DOI: 10.1002/adsc.200800517

Ligand-Free Iron/Copper Cocatalyzed Alkynylation Coupling Reactions

Jincheng Mao,[a,*] Guanlei Xie,[a] Minyan Wu,[a] Jun Guo,[a] and Shunjun Ji[a]

[a] Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215123, People's Republic of China
Fax: (+86)-512-6588-0089; phone: (+86)-512-6588-0403; e-mail: jcmao@suda.edu.cn

Received: August 15, 2008; Revised: October 9, 2008; Published online: November 4, 2008

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.200800517.

Abstract: Ligand-free iron/copper cocatalyzed cross-coupling reactions of aryl halides with terminal alkynes were carried out to provide the corresponding coupling products in good yields (up to 99%). Noteworthy is that this low-cost, effective and environmentally friendly protocol was the first to be employed in alkynylation couplings.

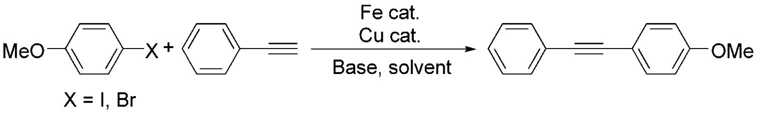
Keywords: alkynylation coupling; aryl halides; cross-coupling; ligand-free conditions; terminal alkynes

Since the original report in the early 1970s,[1] the Sonogashira coupling between terminal alkynes with aryl or vinyl halides has been applied widely in the synthesis of molecules containing an acetylenic moiety, which is found in various functional organic materials as well as biologically important molecules.[2,3] Due to the importance of the formation of carbon-carbon bonds using this method, many catalytic systems have been developed for this coupling reaction.[4] One of the most commonly used catalytic systems for this transformation is $Pd(PPh_3)_2Cl_2$/CuI cocatalysts together with amines as the solvents or cosolvents.[5] During the past few years, several modified protocols have been revealed, such as a copper-free Pd catalytic system,[6] a Pd/Ni bimetallic system[7] and a Pd-C/CuI system.[8] However, the drawbacks of the Pd catalyst systems, such as high cost and toxicity, limit their massive applications on the industrial scale. Thus, chemists have tried to reduce the loading of active metal (10^{-4} mol% of palldium).[9] Meanwhile, the use of a cheaper metal instead of palladium provides another possible route.[10] Among them, copper-based alternatives are particularly attractive, due to their orders of magnitude lower cost and their less harmful impact on the environment than any noble metal.[11] Thus, great progress has been made in the copper-catalyzed alkynylation coupling reactions in the past decades.[12] Recently, novel catalytic systems, including $Ni(0)/CuI/PPh_3$,[13] an Au complex[14] and Ru/Al_2O_3 heterogeneous systems,[15] have also been successfully developed for such coupling reactions.

Iron as an abundant, economical, and environmental friendly metal shows increasing and promising catalytic abilities in many organic transformations, in particular for C–C bond-forming reactions.[16] Recently, Taillefer et al. showed an efficient Fe/Cu catalytic catalyst for the *N*-arylation of nitrogen-containing heterocycles with aryl halides.[17] Wakharkar's group has also developed an efficient C–N coupling between amines with aryl halides in the presence of a heterogeneous recyclable Cu-Fe hydrotalcite catalyst.[18] Independently, Bolm and co-workers reported the iron-catalyzed *N*-arylation of N-nucleophiles with aryl iodides using *N,N'*-dimethylethylenediamine (demeda) as the ligand.[19] Subsequently, they successfully applied their methodology to C–O and C–S cross-coupling reactions.[20] Thus, iron catalysts show great potential.[21] However, according to our knowledge, there are few examples of the Sonogashira coupling using this inexpensive catalyst as an economical and effective method.[22] Based on our research on various cross-coupling reactions,[12i,23] herein, we report an efficient Fe/Cu cocatalytic system for ligand-free Sonogashira couplings.

