C–H Activation

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Rhodium(I)-Catalyzed Tertiary Phosphine Directed C–H Arylation: Rapid Construction of Ligand Libraries

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Abstract: *Modification of commercially available monophosphine ligands with either aryl bromides or chlorides by rhodium(I)-catalyzed, tertiary phosphine directed C–H activation is described. A series of ligand libraries containing mono- and diaryl-substituted groups, having different steric and electronic properties, were obtained in high yields. Based on the outstanding properties of their parent scaffolds, the modified ligands have been found to be powerful in organic reactions.*

Advances in transition-metal catalysis are closely related to the development of new ligands enabling previously impossible transformations. In the ever-growing catalogue of available ligands for cross-coupling reactions, tertiary phosphines (PR_3) remain the most widely used, because their electronic and steric properties can be altered in a systematic and predictable way by varying the R group(s).[1] Among them, the elegantly designed monophosphines reported by the groups of Buchwald,[2] Beller,[3] and Kwong[4] have been widely applied as supporting ligands in a variety of transformations, especially in palladium-catalyzed carbon–carbon and carbon–heteroatom bond-formation reactions.

Ligand modification is a powerful approach for designing new ligands with excellent reactivity, although it occurs seldom and unexpectedly. As early as 2000, the group of Hartwig found that a modified phosphine, $Ar_5FcP(tBu)_2$, generated in situ, served as the actual supporting ligand in aromatic C–O bond formation catalyzed by $[Pd(dba)_2]$ and $FcP(tBu)_2$.[5] This discovery led to the development of widely used Q-Phos ligands.[6] Recently, Buchwald et al. confirmed that the pre-ligand AdBrettPhos underwent in situ ligand modification by dearomatization and arylation during the palladium-catalyzed fluorination of aryl triflates.[7] This discovery resulted in the design of a new ligand, AlPhos, which allowed a highly efficient fluorination process.[8] Herein, we report a general method for modification of commercially available tertiary phosphine ligands by rhodium-catalyzed, P-atom-directed C–H arylation.[9]

This research was inspired by an accidental discovery in the stoichiometric characterization of rhodium phosphine complexes (Figure 1a). The reaction of a $[\{Rh(cod)Cl\}_2]$ dimer with CyJohnPhos (**1a**) in DCM at room temperature generated a yellow complex, [Rh(cod)(CyJohnPhos)Cl] (**1a′**), in 82% yield, and it was the precursor to **1a″**.[10] Treatment of this isolated intermediate **1a″** with 1.0 equivalent of bromobenzene (**2a**) and 3.0 equivalents of LiO*t*Bu[11] in 1,4-dioxane at 110 °C led to the formation of the direct arylation product **3aa**, which was characterized by NMR spectroscopy. It is noted that our group and as well as that of others have recently reported N–P(O)*t*Bu[12]- and $P(O)R_2$-directed[13] (e.g. Figure 1b) C–H activation reactions in which O atoms act as directors for coordination with the metal centers.[14] If the P-atom-directed C–H arylation can be achieved in a catalytic process,[15] this late-stage modification[16] by catalytic P-atom-directed C–H arylation would greatly improve the atom and step economy for building aryl-substituted phosphine ligands, as compared to the traditional routes (Figure 1b and c[17]).

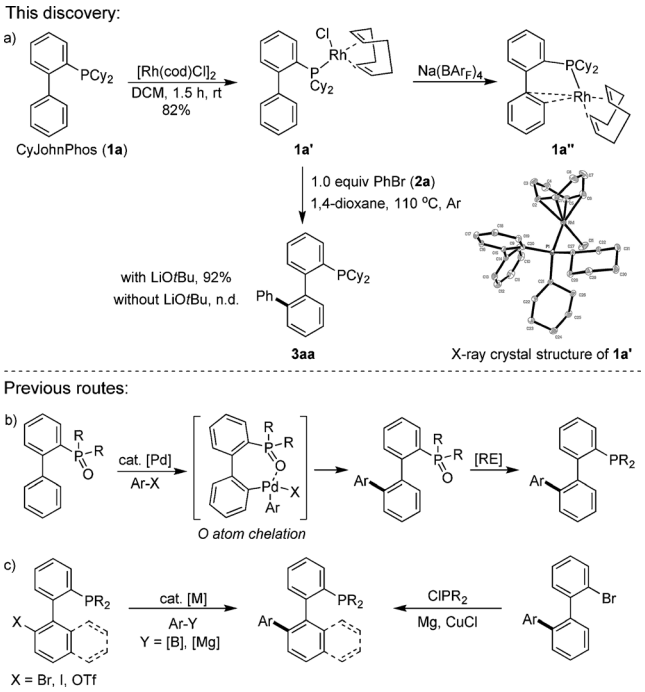

Figure 1. Synthesis of aryl-substituted biaryl phosphines. DCM = dichloromethane, cod = 1,5-cyclooctadiene.

