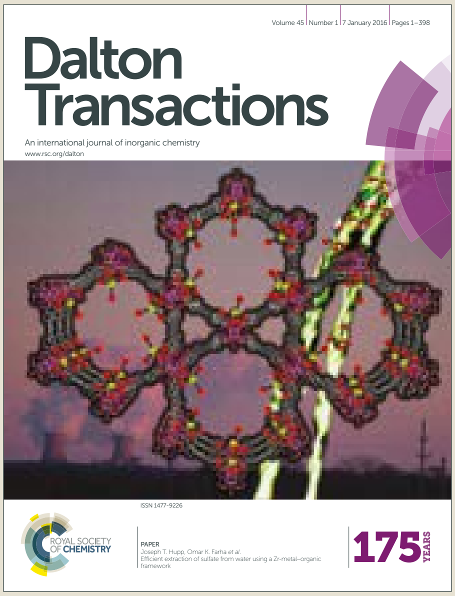
Check for updates

View Article Online
View Journal

Dalton Transactions

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: V. Hardouin Duparc and F. Schaper, *Dalton Trans.*, 2017, DOI: 10.1039/C7DT02260C.



Volume 45 | Number 1 | 7 January 2016 | Pages 1–398
Dalton Transactions
An international journal of inorganic chemistry
www.rsc.org/dalton
ISSN 1477-9226
ROYAL SOCIETY OF CHEMISTRY
PAPER
Joseph T. Hupp, Omar K. Farha et al.
Efficient extraction of sulfate from water using a Zr-metal–organic framework
175 YEARS

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the author guidelines.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the ethical guidelines, outlined in our author and reviewer resource centre, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

View Article Online
DOI: 10.1039/C7DT02260C

Journal Name

COMMUNICATION

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Sulfonato-imino copper(II) complexes : fast and general Chan-Evans-Lam coupling of amines and anilines

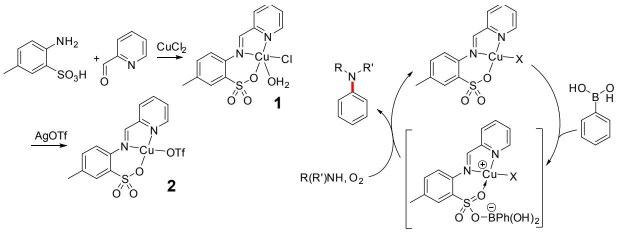
V. Hardouin Duparc,[a] and F. Schaper[a,*]

Sulfonato-imine copper complexes with either chloride or triflate counteranions were prepared in a one-step reaction followed by anion-exchange. They are highly active in Chan-Evans-Lam couplings under mild conditions with a variety of amines or anilines, in particular with sterically hindered substrates. No optimization of reaction conditions other than time and/or temperature is required.

Palladium-catalyzed bond formations are in general without competition with regard to scope and reactivity, but the toxicity and high reactivity of trace amounts of palladium raised concerns, in particular in the pharmaceutical industry.[1] The copper-catalyzed Chan-Evans-Lam coupling of boronic acids with alcohols, amines or other nucleophiles to form carbon-heteroatom bonds provides an alternative bond-forming reaction, using milder conditions compared to the related Ullmann-Goldberg reaction[2] or to the analogous Buchwald-Hartwig coupling using Pd.[3, 4] Following the original work of Chan, Evans and Lam,[5-7] a large number of studies have opened a wide substrate scope and allowed reactions using catalytic amounts of copper.[8-16] With regard to catalyst performance, copper salts with acetates and or triflate counterions are often preferable over halogens or perchlorate anions,[17, 18] possibly due to pre-coordination of boronic acid to the anion.[18-20] Chan-Evans-Lam couplings also often require the addition of base, but its mechanistic implication is unclear and one of its roles might be that of a ligand activating dinuclear $Cu_2(OAc)_2$.[19] For these reasons, Chan-Evans-Lam couplings using $Cu(OAc)_2$ or other simple copper salts react strongly to changes in reaction conditions such as solvent and the nature of the base used. Yields and rates can vary unpredictably, even for closely related substrates,[12] and reaction conditions have to be adapted accordingly.[8] Even then, several substrates show only low or no reactivity.[9]