Initial examinations were carried out on the reaction of 4-iodoanisole with phenylacetylene in DMF (dimethylformamide) catalyzed by different iron catalysts, including $FeCl_3$ and $Fe(acac)_3$. TLC showed that the reactions did not proceed at all (Table 1, entry 1). Another blank test was performed only with CuI and showed that he corresponding product was obtained in 42% yield and the homocoupling product of alkyne was also formed (entry 2). To our surprise, CuI in

Table 1. The coupling of 4-iodoanisole or 4-bromoanisole and phenylacetylene catalyzed by Fe/Cu systems.[a]



Entry	X	Fe catalyst [mol%][b]	Cu catalyst [mol%]	Base	Solvent	Yield [%][c]
1	I	**A**, **B** (30)	–	K_2CO_3	DMF	trace
2	I	–	CuI (10)	K_2CO_3	DMF	42
3	I	**A** (30)	CuI (10)	K_2CO_3	DMF	68
4	I	**A** (30)	CuI (10)	K_2CO_3	DMSO	>99
5	I	**A** (30)	CuI (10)	K_2CO_3	NMP	35
6	I	**A** (30)	CuI (10)	K_2CO_3	PEG-400	trace
7	I	**B** (30)	CuI (10)	K_2CO_3	DMSO	98
8	I	–	CuI (10)	K_2CO_3	DMSO	76
9	I	**A** (20)	CuI (10)	K_2CO_3	DMSO	85
10	I	**A** (30)	CuBr (10)	K_2CO_3	DMSO	69
11	I	**A** (30)	CuCl (10)	K_2CO_3	DMSO	40
12	Br	**A** (30)	CuI (10)	K_2CO_3	DMSO	6
13	Br	**A** (30)	CuI (10)	K_2CO_3	DMSO	trace
14	Br	**A** (30)	CuI (10)	Cs_2CO_3	DMSO	trace
15	Br	**A** (30)	CuI (10)	K_3PO_4	DMSO	13
16	Br	**A** (30)	CuI (20)	K_3PO_4	DMSO	19
17	Br	**A** (20)	CuI (20)	K_3PO_4	DMSO	23
18[d]	Br	**A** (20)	CuI (20)	K_3PO_4	DMSO	36
19[e]	Br	**A** (20)	CuI (20)	K_3PO_4	DMSO	12
20[d]	Br	**A** (20)	Cu (20)	K_3PO_4	DMSO	trace
21[d]	Br	**A** (20)	$Cu(OAc)_2$ (20)	K_3PO_4	DMSO	33
22[d]	Br	**A** (20)	Cu_2O (20)	K_3PO_4	DMSO	8

[a] *Reaction conditions:* argon, aryl halide (0.5 mmol), phenylacetylene (0.6 mmol), base (1.0 mmol), solvent (2 mL), 140 °C, 24 h.

[b] **A**: $Fe(acac)_3$, **B**: $FeCl_3$.

[c] Isolated yield (based on aryl halide).

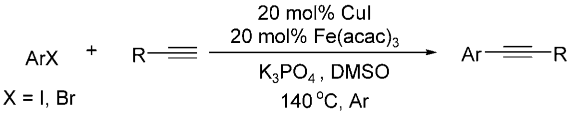
[d] Iodine (10 mol%) as the additive.

[e] TBAB (10 mol%) as the additive.