We first established the feasibility of this proposed transformation (Table 1). The reaction was carried out with CyJohnPhos (**1a**, 1.0 equiv) and bromobenzene (**2a**,

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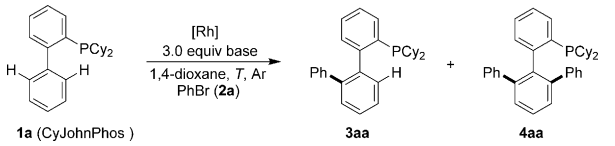
Table 1: Reaction development.[a]

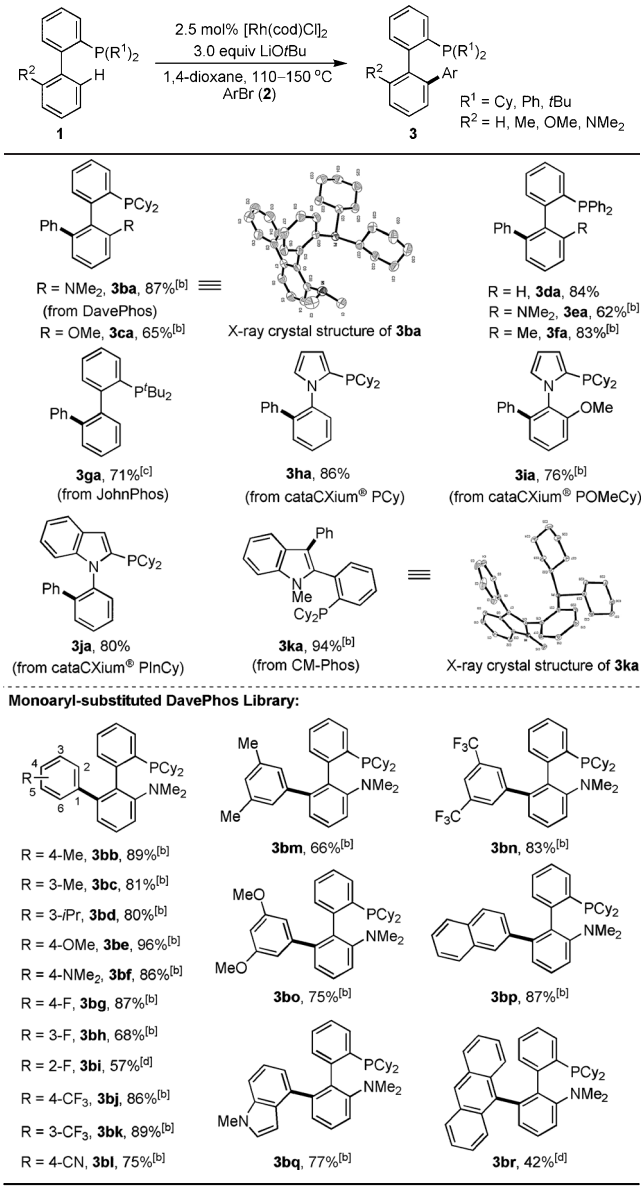


1a (CyJohnPhos) 3aa 4aa

Entry	[Rh] (mol %)	1a/2a	Base	T [°C]	3aa/4aa[b]	Yield [%][c]
1	[{Rh(cod)Cl}$_2$] (100)	1:1	LiO*t*Bu	110	95:5	94
2	[{Rh(cod)Cl}$_2$] (5)	1:1	LiO*t*Bu	110	99:1	88
3	[{Rh(cod)Cl}$_2$] (2.5)	1:1	LiO*t*Bu	110	99:1	86
4	[{Rh(cod)Cl}$_2$] (1.5)	1:1	LiO*t*Bu	110	100:0	71
5	[{Rh(cod)Cl}$_2$] (2.5)	1:1	LiO*t*Bu	80	100:0	52
6	[{Rh(cod)Cl}$_2$] (2.5)	1:1	KO*t*Bu	110	100:0	65
7	[{Rh(cod)Cl}$_2$] (2.5)	1:2.4	LiO*t*Bu	110	15:85	72
8	[{Rh(cod)Cl}$_2$] (2.5)	1:2.4	LiO*t*Bu	140	1:99	94
9	[Rh(PPh$_3$)$_3$Cl] (5)	1:2.4	LiO*t*Bu	140	1:99	80
10[d]	[{Rh(cod)Cl}$_2$] (2.5)	1:5.0	LiO*t*Bu	150	1:99	92
11	[Pd(dba)$_2$] (5)	1:2.4	LiO*t*Bu	140	–	–
12	[Ir(cod)OMe]$_2$ (5)	1:2.4	LiO*t*Bu	140	–	–

