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Pd-catalyzed decarboxylative couplings of arenecarboxylic acids with aryl iodides

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ABSTRACT

The combination of palladium chloride with BINAP shows high efficiency in the decarboxylative cross-coupling reactions of arenecarboxylic acids with aryl iodides. The reactions proceed smoothly to generate the corresponding biaryl compounds in good to excellent yields.

1. Introduction

Palladium-catalyzed coupling has become a principal method of forming a C–C bond.[1] Recently, the palladium-catalyzed decarboxylative cross-coupling reaction is attracting increasing interest since it provides an important alternative route for carbon–carbon bond formation. As highlighted by Baudoin,[2] this method has several advantages over the conventional transition metal-catalyzed cross-coupling reactions and the direct arylation through C-H activation, concerning the regioselectivity as well as atom and step economy issues. Since Nilsson reported the first example for transition-metal mediated decarboxylative biaryl coupling,[3] breakthroughs have been achieved by Myers,[4] Goossen,[5] and others[6,7] in the development of Pd-catalyzed decarboxylative cross-coupling reactions. For instance, Myers reported a versatile decarboxylative Heck-type reaction between arenecarboxylic acids and olefins under palladium catalysis.[4] Goossen and co-workers have described the efficient preparation of biaryls or ketones via a Pd/Cu co-catalyzed decarboxylative coupling of arenecarboxylic acids and aryl halides.[5] The reactions usually finished in 24 h at 120–170 °C with limited substrate scope. The group of Forgione and Bilodeau reported Pd-catalyzed arylation of heteroaromatic carboxylic acids.[6d] Becht and Wagner described the decarboxylative couplings of arenecarboxylic acids with aryl iodides catalyzed by the combination of $PdCl_2$ and $AsPh_3$ in the presence of Ag_2CO_3 in DMSO.[7a] However, 30 mol % of $PdCl_2$ and 60 mol % of highly toxic $AsPh_3$ had to be utilized in the reaction to obtain respectable yields. Moreover, aryl bromide was not effective under the conditions. Subsequently, they presented Pd-catalyzed couplings of arenecarboxylic acids with diaryliodonium triflates.[7d] Again, high loading of palladium catalyst (20 mol %) and ligand was employed. Thus, it is still desired to develop general and efficient methods for this type of decarboxylative coupling. As part of a continuing effort in our laboratory for C–C bond formation,[8] we became interested in developing efficient methods via transition metal-catalyzed decarboxylative coupling of carboxylic acids with aryl halides. Herein, we disclose our recent efforts for decarboxylative cross-coupling of arenecarboxylic acids with aryl iodides catalyzed by the combination of $PdCl_2$ and BINAP. The reactions usually finished in 0.5–2 h with good to excellent isolated yields.

2. Results and discussion

Initially, the reaction was conducted using 2-nitrobenzoic acid **1a** and 4-iodoanisole **2a** as model substrates in the presence of palladium chloride as catalyst (Table 1). At the outset, various ligands were screened in the presence of Ag_2CO_3 as additive at 150 °C. Gratifyingly, in the presence of S-Phos (10 mol %) this reaction proceeded smoothly in DMA to afford the corresponding product **3a** in 59% yield (Table 1, entry 1). Further investigation revealed that the result could be dramatically improved when BINAP was employed in the reaction (83% yield, Table 1, entry 4). In addition, this reaction went to completion in less than 2 h. Other phosphine ligands utilized in this decarboxylative cross-coupling

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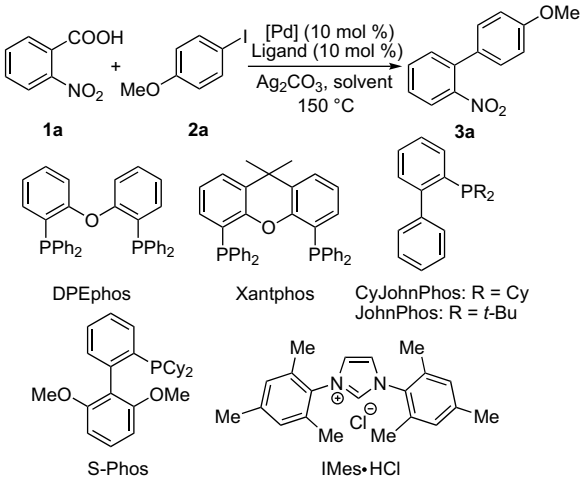
Table 1
Initial studies for Pd-catalyzed decarboxylative coupling of 2-nitrobenzoic acid **1a** and 4-iodoanisole **2a**



