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C–N Coupling of Indoles and Carbazoles with Aromatic Chlorides Catalyzed by a Single-Component NHC-Nickel(0) Precursor

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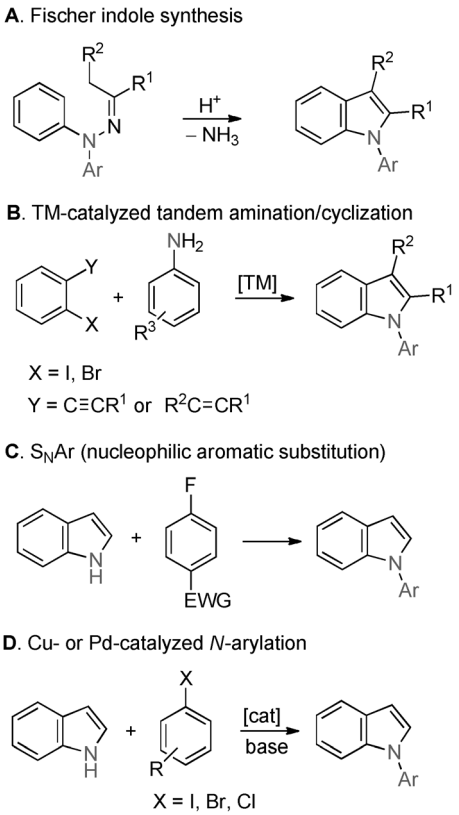
Abstract: A new and efficient nickel-based protocol for the *N*-arylation of indoles and carbazoles with aromatic chlorides, the least expensive of the aryl halides, is described. The procedure provides selectively *N*-(hetero)arylation products in good to high yields, in short reaction times and without adding an excess of ligands.

Keywords: aryl chlorides; C–N bond formation; N-heterocyclic carbenes; nickel catalysts

The indole core is probably the most abundant, nitrogen-containing heterocycle occurring in bioactive natural products.[1] In this context, *N*-arylindoles are pharmaceutically valuable compounds due to their interesting biological activities including antifungal,[2] antiviral,[3] antipsychotic,[4] antiallergic,[5] enzymes inhibitory,[6] and antigiotensin II-1 antagonistic.[7] In addition, structurally related *N*-arylcarbazoles exhibit remarkable electroluminescense properties and have been applied in the preparation of LEDs[8] and charge-transporting/host materials.[9]

N-Arylindoles can be prepared by an annulation reaction of enolizable *N,N*-diarylhydrazones under acidic conditions (classical Fischer indole synthesis[10]) (Scheme 1A).[11] The poor commercial availability and toxicity of *N,N*-diarylhydrazine precursors limited the scope of this transformation. As a result, methods for the synthesis of arylhydrazones involving the use of transition metal catalysts have been devised.[11b,c] Another synthetic strategy makes use of *ortho*-alkynylhaloarenes or *ortho*-alkenylhaloarenes and *N*-arylanilines as reactants, which are transformed into the *N*-arylindole framework by palladium- or copper-mediated tandem amination/cyclization processes (Scheme 1B).[12] The main drawback of this method lies in the need to preform the *ortho*-disubstituted



Scheme 1. General methods for *N*-arylindole synthesis.

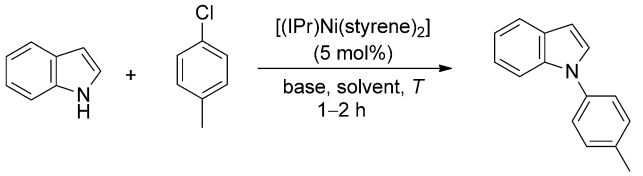
arene precursor for the assembly of the indole nucleus. In recent years, procedures based on the use of monosubstituted or *ortho*-disubstituted benzenoid precursors other than those described above have appeared in the literature.[13]