combination with $Fe(acac)_3$ led to obvious enhancement of the catalytic efficiency (68% yield) (entry 3). Noteworthy is that no homocoupling product of the alkyne was obtained at this time. In other words, the iron catalyst could suppress the homocoupling byproduct.[24] Thus, different commonly used solvents were investigated, such as DMSO (dimethyl sulfoxide), NMP (*N*-methyl-2-pyrrolidone) and PEG-400 [poly(ethylene glycol-400)] (entries 4–6). It can be seen that the catalyitc reaction performed in DMSO afforded a quantitative yield of the product (entry 4) and it also indicated that the amide solvents are not suitable for the catalytic reactions (entries 3 and 5). Thus DMSO was used as the solvent for the following experiments. $FeCl_3$ together with CuI also gave a satisfactory result (98% yield) (entry 7). Although good results were obtained already, we still wanted to conduct the same reaction in DMSO only using 20 mol% of CuI as the catalyst. A comparatively moderate yield (76%) was obtained (entry 8). Meanwhile, we wondered whether the catalytic reaction could be accelerated with lower loading of $Fe(acac)_3$. However, a reduced yield of the desired product was observed (entry 9). Under the same conditions, CuCl or CuBr gave dissapointing results (entries 10 and 11). Since the alkynylation of aryl iodide could go smoothly, we wondered whether these optimized catalytic conditions would be suitable for the alkynylation of aryl bromide. To our disappointment, the desired product was obtained with only 6% yield (entry 12). $FeCl_3$/CuI could hardly catalyze the coupling reaction (entry 13). Furthermore, the experiments showed that various widely used bases such as Cs_2CO_3 and K_3PO_4 had a remarkable effect on the coupling reactions (entries 14 and 15), and K_3PO_4 was the best among the bases (entry 15). The amount of these two metal salts has also been studied (entries 16 and 17). The results showed that equal equivalent ratios (20 mol%:20 mol%) was the optimal (entry 17). Iodine and TBAB (tetrabutyl ammonium bromide) were employed as the additives in the couplings (entries 18 and 19). It can be seen that 10 mol% of iodine was beneficial for the conversion of the catalytic reaction (entry 18). Using copper salts with different valence states afforded disappointing results (entries 20–22). In addition, the catalytic reactions performed in air obviously afforded a great amount of the homocoupling product of the alkyne. Thus, all of the following experiments were conducted under an argon atmosphere.

Based on the above-mentioned optimal conditions, a variety of substrates were examined in the alkynylation coupling reaction and the results are listed in Table 2. It can be seen that the Fe/Cu system efficiently promotes cross-coupling reactions between aryl iodides with alkynes. From an experimental point

Table 2. The coupling reactions of various aryl halides and alkynes catalyzed by Fe(acac)$_3$/CuI.[a]



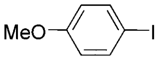
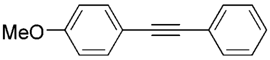
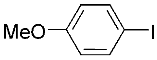
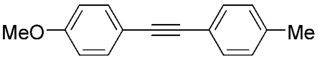
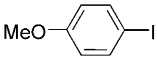
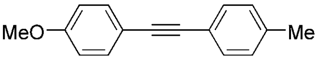
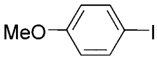
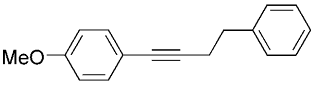
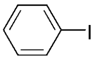
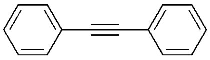
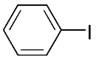
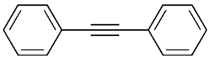
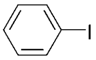
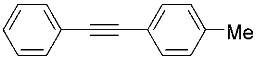
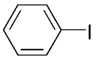
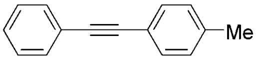
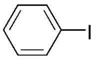
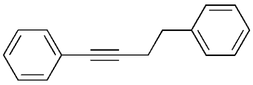
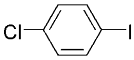
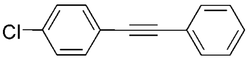
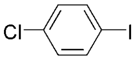
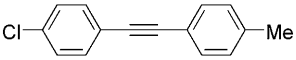
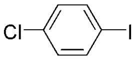
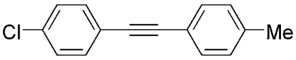
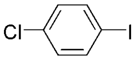
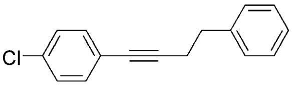
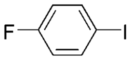
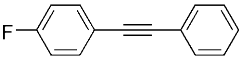
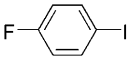
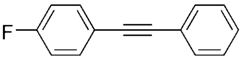
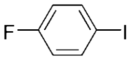
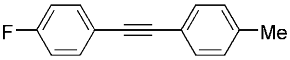
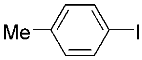
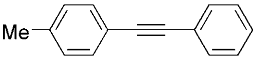
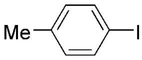
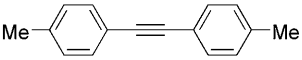
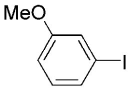
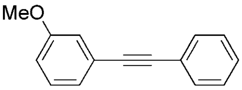
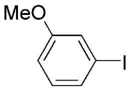
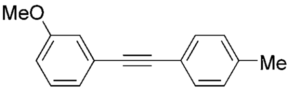
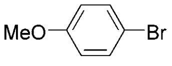
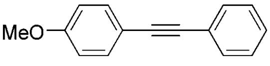
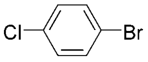
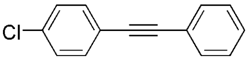
Entry	ArX	Product	Time [h]	Yield [%][b]
1			24	99
2			24	63
3			36	83
4			24	37
5			24	96
6[c]			24	84
7			24	80
8			36	88
9			36	40
10			24	90
11			24	67
12			36	82
13			36	47
14			24	73
15			36	75
16			36	78
17			24	96
18			36	85
19			24	93

