

Cite this: *Chem. Sci.*, 2018, 9, 904

# Ni-catalysed regioselective 1,2-diarylation of unactivated olefins by stabilizing Heck intermediates as pyridylsilyl-coordinated transient metallacycles†

Surendra Thapa,‡ Roshan K. Dhungana,‡ Rajani Thapa Magar, Bijay Shrestha, Shekhar KC and Ramesh Giri \*

We report a Ni-catalysed diarylation of unactivated olefins in dimethylpyridylvinylsilane by intercepting Heck C(sp<sup>3</sup>)-NiX intermediates, derived from aryl halides, with arylzinc reagents. This approach utilizes a modifiable pyridylsilyl moiety as a coordinating group that plays a dual role of intercepting oxidative addition species to promote Heck carbometallation, and stabilizing the Heck C(sp<sup>3</sup>)-NiX intermediates as transient metallacycles to suppress β-hydride elimination, and facilitate transmetalation/reductive elimination. This method affords 1,2-diarylethylsilanes, which can be readily oxidized to 1,2-diarylethanol that occur as structural motifs in 3-aryl-3,4-dihydroisocoumarin and dihydrostilbenoid natural products.

Received 7th October 2017  
Accepted 26th November 2017

DOI: 10.1039/c7sc04351a

rsc.li/chemical-science

## Introduction

Interception of Heck C(sp<sup>3</sup>)-[M] intermediates with carbon nucleophiles by cross-coupling is an attractive approach to construct simultaneously two carbon-carbon (C-C) bonds across an olefin in one synthetic step.<sup>1</sup> This olefin dicarbofunctionalization process integrates the Heck reaction and cross-coupling in one synthetic platform (Scheme 1, path A) to rapidly build molecular complexity, an endeavour that would otherwise require a multi-step process if pursued through traditional synthetic disconnection strategies. However, execution of such a process on an unactivated olefin remains formidably challenging especially with transition metals such as Pd. The difficulty arises due to the sheer requirement to overcome two of the most fundamental Pd-catalysed processes as side reactions – direct cross-coupling between an organohalide and an organometallic reagent prior to olefin insertion (Scheme 1, path B), and the Heck reaction by β-hydride (β-H) elimination from the C(sp<sup>3</sup>)-[M] intermediates formed after carbometallation to an olefin (Scheme 1, path C).

Prior reports have exploited two strategies to overcome these problems and enable the transition metal-catalysed three-component olefin dicarbofunctionalization reactions – (1) the use of dienes and styrenes as substrates that would stabilize the

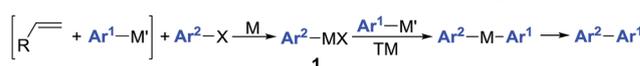
Heck C(sp<sup>3</sup>)-[M] intermediates by intrinsic π-allyl and π-benzyl formation,<sup>2</sup> and (2) the generation and addition of alkyl radicals to olefins.<sup>3</sup> In simple olefins that lack the means to stabilize the Heck C(sp<sup>3</sup>)-[M] intermediates,<sup>4</sup> reactions generally follow the Heck carbometallation/β-H elimination/M-H reinsertion cascade to furnish 1,1-dicarbofunctionalized products.<sup>5</sup>

Recently, we<sup>6</sup> developed a (cod)<sub>2</sub>Ni-catalysed three-component dicarbofunctionalization of olefins in which we strategically employed imines as a readily removable coordinating group to facilitate the reaction.<sup>7</sup> The idea was to intercept the organonickel species 3 by a bidentate coordination mode, promote intramolecular Heck carbonylation onto the bound olefin and stabilize the resultant Heck C(sp<sup>3</sup>)-[Ni] intermediate 6 as a transient metallacycle (Scheme 2). We envisioned that

**Path A: Olefin diarylation by combined Heck reaction and cross-coupling**



**Path B: leads to undesired coupling products by bypassing olefin insertion**



**Path C: leads to undesired Heck products after β-H elimination**



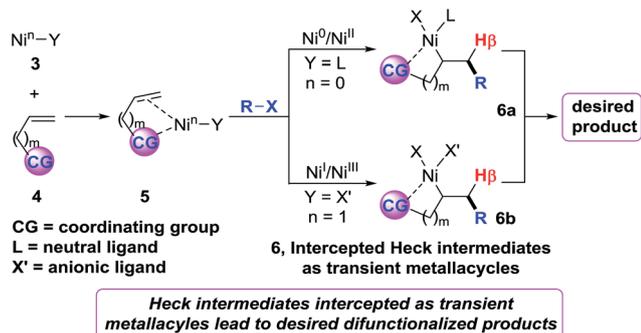
Scheme 1 Two well-known transformations working as side reactions during regioselective olefin diarylation.

