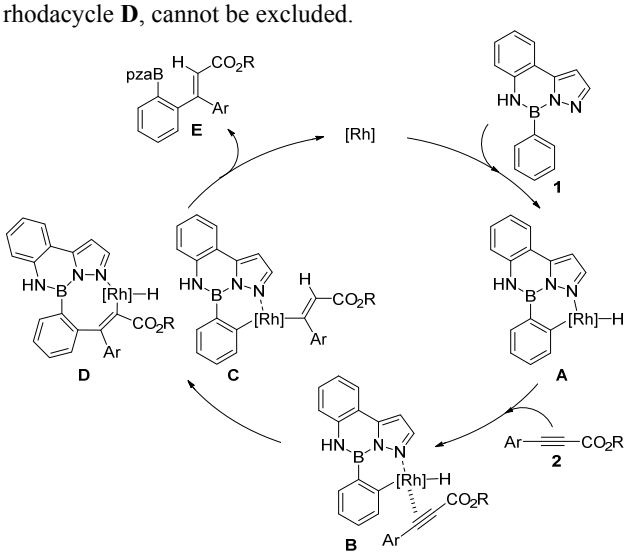


(2)



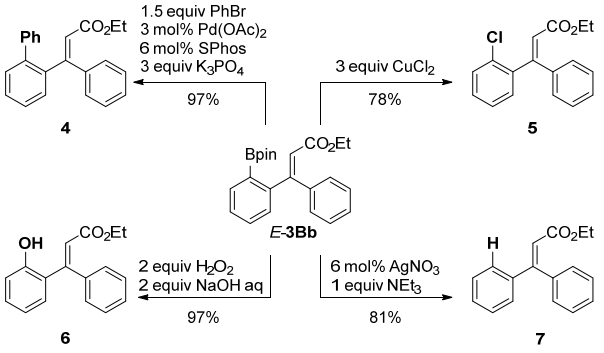
(3)

According to our experimental results, along with previous studies by other groups,[4j, 16] a plausible reaction mechanism is shown in Scheme 2. Coordination of the sp^2-nitrogen atom of the pyrazoryl group of Bpza to the Rh(I) complex followed by oxidative addition of the *o*-C–H bond to Rh provides six-membered rhodacycle **A**. Subsequent coordination of alkyne **2** to **A** gives intermediate **B**, from which insertion of the alkyne to the Rh–H bond forms rhodacycle **C**. Subsequent reductive elimination provides alkenylation product **E**. The possibility of alkyne insertion to the C–Rh bond of **B**, which forms eight-membered rhodacycle **D**, cannot be excluded.



Scheme 2. Proposed Reaction Mechanism

The obtained ethyl 3,3-diarylacrylate **3Bb** bearing an *o*-boryl group serves as a versatile synthetic intermediate for the synthesis of 3,3-diarylacrylates (Scheme 3). Suzuki–Miyaura cross-coupling of *E*-**3Bb** with phenyl bromide afforded biaryl compound **4** in 97% yield. Chlorination of *E*-**3Bb** using $CuCl_2$ afforded the corresponding product **5** in 78% yield. The Bpin group was also converted to a hydroxyl group by oxidation, giving a phenol derivative **6** in 97% yield. In these reactions, *E*/*Z* isomerization of alkene was not observed. In addition, the Bpza group was removed by silver-catalyzed protodeborylation,[17] giving 2,2-diphenylacrylate **7** in 81% yield.



Scheme 3. Synthetic Application

In summary, we demonstrated Rh-catalyzed *o*-C–H alkenylation of arylboronic acids using PZA as a temporary directing group on the boron atom. After replacement of the PZA group with pinacol, the boron functionality was converted to hydrogen, phenyl, chloro, and hydroxy groups. The present protocol based on the *o*-C–H borylation of arylboronic acids provides a new access to *o*-functionalized 3,3-diarylacrylates and triarylethenes.

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Supporting Information is available on http://dx.doi.org/10.1246/cl.******.