We decided to investigate copper coordination complexes with imino-sulfonate ligands (Scheme 1) as potential catalysts for Chan-Evans-Lam couplings. The chelating ligand removes the need for external "base" as ligand and reduces dependence of catalyst performance on the solvent. The sulfonate group incorporated in the ligand enables coordination to boronic acid (see the proposed intermediate in Scheme 1), which should make the choice of counter-ion less important. Although several studies reported improved catalytic performance when nitrogen ligands, such as TMEDA, were added to Chan-Evans-Lam couplings,[21-25] only a very limited amount of studies used preformed coordination complexes instead of simple copper salts.[26-32] Of these, $[Cu(DMAP)_4I]I$, recently reported by Phukan, displayed high activity to a variety of amines and anilines.[32]

Scheme 1



---

[a] Centre in Green Chemistry and Catalysis, Department of chemistry, Université de Montréal, C. P. 6128 Succ. Centre-Ville, Montréal, QC, H3T 3J7, Canada.

* Frank.Schaper@umontreal.ca

Electronic Supplementary Information (ESI) available: Additional figures and tables, experimental details and X-ray diffraction analyses (CIF)]. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C7DT02260C

Chloride complex **1** can be readily prepared in a one-pot reaction from commercially available starting materials, following protocols for similar complexes.[33] Anion exchange provided the triflate complex **2** (Scheme 1). The crystal structure of **2** shows a tetragonally distorted octahedral coordination geometry around copper (Fig. 1). The triflate anion is coordinated in the equatorial plane with a Cu-O distance comparable to that of the sulfonate ligand (1.929(1) and 2.015(1), respectively). Bridging coordination of the triflate and sulfonate ligands of neighbouring molecules to the apical positions ($d_{\text{Cu-O}}$ = 2.4 – 2.5 Å) leads to formation of a 1D-coordination polymer along the crystallographic *b*-axis (Fig. S1). The increased Lewis acidity of copper due to the weakly coordinating triflate anion is likely responsible for the octahedral coordination environment and the slightly shorter bond distances in **2** when compared to similar Cu complexes with chloride or carboxylate counteranions, which show square-pyramidal coordination geometries without bridging sulfonate groups.[33-37] It should be noted that the formation of the coordination polymer strongly resembles the interaction of **2** with boronic acid proposed in Scheme 1: bridging coordination of the sulfonate group to a Lewis-acidic centre (Cu or B, Fig. 1) and interaction of an anionic group on this centre with copper (triflate or Ph). Chloride complex **1** shows square-pyramidal coordination geometry (τ = 0.1, Fig. S2) and is very similar to that of the related complex without the 3-methyl group, in which water is replaced by a μ-chloride ligand.[34]