Department of Chemistry & Chemical Biology, The University of New Mexico, Albuquerque, NM 87131, USA. E-mail: rgiri@unm.edu

† Electronic supplementary information (ESI) available: Experimental procedures and characterization, and the <sup>1</sup>H and <sup>13</sup>C NMR spectra of new compounds. See DOI: 10.1039/c7sc04351a

‡ These authors contributed equally.





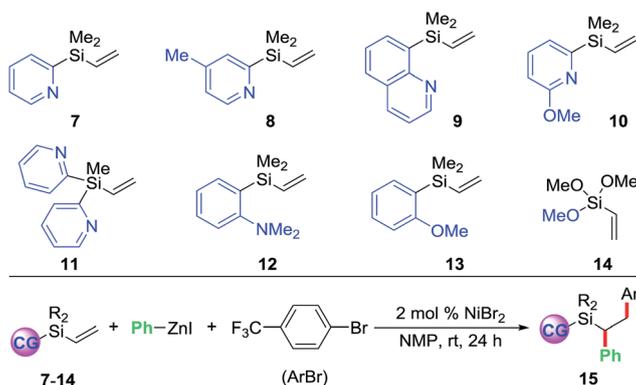
Scheme 2 Strategy for olefin dicarbonylation.

this strategy would afford sufficient residence time for the Heck  $C(sp^3)$ -[Ni] species **6** in order to promote the requisite transmetalation/reductive elimination steps, and furnish the expected product. We believe that this approach should operate regardless of the reaction proceeding *via* a  $Ni^0/Ni^{II}$  or  $Ni^I/Ni^{III}$  catalytic cycle. Herein, we report diarylation of unactivated olefins in pyridylvinylsilanes that relies upon the same strategy

of stabilizing the Heck  $C(sp^3)$ -[Ni] intermediates as transient five-membered metallacycles by pyridylsilyl coordination.<sup>8</sup>

## Results and discussion

Towards our long-term goal of olefin dicarbonylation by cross-coupling,<sup>4a,k</sup> we aspired to expand the scope of our three-component arylation of olefins to silicon-based molecules. We believe that development of such a method could provide rapid access to complex differently substituted 1,2-diarylethylsilanes, which are difficult to synthesize.<sup>9</sup> The 1,2-diarylethylsilanes could then be readily oxidized to 1,2-diarylethanol that occur as structural motifs in wide range of 3-aryl-3,4-dihydroisocoumarin and dihydrostilbenoid natural products.<sup>10</sup> In this process, we examined the diarylation of pyridylvinylsilane **7** with 4-bromobenzotrifluoride and  $PhZnI$  (Table 1). Examination of various parameters revealed that the reaction furnished the expected product **15a** in best yield (79%) using 2 mol%  $NiBr_2$  as a catalyst in NMP at room temperature (entry 1). We then investigated substituted pyridyl (**8** and **10**), 8-quinolyl (**9**), dipyriddy (**11**), *N,N*-dimethylaniliny (**12**), *o*-