References and Notes

1. (a) V. Ritleng, C. Sirlin, M. Pfeffer, *Chem. Rev.* **2002**, *102*, 1731. (b) F. Kakiuchi, T. Kochi, *Synthesis* **2008**, 3013. (c) T. Kitamura, *Eur. J. Org. Chem.* **2009**, 1111. (d) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624. (e) F. Kakiuchi, T. Kochi, S. Murai, *Synlett* **2014**, *25*, 2390. (f) Z. X. Huang, H. N. Lim, F. Y. Mo, M. C. Young, G. B. Dong, *Chem. Soc. Rev.* **2015**, *44*, 7764.
2. F. Kakiuchi, Y. Yamamoto, N. Chatani, S. Murai, *Chem. Lett.* **1995**, 681.
3. (a) Y. Hashimoto, T. Ueyama, T. Fukutani, K. Hirano, T. Satoh, M. Miura, *Chem. Lett.* **2011**, *40*, 1165. (b) P. B. Arockiam, C. Fischmeister, C. Bruneau, P. H. Dixneuf, *Green Chem.* **2011**, *13*, 3075. (c) K. Padala, M. Jeganmohan, *Org. Lett.* **2011**, *13*, 6144. (d) Y. Hashimoto, T. Ortloff, K. Hirano, T. Satoh, C. Bolm, M. Miura, *Chem. Lett.* **2012**, *41*, 151. (e) B. Li, J. F. Ma, N. C. Wang, H. L. Feng, S. S. Xu, B. Q. Wang, *Org. Lett.* **2012**, *14*, 736. (f) K. Padala, M. Jeganmohan, *Org. Lett.* **2012**, *14*, 1134. (g) Y. Hashimoto, K. Hirano, T. Satoh, F. Kakiuchi, M. Miura, *Org. Lett.* **2012**, *14*, 2058. (h) M. C. Reddy, M. Jeganmohan, *Chem. Commun.* **2013**, *49*, 481. (i) M. C. Reddy, M. Jeganmohan, *Eur. J. Org. Chem.* **2013**, 1150. (j) C. Suzuki, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2013**, *15*, 3990. (k) R. Manikandan, M. Jeganmohan, *Org. Lett.* **2014**, *16*, 912. (l) X. G. Li, K. Liu, G. Zou, P. N. Liu, *Eur. J. Org. Chem.* **2014**, 7878. (m) K. Padala, M. Jeganmohan, *Chem. Commun.* **2014**, *50*, 14573. (n) M. C. Reddy, M. Jeganmohan, *Chem. Commun.* **2015**, *51*, 10738. (o) L. B. Huang, A. Biafora, G. D. Zhang, V. Bragoni, L. J. Goossen, *Angew. Chem. Int. Ed.* **2016**, *55*, 6933.
4. (a) N. Umeda, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2009**, *74*, 7094. (b) F. W. Patureau, T. Besset, F. Glorius, *Angew. Chem. Int. Ed.* **2011**, *50*, 1064. (c) S. H. Park, J. Y. Kim, S. Chang, *Org. Lett.* **2011**, *13*, 2372. (d) C. Feng, T. P. Loh, *Chem. Commun.* **2011**, *47*, 10458. (e) N. Schroder, T. Besset, F. Glorius, *Adv. Synth. Catal.* **2012**, *354*, 579. (f) C. M. Wang, H. Chen, Z. F. Wang, J. A. Chen, Y. Huang, *Angew. Chem. Int. Ed.* **2012**, *51*, 7242. (g) Y. Y. Shen, G. X. Liu, Z. Zhou, X. Y. Lu, *Org. Lett.* **2013**, *15*, 3366. (h) G. Liu, Y. Shen, Z. Zhou, X. Lu, *Angew. Chem. Int. Ed.* **2013**, *52*, 6033. (i) X. Huang, J. Huang, C. Du, X. Zhang, F. Song, J. You, *Angew. Chem. Int. Ed.* **2013**, *52*, 12970. (j) A. M. Martinez, J. Echavarren, I. Alonso, N. Rodriguez, R. G. Arrayas, J. C. Carretero, *Chem. Sci.* **2015**, *6*, 5802. (k) R. Morioka, T. Satoh, M. Miura, *Chem. Lett.* **2016**, *45*, 682. (l) C. Q. Wang, C. Feng, T. P. Loh, *Asian J. Org. Chem.* **2016**, *5*, 1002.
5. K. Tsuchikama, M. Kasagawa, Y.-K. Hashimoto, K. Endo, T. Shibata, *J. Organomet. Chem.* **2008**, *693*, 3939.
6. (a) M. D. K. Boele, G. P. F. van Strijdonck, A. H. M. de Vries, P. C. J. Kamer, J. G. de Vries, P. van Leeuwen, *J. Am. Chem. Soc.* **2002**, *124*, 1586. (b) G. Cai, Y. Fu, Y. Li, X. Wan, Z. Shi, *J. Am. Chem. Soc.* **2007**, *129*, 7666. (c) K. M. Engle, D. H. Wang, J. Q. Yu, *Angew. Chem. Int. Ed.* **2010**, *49*, 6169; (d) D.-H. Wang, K. M. Engle, B.-F. Shi, J.-Q. Yu, *Science* **2010**, *327*, 315. (e) A. Garcia-Rubia, M. A. Fernandez-Ibanez, R. G. Arrayas, J. C. Carretero, *Chem. Eur. J.* **2011**, *17*, 3567. (f) A. Garcia-Rubia, B. Urones, R. G. Arrayas, J. C. Carretero, *Angew. Chem. Int. Ed.* **2011**, *50*, 10927. (g) C. Huang, B. Chattopadhyay, V. Gevorgyan, *J. Am. Chem. Soc.* **2011**, *133*, 12406. (h) M. Mewald, J. A. Schiffner, M. Oestreich, *Angew. Chem. Int. Ed.* **2012**, *51*, 1763. (i) P. Gandeepan, C. H. Cheng, *J. Am. Chem. Soc.* **2012**, *134*, 5738. (j) X. Cong, J. You, G. Gao, J. Lan, *Chem. Commun.* **2013**, *49*, 662. (k) H. X. Dai, G. Li, X. G. Zhang, A. F. Stepan, J. Q. Yu, *J. Am. Chem. Soc.* **2013**, *135*, 7567. (l) M. Hasegawa, A. Nomoto, T. Suga, T. Soeta, Y. Ukaji, *Chem. Lett.* **2017**, *46*, 45.
7. F. Zhang, D. R. Spring, *Chem. Soc. Rev.* **2014**, *43*, 6906.
8. (a) H. Ihara, M. Suginome, *J. Am. Chem. Soc.* **2009**, *131*, 7502. (b) H. Ihara, A. Ueda, M. Suginome, *Chem. Lett.* **2011**, *40*, 916. (c) T. Yamamoto, A. Ishibashi, M. Suginome, *Org. Lett.* **2017**, *19*, 886.
9. (a) H. Ihara, M. Koyanagi, M. Suginome, *Org. Lett.* **2011**, *13*, 2662. (b) M. Koyanagi, N. Eichenauer, H. Ihara, T. Yamamoto, M. Suginome, *Chem. Lett.* **2013**, *42*, 541.
10. (a) P. Tolstoy, M. Engman, A. Paptchikhine, J. Bergquist, T. L. Church, A. W. M. Leung, P. G. Andersson, *J. Am. Chem. Soc.* **2009**, *131*, 8855. (b) K. Itoh, A. Tsuruta, J. Ito, Y. Yamamoto, H. Nishiyama, *J. Org. Chem.* **2012**, *77*, 10914.
11. (a) C. G. Jia, W. J. Lu, J. Oyamada, T. Kitamura, K. Matsuda, M. Irie, Y. Fujiwara, *J. Am. Chem. Soc.* **2000**, *122*, 7252. (b) C. G. Jia, D. G. Piao, J. Z. Oyamada, W. J. Lu, T. Kitamura, Y. Fujiwara, *Science* **2000**, *287*, 1992. (c) M. Y. Yoon, J. H. Kim, D. S. Choi, U. S. Shin, J. Y. Lee, C. E. Song, *Adv. Synth. Catal.* **2007**, *349*, 1725. (d) Y. Ashida, Y. Sato, T. Suzuki, K. Ueno, K. Kai, H. Nakatsuji, Y. Tanabe, *Chem. Eur. J.* **2015**, *21*, 5934. (e) A. Morinaga, K. Nagao, H. Ohmiya, M. Sawamura, *Angew. Chem. Int. Ed.* **2015**, *54*, 15859.
12. (a) M. MorenoManas, M. Perez, R. Pleixats, *Tetrahedron Lett.* **1996**, *37*, 7449. (b) C. Gurtler, S. L. Buchwald, *Chem. Eur. J.* **1999**, *5*, 3107. (c) G. Battistuzzi, S. Cacchi, G. Fabrizi, *Synlett*

