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A General and Efficient Palladium-Catalyzed Carbonylative Synthesis of 2-Aryloxazolines and 2-Aryloxazines from Aryl Bromides

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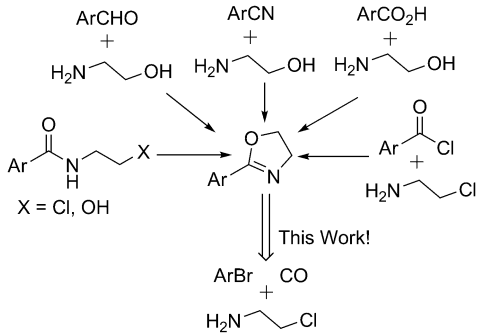
Palladium-catalyzed coupling reactions offer a powerful toolbox for the construction of C–X (X = C, N, O, etc.) bonds, which are frequently applied for the synthesis of pharmaceuticals, agrochemicals, and advanced materials.[1,2] With the importance of these reactions in mind, both academic and industrial chemists are continuously investigating and developing new applications. Among the palladium-catalyzed coupling reactions, palladium-catalyzed carbonylation reactions are elegant in the preparation of carbonyl-containing compounds.[3] By applying CO as a cheap C1 source, the carbon chain of the parent molecules can be easily increased, introducing one or more carbonyl groups into the molecules.

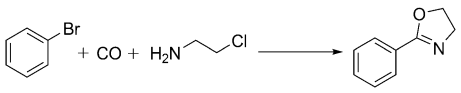
Oxazolines are an important family of chemicals that exist in naturally occurring iron chelators, cytotoxic cyclic peptides, and antimitotic and neuroprotective agents.[4] They also contribute to the flavor of a numbers of foods.[5] Moreover, oxazolines are valuable intermediates in various organic transformations.[6] Because of the importance of oxazolines, a number of methodologies have been developed for the production of these compounds (Scheme 1);[7] they are generally prepared from the corresponding carboxylic acids, carboxylic esters, nitriles, aldehydes, or other carbonyl-containing chemicals. However, it would be extremely interesting if a methodology could be found that can apply CO as the carbonyl source to react with more available aryl bromides as the starting materials, instead of using chemicals that already contain a carbonyl group. To the best of our knowledge, no report on the carbonylative synthesis of 2-oxazolines has been published.[8] Because of the importance of 2-oxazolines, and our ongoing interest in palladium-catalyzed carbonylation reactions,[9] we wish to report, herein, a general and efficient palladium-catalyzed carbonylative synthesis of 2-oxazolines.

The first set of reactions were carried out with six different ligands (Table 1, entries 1–6), in the presence of Pd-



Scheme 1. Methods for oxazoline synthesis.

Table 1. Palladium-catalyzed carbonylative synthesis of oxazolines: Examination of ligands and solvents.[a]



Entry	Ligand ([mol%])	Solvent	Yield [%][b]
1	$BuPAd_2$ (6)	dioxane	36
2	PCy_3 (6)	dioxane	13
3	$P(tBu)_3$ (6)	dioxane	27
4	DPPP (3)	dioxane	27
5	DPPF (3)	dioxane	32
6	DPEphos (3)	dioxane	29
7	$BuPAd_2$ (6)	toluene	51
8	$BuPAd_2$ (6)	DMF	<1
9	$BuPAd_2$ (6)	DMSO	<1
10	$BuPAd_2$ (6)	DMAc	<1
11	$BuPAd_2$ (6)	NMP	<1
12	$BuPAd_2$ (6)	CH_3CN	<1

[a] $Pd(OAc)_2$ (2 mol%), a ligand, a solvent (2 mL), NEt_3 (3 mmol), CO (5 bar), bromobenzene (1 mmol), 2-chloroethylamine hydrochloride (1 mmol), 110 °C, 16 h. Ad = adamantyl; Cy = cyclohexyl; DPPP = 1,3-bis(diphenylphosphino)propane; DPPF = 1,1′-bis(diphenylphosphino)ferrocene; DPEphos = bis(diphenylphosphinophenyl)ether; DMAc = dimethylacetamide; NMP = *N*-methylpyrrolidone. [b] The yields, based on the amount of bromobenzene used, were determined by GC using hexadecane as the internal standard.