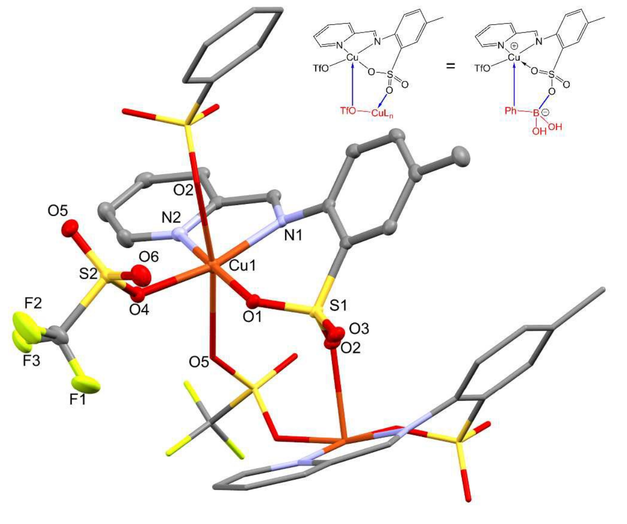


Figure 1. X-ray structure of **2**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and co-crystallized dichloromethane were omitted for clarity. Selected bond distances (Å) and angles (°): Cu-N1 = 2.0261(13), Cu-N2 = 1.967(1), Cu-O1 = 1.929(1), Cu-O4 = 2.015(1), Cu-O2= 2.379(1), Cu-O4 = 2.488(1), N1-Cu-N2 = 81.89(5), N2-Cu-O4 = 93.58(5), O1-Cu-O4 = 91.38(5), N1-Cu-O1 = 94.25(5), X-Cu-O2 = 82.18(4)-94.18(5).

Catalytic performance. Complex **1** catalyses the Chan-Evans-Lam coupling of aniline with phenyl boronic acid in a variety of solvents (Table S1). Increasing polarity led to higher activity (until deactivation in acetonitrile, probably by solvent coordination to copper), but variations were relatively small. We were grateful to note that addition of external base was indeed not necessary. To the contrary, its presence even in catalytic amounts drastically reduced activity (Table S1), in agreement with the mechanistic interpretation that nitrogen bases employed in Chan-Evans-Lam couplings act as a ligands. Presence of water was tolerated and addition of molecular sieves did not improve the reaction (Table S1). Complex **2** was slightly more active than **1** with 98% and 86% conversion, respectively, after 320 min (Table S1). Kinetic studies showed that this was mainly due to a longer induction period for **1** (40 min vs. 10 min for **2**), after which the reaction proceeded with very similar rates ($k_{\text{obs}}(\mathbf{1})$ = 0.37(3) h^{-1}, $k_{\text{obs}}(\mathbf{2})$ = 0.49(1) h^{-1}, Fig. S3). Similar rates, but different induction periods indicate that the anion most likely dissociates from copper and does not further participate in the reaction mechanism. The presence of the chelating sulfonate ligand thus eliminated the requirement of an acetate or triflate counteranion, catalytic performance was good in a variety of solvents and no additional base/ligand was needed. Together with the tolerance towards water, this removed the main variables which typically need to be optimized in Chan-Evans-Lam couplings and which required different protocols even for substrates as closely related as amines and anilines.[38, 39] Complex **2** could thus be applied in base-free Chan-Evans-Lam couplings without any optimization of reaction conditions and the arylation of anilines, primary and secondary amines proceeded with quantitative conversion (Chart 1, isolated yields >85%) at room temperature and in 12 h reaction time.