Table 2. (Continued)

Entry	ArX	Product	Time [h]	Yield [%][b]
20			36	75
21[d]			24	36
22[d]			48	50

[a] *Reaction conditions:* argon, aryl halide (0.5 mmol), akyne (0.6 mmol), K_3PO_4 (1.0 mmol), DMSO (2 mL), 140 °C, 24–48 h.

[b] Isolated yield (based on aryl halides).

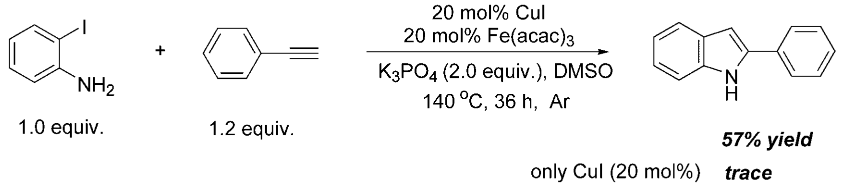
[c] $Cu(OAc)_2$ instead of CuI.

[d] Iodine (10 mol%) as the additive.

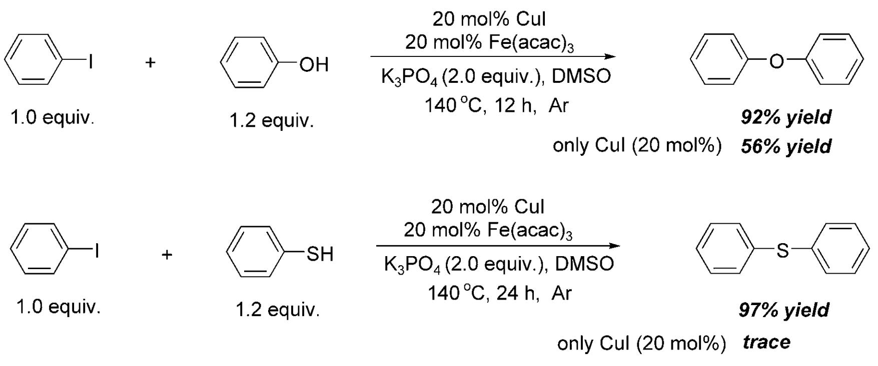
of view, the reactivity of the alkynes would be in the following order (phenylacetylene > *p*-tolylacetylene > 4-phenyl-1-butyne) (entries 1–4). The longer reaction times resulted in higher yields of the corresponding products (entries 3, 8, 12, 15). The catalytic activity of Fe/Cu system for the reactions of aryl bromides was decreased to some extent (entries 21–22). Using 10 mol% of iodine as the additive, a moderate yield (50%) of the desired product was isolated when the coupling of 1-bromo-4-chlorobenzene was performed with phenylacetylene (entry 22). Although iodine was used for halogen exchange,[25] to our disappointment, this catalytic system was not suitable for the coupling of less expensive substrates, such as aryl chlorides.