$(OAc)_2$ (2 mol%), NEt_3 (3 mmol), and bromobenzene (1 mmol), in dioxane (2 mL), under a CO (5 bar) atmosphere, at 110 °C for 16 h. The ligand $BuPAd_2$ gave a 36% yield of 2-phenyloxazoline (Table 1, entry 1). Bidentate ligands showed similar results (Table 1, entries 4–6). Next, we applied $BuPAd_2$ as the ligand to check the effect of other solvents on the reaction (27–32% yield; Table 1, entries 7–

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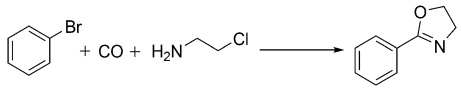
12). Nevertheless, a 51% yield of oxazoline was produced by using toluene as the solvent (Table 1, entry 7), but the other tested solvents resulted in only traces of the desired product. Herein, all of the reactions gave full conversion of bromobenzene and the rest of the starting material was transformed into the dehalogenation product (benzene) instead of into oxazoline.

Next, we chose $BuPAd_2$ in toluene to determine the effect of using different bases (Table 2, entries 1–5), but no better

Table 2. Palladium-catalyzed carbonylative synthesis of oxazolines: Examination of bases and additives.[a]



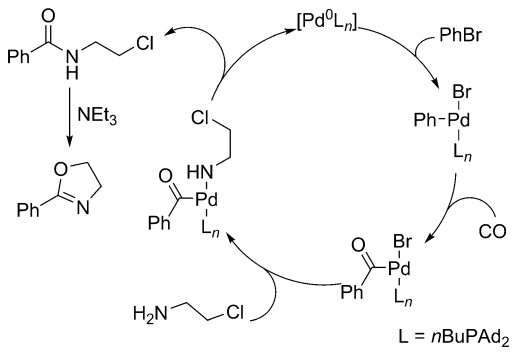
Entry	Base (3 mmol)	Additive (1 mmol)	CO [bar]	Yield [%][b]
1	DiPEA	–	5	40
2	DBU	–	5	0
3	TMEDA	–	5	33
4	DBACO	–	5	0
5	DMAP	–	5	0
6	NEt_3	–	5	55[c]
7	NEt_3	$MgSO_4$	5	60[c]
8	NEt_3	Na_2SO_4	5	44[c]
9	NEt_3	$MgSO_4$	10	80[c]
10	NEt_3	$MgSO_4$	10	66[d]
11	NEt_3	$MgSO_4$	10	45[e]

[a] $Pd(OAc)_2$ (2 mol%), $BuPAd_2$ (6 mol%), toluene (2 mL), base, CO, bromobenzene (1 mmol), 2-chloroethylamine hydrochloride (1 mmol), 110°C, 16 h. DiPEA = *N*,*N*-diisopropylethylamine; DBU = 1,8-diazabicycloundec-7-ene; TMEDA = tetramethylethylenediamine; DABCO = 1,4-diazabicyclo[2.2.2]octane; DMAP = 4-dimethylaminopyridine. [b] The yields, based on the amount of bromobenzene used, were determined by GC using hexadecane as the internal standard. [c] Toluene (4 mL). [d] $Pd(OAc)_2$ (1 mol%), $BuPAd_2$ (3 mol%), toluene (4 mL). [e] 100°C, toluene (4 mL).

yield was observed. The use of 4 mL of toluene can increase the yield of the desired product to 55% (Table 2, entry 6). $MgSO_4$ and Na_2SO_4 were tested as additives; $MgSO_4$ improved the yield of oxazoline to 60% (Table 2, entry 6), but Na_2SO_4 decreased the yield of oxazoline to 44%. To our delight, the yield was improved to 80% by running the reaction under 10 bar of CO (Table 2, entry 9). A 66% yield of oxazoline could still be formed in the presence of only 1 mol% $Pd(OAc)_2$ (Table 2, entry 10).

