# Nickel-Catalyzed Cross-Coupling of Arene- or Heteroarenecarbonitriles with Aryl- or Heteroarylmanganese Reagents through C–CN Bond Activation

Ning Liu<sup>a</sup> and Zhong-Xia Wang<sup>a,\*</sup>

<sup>a</sup> CAS Key Laboratory of Soft Matter Chemistry and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China Fax: (+86)-551-360-1592; e-mail: zxwang@ustc.edu.cn

Received: April 27, 2012; Published online: June 5, 2012

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201200369.

**Abstract:** The nickel-catalyzed cross-coupling reaction of arene- or heteroarenecarbonitriles with arylor heteroarylmanganese reagents *via* C–CN bond activation has been developed. Both electron-rich and electron-deficient nitriles can be employed as the electrophilic substrates. The reaction tolerates a range of functional groups and aromatic heterocycles.

**Keywords:** catalysis; C–CN bond activation; crosscoupling; nickel; nitriles; organomanganese reagents

Transition metal-catalyzed cross-coupling reactions are powerful tools used to construct new carboncarbon bonds in modern organic synthesis.<sup>[1]</sup> The nucleophiles for the cross-couplings are normally Grignard reagents, organozinc reagents, organotin reagents, organoboron reagents and organosilicon reagents. Relatively recently, organomanganese reagents were used as a nucleophilic partner in some cross-coupling reactions.<sup>[2]</sup> Electrophiles used in the reactions include organic halides,<sup>[3]</sup> aryl-oxygen deriv-atives (triflates, mesylates, tosylates<sup>[4]</sup> and carboxylates<sup>[5]</sup>) and aryl-nitrogen derivatives (diazonium salts<sup>[6]</sup> and aryltrimethylammonium salts<sup>[7]</sup>). In 2001 Miller et al. disclosed several nickel-catalyzed crosscoupling reactions of arenecarbonitriles with aryl-, alkenyl- and alkyl-Grignard reagents or alkynylzinc reagents through C-CN bond cleavage.<sup>[8]</sup> In the former case the addition of t-BuOLi or PhSLi was required to suppress the nucleophilic addition of the organomagnesium reagent to the nitrile group. Shi et al. reported the cross-coupling of arenecarbonitriles and arylboronic esters catalyzed by Ni(PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>.<sup>[9]</sup> Chatani et al. carried out the rhodium-catalyzed alkenylation

of arenecarbonitriles via silicon-assisted C-CN bond cleavage.<sup>[10]</sup> Knochel et al. found an efficient iron-catalyzed reaction of aroyl cyanides with aryl-Grignard reagents, forming diaryl ketones in good to excellent yields.<sup>[11]</sup> In addition to carbon-carbon bond forming reactions, aryl cyanides can be converted into C-N,<sup>[8c]</sup> C-Si,<sup>[12]</sup> C-B<sup>[13]</sup> and C-H<sup>[14]</sup> bonds through catalytic activation of the C-CN bonds. We became interested in the C-CN bond activation and transformation of arenecarbonitriles because (i) functional group transformation is a central issue in organic synthesis. Removal or transformation of the cyano group in an aryl nitrile is of significance from this viewpoint; (ii) the activation of C-CN bonds is challenging due to their low reactivity (BDE of Ph-CN is ca. 133 kcal  $mol^{-1}$ ;<sup>[15]</sup> (iii) the nucleophiles used in the C–C coupling reactions of arenecarbonitriles are still limited. Herein we report an efficient cross-coupling reaction of arene- or heteroarenecarbonitriles with aryl- or heteroarylmanganese reagents.