Due to the increasing interest in the activity of indole derivatives for biological, medicinal and pharmaceutical applications,[26] there has been a great effort to develop more general and versatile methods to synthesize this class of compounds.[27] Among them, an attactive way was *via* the direct coupling reaction of 2-iodoaniline and arylacetylenes. In this paper, we also show such examples of the Fe/Cu co-catalyzed coupling reaction (see Scheme 1). The desired 2-phenyl-1*H*-indole was obtained in 57% yield. Under the same conditions, only a trace of product was obtained when CuI was employed as the sole catalyst.

In order to extend the application of our methodology, we attempted to apply the Fe/Cu catalytic system to other coupling reactions, such as C–O or C–S bond-forming reactions. As shown in Scheme 2, under the non-optimized condition, a 92% yield of the desired diphenyl ether was obtained from the coupling between iodobenzene and phenol. Without using an iron catalyst, we only obtained diphenyl ether in modest yield. In addition, our catalytic sytem was also



Scheme 1.



Scheme 2.

suitable for the cross-coupling of iodobenzene and thiophenol and the desired diphenyl sulfide was isolated with 97% yield. Under the same conditions, the reaction did not occur without the iron catalyst. Thus, it was encouraging to reveal that our catalytic system could be efficient in other coupling reactions. Further work is underway in our laboratory.

In summary, we have developed an effective and promising Fe/Cu catalytic system for the coupling of aryl halides including aryl iodides and bromides with various alkynes. A noteworthy finding is that for the first time the iron-catalyzed alkynylation reactions could be performed without using any ligand. Thus, the low-cost, benign character and easy availability of the catalyst makes this method potentially very useful, which could be amenable to scale-up. Further work is in progress in this laboratory with the aim of reducing the loading of catalysts, mechanistic studies and extending the application of these readily available catalytic systems in other coupling transformations.

Experimental Section

General Experimental Methods

All reactions were carried out under an argon atmosphere. Solvents were dried and degassed by the standard methods and all aryl and heteroaryl halides were purchased from Aldrich or Alfa. Aryl halides and alkynes are readily available. Flash column chromatography was performed using silica gel (300–400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). NMR spectra were recorded in $CDCl_3$ on a Varian Inova-400 NMR spectrometer (400 MHz or 300 MHz) with TMS as an internal reference. Products were characterized by comparison of ^{1}H NMR and HR-MS data with those in the literature.

Typical Experimental Procedure for the Fe/Cu Cocatalyzed Alkynylation Coupling Reaction

A mixture of aryl halide (1.0 equiv.), alkyne (1.2 equiv.), CuI (20 mol%), $Fe(acac)_3$ (20 mol%), K_3PO_4 (2.0 equiv.), and DMSO (2 mL) in a Schlenk tube was stirred under an argon atmosphere at 140 °C for the desired time until complete consumption of starting material as monitored by TLC. After that the mixture was poured into ether, then washed with water, extracted with ethyl acetate, dried by anhydrous $MgSO_4$, then filtered and evaporated under vacuum, the residue was purified by flash column chromatography (petroleum ether or petroleum ether/ethyl acetate) to afford the corresponding coupling products.