Based on our experiments, the most probable reaction mechanism is proposed in Scheme 2. The first step is the oxidative addition of bromobenzene to the Pd^0 species, followed by the coordination and insertion of CO to form the acylpalladium intermediate. After nucleophilic attack of 2-chloroethylamine and reductive elimination, *N*-(2-chloroethyl)arylamide is formed as the key intermediate. Under the assistance of a base and high temperatures, 2-aryloxazoline is produced as the final product.

With the best reaction conditions in hand, we tested different substrates in the reaction (Table 3). The generality and variability of this methodology was proven by the synthesis of 27 different oxazolines.



Scheme 2. Proposed reaction mechanism.

Para-methyl- and *ortho*-isopropylbromobenzene gave yields of 70 and 65%, respectively, of the corresponding oxazolines (Table 3, entries 2 and 3). Good yields of the desired products were also produced from the corresponding naphthyl substrates (Table 3, entries 4–6). Methoxyl-, methylthiol-, and *N*,*N*-methyldiamino-substituted aryl bromides were transformed into oxazolines in 65–89% yield (Table 3, entries 7–10). Not only electron-donating groups, but also electron-withdrawing groups were tolerated in the reaction and gave the corresponding products in good yields (Table 3, entries 11–19; 61–85% yield). In addition, eight different heterocycles were successfully transformed into 2-heterocycle-substituted oxazolines in moderate to good yields (Table 3, entries 20–27; 50–89% yield).

Not only five-membered-ring oxazolines, but also six-membered-ring oxazines can be synthesized by using this procedure (Table 4). Both electron-donating- and electron-withdrawing-group-substituted aryl bromides were reacted and gave the corresponding products in good yield (Table 4, entries 2–7; 74–85% yield). Furthermore, four heterocycle-containing aryl bromides were reacted with the aminochloride to give the desired products in good yields (Table 4, entries 8–11; 60–89% yield).

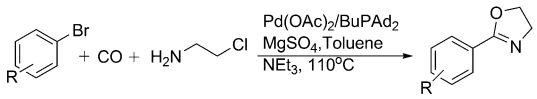
In conclusion, a general and efficient methodology has been developed for the synthesis of oxazolines. This allowed the preparation of 27 five-membered-ring heterocycles and 11 six-membered-ring heterocycles in moderate to good yields.

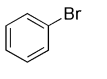
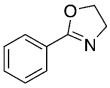
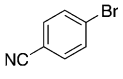
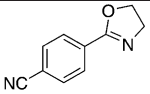
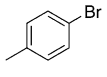
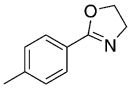
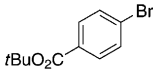
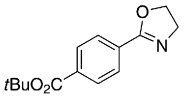
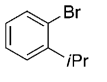
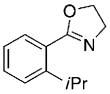
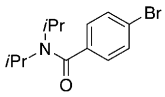
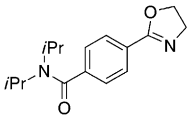
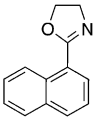
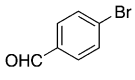
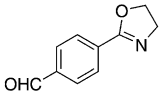
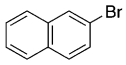
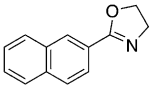
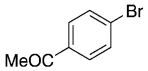
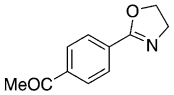
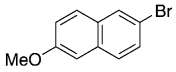
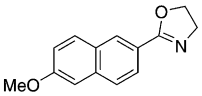
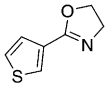
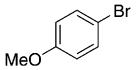
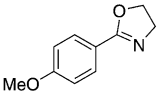
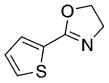
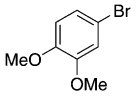
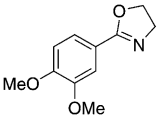
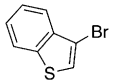
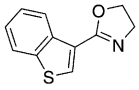
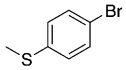
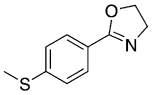
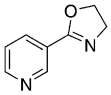
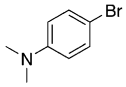
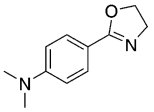
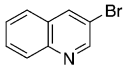
Experimental Section