[a] Reaction conditions: **1a** (0.20 mmol), **2a** (1.0–2.4 equiv) and 3.0 equiv base in solvent at 110 °C for 12 h under argon. [b] Ratios were determined by GC. [c] Yields of the isolated major products. [d] Using PhCl (**2a′**) instead of PhBr (**2a**). dba = dibenzylideneacetone.

Table 2: The scope of monoselective direct arylation.[a]



[a] Reaction conditions: 2.5 mol% [{Rh(cod)Cl}$_2$], **1** (0.20 mmol), **2** (0.20 mmol), and LiO*t*Bu (0.6 mmol) in 1 mL 1,4-dioxane at 110 °C under argon, 24 h. Yields of products isolated after chromatography. [b] 1.5 equiv **2**, 140 °C, 36 h. [c] 2.0 equiv **2**, 150 °C, 24 h. [d] 5.0 equiv **2**, 150 °C, 36 h. For X-ray structures the ellipsoids are set at 30% probability.[23]

1.0 equiv) in the presence of 1.0 equivalents [{Rh(cod)Cl}$_2$] and 3.0 equivalents LiO*t*Bu, at 110 °C under an Ar atmosphere in 1,4-dioxane. Gratifyingly, the desired arylation product **3aa** (mono/di = 99:1) was isolated in 94% yield (entry 1). To our delight, a catalytic amount of [{Rh(cod)Cl}$_2$] (5 mol%) furnished the direct arylation product **3aa** in 88% yield (entry 2). The catalyst loading could also be further reduced to 2.5 mol% without affecting the reactivity (entry 3), but additional lowering to 1.5 mol% led to decreased reactivity (entry 4). An examination of the temperature revealed that a much lower yield (52%) was obtained at 80 °C (entry 5). Screening with another base, such as KO*t*Bu, confirmed LiO*t*Bu to be the optimal additive for this reaction (entry 6). With 2.4 equivalents of **2a**, the ratio of the mono- and disubstituted products **3aa** and **4aa**, respectively, was changed to 15:85 (entry 7). To increase the di-selectivity to a more synthetically useful level, we increased the reaction temperature to 140 °C, and it afforded **4aa** in 94% yield (entry 8). Another rhodium source, such as [Rh(PPh$_3$)$_3$Cl], was also successful (entry 9). Further screening showed that this transformation also occurred in high conversion with the less reactive chlorobenzene (**2a′**) and afforded **4aa** in 92% yield (entry 10). Notably, other transition metals, such as [Pd(dba)$_2$][5] and [{Ir(cod)OMe}$_2$][18] were completely ineffective in this transformation (entries 11 and 12).