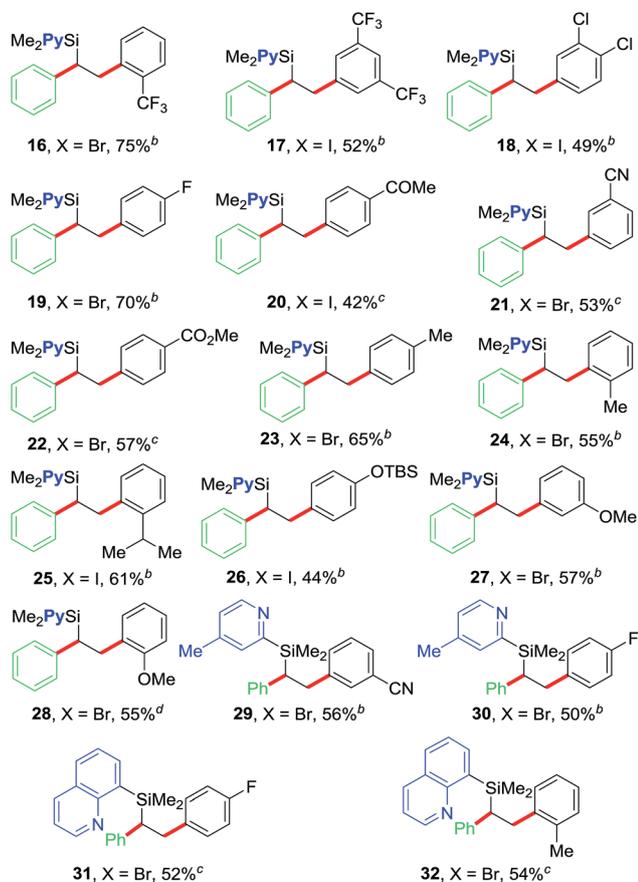
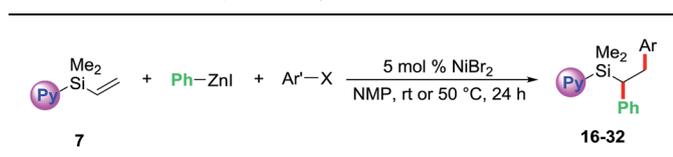
Table 1 Optimization of reaction conditions<sup>a</sup>

Entry	Reaction condition deviation	Vinylsilanes	Product	Yields of <b>15</b> (%)
1	None	<b>7</b>	<b>15a</b>	79 (72)
2	None	<b>8</b>	<b>15b</b>	51
3	None	<b>9</b>	<b>15c</b>	56
4	None	<b>10</b>	<b>15d</b>	0
5	None	<b>11</b>	<b>15e</b>	0
6	None	<b>12</b>	<b>15f</b>	0
7	None	<b>13</b>	<b>15g</b>	0
8	None	<b>14</b>	<b>15h</b>	0
9	15 h	<b>7</b>	<b>15a</b>	62
10	(cod) <sub>2</sub> Ni instead of $NiBr_2$	<b>7</b>	<b>15a</b>	35
11	( $Ph_3P$ ) <sub>4</sub> Ni instead of $NiBr_2$	<b>7</b>	<b>15a</b>	30
12	DMF or DMA instead of NMP	<b>7</b>	<b>15a</b>	40–44
13	DMSO, dioxane or MeCN instead of NMP	<b>7</b>	<b>15a</b>	10–15
14	Benzene of THF instead of NMP	<b>7</b>	<b>15a</b>	<5
15	CuI or $FeCl_3$ instead of $NiBr_2$	<b>7</b>	<b>15a</b>	0
16	$Pd(OAc)_2$ or $Co(OAc)_2$ instead of $NiBr_2$	<b>7</b>	<b>15a</b>	0 <sup>b</sup>

<sup>a</sup> Yields were determined by <sup>1</sup>H NMR using pyrene as an internal standard. Value in parenthesis is the isolated yield from a 0.5 mmol scale reaction.

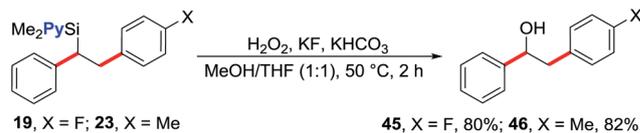
<sup>b</sup> Heck product was formed in >90% NMR yield with  $Co(OAc)_2$ .



Table 2 Reaction scope with aryl halides<sup>a</sup>

<sup>a</sup> Values are isolated yields from 0.5 mmol scale reactions. <sup>b</sup> 50 °C. <sup>c</sup> Room temperature. <sup>d</sup> 80 °C.

anisoyl (13) and trimethoxysilyl (14) as coordinating groups where the nitrogen or oxygen atoms could coordinate to Heck C(sp<sup>3</sup>)-[Ni] intermediates to generate 4-, 5- or 6-membered transient metallacycles (entries 2–8). Among them, only the 4-methylpyridyl (8) and 8-quinolinyl (9) afforded the expected products 15b–c in good yields (entries 2–3).<sup>11</sup> Running the reaction for a shorter time (15 h) formed the product in slightly lower yield (entry 9). Other Ni-catalysts such as Ni(cod)<sub>2</sub> and Ni(PPh<sub>3</sub>)<sub>4</sub> also generated the product in lower yields (entries 10 and 11). The lower yields with Ni(cod)<sub>2</sub> and Ni(PPh<sub>3</sub>)<sub>4</sub> could be rationalized based on difficulty to displace strongly coordinating ligands such as 1,5-cyclooctadiene (cod) and Ph<sub>3</sub>P by the substrate imine or olefin. Using DMF or DMA as a solvent furnished product 15a in moderate yields (entry 12). Other solvents such as DMSO, dioxane, MeCN, benzene and THF formed the product 15a in <15% yield (entries 13 and 14). The use of a Ni-catalyst was found to be critical for this transformation as other