General information: All reactions were performed by using standard Schlenk techniques (argon). Gas chromatography was performed on a Hewlett–Packard HP 6890N chromatograph with an HP5 column. Chemicals were purchased from Fluka, Aldrich, and Strem and used as received. The cataCXium A ligand is available from Strem or directly from Solvias. Toluene was distilled from CaH_2.

General procedure: A vial (12 mL) was charged with $Pd(OAc)_2$ (2 mol%), $BuPAd_2$ (6 mol%), $MgSO_4$ (1 mmol), 2-chloroethylamine hydrochloride (1 mmol), and a stirring bar. Then, toluene (4 mL), an aryl bromide (1 mmol), and NEt_3 (3 mmol) were injected by syringe. The vial (or several vials) was (were) placed in an alloy plate, which was transfer-

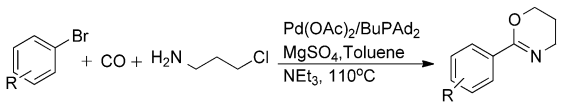
Table 3. Palladium-catalyzed carbonylative synthesis of 2-aryl-4,5-dihydrooxazoles.[a]

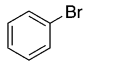
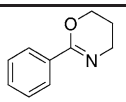
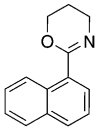
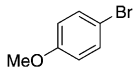
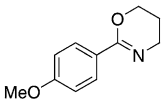
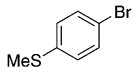
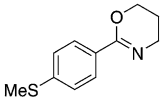
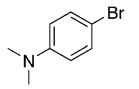
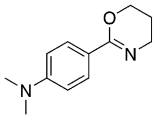
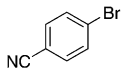
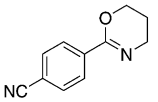
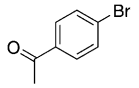
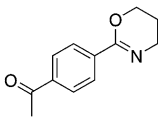
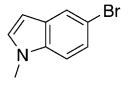
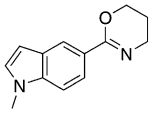
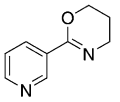
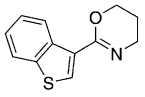
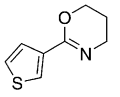


Entry	Aryl bromide	Oxazoline	Yield [%][b]	Entry	Aryl bromide	Oxazoline	Yield [%][b]
1			78[c]	15			61
2			70	16			70
3			65	17			82
4			85	18			71
5			80	19			74
6			83	20			57
7			72	21			52
8			89	22			80
9			70	23			50
10			65	24			70
11			85	25			89
12			81	26			74
13			81	27			68
14			78				

[a] $Pd(OAc)_2$ (2 mol%), $BuPAd_2$ (6 mol%), toluene (4 mL), NEt_3 (3 mmol), CO (10 bar), aryl bromide (1 mmol), 2-chloroethylamine hydrochloride (1 mmol), 110 °C, 16 h. [b] The yields, based on the amount of aryl bromide used, were determined by NMR spectroscopy. [c] Yield of the isolated product.