The catalysts and solvents were first screened using the reaction of 3-methoxybenzonitrile with p-MeC<sub>6</sub>H<sub>4</sub>MnCl (Table 1). A series of nickel, palladium and cobalt complexes bearing phosphine ligands such as PCy<sub>3</sub>, PEt<sub>3</sub>, PMe<sub>3</sub> and Ph<sub>2</sub>POH was used as the catalyst precursor. It was found Ni(PMe<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> is superior to Ni(PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and Ni(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (Table 1, entries 1– 3). 10 mol% of the former could lead to a 98% product yield in THF at room temperature. Further experiments proved that 5 mol% of Ni(PMe<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> afforded a very similar product yield (Table 1, entry 4). In these reactions, p-MeC<sub>6</sub>H<sub>4</sub>MnCl was prepared from *p*-MeC<sub>6</sub>H<sub>4</sub>Li and Li<sub>2</sub>MnCl<sub>4</sub>. If *p*-MeC<sub>6</sub>H<sub>4</sub>MnCl was prepared from p-MeC<sub>6</sub>H<sub>4</sub>MgBr, a lower crosscoupling yield was observed (Table 1, entry 5). It seems that  $Mg^{2+}$  has a negative effect in this reaction. 2.5 equivalents of p-MeC<sub>6</sub>H<sub>4</sub>MnCl are necessary for the reaction to go to completion, lower amounts of arylmanganese reagent resulting in lower product yields

WILEY CONLINE LIBRARY

Table 1. Screening of catalysts and solvents.<sup>[a]</sup>

CN	MnCl	cat. (10 mol%)	OMe Me
OMe +	Me	solvent, 25 °C, 12 h	

Entry	Catalyst	Solvent	Yield <sup>[f]</sup> [%]
1	$Ni(PCy_3)_2Cl_2$	THF	19
2	Ni(PEt <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	THF	40
3	$Ni(PMe_3)_2Cl_2$	THF	98
4 <sup>[b]</sup>	$Ni(PMe_3)_2Cl_2$	THF	96
5 <sup>[c]</sup>	$Ni(PMe_3)_2Cl_2$	THF	88
6 <sup>[d]</sup>	Ni(PMe <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	THF	92
7	$Ni(acac)_2 + 2PMe_3$	THF	91
8	$Ni(acac)_2 + 2Ph_2POH$	THF	47
9	$Ni(COD)_2 + 2PMe_3$	THF	76
10	$Pd(OAc)_2 + 2PMe_3$	THF	trace
11	$Pd_2(dba)_3 + 2PMe_3$	THF	trace
12	$Co(acac)_3 + 2PMe_3$	THF	22
13	$Ni(PMe_3)_2Cl_2$	THF-MTBE	94
	( -/	(1:1)	
14	$Ni(PMe_3)_2Cl_2$	THF-NMP (1:1)	24
15	$Ni(PMe_3)_2Cl_2$	toluene	45
16 <sup>[b,e]</sup>	$Ni(PMe_3)_2Cl_2$	THF	96

[a] Unless otherwise specified, the reactions were carried out on a 0.5 mmol scale according to the conditions indicated by the above equation and *p*-MeC<sub>6</sub>H<sub>4</sub>MnCl was prepared from *p*-MeC<sub>6</sub>H<sub>4</sub>Li and Li<sub>2</sub>MnCl<sub>4</sub>; 2.5 equiv. of *p*-MeC<sub>6</sub>H<sub>4</sub>MnCl were employed.

<sup>[b]</sup> 5 mol% catalyst was employed.

- <sup>[c]</sup> *p*-MeC<sub>6</sub>H<sub>4</sub>MnCl was prepared from *p*-MeC<sub>6</sub>H<sub>4</sub>MgBr and Li<sub>2</sub>MnCl<sub>4</sub>.
- <sup>[d]</sup> 2 equiv. of p-MeC<sub>6</sub>H<sub>4</sub>MnCl were employed.
- <sup>[e]</sup> 5 mmol m-MeOC<sub>6</sub>H<sub>4</sub>CN were employed.
- <sup>[f]</sup> Yields of isolated products.

(Table 1, entry 6). Ni(acac)<sub>2</sub>/2 PMe<sub>3</sub> afforded a slightly lower yield than Ni(PMe<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> under the same conditions, whereas Ni(acac)<sub>2</sub>/2Ph<sub>2</sub>POH led to a much lower yield (Table 1, entries 7 and 8). Somewhat surprisingly, Ni(COD)<sub>2</sub>/2 PMe<sub>3</sub> was not as effective as Ni- $(PMe_3)_2Cl_2$  for this transformation (Table 1, entry 9). Palladium and cobalt complexes showed less activity than the nickel complexes tested. A combination of either  $Pd(OAc)_2$  or  $Pd_2(dba)_3$  and  $PMe_3$  resulted in only a trace amount of product (Table 1, entries 10 and 11).  $Co(acac)_3/2PMe_3$  is not an effective catalyst for this reaction. It led to only 22% product yield under the standard conditions (Table 1, entry 12). Solvent effects were also tested. The reaction in a 1:1 mixture of THF and methyl tert-butyl ether (MTBE) gave a yield close to that in THF, whereas use of toluene or a mixed solvent of THF and NMP (1:1) resulted in much poorer results (Table 1, entries 13-15). In addition, the reaction using a 5-mmol scale of 3-methoxybenzonitrile gave a similar yield under the same conditions as those of entry 4 in Table 1 (Table 1, entry 16).