Scheme 3 Transformation of silyl group to alcohol.

catalysts based on Pd, Co, Fe and Cu did not catalyse the reaction (entries 15 and 16).

We note that the reaction does not form products arising from the Hiyama coupling<sup>12</sup> despite the fact pyridylvinylsilanes are known to undergo such a reaction.<sup>13</sup> The current reaction also proceeds with absolute regioselectivity with terminal arylation during Heck carbometallation, a result that is in sharp contrast to the undirected Ni-catalysed Heck reactions that proceed with excellent selectivity for internal arylation.<sup>14</sup> The regioselectivity of the products was confirmed by oxidation of 1,2-diarylethylsilanes 19 and 23 (Table 2) to the corresponding known 1,2-diarylethanol 45 and 46 (*vide infra*, Scheme 3), respectively.<sup>15</sup> We hypothesize that the remarkable terminal selectivity for Heck carbometallation in our reaction could be a function of both the coordinating effect of the pyridyl group that strives for forming stable and tight five-membered metallacycles after carbometallation on the vinyl group, and the  $\beta$ -cation stabilizing effect of Si due to hyperconjugation.<sup>16</sup> Prior work on Pd- and Fe-catalysed, directed Heck reaction of dimethyl(2-pyridyl)vinylsilane has also shown that the reaction proceeds with high regioselectivity for terminal arylation.<sup>17</sup>

After optimizing the reaction conditions, we examined the scope of the current olefin diarylation reaction (Table 2). In general, reactions of electron-deficient aryl halides reacted at room temperature (20–22, 29 and 31) and those with electron-rich substituents required 50 °C (23–28 and 30). In addition, reactions typically required 2–5 mol% NiBr<sub>2</sub>. A wide variety of electron-rich, neutral and electron-deficient aryl iodides can be utilized as coupling partners along with the pyridylvinylsilane 7, which furnishes variously substituted 1,2-diarylethylsilanes 16–28 in good yields.<sup>18</sup> The reaction tolerates a variety of functional groups such as Me, OMe, OTBS, CF<sub>3</sub>, F, Cl, COMe, CO<sub>2</sub>Me and CN. The reaction also works well with aryl halides containing *ortho*-substituents (16, 24, 28 and 32) including sterically hindered isopropyl group (25).

We further examined the scope of the reaction with respect to arylzinc reagents (Table 3). Electron-rich, deficient and neutral arylzinc reagents containing Me, OMe, F and CF<sub>3</sub> can be used as coupling partners<sup>19</sup> along with aryl halides bearing various functional groups like Me, OMe, CF<sub>3</sub>, Cl, COMe, CO<sub>2</sub>Me and CN, which afford the 1,2-diarylated products in good yields (33–44). The reaction also tolerates *ortho*-substituted arylzinc reagents (43 and 44).

The 1,2-diarylethylsilane products can be readily transformed into 1,2-diarylethanol by oxidation (Scheme 3). For example, we show that the products 19 and 23 can be efficiently oxidized to 2-(4-fluorophenyl)-1-phenylethanol (45) and 1-phenyl-2-(*p*-tolyl)ethanol (46), respectively, in excellent yields by reacting them with H<sub>2</sub>O<sub>2</sub> in the presence of KF and KHCO<sub>3</sub>.<sup>20</sup>





addition/reductive elimination or migratory insertion/oxidative addition/reductive elimination sequence can be readily discounted because such a process would lead to products where the regioselectivity would be either lost or opposite to the one observed experimentally.

## Conclusions

In summary, we have developed a Ni-catalysed diarylation of unactivated olefins in pyridylvinylsilanes by cross-coupling using aryl halides and arylzinc reagents as carbon sources. The reaction affords 1,2-diarylethylsilanes, which can be readily converted to 1,2-diarylethanol that are structural motifs in natural products and biologically important molecules. The reaction also tolerates various functional groups that are synthetically important. Preliminary studies indicate that the reaction proceeds *via* a Ni(0)/Ni(II) catalytic cycle.