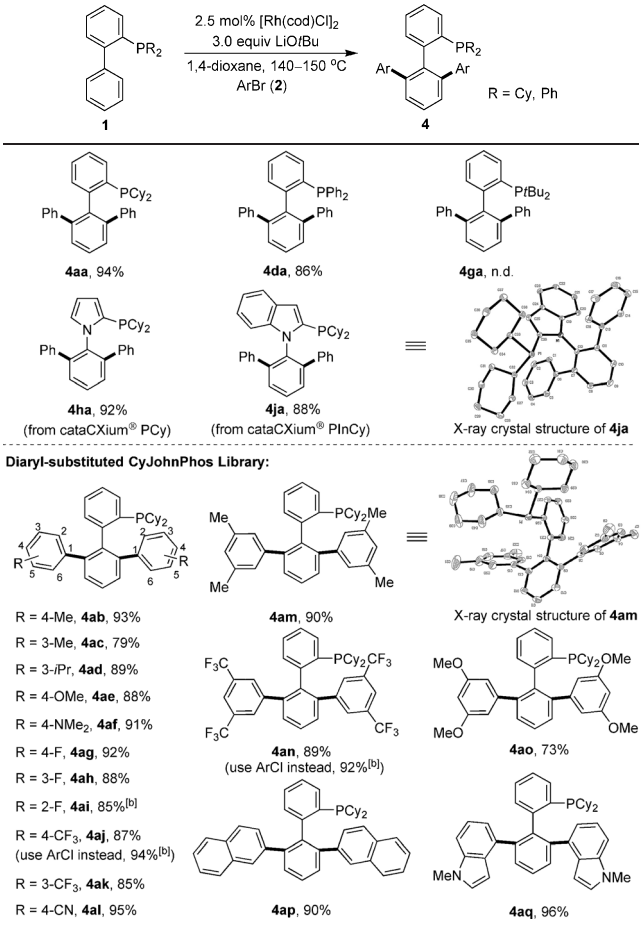
The scope of the monosubstituted products was first examined using a wide range of commercially available phosphine ligands (Table 2). As one of the most widely used ligands, Davephos (**1b**), bearing an NMe$_2$ substituent, underwent facile arylation to afford the corresponding product **3ba** in 87% yield. Methoxy-substitution on the substrate delivered the coupled product **3ca** in 65% yield. The substrates **1d–f**, containing a diphenylphosphino group, were compatible in forming the desired products **3da–fa** in good yields. Gratifyingly, JohnPhos (**1g**), having a sterically hindered directing group, also produced the terphenyl product **3ga** in 71% yield, and was prepared from 2-bromobiphenyl in three steps with 10% total yield according to the previous route.[17a] The cataCxium series ligands including cataCXium® PCy (**1h**), POMeCy (**1i**), and PInCy (**1j**) generated the desired biphenyl products **3ha–ja** in high yields, while CM-Phos (**1k**) was successfully arylated over the indole core to deliver **3ka** in 94% yield as a single regioisomer. These results reflected the importance of the P atom as the sole director for the regioselectivity.

Given the importance of DavePhos, we subjected it to various arylbromides for the direct arylation process (Table 2). Aromatic groups bearing electron-neutral and electron-donating substituents (**3bb–bf**) underwent facile transformation to afford the desired products in excellent yields. Aryl groups with electron-withdrawing groups (**3bg–bl**) could be installed on the Davephos core without any compromise. Disubstituted arylbromides (**2m–o**) were efficiently coupled. The naphthalene- and indole-containing substrates **2p–q** were also found tolerable. In addition, reactivity was achieved with a very sterically hindered 9-bromoanthracene (**1r**), thus providing the compound **3br** in 42% yield. These results are notable because a library of aryl-substituted Davephos analogues having different steric and electronic properties can be generated efficiently and rapidly.

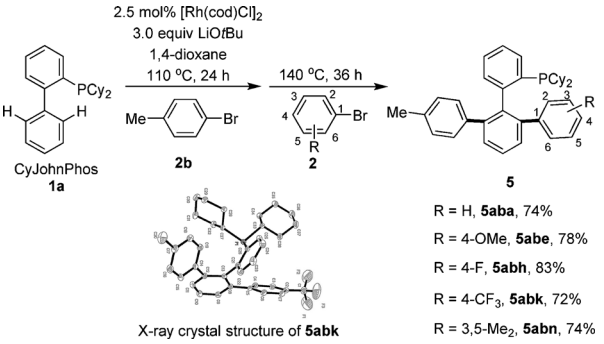
We next studied scope of the disubstituted products, and a variety of PCy_2- and PPh_2-based ligands could be coupled in excellent yields and high selectivity (Table 3). However, the sterically hindered JohnPhos (**1g**), with a P*t*Bu_2 group, could not generate the corresponding diarylation product **4ga**. Under these reaction conditions, a library of diaryl-substituted CyJohnphos was also developed. A number of arylbromides with various electronic and steric properties (**4ab–aq**) could be coupled to provide the disubstituted products with excellent selectivity. In this case, 9-bromoanthracene (**1r**) only yielded the monosubstituted product (not shown in the table). To demonstrate the efficacy of this rhodium catalyst system, we have also prepared the compounds from aryl chlorides such as **4aj** and **4an**.

We also sought to explore the dual C–H activation of phosphine ligands coupling with two different arylbromides (Scheme 1). CyJohnphos (**1a**) was coupled with 4-bromotoluene (**2b**) under monoselective direct arylation conditions and subsequently coupled with another arylbromide, such as **2a**, **2e**, **2h**, **2k**, and **2n** in one pot to afford the desired products in 72–83% yields.