We next examined the scope of arene- and heteroarenecarbonitriles in THF using p-MeC<sub>6</sub>H<sub>4</sub>MnCl as a nucleophile and Ni(PMe<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> as a catalyst (Table 2). Both benzonitrile and 2-naphalenecarbonitrile exhibited good reactivity and their reactions gave excellent product yields at 25 °C with a 5 mol% of catalyst loading (Table 2, entries 1 and 2). 4-Methoxybenzonitrile showed a lower reactivity than 3-methoxybenzonitrile. Reaction of the former with p-MeC<sub>6</sub>H<sub>4</sub>MnCl in the presence of 10 mol% Ni(PMe<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> afforded 75–77% yields even at elevated reaction temperatures or prolonged reaction times (Table 2, entries 3 and 4). It was also noted that at 70°C the reaction of 4-methoxybenzonitrile afforded the homocoupling product of 4-methoxybenzonitrile, 4,4'-dimethoxybiphenyl, in 12% yield besides the cross-coupling product. The reaction of 3,4-dimethoxybenzonitrile gave a slightly higher yield than that of 4-methoxybenzonitrile, whereas the reaction 4-(dimethylamino)benzonitrile afforded an excellent result at 70°C (Table 2, entries 5 and 6). Electron-deficient arenecarbonitriles, including ethyl 4-cyanobenzoate, 4-cyano-N,N-dimethylbenzamide, 4-fluorobenzonitrile and 4-(trifluoromethyl)benzonitrile, displayed higher reactivity than electron-rich ones.

Their reactions with *p*-MeC<sub>6</sub>H<sub>4</sub>MnCl could proceed at room temperature with a 5 mol% catalyst loading, giving 86–96% product yields (Table 2, entries 7–10). In these reactions, functional groups such as  $F, CF_3$ , COOEt and  $C(O)NEt_2$  can be tolerated. Attempts to perform the catalytic reactions using n- $RC(O)C_6H_4CN$  (R=H, Me, Ph) and  $p-O_2NC_6H_4CN$ as the electrophiles were unsuccessful. Reaction of p-CHOC<sub>6</sub>H<sub>4</sub>CN with *p*-MeC<sub>6</sub>H<sub>4</sub>MnCl generated an additional product of the formyl group; whereas  $RC(O)C_6H_4CN$  (R = Me, Ph) and p-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CN did not react with an arylmanganese reagent under the standard catalytic conditions. Heteroarenecarbonitriles reacted smoothly with p-MeC<sub>6</sub>H<sub>4</sub>MnCl under appropriate conditions. Reaction of both 3- and 4-cyanopyridines with p-MeC<sub>6</sub>H<sub>4</sub>MnCl in THF at room temperature gave excellent product yields with a 10 mol% catalyst loading (Table 2, entries 11 and 12). However, similar reaction using 2-cyanopyridine as electrophilic partner led to relatively low yield. Further studies showed that at 70°C and in a mixed solvent of THF and NMP (1:1) the reaction afforded an almost quantitative yield (Table 2, entries 13 and 14). The improved reaction conditions are also applicable to the reaction of 2-cyanoquinoline and pyrimidine-2-carbonitrile, which gave 99% and 92% yields, respectively (Table 2, entries 15 and 16).