1-[2-(4-Methoxyphenyl)ethynyl]benzene: Yellow solid; mp 57–59 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.52–7.50$ (m, 2H, ArH), 7.47 (d, $J = 8.8$ Hz, 2H, ArH), 7.36–7.32 (m, 3H, ArH), 6.88 (d, $J = 8.8$ Hz, 2H, ArH), 3.83 (s, 3H, CH_3); HR-MS (ESI$^+$): $m/z = 208.0896$, calcd. for $[C_{15}H_{12}O]^+$: 208.0888.

Acknowledgements

We are grateful to the grants from the Natural Science Foundation of Education Committee of Jiangsu Province (06KJB150099), the National Natural Science Foundation of China (No. 20802046) and the Key Laboratory of Organic Synthesis of Jiangsu Province for financial support.

References

[1] K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, 4467–4470.

[2] a) R. Chinchilla, C. Najera, *Chem. Rev.* **2007**, *107*, 874–922; b) H. Doucet, J.-C. Hierso, *Angew. Chem.* **2007**, *119*, 850–880; *Angew. Chem. Int. Ed.* **2007**, *46*, 834–871.

[3] S. M. Thacher, S. Nagpal, E. S. Klein, T. Arefieg, G. Krasinski, D. DiSepio, C. Agarwal, A. Johnson, K. L. Eckert, R. A. S. Chandraratna, *Cell Growth & Differentiation* **1999**, *10*, 255–262.

[4] a) M. W. Miller, C. R. Johnson, *J. Org. Chem.* **1997**, *62*, 1582–1583; b) M. Xia, Y.-G. Wang, *Chin. J. Org. Chem.* **2003**, *23*, 609–612; c) O. S. Miljanic, K. P. C. Vollhardt, G. D. Whitener, *Synlett* **2003**, 29–34; d) D. A. Shultz, K. P. Gwaleney, *J. Org. Chem.* **1998**, *63*, 4034–4038; e) K. L. Yu, S. Chen, J. Ostrowski, *Bioorg. Med. Chem. Lett.* **1996**, *6*, 2859–2864; f) L. Wang, P. H. Li, *Chin. J. Chem.* **2003**, *21*, 474–476.

[5] a) S. Thorand, N. Krause, *J. Org. Chem.* **1998**, *63*, 8551–8553; b) A. S. Karpov, F. Rominger, T. J. J. Muller, *J. Org. Chem.* **2003**, *68*, 1503–1511; c) A. Elangovan, Y. H. Wang, *Org. Lett.* **2003**, *5*, 1841–1844; d) J. F. Nguefack, V. Bollet, D. Sinou, *Tetrahedron Lett.* **1996**, *37*, 5527–5530; e) Y. Koseki, K. Omino, S. Anzai, *Tetrahedron Lett.* **2000**, *41*, 2377–2380.

[6] a) J.-H. Li, Q.-M. Zhu, Y.-X. Xie, *J. Org. Chem.* 2005, **70**, 4393–4396; b) J.-H. Li, D.-P. Wang, Y.-X. Xie, *Eur. J. Org. Chem.* 2005, 4256–4259; c) T. Fukuyama, M. Shinmen, S. Nishitani, *Org. Lett.* 2002, **4**, 1691–1694; d) J.-H. Li, D.-P. Wang, Y.-X. Xie, *J. Org. Chem.* 2006, **71**, 379–381; e) L. Anastasia, E. Negishi, *Org. Lett.* 2001, **3**, 3111–3113.

[7] S. U. Son, Y. Jang, J. Park, H. B. Na, H. M. Park, H. J. Yun, J. Lee, T. Hyeon, *J. Am. Chem. Soc.* 2004, **126**, 5026–5027.

[8] R. Soler, . S. Cacchi, G. Fabrizi, G. Forte, L. Martín, S. Martínez, E. Molins, M. Moreno-Mañas, F. Petrucci, A. Roig, R. M. Sebastián, A. Vallribera, *Synthesis* **2007**, 3068–3072.