Table 3: The scope of di-selective direct arylation.[a]



[a] Reaction conditions: 2.5 mol% $[Rh(cod)Cl]_2$, **1** (0.20 mmol), **2** (0.48 mmol), and LiO*t*Bu (0.6 mmol) in 1 mL 1,4-dioxane at 140 °C under argon, 36 h. Yields of products isolated after chromatography. [b] 5.0 equiv ArCl (**2a′**), 150 °C, 36 h. For X-ray structures the ellipsoids are set at 30% probability.[23]

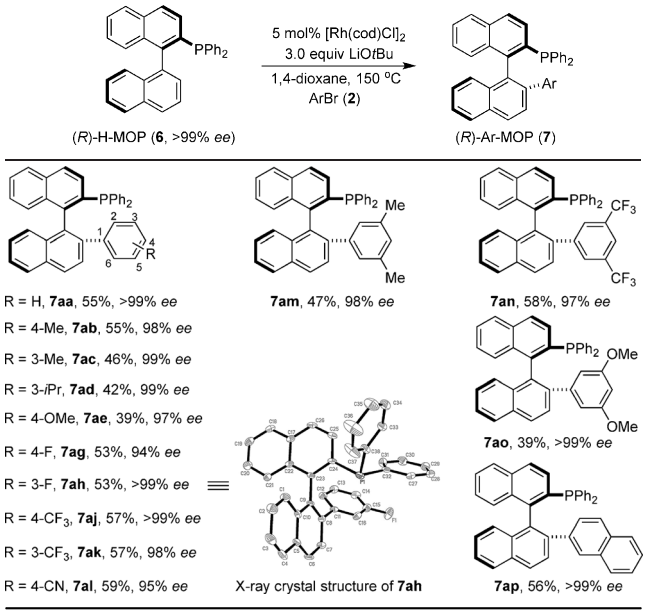


Scheme 1. One-pot synthesis of nonsymmetrical diaryl phosphines. For X-ray structures the thermal ellipsoids are shown at 30% probability.[23]

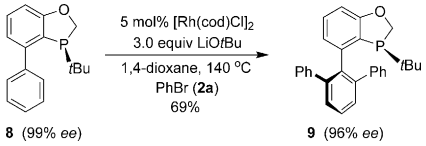
The biaryl axially chiral monophosphine ligands play an important role in catalytic asymmetric reactions. Aiming to rapidly construct synthetically useful chiral ligands, we extended this methodology to build an aryl-substituted MOP ligand library (Table 4).[19] When (*R*)-H-MOP (**6**) was employed, the direct arylation product (*R*)-Ph-MOP (**7aa**) was generated in 55% yield without erosion of the *ee* value. A wide range of aryl bromides bearing both electron-donating (**7ab–ae**) and electron-withdrawing groups (**7ag–al**) proved to be suitable coupling partners for this reaction with acceptable yields and excellent stereochemical reliability. Disubstituted aryl bromides (**7am–ao**), and 2-naphthyl bromide (**7ap**) were also compatible with this stereospecific process. In addition, this method also allowed direct arylation of the P-stereogenic monophosphine **8**,[20] thus affording a bulky and stable chiral ligand **9** with excellent yield and enantioselectivity (Scheme 2).

Finally, we tested the newly constructed ligand libraries in two important catalytic transformations (Scheme 3). In palladium-catalyzed arylation of the carboxylic ester **11**, β-arylation was predominantly observed with *o*-fluorobromobenzene (**10′**), whereas α-arylation was primarily observed with *m*-fluorobromobenzene (**10**) for all ligands except with DavePhos (**1b**), which gave a 47:53 mixture of the α- and β-arylated products **12** and **13**, respectively.[21] After a preliminary screening of the modified phosphine ligands in Table 2,

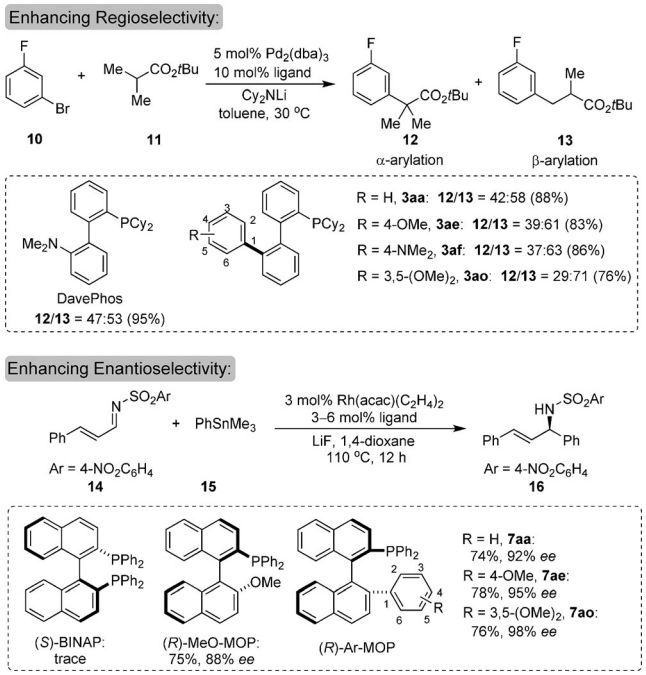
Table 4: Construction of (*R*)-Ar-MOP library.