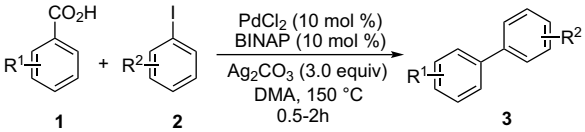
Entry	[Pd]	Ligand	Solvent	Yield[a] (%)
1	$PdCl_2$	S-Phos	DMA	59
2	$PdCl_2$	JohnPhos	DMA	37
3	$PdCl_2$	CyJohnPhos	DMA	63
4	$PdCl_2$	BINAP	DMA	83
5	$PdCl_2$	PCy_3	DMA	39
6	$PdCl_2$	$P(o\text{-tolyl})_3$	DMA	47
7	$PdCl_2$	DPPP	DMA	49
8	$PdCl_2$	DPPF	DMA	55
9	$PdCl_2$	Xantphos	DMA	49
10	$PdCl_2$	DPEphos	DMA	52
11	$PdCl_2$	IMes•HCl	DMA	42
12	$Pd(OAc)_2$	BINAP	DMA	58
13	$Pd(PPh_3)_2Cl_2$	BINAP	DMA	52
14	$Pd(dppf)Cl_2$	BINAP	DMA	61
15	$PdCl_2$	BINAP	DMSO	64
16	$PdCl_2$	BINAP	DMF	61
17	$PdCl_2$	/	DMA	30

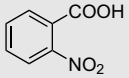
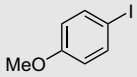
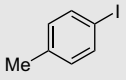
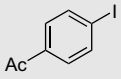
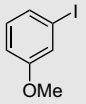
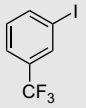
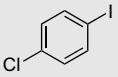
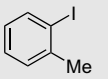
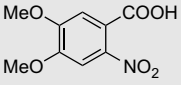
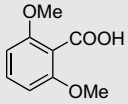
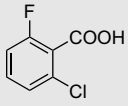
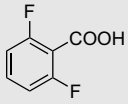
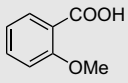
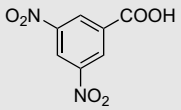
[a] Isolated yield based on 2-Nitrobenzoic Acid **1a**.

reaction showed inferior results. Lower yields were observed when *N*-heterocyclic carbene[9] was used as a replacement (Table 1, entry 11). We also tested other palladium catalysts, and $PdCl_2$ was the best choice (Table 1, entries 12–14). Reactions in other solvents (such as DMSO and DMF, Table 1, entries 15 and 16) or at lower temperatures (data not shown in Table 1) either occurred to afford lower conversions, required longer reaction times, or both. In the absence of ligand or decreasing the amount of palladium catalyst the yield was diminished. We also tested other additives (such as CuI, $Cu(OAc)_2$, AgOAc) as replacement of Ag_2CO_3. However, the yield could not be improved (data not shown in Table 1).

Having demonstrated the viability of this catalytic strategy we next investigated the scope of the transformation under the

Table 2
Pd-catalyzed decarboxylative cross-coupling reactions of arenecarboxylic acids **1** with aryl iodides **2**

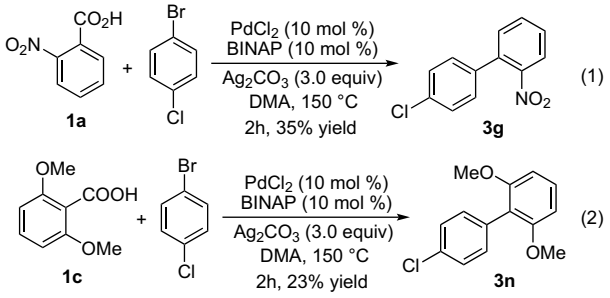


Entry	Carboxylic acid **1**	Aryl iodide **2**	Product	Yield[a] (%)
1	 **1a**	 **2a**	**3a**	83
2	**1a**	 **2b**	**3b**	96
3	**1a**	 **2c**	**3c**	95
4	**1a**	 **2d**	**3d**	91
5	**1a**	 **2e**	**3e**	87
6	**1a**	 **2f**	**3f**	85
7	**1a**	 **2g**	**3g**	89
8	**1a**	 **2h**	**3h**	60
9	 **1b**	**2a**	**3i**	72
10	**1b**	**2b**	**3j**	82
11	**1b**	**2d**	**3k**	75
12	 **1c**	**2a**	**3l**	63
13	**1c**	**2c**	**3m**	76
14	**1c**	**2g**	**3n**	91
15	 **1d**	**2a**	**3o**	75
16	 **1e**	**2a**	**3p**	54
17	 **1f**	**2c**	**3q**	41
18	 **1g**	**2c**	**3r**	40