A different approach to the synthesis of *N*-arylindoles consists of the direct C–N functionalization of the preformed indole rings. Classically, this strategy has been achieved through S_NAr (nucleophilic aromatic substitution) of π-electron rich NH-indoles with electron-deficient fluorobenzenes (Scheme 1C),[14] or through stoichiometric Ullmann condensations.[15] With the development of metal-mediated catalytic procedures for C–N bond formation, limitations associated with those traditional methods such as narrow substrate scope, high reaction temperatures and the need for stoichiometric amounts of copper salts have been partially overcome. Copper and palladium are the metals of choice to catalyze the *N*-arylation of indoles (Scheme 1D).[16] Copper-mediated protocols make use of simple, cost-effective nitrogen-based ligands like diamines,[17a–c] α-amino acids,[17d] Schiff bases[17e] oximes,[17f,g] etc., and require temperatures between 80–120 °C[18] and catalyst loadings between 5–20 mol%. However, they are limited almost exclusively to the use of aryl iodides and bromides as coupling partners.[19] Compared to copper, the number of palladium-based catalytic systems able to perform the *N*-arylation of indoles in an effective manner remains scarce.[12f–20] This could be attributed to the poor nucleophilicity, high acidity and strong coordination ability of the NH group of indole to the Pd center.[21] Moreover, selectivity problems associated with competing *N*- and *C*-arylation have also been observed.[20b,c] To avoid these problems, reactions have to be carried out using loadings of 1–8 mol% Pd and excess of ligands, generally phosphines (Pd/L ratio up to 1:4).

C–N coupling reactions catalyzed by nickel complexes have received increased attention in the past few years.[22] Recently, we became interested in the development of single-component nickel catalysts for C–C[23a] and C–N[23b,c] bond couplings. We reported that the Ni(0) complex [(IPr)Ni(styrene)$_2$] [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] efficiently catalyzed the coupling of aryl tosylates with cyclic secondary amines and anilines.[23c] Since no nickel catalyst showing a wide scope for the *N*-arylation of indole has been reported so far, we decided to explore the use of our IPr-Ni(0) complex as catalyst in this challenging C–N coupling. As nickel(0) complexes are highly reactive toward the oxidative addition of aryl chlorides, the most affordable and available among the aryl halides, we focused on the *N*-arylation of indoles with chloroarenes.

Using 5 mol% of IPr-Ni(0) precatalyst, 4-chlorotoluene (1 equiv.) and indole (1.2 equiv.) reacted in dioxane at 80 °C in the presence of LiO-*t*-Bu (1.2 equiv.) giving the expected coupling product in low yield (25%) within 1 hour (Table 1, entry 1). Increasing the temperature up to 110 °C produced a notable enhancement of the reaction yield (entry 2). Different bases were tested but LiO-*t*-Bu proved to be the most effective (entries 3 and 4). Moreover, the *N*-arylation reaction was successfully conducted in toluene although the yield did not change substantially (entry 5). Finally, the highest yield of the coupling product was obtained when the reaction was carried out for 2 h (entry 6).

Table 1. Optimization studies for the *N*-arylation of indole with 4-chlorotoluene catalyzed by [(IPr)Ni(styrene)$_2$].[a]