[9] Leading examples, see: a) M. Feuerstein, F. Berthiol, H. Doucet, M. Santelli, *Org. Biomol. Chem.* **2003**, *1*, 2235–2237; b) J.-C. Hierso, A. Fihri, R. Amardell, P. Meunier, *Org. Lett.* **2004**, *6*, 3473–3476; c) J.-C. Hierso, A. Fihri, R. Amardell, P. Meunier, H. Doucet, M. Santelli, *Tetrahedron* **2005**, *61*, 9759–9766; d) J.-C. Hierso, M. Beaupéin, P. Meunier, *Eur. J. Inorg. Chem.* **2007**, 3767–3780; e) A. Köllhofer, H. Plenio, *Adv. Synth. Catal.* **2005**, *347*, 1295–1300.

[10] I. P. Beletskaya, G. V. Latyshev, A. V. Tsvetkov, N. V. Lukashev, *Tetrahedron Lett.* **2003**, *44*, 5011–5013.

[11] For special reviews on copper-catalyzed cross-couplings, see: a) P. Siemsen, R. C. Livingston, F. Diederich, *Angew. Chem.* **2000**, *112*, 2740–2767; *Angew. Chem. Int. Ed.* **2000**, *39*, 2632–2657; b) J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359–1470; c) S. V. Ley, A. W. Thomas, *Angew. Chem.* **2003**, *115*, 5558–5607; *Angew. Chem. Int. Ed.* **2003**, *42*, 5400–5449; d) I. P. Beletskaya, A. V. Cheprakov, *Coord. Chem. Rev.* **2004**, *248*, 2337–2364; e) F. Monnier, F. Turtaut, L. Duroure, M. Taillefer, *Org. Lett.* **2008**, *10*, 3203–3206.

[12] a) S. Cacchi, G. Fabrizi, L. M. Parisi, *Org. Lett.* **2003**, *5*, 3843–3846; b) M. B. Thathagar, J. Beckers, G. Rothenberg, *Green. Chem.* **2004**, *6*, 215–218; c) K. Okaro, M. Furuune, M. Enna, M. Miura, M. Nomura, *J. Org. Chem.* **1993**, *58*, 4716–4721; d) B.-X. Tang, F. Wang, J.-H. Li, Y.-X. Xie, M.-B. Zhang, *J. Org. Chem.* **2007**, *72*, 6294–6297; e) C. G. Bates, P. Saejueng, J. M. Murphy, D. Venkataraman, *Org. Lett.* **2002**, *4*, 4727–4729; f) Y. F. Wang, W. Deng, L. Liu, Q. X. Guo, *Chin. Chem. Lett.* **2005**, *16*, 1197–1200; g) J.-H. Li, J.-L. Li, D.-P. Wang, S.-F. Pi, Y.-X. Xie, M.-B. Zhang, X.-C. Hu, *J. Org. Chem.* **2007**, *72*, 2053–2057; h) D. Ma, F. Liu, *Chem. Commun.* **2004**, 1934–1935; i) J. Mao, J. Guo, S.-J. Ji, *J. Mol. Catal. A: Chem.* **2008**, *284*, 85–88; j) H. Plenio, *Angew. Chem.* **2008**, *120*, 7060–7063; *Angew. Chem. Int. Ed.* **2008**, *47*, 6954–6956; k) F. Monnier, M. Taillefer, *Angew. Chem.* **2008**, *120*, 3140–3143; *Angew. Chem. Int. Ed.* **2008**, *47*, 3096–3099; l) P. Saejueng, C. G. Bates, D. Venkataraman, *Synthesis* **2005**, 1706–1712; m) F. Liu, D. Ma, *J. Org. Chem.* **2007**, *72*, 4844–4850.

[13] L. Wang, P. Li, Y. Zhang, *Chem. Commun.* **2004**, 514–515.

[14] A. Corma, C. González-Arellano, M. Iglesias, F. Sánchez, *Angew. Chem.* **2007**, *119*, 1558–1560; *Angew. Chem. Int. Ed.* **2007**, *46*, 7820–7822.