The scope of the manganese reagents was also tested, including electron-rich and electron-deficient arylmanganese chlorides as well as heteroarylmanga-

Table 2. Nickel-catalyzed	coupling of	arene- or	heteroarene-
carbonitriles with $p$ -MeC <sub>6</sub>	H <sub>4</sub> MnCl. <sup>[a]</sup>		

ArCN	+ MnCl	Ni(PMe <sub>3)2</sub> Cl <sub>2</sub>	e Ar
Entry	ArCN	Catalyst loading	Yield <sup>[e]</sup> [%]
1	CN CN	5 mol%	90
2	CN	5 mol%	93
3 <sup>[b]</sup>	MeO	10 mol%	77
4 <sup>[c]</sup>		10 mol%	75
5 <sup>[b]</sup>		10 mol%	80
6 <sup>[c]</sup>	Me <sub>2</sub> N-CN	10 mol%	89
7		5 mol%	96
8		5 mol%	87
9	F-CN	5 mol%	86
10	F <sub>3</sub> C-CN	5 mol%	92
11	≪CN	10 mol%	89
12	NCN	10 mol%	86
13	CN N	10 mol%	53
14 <sup>[c,d]</sup>	CN N	10 mol%	99
15 <sup>[c,d]</sup>	N CN	10 mol%	99
16 <sup>[c,d]</sup>	⟨_N _N⊂N	10 mol%	92

<sup>[a]</sup> The reactions were carried out on a 0.5-mmol scale according to the conditions indicated by the above equation unless otherwise specified; 2.5 equiv. of *p*-MeC<sub>6</sub>H<sub>4</sub>MnCl were employed; *p*-MeC<sub>6</sub>H<sub>4</sub>MnCl was prepared from *p*-MeC<sub>6</sub>H<sub>4</sub>Li and Li<sub>2</sub>MnCl<sub>4</sub>.

<sup>[b]</sup> Reaction was run for 24 h.

- <sup>[c]</sup> Reaction was carried out at 70 °C.
- <sup>[d]</sup> Reaction was run in a mixed solvent of THF and NMP (1:1).
- <sup>[e]</sup> Yields of isolated products.

nese chlorides. The electron-rich manganese reagents, p-MeOC<sub>6</sub>H<sub>4</sub>MnCl and p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>MnCl, were prepared from the corresponding Grignard reagents and Li<sub>2</sub>MnCl<sub>4</sub>, which gave better coupling results; whereas all other aryl- and heteroarylmanganese reagents were prepared from the corresponding organolithium reagents and Li<sub>2</sub>MnCl<sub>4</sub>. Reaction of *p*-MeOC<sub>6</sub>H<sub>4</sub>MnCl or p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>MnCl with PhCN in THF at 70°C using 10 mol% Ni(PMe<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> as a catalyst afforded the corresponding cross-coupling products in 67% and 82% yields, respectively. Reaction of p- $Me_2NC_6H_4MnCl$  with *m*-MeOC<sub>6</sub>H<sub>4</sub>CN under the same conditions gave the desired product in 72% yield (Table 3, entries 1-3). Usually an electron-rich nucleophilic reagent should behave with stronger nucleophilicity. However, the above results showed that *p*-MeOC<sub>6</sub>H<sub>4</sub>MnCl the reactivity of and p- $Me_2NC_6H_4MnCl$  was lower than that of p-MeC<sub>6</sub>H<sub>4</sub>MnCl. A supposed reason is the coordination of the oxygen atom of p-MeOC<sub>6</sub>H<sub>4</sub>MnCl or the nitrogen atom of p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>MnCl to a metal center (e.g., magnesium, lithium or manganese ion), which decreases the nucleophilicity of the aryl anions. The electron-deficient p-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>MnCl is less reactive than p-MeC<sub>6</sub>H<sub>4</sub>MnCl as expected. Reaction of p- $CF_3C_6H_4MnCl$ with *p*-EtO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>CN or m-MeOC<sub>6</sub>H<sub>4</sub>CN resulted in 63% and 76% yields, respectively (Table 3, entries 4 and 5). The catalytic reaction is sensitive to steric hindrance of the arylmanganese reagents. Reaction of o-MeC<sub>6</sub>H<sub>4</sub>MnCl with p-(t-BuO<sub>2</sub>C)C<sub>6</sub>H<sub>4</sub>CN afforded only 51% yield of crosscoupling product. Heteroarylmanganese reagents are applicable to the cross-coupling. Reaction of 2-furylmanganese chloride with 2-naphthalenecarbonitrile, p-EtO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>CN or *m*-MeOC<sub>6</sub>H<sub>4</sub>CN gave the corresponding products in 77-92% yields (Table 3, entries 7–9). In the reactions, 2-naphthalenecarbonitrile exhibited the highest reactivity; whereas the reaction of p-EtO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>CN led to the lowest yield for as yet unclear reasons. These results also showed that electron-rich 2-furylmanganese chloride is less reactive than p-MeC<sub>6</sub>H<sub>4</sub>MnCl. This may be due to the same p-MeOC<sub>6</sub>H<sub>4</sub>MnCl reason as for and p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>MnCl. Thus, the coordination of the oxygen atom of the furyl group to a metal ion like Li<sup>+</sup> and Mn<sup>2+</sup> decreases the nucleophilicity of the 2-furyl anion. 2-Thienvlmanganese chloride showed higher reactivity than 2-furylmanganese chloride. Its reaction with both activated and deactivated arenecarbonitriles gave excellent results (Table 3, entries 10–13). It was also proven through reaction of 2-naphthalenecarbonitrile and 2-thienylmanganese chloride that the reaction can tolerate larger amounts of substrates without a reduction of yield (Table 3, entry 14). Benzothien-2-ylmanganese chloride can also be used as a nucleophile in the transformation. Its reaction with PhCN or  $3,4-(MeO)_2C_6H_3CN$  gave the corresponding cross-coupling products in 91% and 84% yields, respectively (Table 3, entries 15 and 16). The reaction activity is approximately comparable to that of p-MeC<sub>6</sub>H<sub>4</sub>MnCl.