## Conflicts of interest

There are no conflicts of interest to declare.

## Acknowledgements

We thank the University of New Mexico (UNM) and the National Science Foundation (NSF CHE-1554299) for financial support, and upgrades to the NMR (NSF grants CHE08-40523 and CHE09-46690) and MS Facilities.

## Notes and references

- For dicarbofunctionalization of activated olefins by conjugate addition/enolate interception, see: (a) H.-C. Guo and J.-A. Ma, *Angew. Chem., Int. Ed.*, 2006, **45**, 354; (b) T. Qin, J. Cornella, C. Li, L. R. Malins, J. T. Edwards, S. Kawamura, B. D. Maxwell, M. D. Eastgate and P. S. Baran, *Science*, 2016, **352**, 801.
- (a) L. Liao, R. Jana, K. B. Urkalan and M. S. Sigman, *J. Am. Chem. Soc.*, 2011, **133**, 5784; (b) X. Wu, H.-C. Lin, M.-L. Li, L.-L. Li, Z.-Y. Han and L.-Z. Gong, *J. Am. Chem. Soc.*, 2015, **137**, 13476; (c) Z. Kuang, K. Yang and Q. Song, *Org. Lett.*, 2017, **19**, 2702; (d) J. Terao, S. Nii, F. A. Chowdhury, A. Nakamura and N. Kambe, *Adv. Synth. Catal.*, 2004, **346**, 905; (e) K. Mizutani, H. Shinokubo and K. Oshima, *Org. Lett.*, 2003, **5**, 3959.
- (a) A. García-Domínguez, Z. Li and C. Nevado, *J. Am. Chem. Soc.*, 2017, **139**, 6835; (b) J.-W. Gu, Q.-Q. Min, L.-C. Yu and X. Zhang, *Angew. Chem., Int. Ed.*, 2016, **55**, 12270; (c) B. J. Stokes, L. Liao, A. M. de Andrade, Q. Wang and M. S. Sigman, *Org. Lett.*, 2014, **16**, 4666.
- For examples of two-component dicarbofunctionalizations of tethered olefins, see: (a) R. K. Dhungana, B. Shrestha, R. Thapa-Magar, P. Basnet and R. Giri, *Org. Lett.*, 2017, **19**, 2154; (b) G. Balme, D. Bouyssi, T. Lomberget and N. Monteiro, *Synthesis*, 2003, **2003**, 2115; (c) G. Fournet, G. Balme and J. Gore, *Tetrahedron Lett.*, 1987, **28**, 4533; (d) J. G. Kim, Y. H. Son, J. W. Seo and E. J. Kang, *Eur. J. Org. Chem.*, 2015, **2015**, 1781; (e) V. B. Phapale, E. Buñuel, M. García-Iglesias and D. J. Cárdenas, *Angew. Chem., Int. Ed.*, 2007, **46**, 8790; (f) M. Nakamura, S. Ito, K. Matsuo and E. Nakamura, *Synlett*, 2005, **2005**, 1794; (g) K. Wakabayashi, H. Yorimitsu and K. Oshima, *J. Am. Chem. Soc.*, 2001, **123**, 5374; (h) C.-S. Yan, Y. Peng, X.-B. Xu and Y.-W. Wang, *Chem.-Eur. J.*, 2012, **18**, 6039; (i) B. Seashore-Ludlow and P. Somfai, *Org. Lett.*, 2012, **14**, 3858; (j) R. Grigg, J. Sansano, V. Santhakumar, V. Sridharan, R. Thangavelanthum, M. Thornton-Pett and D. Wilson, *Tetrahedron*, 1997, **53**, 11803; (k) S. Thapa, P. Basnet and R. Giri, *J. Am. Chem. Soc.*, 2017, **139**, 5700; (l) W. You and M. K. Brown, *J. Am. Chem. Soc.*, 2015, **137**, 14578; (m) W. You and M. K. Brown, *J. Am. Chem. Soc.