[a] Isolated yield based on arenecarboxylic acid **1**.

preliminary optimized conditions [$PdCl_2$ (10 mol %), BINAP (10 mol %), Ag_2CO_3 (3.0 equiv), DMA, 150 °C], and the results are summarized in Table 2. To assess the impact of the structural and functional motifs on the reaction we tested a range of linking units between arenecarboxylic acids **1** and aryl iodides **2**. From Table 2, it was found that for most cases, the reactions furnished the corresponding biaryl compounds **3** in good to excellent yields. For example, reaction of 2-nitrobenzoic acid **1a** with 1-iodo benzene **2b** gave rise to product **3b** in 96% yield (Table 2, entry 2). A similar result was observed when 1-iodo-4-methylbenzene **2c** was employed in the reaction of 2-nitrobenzoic acid **1a** (95% yield, Table 2, entry 3). Additionally, for the reactions of 2-nitrobenzoic acid **1a**, a range of different groups was tolerated in aryl iodides with different electronic demands on the aromatic rings involving electron-donating and electron-withdrawing groups. For instance, reaction of acetyl-substituted aryl iodide **2d** proceeded smoothly, which gave rise to the desired product **3d** in good yield (91% yield, Table 2, entry 4). 3-Substituted aryl iodides, such as **2e** or **2f**, were also suitable partners in this process, and the desired products were furnished in good yield (Table 2, entries 5 and 6). When 4-chlorophenyl iodide **2g** was employed in the reaction of 2-nitrobenzoic acid **1a** under the standard conditions, the chloro group in compound **2g** was retained during the transformation, and the product **3g** was afforded in 89% yield (Table 2, entry 7). The aryl iodide bearing *ortho*-substitution was also employed in the reaction of 2-nitrobenzoic acid **1a** and the desired product **3h** was generated in 60% yield (Table 2, entry 8). Other arenecarboxylic acids were also examined. Reactions of 4,5-dimethoxy-2-nitrobenzoic acid **1b** or 2,6-dimethoxybenzoic acid **1c** with various aryl iodides led to the corresponding products in good yields (Table 2, entries 9–14). Fluoro-substituted arenecarboxylic acid **1d** reacted with 4-iodoanisole **2a**, and gave rise to the biaryl product **3o** in 75% yield (Table 2, entry 15). However, only a moderate yield was observed when 2,6-difluorobenzoic acid **1e** was used in the reaction (54% yield, Table 2, entry 16). Reaction of 2-methoxybenzoic acid **1f** or 3,5-dinitrobenzoic acid **1g** with 1-iodo-4-methylbenzene **2c** led to the formation of product **3q** or **3r** in 41% or 40% yield, respectively (Table 2, entries 17 and 18).

We also examined the palladium-catalyzed decarboxylative cross-coupling reactions of arenecarboxylic acids with activated aryl bromide under the standard conditions shown in Table 2 (Scheme 1). Interestingly, the desired product was also generated, although the yield was low.



Scheme 1. Pd-catalyzed decarboxylative cross-coupling reactions of arenecarboxylic acids with aryl bromide.

3. Conclusions

In summary, we have described an efficient method for the decarboxylative cross-coupling reaction of arenecarboxylic acids with aryl iodides catalyzed by the combination of $PdCl_2$ and BINAP in the presence of Ag_2CO_3 as an additive. The reactions showed high efficiency and usually finished in 0.5–2 h with good to excellent isolated yields. Currently, investigations utilizing unactivated aryl bromides and aryl chlorides as substrates in palladium-catalyzed decarboxylative cross-coupling reactions of arenecarboxylic acids are ongoing, and the results will be reported in due course.

4. Experimental section

4.1. General method

All reactions were performed in reaction tubes under nitrogen atmosphere. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63 μm, standard grade). Analytical thin-layer chromatography was performed using glass plates precoated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin-layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr (house vacuum) at 25–35 °C. Commercial reagents and solvents were used as received. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale.