Adv. Synth. Catal. 2012, 354, 1641-1645

 $\ensuremath{\mathbb C}$  2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 3. Nickel-catalyzed coupling of arenecarbonitriles	with
aryl- or heteroarylmanganese reagents. <sup>[a]</sup>	

		i(PMe <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (10 mol%)	Ar
μ	+ Anwinci –	THF, 70 °C, 12 h	n
Entry	ArMnCl	Arenecarbonitrile	Yield <sup>[d]</sup> [%]
1 <sup>[b]</sup>	MeOMnCl	CN CN	67
2 <sup>[b]</sup>	Me <sub>2</sub> N-MnCl		82
3 <sup>[b]</sup>	Me <sub>2</sub> N-MnCl	MeO	72
4	F <sub>3</sub> C-/MnCl		63
5	F <sub>3</sub> C-MnCl	MeO	76
6	MnCl	t-BuOOC	51
7	MnCl	CN	92
8	MnCl	EtOOC-CN	77
9	MnCl	MeO	80
10	MnCl	CN CN	95
11	MnCl	CN	94
12	MnCl	MeO	87
13	MnCl	F <sub>3</sub> C-CN	95
14 <sup>[c]</sup>	MnCl	CN	98
15	MnCl	CN CN	91
16	MnCl	MeO MeO CN	84

[a] The reactions were carried out on a 0.5-mmol scale according to the conditions indicated by the above equation and ArMnCl was prepared from ArLi and Li<sub>2</sub>MnCl<sub>4</sub> unless otherwise specified; 2.5 equiv. of arylmanganese reagents were employed.

- <sup>[b]</sup> ArMnCl was prepared from ArMgBr and Li<sub>2</sub>MnCl<sub>4</sub>.
- <sup>[c]</sup> 5 mmol 2-naphthalenecarbonitrile were employed.

<sup>[d]</sup> Yields of isolated products.

In summary, we have developed a simple and highly efficient process for the nickel-catalyzed crosscoupling of arene- or heteroarenecarbonitriles and aryl- or heteroarylmanganese reagents. The cross-coupling can be carried out under mild conditions, does not require any additives, displays a broad substrate scope and tolerates functional groups such as ester, amide, trifluoromethyl, fluoride, methyloxy, and dimethylamino groups and aromatic heterocycles.