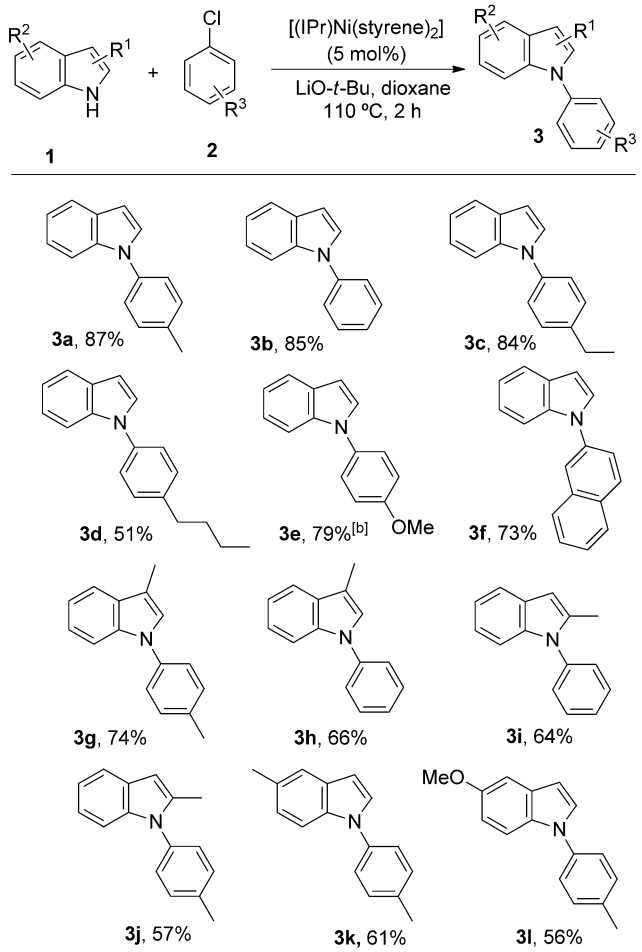
Entry	Base	Temperature [°C]	Time [h]	Yield [%][b]
1	LiO-*t*-Bu	80	1	25
2	LiO-*t*-Bu	110	1	81
3	NaO-*t*-Bu	110	1	<5
4	Cs_2CO_3	110	1	<5
5	LiO-*t*-Bu	110	1	78[c]
6	LiO-*t*-Bu	110	2	87

[a] *Reaction conditions:* indole (1.2 mmol); 4-chlorotoluene (1.0 mmol); base (1.2 mmol); catalyst (5 mol%); dioxane (1 mL).
[b] Yields of isolated products.
[c] The reaction was performed in toluene.

To examine the scope of this nickel precatalyst for the preparation of *N*-arylindoles, a selection of aryl chlorides was reacted with several indoles under the optimized conditions. The results of the couplings are presented in Table 2. Reactions were accomplished within a fairly short time, 2 h in most cases. Electron-neutral and electron-rich aryl chlorides reacted with the parent indole affording the coupling products in high yields (**3a**–**3f**), whereas for substituted indoles yields were slightly lower (**3g**–**3l**). In such cases, no further improvement of yields was observed by extending the reaction time, as previously observed for other Ni-catalyzed amination reactions.[22c,d] It is worth noting that competing *C*-arylation products were not observed for reactions of 2-methylindole.[20c] Finally, no desired product was obtained with aryl chlorides containing electron-withdrawing groups (CF_3 and COPh) or substituents in *ortho* positions of the ring[20c] even under prolonged reaction times.

The results depicted in Table 2 compare well with those described recently by the group of Stradiotto using the BippyPhos/[Pd(cinnamyl)Cl]$_2$ catalytic sys-

Table 2. Scope of *N*-arylation of indoles with aryl chlorides catalyzed by [(IPr)Ni(styrene)$_2$].[a]