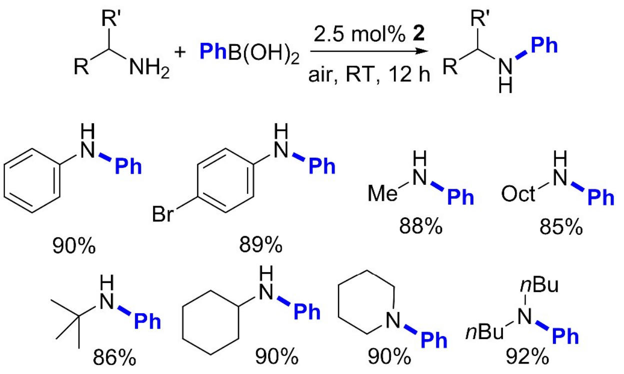
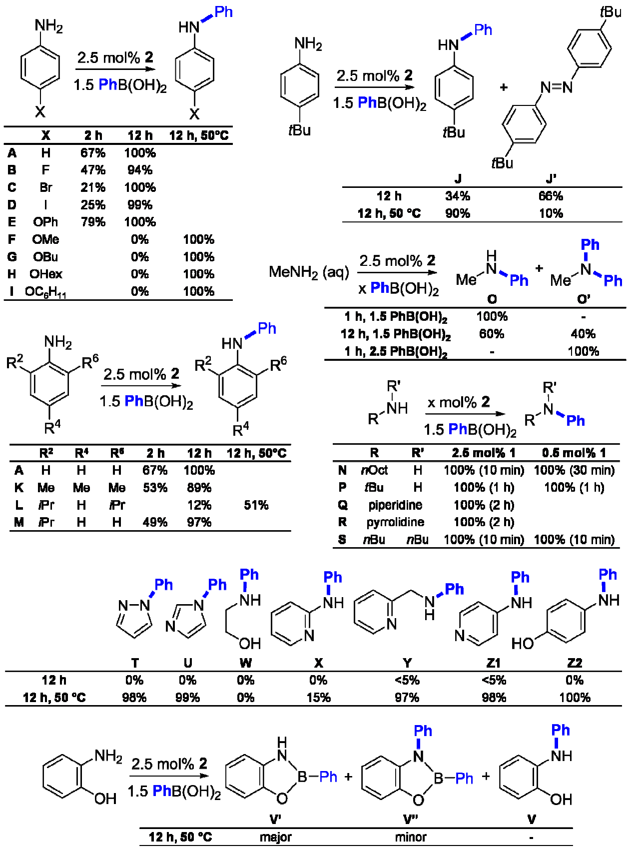


Chart 1. Isolated yields for arylations with **2**

Reactivity studies. Given the good reactivity towards amines and anilines in general, the reactivity of different substrates was investigated in more detail with particular attention towards substrates reported to be less reactive. Complex **2** was chosen for these studies, since its shorter induction time facilitates reactivity comparisons at short reaction times. Poorer nucleophiles are generally more difficult to react in Chan-Evans-Lam couplings,[30, 39-41] but *para*-fluoro, -bromo or -iodo anilines reacted only slightly slower than unsubstituted aniline (Chart 2, **A**-**D**). While *para*-phenoxy aniline reacted readily at room temperature (**E**), anilines carrying alkoxy substituents in *para*-position surprisingly only yielded starting

View Article Online
DOI: 10.1039/C7DT02260C



	X	2 h	12 h	12 h, 50°C
A	H	67%	100%	
B	F	47%	94%	
C	Br	21%	100%	
D	I	25%	99%	
E	OPh	79%	100%	
F	OMe		0%	100%
G	OBu		0%	100%
H	OHex		0%	100%
I	OC_6H_{11}		0%	100%

	J	J'
12 h	34%	66%
12 h, 50 °C	90%	10%

	O	O'
1 h, 1.5 $PhB(OH)_2$	100%	-
12 h, 1.5 $PhB(OH)_2$	60%	40%
1 h, 2.5 $PhB(OH)_2$	-	100%

	R^2	R^4	R^6	2 h	12 h	12 h, 50°C
A	H	H	H	67%	100%	
K	Me	Me	Me	53%	89%	
L	*i*Pr	H	*i*Pr		12%	51%
M	*i*Pr	H	H	49%	97%	

	R	R'	2.5 mol% 1	0.5 mol% 1
N	*n*Oct	H	100% (10 min)	100% (30 min)
P	*t*Bu	H	100% (1 h)	100% (1 h)
Q	piperidine		100% (2 h)	
R	pyrrolidine		100% (2 h)	
S	*n*Bu	*n*Bu	100% (10 min)	100% (10 min)

	T	U	W	X	Y	Z1	Z2
12 h	0%	0%	0%	0%	<5%	<5%	0%
12 h, 50 °C	98%	99%	0%	15%	97%	98%	100%

	V'	V''	V
12 h, 50 °C	major	minor	-

Chart 2. Conversion to product (determined by GC-MS vs. internal calibrated standard) for the coupling of nitrogen nucleophiles with phenyl boronic acid.