## **Experimental Section**

#### **Typical Procedure (Table 1, entry 4)**

A Schlenk tube was charged with Ni(PMe<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (7.0 mg, 0.025 mmol), 3-methoxybenzonitrile (0.0675 g, 0.5 mmol) and THF (0.5 mL). To the solution was added dropwise a solution of p-MeC<sub>6</sub>H<sub>4</sub>MnCl (2.5 mL, 0.5 M in THF, 1.25 mmol) at 25 °C with stirring. After stirring at this temperature for 12 h, water (10 mL) and several drops of acetic acid were successively added. The resulting mixture was extracted with Et<sub>2</sub>O (3×10 mL). The extract was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated by rotary evaporation. The residue was purified by column chromatography (silica gel, eluted using petroleum ether) to afford 3-methoxy-4'-methylbiphenyl; yield: 0.095 g (96%).

#### Acknowledgements

We gratefully acknowledge financial support by the National Natural Science Foundation of China (grant no. 21172208) and National Basic Research Program of China (grant no. 2009CB825300).

### References

- [1] a) Metal-Catalyzed Cross-Coupling Reactions, (Eds.: F. Diederich, P. J. Stang), VCH, Weinheim, 1998; b) Metal-Catalyzed Cross-Coupling Reactions, 2nd edn., (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, 2004; c) Handbook of Organopalladium Chemistry for Organic Synthesis (Ed.: E. Negishi), Wiley, New York, 2002; d) J. Hassan, M. Sévignon, C. Gozzi, E. Schulz, M. Lemaire, Chem. Rev. 2002, 102, 1359-1470; e) J. Corbet, G. Mignani, Chem. Rev. 2006, 106, 2651-2710; f) A. F. Littke, G. C. Fu, Angew. Chem. 2002, 114, 4350-4386; Angew. Chem. Int. Ed. 2002, 41, 4176-4211; g) A. C. Frisch, M. Beller, Angew. Chem. 2005, 117, 680-695; Angew. Chem. Int. Ed. 2005, 44, 674-688; h) S. Würtz, F. Glorius, Acc. Chem. Res. 2008, 41, 1523-1533; i) G. C. Fu, Acc. Chem. Res. 2008, 41, 1555-1564; j) K. C. Nicolaou, P. G. Bulger, D. Sarlah, Angew. Chem. 2005, 117, 4516–4563; Angew. Chem. Int. Ed. 2005, 44, 4442-4489; k) S. E. Denmark, C. S. Regens, Acc. Chem. Res. 2008, 41, 1486-1499.
- [2] a) G. Cahiez, C. Duplais, J. Buendia, *Chem. Rev.* 2009, 109, 1434–1476; b) E. Riguet, M. Alami, G. Cahiez, *Tetrahedron Lett.* 1997, 38, 4397–4400; c) A. Leleu, Y.

Fort, R. Schneider, Adv. Synth. Catal. 2006, 348, 1086–1092.

- [3] a) C. Dai, G. C. Fu, J. Am. Chem. Soc. 2001, 123, 2719-2724; b) A. Gavryushin, C. Kofink, G. Manolikakes, P. Knochel, Org. Lett. 2005, 7, 4871-4874; c) J. E. Milne, S. L. Buchwald J. Am. Chem. Soc. 2004, 126, 13028-13032; d) G. Manolikakes, Z. Dong, H. Mayr, J. Li, P. Knochel, Chem. Eur. J. 2009, 15, 1324-1328; e) B. H. Lipshutz, P. A. Blomgren, J. Am. Chem. Soc. 1999, 121, 5819-5820; f) L. Wang, Z.-X. Wang, Org. Lett. 2007, 9, 4335-4338; g) N. Liu, L. Wang, Z.-X. Wang, Chem. Commun. 2011, 47, 1598-1600; h) A. Gavryushin, C. Kofink, G. Manolikakes, P. Knochel, Tetrahedron 2006, 62, 7521-7533; i) Z. Xi, Y. Zhou, W. Chen J. Org. Chem. 2008, 73, 8497-8501; j) S. C. Calimsiz, M. Sayah, D. Mallik, M. G. Organ, Angew. Chem. 2010, 122, 2058-2061; Angew. Chem. Int. Ed. 2010, 49, 2014-2017; k) J. L. Bolliger, C. M. Frech, Chem. Eur. J. 2010, 16, 11072-11081; l) Z. Tan, E. Negishi, Angew. Chem. 2006, 118, 776-779; Angew. Chem. Int. Ed. 2006, 45, 762-765; m) S. Son, G. C. Fu, J. Am. Chem. Soc. 2008, 130, 2756-2757.
- [4] a) J. Terao, H. Todo, H. Watanabe, A. Ikumi, N. Kambe, Angew. Chem. 2004, 116, 6306–6308; Angew. Chem. Int. Ed. 2004, 43, 6180–6182; b) M. G. Organ, S. Avola, I. Dubovyk, N. Hadei, E. Assen, B. Kantchev, C. J. O'Brien, C. Valente, Chem. Eur. J. 2006, 12, 4749–4755; c) S. A. Savage, A. P. Smith, C. L. Fraser, J. Org. Chem. 1998, 63, 10048–10051; d) C. Gómez-Reino, C. Vitale, M. Maestro, A. Mouriño, Org. Lett. 2005, 7, 5885–5887; e) L. Melzig, A. Gavryushin, P. Knochel, Org. Lett. 2007, 9, 5529–5532; f) X. Li, F. Shen, H. Fu, Y. Jiang, Y. Zhao, Synlett 2006, 630–632; g) H. Shimizu, K. Manabe, Tetrahedron Lett. 2006, 47, 5927–5931.