2002, 439. (d) I. Kondolff, H. Doucet, M. Santelli, *Tetrahedron Lett.* **2003**, *44*, 8487. (e) J. C. Pastre, C. R. D. Correia, *Adv. Synth. Catal.* **2009**, *351*, 1217. (f) V. Calo, A. Nacci, A. Monopoli, P. Cotugno, *Angew. Chem. Int. Ed.* **2009**, *48*, 6101. (g) Z. He, S. Kirchberg, R. Froehlich, A. Studer, *Angew. Chem. Int. Ed.* **2012**, *51*, 3699.

13. (a) Y. Yamamoto, N. Kirai, Y. Harada, *Chem. Commun.* **2008**, 2010. (b) T. Murayama, M. Shibuya, Y. Yamamoto, *Adv. Synth. Catal.* **2016**, *358*, 166.
14. T. Satoh, Y. Nishinaka, M. Miura, M. Nomura, *Chem. Lett.* **1999**, 615.
15. (a) H. Noguchi, K. Hojo, M. Suginome, *J. Am. Chem. Soc.* **2007**, *129*, 758. (b) H. Noguchi, T. Shioda, C.-M. Chou, M. Suginome, *Org. Lett.* **2008**, *10*, 377. (c) N. Iwadate, M. Suginome, *Org. Lett.* **2009**, *11*, 1899.
16. (a) D. A. Colby, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2008**, *130*, 3645. (b) L. Li, Y. Z. Jiao, W. W. Brennessel, W. D. Jones, *Organometallics* **2010**, *29*, 4593. (c) M. Valencia, M. Martin-Ortiz, M. Gomez-Gallego, C. R. de Arellano, M. A. Sierra, *Chem. Eur. J.* **2014**, *20*, 3831. (d) F. Y. Mo, G. B. Dong, *Science* **2014**, *345*, 68. (e) F. Y. Mo, H. N. Lim, G. B. Dong, *J. Am. Chem. Soc.* **2015**, *137*, 15518.
17. C. Liu, X. M. Li, Y. H. Wu, *Rsc Adv*. **2015**, *5*, 15354.