material (**F**-**I**). Since formation of diphenyl side product was likewise suppressed in these reactions, electron-rich anilines probably coordinate to either copper or boron in an unproductive off-cycle complex. Dissociation of these complexes would be more favourable at higher temperatures and full conversion can be achieved by conducting the reaction at 50 °C (**F**-**I**).‡ In the case of *para*-*tert*-butyl aniline, the reaction yielded a 1:2 mixture of the coupling product (**J**) and 4,4'-di(*tert*-butyl)azobenzene (**J'**). Cu-catalyzed formation of azabenzenes by aerial oxidation of anilines is well established,[42, 43] but has not been reported as a side reaction in Chan-Evans-Lam couplings. At 50 °C, aza-benzene formation was reduced to 10%, but could not be suppressed completely.

Chan-Evans-Lam couplings of sterically demanding *ortho*-disubstituted anilines are typically difficult[32, 38, 39, 44-48] and only few optimized protocols report yields above 80%.[39, 45, 46, 48] Complex **2** coupled 2,4,6-dimethylaniline (**K**) with only slightly lower activity than aniline. 2,6-Diisopropyl aniline reacted more slowly and only partial conversion of 51% was observed even after 12 h at 50 °C (**L**). We are aware of only one other Cu-catalyzed coupling of diisopropylaniline with arylboronic acid.[49] If one *i*Pr-substituent is removed, coupling proceeds readily at room temperature (**M**).

Amines react in general faster and easier than anilines. Primary amines typically reached full conversion in less than 2 h at ambient temperature. Catalytic activity was investigated in more detail with octylamine (**N**) and full conversion could be achieved in 30 min with a reduced catalyst loading of 0.5 mol%. The tolerance of water in Chan-Evans-Lam couplings with **2** allowed the use of an aqueous solution of methylamine, which readily reacted in 1 h to MeN(Ph)H (**O**). To the best of our knowledge, no copper-catalyzed coupling of boronic acids with methylamine has been reported. Prolonged reaction times led in this case to the appearance of the double coupling product, $MeNPh_2$ (**O'**). The second coupling is, however, notably slower and formation of $MeNPh_2$ can be avoided by controlling reaction time or reducing the excess of phenyl boronic acid. With 2.5 equiv of phenyl boronic acid, full conversion to $MeNPh_2$ (**O'**) was observed after 12 h. The same product was obtained from coupling of *N*-methyl aniline.

Increased steric hindrance typically overcomes the increase in nucleophilicity and tertiary alkyl amines show very low activities in Chan-Evans-Lam couplings.[38] Couplings of *tert*-butyl amine have been reported with (isolated) yields of 28% – 60% using reaction temperatures of 40 – 80 °C and 20 – 24 h reaction time.[50-52] Coupling of *tert*-butyl amine with phenyl boronic acid using **2** proceeds with drastically higher activity and full conversion is achieved at room temperature in 1 h, even at lowered catalyst loadings of 0.5 mol% (**P**).

Cyclic secondary amines, such as piperidine (**Q**) and pyrrolidine (**R**), undergo Chan-Evans-Lam couplings readily,[5] and full conversion is also obtained with **2** at room temperature in 2 h. Low reactivity of acyclic secondary amines, on the other hand, has been reported as a "*major restriction*" in copper-catalyzed coupling reactions.[9] Reactions with $Cu(OAc)_2$ as a catalyst typically require longer reaction times at elevated temperature and yields vary between traces to 60%.[39, 41, 45, 50, 51, 53-56] Using (Xantphos)Cu(O*t*Bu) as catalyst, Lalic obtained iPr_2NAr from benzoyloxy diisopropylamine in 94% conversion at 60 °C.[48] Phukan reported yields of 83% – 94% in 5 – 10 min for the coupling of *N*-methyl-benzylamine to various arylboronic acids using 2 mol% of a highly active $[(DMAP)_4CuI]I$ catalyst.[32] Using **2**, dibutylamine showed full conversion to nBu_2NPh in 10 min at room temperature at reduced catalyst loadings of 0.5% (**S**).