General procedure for palladium-catalyzed decarboxylative cross-coupling reaction of arenecarboxylic acid **1** with aryl iodide **2**. A mixture of arenecarboxylic acid **1** (0.30 mmol), aryl iodide **2** (0.33 mmol, 1.1 equiv), Ag_2CO_3 (0.90 mmol, 247 mg, 3.0 equiv), BINAP (0.03 mmol, 19 mg, 0.1 equiv), and $PdCl_2$ (0.03 mmol, 5.3 mg, 0.1 equiv) in DMA (2.0 mL) was stirred at 150 °C under nitrogen for 2 h. After completion of reaction as indicated by TLC, the mixture was cooled and filtered with Celite (washed with 10 mL of ethyl acetate). The filtrate was then washed with saturated NH_4Cl, dried with $MgSO_4$, and concentrated under reduced vacuum. The residue was subsequently purified by flash chromatography on silica gel to afford product **3**.

4.1.1. 4′-Methoxy-2-nitrobiphenyl (**3a**)[5b]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.83 (s, 3H), 6.94 (d, *J*=8.3 Hz, 2H), 7.24 (d, *J*=8.3 Hz, 2H), 7.39–7.44 (m, 2H), 7.57 (t, *J*=7.3 Hz, 1H), 7.80 (d, *J*=7.3 Hz, 1H).

4.1.2. 2-Nitrobiphenyl (**3b**)[7d]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.31 (dd, *J*=1.9, 7.8 Hz, 2H), 7.39–7.48 (m, 5H), 7.60 (t, *J*=7.3 Hz, 1H), 7.84 (d, *J*=7.8 Hz, 1H).

4.1.3. 4′-Methyl-2-nitrobiphenyl (**3c**)[5b]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.38 (s, 3H), 7.22–7.24 (m, 4H), 7.41–7.44 (m, 2H), 7.58 (t, *J*=7.8 Hz, 1H), 7.81 (d, *J*=8.3 Hz, 1H).

4.1.4. 4′-Acetyl-2-nitrobiphenyl (**3d**)[5b]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.64 (s, 3H), 7.43 (t, *J*=8.3 Hz, 3H), 7.54 (t, *J*=7.3 Hz, 1H), 7.66 (t, *J*=7.3 Hz, 1H), 7.93 (d, *J*=8.3 Hz, 1H), 7.57 (d, *J*=8.3 Hz, 2H).

4.1.5. 3′-Methoxy-2-nitrobiphenyl (**3e**)[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.81 (s, 3H), 6.85 (s, 1H), 6.88 (d, *J*=7.8 Hz, 1H), 7.82 (dd, *J*=2.4, 8.3 Hz, 1H), 7.32 (t, *J*=7.8 Hz, 1H), 7.44 (d, *J*=7.3 Hz, 1H), 7.47 (d, *J*=7.8 Hz, 1H), 7.59 (t, *J*=7.8 Hz, 1H), 7.82 (d, *J*=8.3 Hz, 1H).

4.1.6. 2′-Nitro-3-trifluoromethylbiphenyl (**3f**)[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.43 (d, *J*=7.8 Hz, 1H), 7.48 (d, *J*=7.3 Hz, 1H), 7.54 (t, *J*=8.3 Hz, 2H), 7.59 (s, 1H), 7.65 (d, *J*=6.3 Hz, 1H), 7.67 (d, *J*=6.3 Hz, 1H), 7.94 (d, *J*=8.3 Hz, 1H).

4.1.7. 4′-Chloro-2-nitrobiphenyl (**3g**)[5b]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.24 (d, *J*=8.3 Hz, 2H), 7.38–7.41 (m, 3H), 7.49 (t, *J*=7.8 Hz, 1H), 7.61 (dt, *J*=0.96, 7.8 Hz, 1H), 7.87 (d, *J*=7.8 Hz, 1H).

4.1.8. 2′-Methyl-2-nitrobiphenyl (**3h**)[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.10 (s, 3H), 7.09 (d, *J*=7.3 Hz, 1H), 7.20–7.28 (m, 3H), 7.32 (t, *J*=7.8 Hz, 1H), 7.51 (t, *J*=7.8 Hz, 1H), 7.63 (t, *J*=7.8 Hz, 1H), 7.98 (d, *J*=7.8 Hz, 1H).

*4.1.9. 4′,4,5,-Trimethoxy-2-nitrobiphenyl (**3i**)*[7a]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.84 (s, 3H), 3.94 (s, 3H), 3.97 (s, 3H), 6.77 (s, 1H), 6.94 (d, J=8.3 Hz, 2H), 7.21 (d, J=8.3 Hz, 2H), 7.51 (s, 1H).