Table 4. Palladium-catalyzed carbonylative synthesis of 2-aryl-5,6-dihydro-4*H*-1,3-oxazines.[a]



Entry	Aryl bromide	Oxazine	Yield [%][b]
1			77[c]
2			74
3			80
4			85
5			70
6			78
7			80
8			89
9			60
10			82
11			68

[a] $Pd(OAc)_2$ (2 mol%), $BuPAd_2$ (6 mol%), toluene (4 mL), NEt_3 (3 mmol), CO (10 bar), aryl bromide (1 mmol), 3-chloropropylamine hydrochloride (1 mmol), 110°C, 16 h. [b] The yields, based on the amount of aryl bromide used, were determined by NMR spectroscopy. [c] Yield of the isolated product.

red into an autoclave (300 mL; 4560 series from Parr Instruments) under an argon atmosphere. After flushing the autoclave three times with CO and adjusting the pressure to 10 bar, the reaction was performed for 16 h at 110°C. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. Then, water (4 mL) was added and the mixture was extracted three times with ethyl acetate. After drying the combined organic phases with $MgSO_4$ and removing the solvent under vacuum, 1,4-dimethoxybenzene (20 mg) was added as an internal standard. A part of the mixture was removed for NMR analysis to determine the yield. All of the products are known compounds.

Representative purification procedure: The solution was extracted 3–5 times with ethyl acetate (2–3 mL). After evaporation of the organic solvent the residue was adsorbed on silica gel and the crude product was purified by column chromatography using *n*-heptane/AcOEt (4:1) as the eluent.

2-Phenyl-4,5-dihydrooxazole: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87–7.97 (m, 2H), 7.28–7.45 (m, 3H), 4.32 (t, 2H, J = 9.3 Hz), 3.97 ppm (t, 2H, J = 9.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.5, 131.2, 128.3, 128.1, 127.8, 67.5, 54.9 ppm; GC-MS (EI, 70 eV): *m*/*z* (%): 147 $[M]^+$ (80), 117 (100), 77 (20), 51 (10).

*2-Phenyl-5,6-dihydro-4*H*-1,3-oxazine*: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93–8.02 (m, 2H), 7.33–7.47 (m, 3H), 4.42 (t, 2H, J = 4.9 Hz), 3.49–3.59 (m, 2H), 2.03 ppm (t, 2H, J = 6.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.4, 132.2, 128.6, 127.6, 127.4, 61.6, 35.8, 27.9 ppm; GC-MS (EI, 70 eV): *m*/*z* (%): 161 $[M]^+$ (50), 160 (50), 105 (100), 77 (45), 51 (10).

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Keywords: aryl bromides · carbonylation · heterocycles · oxazolines · palladium

[1] For selected reviews, see: a) F. Alonso, I. P. Beletskaya, M. Yus, *Tetrahedron* **2008**, *64*, 3047–3101; b) P. Rollet, W. Kleist, V. Dufaud, L. Djakovitch, *J. Mol. Catal.* **2005**, *241*, 39–51; c) A. Zapf, M. Beller, *Chem. Commun.* **2005**, 431–440; d) A. Frisch, M. Beller, *Angew. Chem.* **2005**, *117*, 680–695; *Angew. Chem. Int. Ed.* **2005**, *44*, 674–688; e) E. Negishi, L. Anastasia, *Chem. Rev.* **2003**, *103*, 1979–2017; f) D. S. Surry, S. L. Buchwald, *Angew. Chem.* **2008**, *120*, 6438–6461; *Angew. Chem. Int. Ed.* **2008**, *47*, 6338–6361; g) H. Doucet, J.-C. Hierso, *Angew. Chem.* **2007**, *119*, 850–888; *Angew. Chem. Int. Ed.* **2007**, *46*, 834–871; h) K. C. Nicolaou, P. G. Bulger, D. Sarlah, *Angew. Chem.* **2005**, *117*, 4516–4563; *Angew. Chem. Int. Ed.* **2005**, *44*, 4442–4489; i) A. Roglans, A. Pla-Quintana, M. Moreno-Manas, *Chem. Rev.* **2006**, *106*, 4622–4643; j) X.-F. Wu, P. Anbarasan, H. Neumann, M. Beller, *Angew. Chem.* **2010**, *122*, 9231–9234; *Angew. Chem. Int. Ed.* **2010**, *49*, 9047–9050.