Pyrazol (**T**) and imidazole (**U**) could also be successfully coupled at 50 °C, using the same reaction conditions employed for amines and anilines. *Ortho*-amino phenol, amino ethanol and *ortho*-amino pyridine did not react or only sluggishly (**V**-**X**), probably due to formation of phenyl boronic esters which were identified by GC-MS for *ortho*-aminophenol (**V'**, **V"**). Addition of glycol, of $B(OH)_3$[19] or both, did not change the reaction outcome. Picolylamine (**Y**) was coupled successfully, but was the only alkylamine which required heating. Consequently, *para*-amino pyridine (**Z1**) and *para*-amino phenol (**Z2**), which cannot form chelated boronic esters, were coupled quantitatively at 50 °C. Using $Cu(OAc)_2$ catalyst, couplings of *para*-amino phenol were reported with up to 75% (isolated) yield, but required carefully optimized reaction conditions (dioxane, 90 °C, 12 h, $CsCO_3$, benzoic acid).[57] As with **2**, *ortho*-aminophenols could not be coupled.

View Article Online
DOI: 10.1039/C7DT02260C

In conclusion, use of a chelating ligand containing a sulfonate group able to coordinate to boronic acid afforded a highly active catalyst for Chan-Evans-Lam couplings, which does not require additional base/ligand, tolerates the presence of water and displays only slight dependence of activity on the solvent and the counter-anion. Consequently, no optimization of reaction conditions other than time and temperature was necessary to achieve full conversion to product for the coupling of a large variety of amines and anilines, including substrates generally considered challenging. In particular, sterically crowded substrates, such as 2,4,6-trimethylaniline, *tert*-butylamine and dibutylamine, react readily. Considering also the similarly high activity reported for $[Cu(DMAP)_4I]I$ with amines and anilines,[32] the use of preformed coordination complexes can provide more universal Chan-Evans-Lam coupling protocols than simple copper salt catalysts.

Notes and references

‡ Heated reactions were conducted under oxygen atmosphere. Reactions in open vessels under ambient atmosphere led either to significant evaporation of amine and/or to reduced yields due to reduced oxygen uptake in the presence of solvent vapour.