[15] S. Park, M. Kim, D. H. Koo, S. Chang, *Adv. Synth. Catal.* **2004**, *346*, 1638–1640.

[16] For general reviews, see: a) C. Bolm, J. Legros, J. L. Paih, L. Zani, *Chem. Rev.* **2004**, *104*, 6217–6254; b) A. Fürstner, R. Martin, *Chem. Lett.* **2005**, *34*, 624–629.

[17] M. Taillefer, N. Xia, A. Oualli, *Angew. Chem.* **2007**, *119*, 952–954; *Angew. Chem. Int. Ed.* **2007**, *46*, 934–936.

[18] V. H. Jadhav, D. K. Dumbre, V. B. Phapale, H. B. Borate, R. D. Wakharkar, *Catal. Commun.* **2007**, *8*, 65–68.

[19] a) A. Correa, C. Bolm, *Angew. Chem.* **2007**, *119*, 9028–9031; *Angew. Chem. Int. Ed.* **2007**, *46*, 8862–8865; b) A. Correa, C. Bolm, *Adv. Synth. Catal.* **2008**, *350*, 391–394; c) A. Correa, S. Elmore, C. Bolm, *Chem. Eur. J.* **2008**, *14*, 3527–3529.

[20] C–O coupling, see: a) O. Bistri, A. Correa, C. Bolm, *Angew. Chem.* **2008**, *120*, 596–598; *Angew. Chem. Int. Ed.* **2008**, *47*, 586–588; b) N. Xia, M. Taillefer, *Chem. Eur. J.* **2008**, *14*, 6037–6039; C–S coupling, see: c) A. Correa, M. Carril, C. Bolm, *Angew. Chem.* **2008**, *120*, 2922–2925; *Angew. Chem. Int. Ed.* **2008**, *47*, 2880–2883.

[21] a) Z. Wang, Y. Zhang, H. Fu, Y. Jiang, Y. Zhao, *Org. Lett.* **2008**, *10*, 1863–1866; b) R. Li, S. R. Wang, W. Lu, *Org. Lett.* **2007**, *9*, 2219–2222; c) J. Bonnamour, C. Bolm, *Org. Lett.* **2008**, *10*, 2665–2667.

[22] After we had submitted our manuscript, we found that Bolm and co-workers had reported the $FeCl_3$-catalyzed Sonogashira coupling reaction using dmeda as the ligand. Please see: M. Carril, A. Correa, C. Bolm, *Angew. Chem.* **2008**, *120*, 4940–4943; *Angew. Chem. Int. Ed.* **2008**, *47*, 4862–4865.

[23] a) J. Mao, J. Guo, S.-J. Ji, *Tetrahedron* **2008**, *64*, 1383–1387; b) J. Mao, J. Guo, F. Fang, S.-J. Ji, *Tetrahedron* **2008**, *64*, 3905–3911; c) Z. Xu, J. Mao, Y. Zhang, *Catal. Commun.* **2008**, *9*, 97–100.

[24] D. Evrard, D. Lucas, Y. Mugnier, P. Meunier, J.-C. Hierso, *Organometallics* **2008**, *27*, 2643–2653.

[25] A. Klapars, S. L. Buchwald, *J. Am. Chem. Soc.* **2000**, *122*, 4844–4845.

[26] a) R. R. Gupta, M. Kumar, V. Gupta, *Heterocyclic Chemistry II*. Springer Verlag, Berlin, Heidelberg, **1998**, Vol. 2; b) R. J. Sundberg, *Indoles*, Academic Press, San Diego, **1996**.

[27] a) S. Cacchi, G. Fabrizi, *Chem. Rev.* **2005**, *105*, 2873–2920; b) G. R. Humphrey, J. T. Kuethe, *Chem. Rev.* **2006**, *106*, 2875–2911.