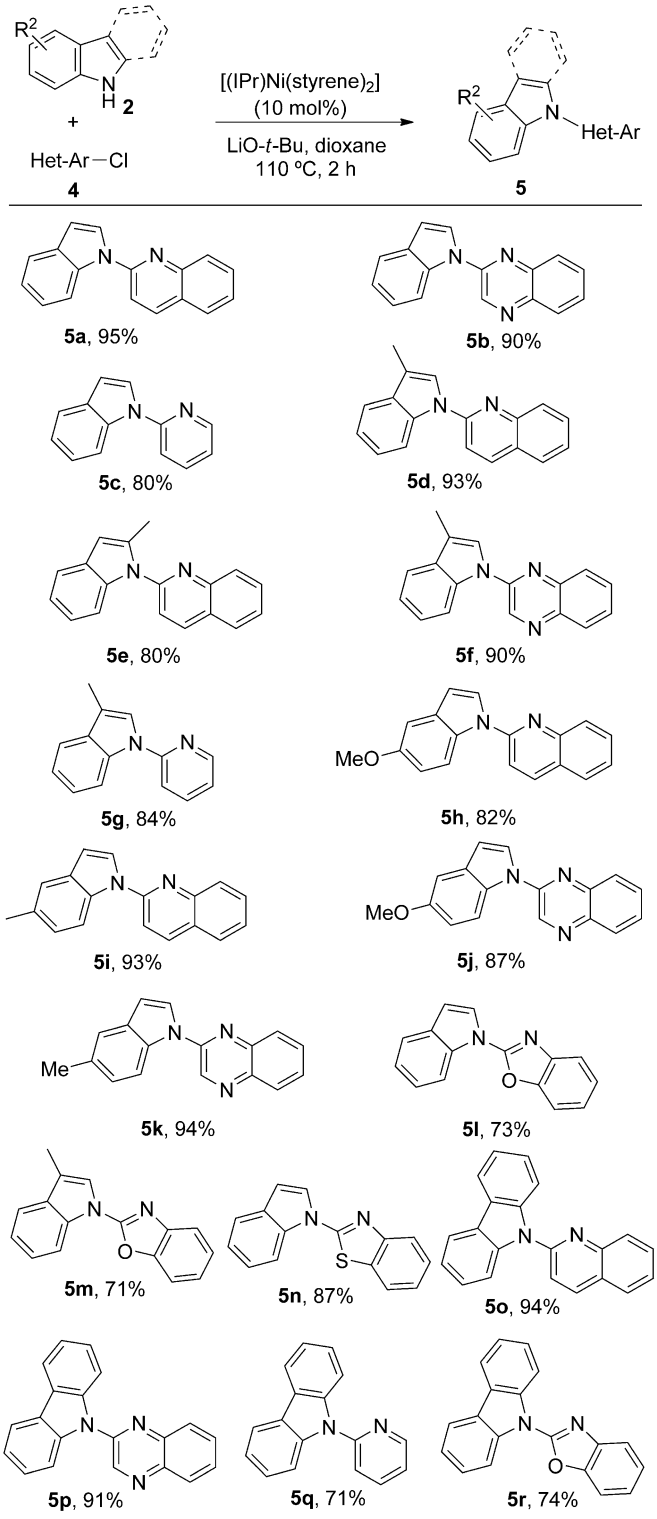


[a] *Reagents and conditions:* indole (1.2 mmol), aryl chloride (1.0 mmol); LiO-*t*-Bu (1.2 mmol), catalyst (5 mol%), dioxane (1 mL), 110 °C, 2 h. Yields of isolated products.
[b] Reaction performed for 3 h.

tem[12f] which shows the widest scope for the *N*-arylation of indoles with chloroarenes ever reported. Reactions were conducted with lower loadings of Pd-based catalyst (1 mol%) as compared to those used here, however a large excess of BippyPhos ligand (4 mol%) was required in order to make effective the couplings in longer reaction times than those displayed in Table 2.

The C–N coupling between two heteroaromatic reagents is a far more challenging process, since the coordination abilities of both heteroaryl groups to the metal center might inhibit the catalysis. Thus, we decided to examine the application of the IPr-Ni(0) precatalyst to the C–N coupling of indoles with heteroaryl chlorides. When conditions outlined in Table 2 were applied to the *N*-arylation of indole with 2-chloroquinoline the expected product was obtained in 51% isolated yield. No significant improvement in

Table 3. Scope of the *N*-arylation of indoles and carbazoles with heteroaryl chlorides catalyzed by [(IPr)Ni(styrene)$_2$].[a]



[a] *Reagents and conditions:* indole (1.2 mmol), heteroaryl chloride (1.0 mmol); LiO-*t*-Bu (1.2 mmol), catalyst (10 mol%), dioxane (1 mL), 110 °C, 2 h. Yields of isolated products.

yield was observed by increasing the reaction time; however, the coupling product was formed quantitatively in 2 h when the reaction was conducted with 10 mol% of IPr-Ni(0) complex (Table 3, **5a**).