*4.1.10. 4,5-Trimethoxy-2-nitrobiphenyl (**3j**)*[7d]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.95 (s, 3H), 3.98 (s, 3H), 6.78 (s, 1H), 7.28–7.30 (m, 2H), 7.38–7.42 (m, 3H), 7.55 (s, 1H).

*4.1.11. 4′-Acetyl-4,5-dimethoxy-2-nitrobiphenyl (**3k**)*

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.64 (s, 3H), 3.96 (s, 3H), 4.00 (s, 3H), 6.76 (s, 1H), 7.39 (d, J=7.8 Hz, 2H), 7.61 (s, 1H), 8.01 (d, J=8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 26.6, 56.4, 56.5, 107.9, 113.1, 128.3, 128.5, 130.3, 136.2, 140.6, 143.3, 148.4, 152.4, 197.5. MS (EI) m/z 301 (M^+). Anal. Calcd for $C_{16}H_{15}NO_5$: C, 63.78; H, 5.02, N, 4.65. Found: C, 63.56; H, 4.95, N, 4.51.

*4.1.12. 2,4′,6-Trimethoxybiphenyl (**3l**)*[7a]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.73 (s, 6H), 3.83 (s, 3H), 6.64 (d, J=8.3 Hz, 2H), 6.95 (d, J=8.8 Hz, 2H), 7.23–7.29 (m, 3H).

*4.1.13. 2,6-Dimethoxy-4′-methylbiphenyl (**3m**)*[7a]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.38 (s, 3H), 3.73 (s, 6H), 6.65 (d, J=8.3 Hz, 2H), 7.22–7.25 (m, 5H).

*4.1.14. 4′-Chloro-2,6-dimethoxybiphenyl (**3n**)*[7a]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.71 (s, 6H), 6.63 (d, J=8.8 Hz, 2H), 7.25–7.29 (m, 3H), 7.35 (d, J=8.3 Hz, 2H).

*4.1.15. 2-Chloro-6-fluoro-4′-methoxybiphenyl (**3o**)*[7a]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.85 (s, 3H), 6.99 (d, J=8.8 Hz, 2H), 7.06 (t, J=8.3 Hz, 1H), 7.21–7.31 (m, 4H).

*4.1.16. 4′-Chloro-2,6-difluorobiphenyl (**3p**)*[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.84 (s, 3H), 6.94 (d, J=7.8 Hz, 2H), 6.99 (d, J=8.8 Hz, 2H), 7.19–7.25 (m, 1H), 7.40 (d, J=8.8 Hz, 2H).

*4.1.17. 4′-Methyl-2-methoxybiphenyl (**3q**)*[5b]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.38 (s, 6H), 3.80 (s, 3H), 6.97 (d, J=8.8 Hz, 1H), 7.01 (dt, J=1.0, 7.3 Hz, 1H), 6.97 (d, J=8.8 Hz, 1H), 7.22 (d, J=7.8 Hz, 2H), 7.28–7.31 (m, 2H), 7.42 (d, J=7.8 Hz, 2H).

*4.1.18. 4′-Methyl-3,5-dinitrobiphenyl (**3r**)*[14]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.45 (s, 3H), 7.36 (d, J=7.8 Hz, 2H), 7.58 (d, J=7.8 Hz, 2H), 8.75 (d, J=1.5 Hz, 2H), 8.97 (s, 1H).

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2009.04.047.