[a] Reaction conditions: 5 mol% [{Rh(cod)Cl}$_2$], **6a** (0.20 mmol), **2** (2.0 mmol), and LiO*t*Bu (0.6 mmol) in 1 mL 1,4-dioxane at 150 °C under argon, 4 days. Yields of products isolated after chromatography. For X-ray structures the thermal ellipsoids are shown at 30% probability.[23]



Scheme 2. Direct arylation of the ligand **8** (Tang's ligand).



Scheme 3. Testing the developed phosphine ligand libraries.

we found that Ph-CyJohnPhos **3aa** could provide a better result on regioselectivity (42:58). Further investigation with the monoaryl-substituted CyJohnPhos library, **3ao** was found to be the best ligand for the β-arylated product **13** (29:71). We also explored the developed Ar-MOP ligand library in rhodium-catalyzed asymmetric arylation of the α,β-unsaturated imine **14** with the arylstannane **15**.[17b,22] Compared to the BINAP ligand, the monodentate ligand MeO-MOP showed good reactivity and afforded the desired product **16** in 75% yield and 88% *ee*. When the ligand was switched to our modified Ar-MOP library, application of the ligand **7ao** dramatically increased the enantioselectivity to 98% with 76% yield. These examples proved the potential of the developed ligand libraries in catalytic reactions.

In summary, a series of monophosphine ligand libraries have been developed by rhodium(I)-catalyzed direct arylation of commercially available ligands, in which the mono- and diselectivity can be controlled. The reaction does not require the addition of an exogenous ligand, and is applicable to the coupling of various aryl bromides and aryl chlorides with the aid of the dialkyl and diaryl phosphino groups from the parent scaffolds. Further exploration of new reactions using these ligand libraries is ongoing in our laboratory.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: arylation · biaryls · C–H activation · P ligands · rhodium

[1] For a very recent example on monophosphine ligand design, see: K. Wu, A. G. Doyle, *Nat. Chem.* **2017**, https://doi.org/10.1002/nchem.2741.

[2] a) P. Ruiz-Castillo, S. L. Buchwald, *Chem. Rev.* **2016**, *116*, 12564; b) A. C. Sather, S. L. Buchwald, *Acc. Chem. Res.* **2016**, *49*, 2146.

[3] a) A. Zapf, R. Jackstell, F. Rataboul, T. Riermeier, A. Monsees, C. Fuhrmann, N. Shaikh, U. Dingerdissen, M. Beller, *Chem. Commun.* **2004**, 38; b) X.-F. Wu, H. Neumann, A. Spannenberg, T. Schulz, H. Jiao, M. Beller, *J. Am. Chem. Soc.* **2010**, *132*, 14596; c) L. Wu, I. Fleischer, R. Jackstell, I. Profir, R. Franke, M. Beller, *J. Am. Chem. Soc.* **2013**, *135*, 14306; d) L. Wu, I. Fleischer, R. Jackstell, M. Beller, *J. Am. Chem. Soc.* **2013**, *135*, 3989; e) H. Li, K. Dong, H. Jiao, H. Neumann, R. Jackstell, M. Beller, *Nat. Chem.* **2016**, *8*, 1159.

[4] a) C. M. So, Z. Zhou, C. P. Lau, F. K. Kwong, *Angew. Chem. Int. Ed.* **2008**, *47*, 6402; *Angew. Chem.* **2008**, *120*, 6502; b) C. M. So, C. P. Lau, F. K. Kwong, *Angew. Chem. Int. Ed.* **2008**, *47*, 8059;