Under these conditions, diverse indoles were coupled with unsubstituted *N*-containing heteroaryl chlorides such as 2-chloroquinoline, 2-chloroquinoxaline and 2-chloropyridine, in good to excellent isolated yields (**5a**–**k**, Table 3). In addition, 2-chlorobenzoxazole and 2-chlorobenzothiazole could be successfully used as coupling partners, affording the corresponding products in high yields (**5l**–**n**). However, non-benzofused five-membered heteroaryl chlorides did not undergo the reaction. Finally, using the same conditions carbazole was effectively coupled with different heteroaryl chlorides in yields ranging from 71–94% (**5o**–**r**). Again, it should be stressed that all these couplings proceed with high yields in only 2 h and without adding an excess of the ligand. To the best of our knowledge, this is the shortest reaction time reported to date for the *N*-arylation of indoles with (hetero)aryl chlorides.

In conclusion, we have developed a new, highly effective method for the C–N couplings of indoles and carbazoles with hetero(aryl) chlorides based on the use of the nickel(0) complex [(IPr)Ni(styrene)$_2$]. Reactions are accomplished in very short reaction times in the presence of 5–10 mol% of the IPr-Ni(0) complex, and without using an excess of the ligand. Competing *C*-arylation processes were not observed and the C–N coupling products were obtained in good to excellent yields using the least expensive and reactive of aryl halides.

Experimental Section

General Catalytic Procedure

The catalyst (0.05 or 0.10 mmol), the base LiO-*t*-Bu (1.2 mmol) and dioxane (1 mL) were added in turn to a vial equipped with a J Young tap and containing a magnetic bar. The indole (1.2 mmol) and the (hetero)aryl chloride (1 mmol) were added under a nitrogen atmosphere. The reaction mixture was stirred at 110 °C for 2 h in an oil bath. The reaction mixture was allowed to cool to room temperature, then diluted with ethyl acetate (10 mL) and filtered through celite. The clean solution was evaporated to dryness, and the residue was purified by flash chromatography or by recrystallization to afford the desired product.

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References

[1] a) S.-M. Li, *Nat. Prod. Rep.* **2010**, *27*, 57–78; b) A. J. Kochanowska-Karamyan, M. T. Hamann, *Chem. Rev.* **2010**, *110*, 4489–4497; c) M. Ishikura, T. Abe, T. Choshi, S. Hibino, *Nat. Prod. Rep.* **2013**, *30*, 694–752; d) S. Lancianesi, A. Palmieri, M. Petrini, *Chem. Rev.* **2014**, *114*, 7108–7149.

[2] a) C.-K. Ryu, J. Y. Lee, S. H. Jeong, J.-H. Nho, *Bioorg. Med. Chem. Lett.* **2009**, *19*, 146–148; b) R. E. Sawy-El, F. A. Bassyouni, S. H. Abu-Bakr, S. A. Abdlla, *Acta Pharm.* **2010**, *60*, 55–71.

[3] a) H. Xu, W. Q. Liu, L. L. Fan, Y. Chen, L. M. Yang, L. Lv, Y. T. Zheng, *Chem. Pharm. Bull.* **2008**, *56*, 720–722; b) M.-Z. Zhang, Q. Chen, G.-F. Yang, *Eur. J. Med. Chem.* **2015**, *89*, 421.

[4] a) R. Sarges, H. R. Howard, B. K. Koe, A. Weissman, *J. Med. Chem.* **1989**, *32*, 437–444; b) J. Perregaard, J. Arnt, K. P. Bogem, J. Hyttel, C. Sánchez, *J. Med. Chem.* **1992**, *35*, 1092–1101; c) K. Andersen, T. Liljefors, J. Hyttel, J. Perregaard, *J. Med. Chem.* **1996**, *39*, 3723–3738.