- [5] B.-J. Li, Y.-Z. Li, X.-Y. Lu, J. Liu, B.-T. Guan, Z.-J. Shi, Angew. Chem. 2008, 120, 10278–10281; Angew. Chem. Int. Ed. 2008, 47, 10124–10127.
- [6] A. Roglans, A. Pla-Quintana, M. Moreno-Mañas, *Chem. Rev.* 2006, 106, 4622–4643.
- [7] a) E. Wenkert, A.-L. Han, C.-J. Jenny, J. Chem. Soc. Chem. Commun. 1988, 975–976; b) J. T. Reeves, D. R. Fandrick, Z. Tan, J. J. Song, H. Lee, N. K. Yee, C. H. Senanayake, Org. Lett. 2010, 12, 4388–4391; c) S. B. Blakey, D. W. C. MacMillan, J. Am. Chem. Soc. 2003, 125, 6046–6047; d) L.-G. Xie, Z.-X. Wang, Angew. Chem. 2011, 123, 5003–5006; Angew. Chem. Int. Ed. 2011, 50, 4901–4904.
- [8] a) J. A. Miller, Tetrahedron Lett. 2001, 42, 6991–6993;
  b) J. A. Miller, J. W. Dankwardt, Tetrahedron Lett. 2003, 44, 1907–1910;
  c) J. A. Miller, J. W. Dankwardt, J. M. Penny, Synthesis 2003, 1643–1648;
  d) J. M. Penney, J. A. Miller, Tetrahedron Lett. 2004, 45, 4989–4992.
- [9] D.-G. Yu, M. Yu, B.-T. Guan, B.-J. Li, Y. Zheng, Z.-H. Wu, Z.-J. Shi, Org. Lett. 2009, 11, 3374–3377.
- [10] Y. Kita, M. Tobisu, N. Chatani, Org. Lett. 2010, 12, 1864–1867.
- [11] C. Duplais, F. Bures, I. Sapountzis, T. J. Korn, G. Cahiez, P. Knochel, Angew. Chem. 2004, 116, 3028–3030; Angew. Chem. Int. Ed. 2004, 43, 2968–2970.
- [12] a) M. Tobisu, Y. Kita, N. Chatani, J. Am. Chem. Soc.
   2006, 128, 8152–8153; b) M. Tobisu, Y. Kita, Y. Ano, N. Chatani, J. Am. Chem. Soc. 2008, 130, 15982–15989.
- [13] M. Tobisu, H. Kinuta, Y. Kita, E. Rémond, Naoto Chatani, J. Am. Chem. Soc. 2012, 134, 115–118.
- [14] a) M. Tobisu, R. Nakamura, Y. Kita, N. Chatani, J. Am. Chem. Soc. 2009, 131, 3174–3175; b) M. Tobisu, R. Nakamura, Y. Kita, N. Chatani, Bull. Korean Chem. Soc. 2010, 31, 582–587.
- [15] A. A. Zavitsas, J. Phys. Chem. A 2003, 107, 897-898.