*, 2014, **136**, 14730; (n) H. Cong and G. C. Fu, *J. Am. Chem. Soc.*, 2014, **136**, 3788; (o) C. M. McMahon, M. S. Renn and E. J. Alexanian, *Org. Lett.*, 2016, **18**, 4148; (p) A. Vaupel and P. Knochel, *J. Org. Chem.*, 1996, **61**, 5743; (q) T. Ishiyama, M. Murata, A. Suzuki and N. Miyaura, *J. Chem. Soc., Chem. Commun.*, 1995, 295; (r) J. A. Walker, K. L. Vickerman, J. N. Humke and L. M. Stanley, *J. Am. Chem. Soc.*, 2017, **139**, 10228.
- (a) V. Saini and M. S. Sigman, *J. Am. Chem. Soc.*, 2012, **134**, 11372; (b) E. W. Werner, K. B. Urkalan and M. S. Sigman, *Org. Lett.*, 2010, **12**, 2848; (c) V. Saini, L. Liao, Q. Wang, R. Jana and M. S. Sigman, *Org. Lett.*, 2013, **15**, 5008; (d) K. B. Urkalan and M. S. Sigman, *Angew. Chem., Int. Ed.*, 2009, **48**, 3146.
- B. Shrestha, P. Basnet, R. K. Dhungana, S. Kc, S. Thapa, J. M. Sears and R. Giri, *J. Am. Chem. Soc.*, 2017, **139**, 10653.
- For other examples of directed olefin difunctionalization, see: with Pd: (a) S. Yahiaoui, A. Fardost, A. Trejos and M. Larhed, *J. Org. Chem.*, 2011, **76**, 2433; (b) E. P. A. Talbot, T. d. A. Fernandes, J. M. McKenna and F. D. Toste, *J. Am. Chem. Soc.*, 2014, **136**, 4101; (c) S. R. Neufeldt and M. S. Sanford, *Org. Lett.*, 2013, **15**, 46; (d) Z. Liu, T. Zeng, K. S. Yang and K. M. Engle, *J. Am. Chem. Soc.*, 2016, **138**, 15122; (e) J. Derosa, V. T. Tran, M. N. Boulous, J. S. Chen and K. M. Engle, *J. Am. Chem. Soc.*, 2017, **139**, 10657.
- For the use of pyridylsilyl as a directing group for C-H activation, see: (a) A. V. Gulevich, F. S. Melkonyan, D. Sarkar and V. Gevorgyan, *J. Am. Chem. Soc.*, 2012, **134**, 5528; (b) N. Chernyak, A. S. Dudnik, C. Huang and V. Gevorgyan, *J. Am. Chem. Soc.*, 2010, **132**, 8270; for a review on the use of pyridylsilyl as a directing group, see: (c) K. Itami and J.-i. Yoshida, *Synlett*, 2006, **2006**, 157.
- For prior reports each showing the synthesis of one 1,2-diarylethylsilane, see: (a) C. K. Hazra, N. Gandhamsetty, S. Park and S. Chang, *Nat. Commun.*, 2016, **7**, 13431; (b) A. Saxena and H. W. Lam, *Chem. Sci.*, 2011, **2**, 2326; (c) S. Nii, J. Terao and N. Kambe, *J. Org. Chem.*, 2004, **69**, 573.
- (a) J. Chen, L. Zhou, C. K. Tan and Y.-Y. Yeung, *J. Org. Chem.*, 2012, **77**, 999; (b) G. C. Tron, T. Pirali, G. Sorba, F. Pagliai, S. Busacca and A. A. Genazzani, *J. Med. Chem.*, 2006, **49**, 3033; (c) J. A. Baur and D. A. Sinclair, *Nat. Rev. Drug Discovery*, 2006, **5**, 493; (d) A. Cirila and J. Mann, *Nat. Prod. Rep.*, 2003, **20**, 558; (e) S. B. Singh and G. R. Pettit, *Synth. Commun.*, 1987, **17**, 877.