[5] a) P. C. Unangst, M. E. Carethers, K. Webster, G. M. Janik, L. J. Robichaud, *J. Med. Chem.* **1984**, *27*, 1629–1633; b) P. C. Unangst, D. T. Connor, S. S. Stabler, R. J. Weikert, M. E. Carethers, J. A. Kennedy, D. O. Thueson, J. C. Chestnut, R. L. Adolphson, M. C. Conroy, *J. Med. Chem.* **1989**, *32*, 1360–1366.

[6] a) H. Sano, T. Noguchi, A. Tanatani, Y. Hashimoto, H. Miyachi, *Bioorg. Med. Chem.* **2005**, *13*, 3079–3091; b) H. Sano, T. Noguchi, A. Miyajima, Y. Hashimoto, H. Miyachi, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 3068–3072; c) T. Tomoo, T. Nakatsuka, T. Katayama, Y. Hayashi, Y. Fujieda, M. Terakawa, K. Nagahira, *J. Med. Chem.* **2014**, *57*, 7244–7262.

[7] S. R. Stabler, Jahangir, *Synth. Commun.* **1994**, *24*, 123–129.

[8] a) Y. Tao, Q. Wang, C. Yang, Q. Wang, Z. Zhang, T. Zou, J. Qin, D. Mac, *Angew. Chem.* **2008**, *120*, 8224–8227; *Angew. Chem. Int. Ed.* **2008**, *47*, 8104–8107; b) J. Lia, A. C. Grimsdale, *Chem. Soc. Rev.* **2010**, *39*, 2399–2410 and references cited therein; c) H.-H. Chou, C.-H. Chen, *Adv. Mater.* **2010**, *22*, 2468–2471; d) H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, *Nature* **2012**, *492*, 234–238.

[9] a) S.-J. Su, H. Sasabe, T. Takeda, J. Kido, *Chem. Mater.* **2008**, *20*, 1691–1693; b) S.-J. Su, C. Cai, J. Kido, *Chem. Mater.* **2011**, *23*, 274–284; c) Y.-T. Lee, Y.-T. Chang, M.-T. Lee, P.-H. Chiang, C.-T. Chen, C.-T. Chen, *J. Mater. Chem. C* **2014**, *2*, 382–391.

[10] a) E. Fischer, F. Jourdan, *Ber. Dtsch. Chem. Ges.* **1883**, *16*, 2241–2245.

[11] a) O. Miyata, Y. Kimura, K. Muroya, H. Hiramatsu, T. Naito, *Tetrahedron Lett.* **1999**, *40*, 3601–3604; b) S. Wagaw, B. H. Yang, S. L. Buchwald, *J. Am. Chem. Soc.* **1999**, *121*, 10251–10263; c) C. Cao, Y. Shi, A. L. Odom, *Org. Lett.* **2002**, *4*, 2853–2856.

[12] a) M. Beller, C. Breindl, T. H. Riermeier, A. Tillack, *J. Org. Chem.* **2001**, *66*, 1403–1412; b) H. Siebeneicher, I. Bytschkov, S. Doye, *Angew. Chem.* **2003**, *115*, 3151–3153; *Angew. Chem. Int. Ed.* **2003**, *42*, 3042–3044; c) N. C. Willis, G. N. Brace, I. P. Holmes, *Angew. Chem.* **2005**, *117*, 407–410; *Angew. Chem. Int. Ed.* **2005**, *44*, 403–406; d) L. Ackermann, *Org. Lett.* **2005**, *7*, 439–442; e) M. C. Willis, G. N. Brace, T. J. K. Findlay, I. P. Holmes, *Adv. Synth. Catal.* **2006**, *348*, 851–856; f) S. M. Crawford, C. B. Lavery, M. Stradiotto, *Chem. Eur. J.* **2013**, *19*, 16760–16771. g) For a nickel-based catalyst see: L. Ackermann, W. Song, R. Sandmann, *J. Organomet. Chem.* **2011**, *696*, 195–201.