[2] For reviews on industrial applications, see: a) C. Torborg, M. Beller, *Adv. Synth. Catal.* **2009**, *351*, 3027–3043; b) A. Zapf, M. Beller, *Top. Catal.* **2002**, *19*, 101–109; c) C. E. Tucker, J. G. de Vries, *Top. Catal.* **2002**, *19*, 111–118.

[3] For reviews on palladium-catalyzed carbonylations, see: a) A. Brennführer, H. Neumann, M. Beller, *Angew. Chem.* **2009**, *121*, 4176–4196; *Angew. Chem. Int. Ed.* **2009**, *48*, 4114–4133; b) A. Brennführer, H. Neumann, M. Beller, *ChemCatChem* **2009**, *1*, 28–41; c) M. Beller in *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed. (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **2002**, pp. 145–156; d) R. Skoda-Foldes, L. Kollar, *Curr. Org. Chem.* **2002**, *6*, 1097–1119; e) M. Beller, B. Cornils, C. D. Frohning, C. W. Kohlpaintner, *J. Mol. Catal. A: Chem.* **1995**, *104*, 17–85; f) R. Grigg, S. P. Mutton, *Tetrahedron* **2010**, *66*, 5515–5548; g) X. F. Wu, H. Neumann, M. Beller, *Chem. Soc. Rev.* **2011**, *40*, 4986–5009.

[4] a) J. P. Genet, S. Thorimbert, A. M. Touzin, *Tetrahedron Lett.* **1993**, *34*, 1159–1162; b) P. Wipf, C. P. Miller, *J. Am. Chem. Soc.* **1992**, *114*, 10975–10977; c) Q. Li, K. W. Woods, A. Claiborne, S. L. Gwaltney,

K. J. Barr, G. Liu, L. Gehrke, R. B. Credo, Y. Hua Hui, J. Lee, R. B. Warner, P. Kovar, M. A. Nukkala, N. A. Zielinski, S. K. Tahir, M. Fitzgerald, K. H. Kim, K. Marsh, D. Frost, S.-C. Ng, S. Rosenberg, H. L. Sham, *Bioorg. Med. Chem. Lett.* **2002**, *12*, 465–469; d) C. Campiani, M. de Angelis, S. Armaroli, C. Fattorusso, B. Catalanotti, A. Ramunno, V. Nacci, E. Novellino, C. Grewer, D. Ionescu, T. Rauen, R. Griffiths, C. Sinclair, E. Fumagalli, T. Mennini, *J. Med. Chem.* **2001**, *44*, 2507–2510; e) C. Minakuchi, J. Suzuki, K. Toda, M. Akamatsu, Y. Nakagawa, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 4080–4084.

[5] T. Shibamoto, *J. Agric. Food Chem.* **1980**, *28*, 237–243.

[6] For reviews on the synthetic utility of 2-oxazolines, see: a) A. I. Meyers, E. D. Mihelich, *Angew. Chem.* **1976**, *88*, 321–332; *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 270–281; b) G. Bhaskar, V. S. Kumar, B. V. Rao, *Tetrahedron: Asymmetry* **2004**, *15*, 1279–1283.

[7] For selected examples, see: a) M. J. Petersson, I. D. Jenkins, W. A. Loughlin, *Org. Biomol. Chem.* **2009**, *7*, 739–746; b) K. Hioki, Y. Takechi, N. Kimura, H. Tanaka, M. Kunishima, *Chem. Pharm. Bull.* **2008**, *56*, 1735–1737; c) I. Mohammadpoor-Baltork, A. R. Khosropour, S. F. Hojati, *Catal. Commun.* **2007**, *8*, 200–204; d) M. Ishihara, H. Togo, *Tetrahedron* **2007**, *63*, 1474–1480; e) M. Durán-Galván, S. A. Worlikar, B. T. Connell, *Tetrahedron* **2010**, *66*, 7707–7719; f) S. Crosignani, A. C. Young, B. Linclau, *Tetrahedron Lett.* **2004**, *45*, 9611–9615; g) Q. Xu, Z. Li, *Tetrahedron Lett.* **2009**, *50*, 6838–6840; h) B. Ilkgul, D. Gunes, O. Sirkecioglu, N. Bicak, *Tetrahedron Lett.* **2010**, *51*, 5313–5315; i) A. Cwik, Z. Hell, A. Hegedüs, Z. Finta, Z. Horváth, *Tetrahedron Lett.* **2002**, *43*, 3985–3987; j) Y. I. Kim, Y. H. Kim, *Synlett* **1997**, 1324–1326; k) I. Mohammadpoor-Baltork, A. R. Khosropour, S. F. Hojati, *Synlett* **2005**, 2747–2750; l) N. N. Karade, G. B. Tiwari, S. V. Gampawar, *Synlett* **2007**, 1921–1924.