Angew. Chem. **2008**, *120*, 8179; c) P. Y. Yeung, C. M. So, C. P. Lau, F. K. Kwong, *Angew. Chem. Int. Ed.* **2010**, *49*, 8918; *Angew. Chem.* **2010**, *122*, 9102.
[5] a) Q. Shelby, N. Kataoka, G. Mann, J. Hartwig, *J. Am. Chem. Soc.* **2000**, *122*, 10718; b) G. Mann, C. Incarvito, A. L. Rheingold, J. F. Hartwig, *J. Am. Chem. Soc.* **1999**, *121*, 3224.
[6] a) T. Hama, X. Liu, D. A. Culkin, J. F. Hartwig, *J. Am. Chem. Soc.* **2003**, *125*, 11176; b) T. Hama, D. A. Culkin, J. Hartwig, *J. Am. Chem. Soc.* **2006**, *128*, 4976; c) Y. Nakao, M. Takeda, T. Matsumoto, T. Hiyama, *Angew. Chem. Int. Ed.* **2010**, *49*, 4447; *Angew. Chem.* **2010**, *122*, 4549; d) S. G. Newman, J. K. Howell, N. Nicolaus, M. Lautens, *J. Am. Chem. Soc.* **2011**, *133*, 14916; e) S. G. Newman, M. Lautens, *J. Am. Chem. Soc.* **2011**, *133*, 1778; f) D. A. Petrone, M. Lischka, M. Lautens, *Angew. Chem. Int. Ed.* **2013**, *52*, 10635; *Angew. Chem.* **2013**, *125*, 10829; g) Q. Li, C. W. Liskey, J. F. Hartwig, *J. Am. Chem. Soc.* **2014**, *136*, 8755.
[7] a) D. A. Watson, M. Su, G. Teverovskiy, Y. Zhang, J. García-Fortanet, T. Kinzel, S. L. Buchwald, *Science* **2009**, *325*, 1661; b) T. J. Maimone, P. J. Milner, T. Kinzel, Y. Zhang, M. K. Takase, S. L. Buchwald, *J. Am. Chem. Soc.* **2011**, *133*, 18106; c) H. G. Lee, P. J. Milner, S. L. Buchwald, *J. Am. Chem. Soc.* **2014**, *136*, 3792.
[8] A. C. Sather, H. G. Lee, V. Y. De La Rosa, Y. Yang, P. Müller, S. L. Buchwald, *J. Am. Chem. Soc.* **2015**, *137*, 13433.
[9] D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624.
[10] For X-ray structural characterization of **1a″** and related structures, see: a) A. R. O'Connor, W. Kaminsky, D. M. Heinekey, K. I. Goldberg, *Organometallics* **2011**, *30*, 2105; b) Z. Liu, H. Yamamichi, S. T. Madrahimov, J. F. Hartwig, *J. Am. Chem. Soc.* **2011**, *133*, 2772.
[11] L. Ackermann, *Chem. Rev.* **2011**, *111*, 1315.
[12] a) Y. Yang, X. Qiu, Y. Zhao, Y. Mu, Z. Shi, *J. Am. Chem. Soc.* **2016**, *138*, 495; b) Y. Yang, L. R. Zhao, Y. Zhao, D. Z. Shi, *J. Am. Chem. Soc.* **2016**, *138*, 8734.
[13] a) R.-B. Hu, H. Zhang, X.-Y. Zhang, S.-D. Yang, *Chem. Commun.* **2014**, *50*, 2193; b) Y.-N. Ma, S.-D. Yang, *Chem. Eur. J.* **2015**, *21*, 6673.
[14] a) H.-Y. Zhang, H.-M. Yi, G.-W. Wang, B. Yang, S.-D. Yang, *Org. Lett.* **2013**, *15*, 6186; b) D. Zhao, C. Nimphius, M. Lindale, F. Glorius, *Org. Lett.* **2013**, *15*, 4504; c) T. Ryu, J. Kim, Y. Park, S. Kim, P. H. Lee, *Org. Lett.* **2013**, *15*, 3986; d) D. Gwon, D. Lee, J. Kim, S. Park, S. Chang, *Chem. Eur. J.* **2014**, *20*, 12421; e) Y. Unoh, T. Satoh, K. Hirano, M. Miura, *ACS Catal.* **2015**, *5*, 6634.
[15] For rhodium-mediated *ortho*-arylation of substituted phenol with either phosphinite or phosphonite as a cocatalyst, see: a) L. N. Lewis, J. F. Smith, *J. Am. Chem. Soc.* **1986**, *108*, 2728; b) R. B. Bedford, S. J. Coles, M. B. Hursthouse, M. E. Limmert, *Angew. Chem. Int. Ed.* **2003**, *42*, 112; *Angew. Chem.* **2003**, *115*, 116; c) S. Oi, S. Watanabe, S. Fukita, Y. Inoue, *Tetrahedron Lett.* **2003**, *44*, 8665; d) R. B. Bedford, M. Betham, A. J. M. Caffyn, J. P. H. Charmant, L. C. Lewis-Alleyne, P. D. Long, D. Polo-Cerónac, S. Prashar, *Chem. Commun.* **2008**, 990; e) J.-F. Yang, R.-H. Wang, Y.-X. Wang, W.-W. Yao, Q.-S. Liu, M. Ye, *Angew. Chem. Int. Ed.* **2016**, *55*, 14116; *Angew. Chem.* **2016**, *128*, 14322.