[13] a) Y. Du, R. Liu, G. Linn, K. Zhao, *Org. Lett.* **2006**, *8*, 5919–5922; b) J. Barluenga, A. Jiménez-Aquino, F. Aznar, C. Valdés, *J. Am. Chem. Soc.* **2009**, *131*, 4031–4041; c) Q. Yan, J. Luo, D. Zhang-Negrerie, H. Li, X. Qi, K. Zhao, *J. Org. Chem.* **2011**, *76*, 8690–8697; d) A. Bunescu, C. Piemontesi, Q. Wang, J. Zhu, *Chem. Commun.* **2013**, *49*, 10284–10286; e) J. M. Knapp, J. S. Zhu, D. J. Tantillo, M. J. Kurth, *Angew. Chem.* **2012**, *124*, 10740; *Angew. Chem. Int. Ed.* **2012**, *51*, 10588; f) N. L. Rotta-Loria, A. Borzenko, P. G. Alsabeh, C. B. Lavery, M. Stradiotto, *Adv. Synth. Catal.* **2015**, *357*, 100.

[14] For representative examples, see: a) S. R. Stabler, Jahangir, *Synth. Commun.* **1994**, *24*, 123–129; b) W. J. Smith III, J. S. Sawyer, *Tetrahedron Lett.* **1996**, *37*, 29–302; c) G. L. Frayne, G. M. Green, *Tetrahedron Lett.* **2008**, *49*, 7328–7329; d) R. Cano, D. J. Ramon, M. Yus, *J. Org. Chem.* **2011**, *76*, 654–660. e) For the use of unactivated fluorobenzenes see: F. Diness, D. P. Fairlie, *Angew. Chem.* **2012**, *124*, 8136–8140; *Angew. Chem. Int. Ed.* **2012**, *51*, 8012–8016.

[15] For recent examples, see: a) F. Bellina, C. Calandri, S. Cauteruccio, R. Rossi, *Eur. J. Org. Chem.* **2007**, 2147–2151; b) G. Pai, A. P. Chattopadhyay, *Tetrahedron Lett.* **2014**, *55*, 941–944.

[16] L. Joucla, L. Djiakovitch, *Adv. Synth. Catal.* **2009**, *351*, 673–714.

[17] For representative examples, see: a) A. Klapars, J. C. Antilla, X. Huang, S. L. Buchwald, *J. Am. Chem. Soc.* **2001**, *123*, 7727–7729; b) J. C. Antilla, A. Klapars, S. L. Buchwald, *J. Am. Chem. Soc.* **2002**, *124*, 11684–11688; c) X. Huang, K. W. Anderson, D. Zim, L. Jiang, A. Klapars, S. L. Buchwald, *J. Am. Chem. Soc.* **2003**, *125*, 6653–6655; d) H. Zhang, Q. Cai, D. Ma, *J. Org. Chem.* **2005**, *70*, 5164–5173; e) H.-J. Cristau, P. P. Cellier, J.-F. Spindler, M. Taillefer, *Chem. Eur. J.* **2004**, *10*, 5607–5622; f) H.-C. Ma, Z.-X. Jiang, *J. Org. Chem.* **2007**, *72*, 8943–8946; g) X. Li, D. Yang, Y. Jiang, H. Fu, *Green Chem.* **2010**, *12*, 1097–1105.