[8] For examples of the palladium-catalyzed carbonylative synthesis of benzoxazoles from aryl halides and 2-aminophenols in two steps, see: a) R. J. Perry, B. D. Wilson, *Organometallics* **1994**, *13*, 3346–3350; b) R. J. Perry, B. D. Wilson, *Macromolecules* **1994**, *27*, 40–44; c) R. J. Perry, B. D. Wilson, R. J. Miller, *J. Org. Chem.* **1992**, *57*, 2883–2887; d) R. J. Perry, B. D. Wilson, *J. Org. Chem.* **1993**, *58*, 7016–7021.

[9] a) X.-F. Wu, H. Neumann, M. Beller, *Adv. Synth. Catal.* **2011**, *353*, 788–792; b) X.-F. Wu, H. Neumann, M. Beller, *Angew. Chem.* **2010**, *122*, 5412–5416; *Angew. Chem. Int. Ed.* **2010**, *49*, 5284–5288; c) X.-F. Wu, P. Anbarasan, H. Neumann, M. Beller, *Angew. Chem.* **2010**, *122*, 7474–7477; *Angew. Chem. Int. Ed.* **2010**, *49*, 7316–7319; d) X.-F. Wu, H. Neumann, M. Beller, *Chem. Asian J.* **2010**, *5*, 2168–2172; e) X.-F. Wu, H. Neumann, M. Beller, *ChemCatChem* **2010**, *2*, 509–513; f) X.-F. Wu, H. Neumann, M. Beller, *Chem. Eur. J.* **2010**, *16*, 9750–9753; g) X.-F. Wu, H. Neumann, M. Beller, *Chem. Eur. J.* **2010**, *16*, 12104–12107; h) X.-F. Wu, B. Sundararaju, H. Neumann, P. H. Dixneuf, M. Beller, *Chem. Eur. J.* **2011**, *17*, 106–110; i) X.-F. Wu, H. Neumann, M. Beller, *Tetrahedron Lett.* **2010**, *51*, 6146–6149; j) X.-F. Wu, H. Neumann, A. Spannenberg, T. Schulz, H. Jiao, M. Beller, *J. Am. Chem. Soc.* **2010**, *132*, 14596–14602; k) X.-F. Wu, H. Jiao, H. Neumann, M. Beller, *ChemCatChem* **2011**, *3*, 726–733.

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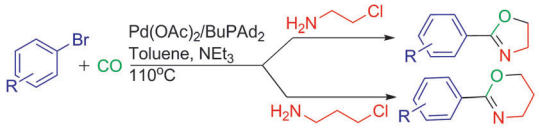
Heterocycle Synthesis

X.-F. Wu, H. Neumann, S. Neumann, M. Beller** ..... ▮▮▮▮–▮▮▮▮

A General and Efficient Palladium-Catalyzed Carbonylative Synthesis of 2-Aryloxazolines and 2-Aryloxazines from Aryl Bromides



Oxazoline is OK! A general and efficient method for the synthesis of oxazolines has been developed (see scheme). This allowed the preparation of 27 five-membered-ring heterocycles and 11 six-membered-ring heterocycles in moderate to good yields.