- 11 Since 2-OMe group is known to decrease the basicity of the pyridyl nitrogen, it could weaken pyridyl N-binding to Ni resulting in no reactivity of the olefin 10. See: R. A. Murphy and R. Sarpong, *Org. Lett.*, 2012, **14**, 632. As such, 23% of direct cross-coupling product was formed in this reaction.
- 12 (a) D. A. Powell and G. C. Fu, *J. Am. Chem. Soc.*, 2004, **126**, 7788; (b) X. Dai, N. A. Strotman and G. C. Fu, *J. Am. Chem. Soc.*, 2008, **130**, 3302.
- 13 K. Itami, T. Nokami and J.-i. Yoshida, *J. Am. Chem. Soc.*, 2001, **123**, 5600.
- 14 (a) R. Matsubara, A. C. Gutierrez and T. F. Jamison, *J. Am. Chem. Soc.*, 2011, **133**, 19020; (b) E. A. Standley and T. F. Jamison, *J. Am. Chem. Soc.*, 2013, **135**, 1585; (c) S. Z. Tasker, A. C. Gutierrez and T. F. Jamison, *Angew. Chem., Int. Ed.*, 2014, **53**, 1858.
- 15 D. K. Nielsen and A. G. Doyle, *Angew. Chem., Int. Ed.*, 2011, **50**, 6056.
- 16 S. G. Wierschke, J. Chandrasekhar and W. L. Jorgensen, *J. Am. Chem. Soc.*, 1985, **107**, 1496.
- 17 (a) K. Itami, K. Mitsudo, T. Kamei, T. Koike, T. Nokami and J.-i. Yoshida, *J. Am. Chem. Soc.*, 2000, **122**, 12013; (b) K. Itami, T. Nokami, Y. Ishimura, K. Mitsudo, T. Kamei and J.-i. Yoshida, *J. Am. Chem. Soc.*, 2001, **123**, 11577; (c) K. Itami, Y. Ushioji, T. Nokami, Y. Ohashi and J.-i. Yoshida, *Org. Lett.*, 2004, **6**, 3695; (d) L. Ilies, J. Okabe, N. Yoshikai and E. Nakamura, *Org. Lett.*, 2010, **12**, 2838; (e) G. Meng and M. Szostak, *Angew. Chem., Int. Ed.*, 2015, **54**, 14518.
- 18 No product was observed when  $\beta$ -bromostyrene or iodoctane was used in place of aryl bromides. Similarly, 2-pyridyldimethylallylsilane bearing olefin unactivated by Si and (*E*)-2-(dimethyl(3-(4-(trifluoromethyl)phenyl)allyl)silyl)pyridine containing internal olefin also did not form any product.
- 19 No product was observed when 2-propylzinc bromide, 2-pyridylzinc bromide or arylzinc iodide bearing nitrile or ester functional group was used.
- 20 K. Itami, K. Mitsudo and J.-i. Yoshida, *J. Org. Chem.*, 1999, **64**, 8709.
- 21 (a) M. R. Harris, M. O. Konev and E. R. Jarvo, *J. Am. Chem. Soc.*, 2014, **136**, 7825; (b) C. Liu, S. Tang, D. Liu, J. Yuan, L. Zheng, L. Meng and A. Lei, *Angew. Chem., Int. Ed.*, 2012, **51**, 3638; (c) S. A. Lebedev, V. S. Lopatina, E. S. Petrov and I. P. Beletskaya, *J. Organomet. Chem.*, 1988, **344**, 253; (d) T. M. Gøgsig, J. Kleimark, S. O. Nilsson Lill, S. Korsager, A. T. Lindhardt, P.-O. Norrby and T. Skrydstrup, *J. Am. Chem. Soc.*, 2012, **134**, 443; (e) A. Trejos, J. Sävmarker, S. Schlummer, G. K. Datta, P. Nilsson and M. Larhed, *Tetrahedron*, 2008, **64**, 8746; (f) A. B. Machotta, B. F. Straub and M. Oestreich, *J. Am. Chem. Soc.*, 2007, **129**, 13455; (g) J.-N. Desrosiers, L. Hie, S. Biswas, O. V. Zatulochynaya, S. Rodriguez, H. Lee, N. Grinberg, N. Haddad, N. K. Yee, N. K. Garg and C. H. Senanayake, *Angew. Chem., Int. Ed.*, 2016, **55**, 11921; (h) K. M. M. Huihui, R. Shrestha and D. J. Weix, *Org. Lett.*, 2017, **19**, 340.
- 22 A. N. Abeywickrema and A. L. J. Beckwith, *J. Chem. Soc., Chem. Commun.*, 1986, 464.
- 23 G. D. Jones, J. L. Martin, C. McFarland, O. R. Allen, R. E. Hall, A. D. Haley, R. J. Brandon, T. Konovalova, P. J. Desrochers, P. Pulay and D. A. Vacic, *J. Am. Chem. Soc.*, 2006, **128**, 13175.