References and notes

1. (a) *Palladium Reagents and Catalysts*; Tsuji, J., 2nd, Ed.; John Wiley & Sons: Chichester, UK, 2004; (b) de Meijere, A.; Diederich, F. *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; John Wiley & Sons: Weinheim, Germany, 2004.
2. Baudoin, O. *Angew. Chem., Int. Ed.* **2007**, *46*, 1373.
3. Nilsson, M. *Acta Chem. Scand.* **1966**, *20*, 423.
4. (a) Myers, A. G.; Tanaka, D.; Mannion, M. R. *J. Am. Chem. Soc.* **2002**, *124*, 11250; (b) Tanaka, D.; Myers, A. G. *Org. Lett.* **2004**, *6*, 433; (c) Tanaka, D.; Romeril, S. P.; Myers, A. G. *J. Am. Chem. Soc.* **2005**, *127*, 10323.
5. (a) Goossen, L. J.; Deng, G.; Levy, L. M. *Science* **2006**, *313*, 662; (b) Goossen, L. J.; Rodriguez, N.; Melzer, B.; Linder, C.; Deng, G.; Levy, L. M. *J. Am. Chem. Soc.* **2007**, *129*, 4824; (c) Goossen, L. J.; Melzer, B. *J. Org. Chem.* **2007**, *72*, 7473; (d) For review, see: Goossen, L. J.; Rudolphi, F.; Oppel, C.; Rodriguez, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 3043; Goossen, L. J.; Rodriguez, N.; Goossen, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 3100.
6. (a) Lalic, G.; Aloise, A. D.; Shair, M. D. *J. Am. Chem. Soc.* **2003**, *125*, 2852; (b) Lou, S.; Westbrook, J. A.; Schaus, S. E. *J. Am. Chem. Soc.* **2004**, *126*, 11440; (c) Rayabarapu, D. K.; Tunge, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 13510; (d) Forgione, P.; Brochu, M.-C.; St-Onge, M.; Thesen, K. H.; Bailey, M. D.; Bilodeau, F. *J. Am. Chem. Soc.* **2006**, *128*, 11350.
7. (a) Becht, J.-M.; Catala, C.; Le Drian, C.; Wagner, A. *Org. Lett.* **2007**, *9*, 1781; (b) Waetzig, S. R.; Tunge, J. A. *J. Am. Chem. Soc.* **2007**, *129*, 14860; (c) Yeagley, A. A.; Chruma, J. J. *Org. Lett.* **2007**, *9*, 2879; (d) Becht, J.-M.; Drian, C. L. *Org. Lett.* **2008**, *10*, 3161; (e) Goossen, L. J.; Rodriguez, N.; Linder, C. *J. Am. Chem. Soc.* **2008**, *130*, 15248; (f) Moon, J.; Jang, M.; Lee, S. *J. Org. Chem.* **2009**, *74*, 1403; (g) Voutchkova, A.; Coplin, A.; Leadbeater, N. E.; Crabtree, R. H. *Chem. Commun.* **2008**, 6312.
8. (a) Zhang, L.; Meng, T.; Wu, J. *J. Org. Chem.* **2007**, *72*, 9346; (b) Zhang, L.; Meng, T.; Fan, R.; Wu, J. *J. Org. Chem.* **2007**, *72*, 7279; (c) Wang, Z.; Fan, R.; Wu, J. *Adv. Synth. Catal.* **2007**, *349*, 1943; (d) Zhang, L.; Wu, J. *J. Am. Chem. Soc.* **2008**, *130*, 12250; (e) Zhang, L.; Qing, J.; Yang, P.; Wu, J. *Org. Lett.* **2008**, *10*, 4971; (f) Zhang, L.; Wu, J. *Adv. Synth. Catal.* **2008**, *350*, 2409.
9. For selected examples, see: (a) *N-Heterocyclic Carbenes in Transition Metal Catalysis*; Glorius, F., Ed.; Springer: Berlin, 2007; (b) Herrmann, W. A. *Angew. Chem., Int. Ed* **2002**, *41*, 1290; (c) Navarro, O.; Kelly, R. A., III; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 16194; (d) Grasa, G. A.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 119; (e) Fructos, M. R.; Belderrain, T. R.; Nicasio, M. C.; Nolan, S. P.; Kaur, H.; Diaz-Requejo, M. M.; Perez, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 10846; (f) Yang, C.; Lee, H. M.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 1511; (g) Singh, R.; Viciu, M. S.; Kramareva, N.; Navarro, O.; Nolan, S. P. *Org. Lett.* **2005**, *7*, 1829; (h) Grasa, G. A.; Hillier, A. C.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 1077; (i) Viciu, M. S.; Germaneau, R. F.; Navarro-Fernandez, O.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2002**, *21*, 5470.
10. Cammidge, A. N.; Goddard, V. H. M.; Gopee, H.; Harrison, N. L.; Hughes, D. L.; Schubert, C. J.; Sutton, B. M.; Watts, G. L.; Whitehead, A. J. *Org. Lett.* **2006**, *8*, 4071.
11. Randle, R. R.; Whiffen, D. H. *J. Chem. Soc.* **1955**, 1311.
12. Gonzalez, R. R.; Liguori, L.; Carrillo, A. M.; Bjorsvik, H.-R. *J. Org. Chem.* **2005**, *70*, 9591.
13. Osakada, K.; Onodera, H.; Nishihara, Y. *Organometallics* **2005**, *24*, 190.
14. Hagiya, K. *PCT Int. Appl.* **2003**, WO 2003066546.