1. K. Koide, in *New Trends in Cross-Coupling: Theory and Applications*, The Royal Society of Chemistry, 2015, DOI: 10.1039/9781782620259-00779, pp. 779.
2. Y. Jiang and D. Ma, in *Copper-Mediated Cross-Coupling Reactions*, John Wiley & Sons, Inc., 2013, DOI: 10.1002/9781118690659.ch1, pp. 1.
3. F. Paul, J. Patt and J. F. Hartwig, *J. Am. Chem. Soc.*, 1994, **116**, 5969.
4. A. S. Guram and S. L. Buchwald, *J. Am. Chem. Soc.*, 1994, **116**, 7901.
5. D. M. T. Chan, K. L. Monaco, R.-P. Wang and M. P. Winters, *Tetrahedron Lett.*, 1998, **39**, 2933.
6. D. A. Evans, J. L. Katz and T. R. West, *Tetrahedron Lett.*, 1998, **39**, 2937.
7. P. Y. S. Lam, C. G. Clark, S. Saubern, J. Adams, M. P. Winters, D. M. T. Chan and A. Combs, *Tetrahedron Lett.*, 1998, **39**, 2941.
8. S. V. Ley and A. W. Thomas, *Angew. Chem., Int. Ed.*, 2003, **42**, 5400.
9. G. Evano, N. Blanchard and M. Toumi, *Chem. Rev.*, 2008, **108**, 3054.
10. F. Bellina and R. Rossi, *Adv. Synth. Catal.*, 2010, **352**, 1223.
11. J. X. Qiao and P. Y. S. Lam, in *Boronic Acids*, Wiley-VCH Verlag GmbH & Co. KGaA, 2011, DOI: 10.1002/9783527639328.ch6, pp. 315.
12. I. P. Beletskaya and A. V. Cheprakov, *Organometallics*, 2012, **31**, 7753.
13. T. R. M. Rauws and B. U. W. Maes, *Chem. Soc. Rev.*, 2012, **41**, 2463.
14. K. Sanjeeva Rao and T.-S. Wu, *Tetrahedron*, 2012, **68**, 7735.
15. L. Neuville, in *Copper-Mediated Cross-Coupling Reactions*, John Wiley & Sons, Inc., 2013, DOI: 10.1002/9781118690659.ch4, pp. 113.
16. P. Y. S. Lam, in *Synthetic Methods in Drug Discovery: Volume 1*, The Royal Society of Chemistry, 2016, vol. 1, pp. 242.
17. D. N. Rao, S. Rasheed, S. Aravinda, R. A. Vishwakarma and P. Das, *RSC Adv.*, 2013, **3**, 11472.
18. A. E. King, B. L. Ryland, T. C. Brunold and S. S. Stahl, *Organometallics*, 2012, **31**, 7948.
19. J. C. Vantourout, H. N. Miras, A. Isidro-Llobet, S. Sproules and A. J. B. Watson, *J. Am. Chem. Soc.*, 2017, **139**, 4769.
20. T. Garnier, R. Sakly, M. Danel, S. Chassaing and P. Pale, *Synthesis*, 2017, **49**, 1223.
21. J. P. Collman and M. Zhong, *Org. Lett.*, 2000, **2**, 1233.
22. J. P. Collman, M. Zhong, C. Zhang and S. Costanzo, *J. Org. Chem.*, 2001, **66**, 7892.
23. S. S. van Berkel, A. van den Hoogenband, J. W. Terpstra, M. Tromp, P. W. N. M. van Leeuwen and G. P. F. van Strijdonck, *Tetrahedron Lett.*, 2004, **45**, 7659.
24. M. Tromp, G. P. F. van Strijdonck, S. S. van Berkel, A. van den Hoogenband, M. C. Feiters, B. de Bruin, S. G. Fiddy, A. M. J. van der Eerden, J. A. van Bokhoven, P. W. N. M. van Leeuwen and D. C. Koningsberger, *Organometallics*, 2010, **29**, 3085.
25. T. Onaka, H. Umemoto, Y. Miki, A. Nakamura and T. Maegawa, *J. Org. Chem.*, 2014, **79**, 6703.
26. B. Liu, B. Liu, Y. Zhou and W. Chen, *Organometallics*, 2010, **29**, 1457.
27. L. Wang, Z. Jiang, L. Yu, L. Li, Z. Li and X. Zhou, *Chem. Lett.*, 2010, **39**, 764.
28. M. Islam, S. Mondal, P. Mondal, A. Roy, K. Tuhina, M. Mobarok, S. Paul, N. Salam and D. Hossain, *Catal. Lett.*, 2011, **141**, 1171.
29. B. Kaboudin, Y. Abedi and T. Yokomatsu, *Eur. J. Org. Chem.*, 2011, **2011**, 6656.
30. A. Gogoi, G. Sarmah, A. Dewan and U. Bora, *Tetrahedron Lett.*, 2014, **55**, 31.
31. Anuradha, S. Kumari and D. D. Pathak, *Tetrahedron Lett.*, 2015, **56**, 4135.
32. S. Roy, M. J. Sarma, B. Kashyap and P. Phukan, *Chem. Commun. (Cambridge, U. K.)*, 2016, **52**, 1170.
33. S. Hazra, S. Mukherjee, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *RSC Adv.*, 2014, **4**, 48449.
34. Y.-M. Ou, Z.-Y. Zhao, Yue-Hua Shi, Y.-L. Zhang and Y.-M. Jiang, *Chin. J. Struct. Chem.*, 2009, **28**, 457.
35. G.-G. Yang, M. Ou-Yang, X.-J. Meng, X.-R. Huang and Y.-M. Jiang, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2009, **65**, m1200.
36. S. Hazra, A. Karmakar, M. d. F. C. Guedes da Silva, L. u. Dlhan, R. Boca and A. J. L. Pombeiro, *New J. Chem.*, 2015, **39**, 3424.
37. S. Hazra, A. P. C. Ribeiro, M. F. C. Guedes da Silva, C. A. Nieto de Castro and A. J. L. Pombeiro, *Dalton Trans.*, 2016, **45**, 13957.
38. T. D. Quach and R. A. Batey, *Org. Lett.*, 2003, **5**, 4397.
39. J. C. Antilla and S. L. Buchwald, *Org. Lett.*, 2001, **3**, 2077.
40. S. Chen, H. Huang, X. Liu, J. Shen, H. Jiang and H. Liu, *J. Comb. Chem.*, 2008, **10**, 358.
41. J. C. Vantourout, R. P. Law, A. Isidro-Llobet, S. J. Atkinson and A. J. B. Watson, *J. Org. Chem.*, 2016, **81**, 3942.
42. A. P. Terent'ev and Y. D. Mogilyanskii, *Zh. Obshch. Khim.*, 1958, **28**, 1959.
43. K. Keiz, *Bull. Chem. Soc. Jpn.*, 1959, **32**, 777.
44. G. C. H. Chiang and T. Olsson, *Org. Lett.*, 2004, **6**, 3079.
45. G. W. Kabalka and L.-L. Zhou, *Letters in Organic Chemistry* 2006, **3**, 320