[16] J. Wencel-Delord, F. Glorius, *Nat. Chem.* **2013**, *5*, 369.
[17] a) A. Aranyos, D. W. Old, A. Kiyomori, J. P. Wolfe, J. P. Sadighi, S. L. Buchwald, *J. Am. Chem. Soc.* **1999**, *121*, 4369; b) T. Hayaship, M. Ishigedani, *Tetrahedron* **2001**, *57*, 2589; c) L. Bonnafoux, F. R. Leroux, F. Colobert, *Beilstein J. Org. Chem.* **2011**, *7*, 1278; d) M. J. Fer, J. Cinqualbre, J. Bortoluzzi, M. Chessé, F. R. Leroux, A. Panossian, *Eur. J. Org. Chem.* **2016**, 4545.
[18] For an iridium-catalyzed phosphine-directed C–H borylation, see: K. M. Crawford, T. R. Ramseyer, C. J. A. Daley, T. B. Clark, *Angew. Chem. Int. Ed.* **2014**, *53*, 7589; *Angew. Chem.* **2014**, *126*, 7719.
[19] a) T. Hayashi, *Acc. Chem. Res.* **2000**, *33*, 354; b) T. Hayashi, J.-W. Han, A. Takeda, J. Tang, K. Nohmi, K. Mukaide, H. Tsuji, Y. Uozumi, *Adv. Synth. Catal.* **2001**, *343*, 279; c) T. Shimada, Y.-H. Cho, T. Hayashi, *J. Am. Chem. Soc.* **2002**, *124*, 13396; d) T. Ohmura, M. Suginome, *Org. Lett.* **2006**, *8*, 2503; e) T. Ohmura, H. Taniguchi, Y. Kondo, M. Suginome, *J. Am. Chem. Soc.* **2007**, *129*, 3518.
[20] a) N. Hu, K. Li, Z. Wang, W. Tang, *Angew. Chem. Int. Ed.* **2016**, *55*, 5044; *Angew. Chem.* **2016**, *128*, 5128; b) W. Fu, M. Nie, A. Wang, W. Tang, *Angew. Chem. Int. Ed.* **2015**, *54*, 2520; *Angew. Chem.* **2015**, *127*, 2550; c) K. Du, P. Guo, Y. Chen, Z. Cao, Z. Wang, W. Tang, *Angew. Chem. Int. Ed.* **2015**, *54*, 3033; *Angew. Chem.* **2015**, *127*, 3076; d) C. Li, D. Chen, W. Tang, *Synlett* **2016**, 2183.
[21] a) A. Renaudat, L. Jean-Gérard, R. Jazzar, C. E. Kefalidis, E. Clot, O. Baudoin, *Angew. Chem. Int. Ed.* **2010**, *49*, 7261; *Angew. Chem.* **2010**, *122*, 7419; b) P. Larini, C. E. Kefalidis, R. Jazzar, A. Renaudat, E. Clot, O. Baudoin, *Chem. Eur. J.* **2012**, *18*, 1932.
[22] a) T. Hayashi, M. Ishigedani, *J. Am. Chem. Soc.* **2000**, *122*, 976.
[23] CCDC 1548865 (**1a′**), 1548866 (**3ba**), 1548867 (**3ka**), 1548868 (**4ja**), 1548869 (**4am**) 1548870 (**5abk**), and 1548872 (**7ah**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Communications

C–H Activation

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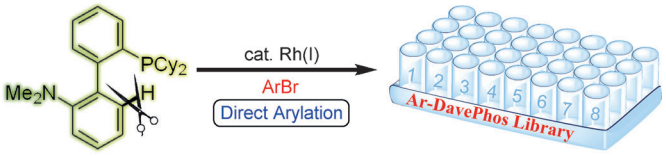
Rhodium(I)-Catalyzed Tertiary Phosphine Directed C–H Arylation: Rapid Construction of Ligand Libraries



Ligand-to-ligand: A catalytic rhodium system has been established for direct and site-selective arylation of commercially available phosphine ligands by tertiary phosphine directed C–H activation. A series of monophosphine ligand libraries containing mono- and diaryl-substituted groups, having different steric and electronic properties, were obtained in high yields.