[18] An impressive photoinduced copper-catalyzed *N*-arylation and *N*-alkylation of carbazoles at 0 °C has been recently described, see: a) S. E. Creutz, K. J. Lotito, G. C. Fu, J. C. Peters, *Science* **2012**, *338*, 648–651; b) A. C. Bissember, R. L. Lundgren, S. E. Creutz, J. C. Peters, G. C. Fu, *Angew. Chem.* **2013**, *125*, 5233–5237; *Angew. Chem. Int. Ed.* **2013**, *52*, 5129–5133.

[19] Examples of the copper-catalyzed *N*-arylation of azoles using aryl chlorides as coupling partners are scarce and involve the use of activated aryl chlorides and fluorides and a heterogeneous copper based system. See: a) S. U. Son, I. K. Park, J. Park, T. Hyeon, *Chem. Commun.* **2004**, 778–779; b) B. M. Choudary, C. Sridhar, M. L. Kantam, G. T. Venkanna, B. Sreedhar, *J. Am. Chem. Soc.* **2005**, *127*, 9948–9949; c) M. L. Kantam, J. Yadav, S. Laha, B. Sreedhar, S. Jha, *Adv. Synth. Catal.* **2007**, *349*, 1938–1942.

[20] a) G. Mann, J. F. Hartwig, M. S. Driver, C. Fernández-Rivas, *J. Am. Chem. Soc.* **1998**, *120*, 827–828; b) J. F. Hartwig, M. Kawatsura, S. I. Hauck, K. H. Shaughnessy, L. M. Alcázar-Román, *J. Org. Chem.* **1999**, *64*, 5575–5580; c) D. W. Old, M. C. Harris, S. L. Buchwald, *Org. Lett.* **2000**, *2*, 1403–1406; d) M. Watanabe, M. Nishiyama, T. Yamamoto, Y. Koie, *Tetrahedron Lett.* **2000**, *41*, 481–483; e) G. A. Grasa, M. S. viciu, J. Huang, S. P. Nolan, *J. Org. Chem.* **2001**, *66*, 7729–7737; f) C. J. Smith, M. W. S. Tsang, A. B. Holmes, R. L. Danheiser, J. W. Tester, *Org. Biomol. Chem.* **2005**, *3*, 3767–3781; g) M. Romero, Y. Harrak, J. Basset, L. Ginet, P. Constans, M. D. Pujol, *Tetrahedron* **2006**, *62*, 9010–9016; h) Y. Monguchi, T. Marumoto, H. Takamatsu, Y. Sawama, H. Sajiki, *Adv. Synth. Catal.* **2014**, *356*, 1866–1872.

[21] I. P. Beletskaya, A. V. Cheprakov, *Organometallics* **2012**, *31*, 7753–7808.

[22] a) G. Manolikakes, A. Gavryushin, P. Knochel, *J. Org. Chem.* **2008**, *73*, 1429; b) A. R. Martin, Y. Makida, S. Meiries, A. M. Z. Slawin, S. P. Nolan, *Organometallics* **2013**, *32*, 6265; c) N. H. Park, G. Teverovskiy, S. L. Buchwald, *Org. Lett.* **2014**, *16*, 220; d) S. Ge, R. A. Green, J. F. Hartwig, *J. Am. Chem. Soc.* **2014**, *136*, 1617; e) N. F. F. Nathel, J. Kim, X. Jiang, N. K. Garg, *ACS Catal.* **2014**, *4*, 3289; f) A. R. Martin, D. J. Nelson, S. Meiries, A. M. Z. Slawin, S. P. Nolan, *Eur. J. Org. Chem.* **2014**, 3127.

[23] a) M. J. Iglesias, A. Prieto, M. C. Nicasio, *Org. Lett.* **2012**, *14*, 4318–4321; b) M. J. Iglesias, A. Prieto, M. C. Nicasio, *Adv. Synth. Catal.* **2010**, *352*, 1949–1954; c) M. J. Iglesias, J. F. Blandez, M. R. Fructos, A. Prieto, E. Álvarez, T. R. Belderrain, M. C. Nicasio, *Organometallics* **2012**, *31*, 6312–6316.