View Article Online
DOI: 10.1039/C7DT02260C

46. K. A. McGarry, A. A. Duenas and T. B. Clark, *J. Org. Chem.*, 2015, **80**, 7193.
47. J. Bao and G. K. Tranmer, *Tetrahedron Lett.*, 2016, **57**, 654.
48. R. P. Rucker, A. M. Whittaker, H. Dang and G. Lalic, *Angew. Chem., Int. Ed.*, 2012, **51**, 3953.
49. W. Zhong, Z. Liu, C. Yu and W. Su, *Synlett*, 2008, **2008**, 2888.
50. T. D. Quach and R. A. Batey, *Org. Lett.*, 2003, **5**, 1381.
51. X.-Q. Yu, Y. Yamamoto and N. Miyaura, *Chemistry – An Asian Journal*, 2008, **3**, 1517.
52. A. Joliton and E. M. Carreira, *Synlett*, 2015, **11**, 737.
53. A. P. Combs, S. Tadesse, M. Rafalski, T. S. Haque and P. Y. S. Lam, *J. Comb. Chem.*, 2002, **4**, 179.
54. S. Benard, L. Neuville and J. Zhu, *Chem. Commun. (Cambridge, U. K.)*, 2010, **46**, 3393.
55. N. Debreczeni, A. Fodor and Z. Hell, *Catal. Lett.*, 2014, **144**, 1547.
56. K. Singh, M. Kumar, E. Pavadai, K. Naran, D. F. Warner, P. G. Ruminski and K. Chibale, *Bioorg. Med. Chem. Lett.*, 2014, **24**, 2985.
57. A. Siva Reddy, K. Ranjith Reddy, D. Nageswar Rao, C. K. Jaladanki, P. V. Bharatam, P. Y. S. Lam and P. Das, *Organic & Biomolecular Chemistry*, 2017, **15**, 801.

View Article Online
DOI: 10.1039/C7DT02260C

Sulfonato-imino copper(II) complexes : fast and general Chan-Evans-Lam coupling of amines and anilines

V. Hardouin Duparc and F. Schaper

Table of Contents

One size fits all: a simple coordination complex allows Chans-Evans-Lam arylations of a wide variety of amines and anilines without optimization of reaction conditions