

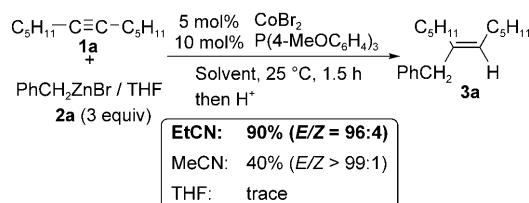
Cobalt-Catalyzed Benzylzincation of Alkynes

Kei Murakami,^[a] Hideki Yorimitsu,*^[a, b] and Koichiro Oshima*^[a]

Multisubstituted alkenes are among the most important structures in organic chemistry. In particular, multisubstituted alkenes bearing a benzyl group are essential fragments present in the key precursors of lignans^[1] and in pharmacologically important molecules.^[2] Although there are numerous methods for the preparation of alkenes, the regio- and stereoselective synthesis of benzylated, multisubstituted alkenes is still challenging. Thus, development of general and efficient routes to benzylated alkenes is in high demand. Herein we wish to report cobalt-catalyzed^[3] benzylzincation^[4–7] of alkynes to afford benzylated multisubstituted alkenes. The reaction is applicable to the regio- and stereoselective synthesis of an estrogen receptor antagonist.

Treatment of 6-dodecyne (**1a**) with benzylzinc bromide (**2a**) in the presence of cobalt(II) bromide and tris(4-methoxyphenyl)phosphine in propionitrile at 25 °C for 1.5 h followed by hydrolysis gave the corresponding benzylated product **3a** in 90 % yield with high *E* selectivity (Scheme 1).^[8–10] The use of propionitrile as the solvent was crucial and the use of acetonitrile significantly retarded the reaction. When the reaction was carried out in THF, no benzylated product was obtained.

The scope of benzylzinc reagents and alkynes was studied, and the results are summarized in Table 1. Symmetrical alkynes, such as 4-octyne (**1b**) and 1,4-dibenzoyloxy-2-butyne (**1c**), participated in the reaction in high yield and with high stereoselectivity (Table 1, entries 1–3). The reaction of ter-



Scheme 1.

Table 1. Scope of benzylzinc reagents and aliphatic alkynes^[a]

R-C≡C-R'		5 mol% CoBr ₂ 10 mol% P(4-MeOC ₆ H ₄) ₃		EtCN, 25 °C, 1.5–5 h		ArCH ₂ ZnBr / THF 2 (3 equiv)		then H ⁺		R R' ArCH ₂ H 3	
1b : R = C ₃ H ₇ , R' = C ₃ H ₇		2b : Ar = 4-MeC ₆ H ₄									
1c : R = BnOCH ₂ , R' = CH ₂ OBn		2c : Ar = 3-MeC ₆ H ₄									
1d : R = <i>t</i> Bu, R' = H		2d : Ar = 2-MeC ₆ H ₄									
1e : R = HO(CH ₂) ₂ , R' = H		2e : Ar = 2-thienyl									
1f : R = C ₆ H ₁₁ CH(OBn), R' = H		2f : Ar = 3-MeOC ₆ H ₄									
1g : R = CH ₃ , R' = C ₆ H ₁₁		2g : Ar = 4-ClC ₆ H ₄									
1h : R = <i>i</i> Pr, R' = C ₆ H ₁₃		2h : Ar = 4-BrC ₆ H ₄									
		2i : Ar = 4-CF ₃ C ₆ H ₄									
1	2	3	Yield [%] ^[b]	<i>E/Z</i> ^[c]	r.r. ^[d]						
1	1b	2a	3b	86	96:4	–					
2 ^[e]	1b	2a	3b	94	95:5	–					
3	1c	2a	3c	88	< 1:99	–					
4	1d	2b	3d	94	–	> 99:1					
5	1e	2a	3e	60	–	93:7					
6	1f	2a	3f	89	–	91:9					
7	1g	2a	3g	83	nd ^[f]	48:52					
8 ^[g]	1h	2a	3h	trace	–	–					
9	1b	2b	3i	93	97:3	–					
10	1b	2c	3j	94	96:4	–					
11	1b	2d	3k	85	97:3	–					
12	1b	2e	3l	79	> 99:1	–					
13	1b	2f	3m	69	> 99:1	–					
14 ^[h]	1b	2g	3n	94	97:3	–					
15 ^[i]	1b	2h	3o	75	96:4	–					
16	1b	2i	3p	trace	–	–					

[a] Performed on a 0.3 mmol scale. [b] Isolated yield. [c] Determined by ¹H NMR spectroscopy. [d] Regioisomeric ratio determined by ¹H NMR spectroscopy. [e] Performed on a 5 mmol scale. [f] Not determined. [g] Performed at 60 °C. [h] CoBr₂ (10 mol%) and P(3,5-Me₂-4-MeOC₆H₂)₃ (20 mol%) were used. [i] CoBr₂ (10 mol%) and P(4-MeOC₆H₄)₃ (20 mol%) were used.

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minal alkynes (**1d–1f**) proceeded regioselectively to yield *gem*-disubstituted alkenes (Table 1, entries 4–6). However, the reaction of 2-octyne (**1g**) provided a 48:52 mixture of regioisomers (Table 1, entry 7). Unfortunately, sterically hindered 2-methyl-3-decyne (**1h**) failed to react (Table 1, entry 8). The reactions with 4-methylbenzyl- and 3-methylbenzylzinc bromide afforded **3i** and **3j** in 93 and 94 % yields, respectively (Table 1, entries 9 and 10). A bulky 2-methylbenzylzinc reagent also participated in the reaction (Table 1, entry 11). The benzylzincation with 2-thienylmethylzinc bromide (**2e**) and 3-methoxybenzylzinc bromide (**2f**) occurred with perfect stereoselectivity (Table 1, entries 12 and 13). The benzylzinc reagent bearing a chloro or bromo group was also applicable to provide the corresponding product without any observable side reactions (Table 1, entries 14 and 15). Attempts on benzylzincation with electron-deficient 4- $\text{CF}_3\text{C}_6\text{H}_4\text{CH}_2\text{ZnBr}$ (**2i**) failed and **1b** was recovered (Table 1, entry 16). It is worth noting that no cyclo-trimerization of the alkyne occurred owing to the mild reaction conditions.^[11]

We next examined the reaction of the more reactive aryl-substituted alkyne **4a** with benzylzinc bromide (**2a**). Although the reaction completed smoothly, the benzylated product was a 41:59 mixture of regioisomers (Table 2,

Table 2. Optimization of arylzincation of 1-phenyl-1-propyne.

Zinc reagent		Solvent	T [°C]	t [h]	Yield [%] ^[a]	r.r. ^[b]
1	PhCH_2ZnBr (2a)	EtCN	25	1.5	78 ^[c]	41:59
2	$\text{PhCH}_2\text{ZnBr}\cdot\text{LiCl}$ (2aa)	EtCN	60	12	33	> 99:1
3	$\text{PhCH}_2\text{ZnBr}\cdot\text{LiBr}$ (2ab)	EtCN	60	12	40	> 99:1
4	$\text{PhCH}_2\text{ZnBr}\cdot\text{MgClBr}$ (2ac)	EtCN	60	12	27	> 99:1
5	$(\text{PhCH}_2)_2\text{Zn}\cdot 2\text{MgClBr}$ (5a)	EtCN	25	12	54	> 99:1
6	$(\text{PhCH}_2)_2\text{Zn}\cdot 2\text{MgClBr}$ (5a)	none	25	12	82	> 99:1
7	PhCH_2MgCl	none	25	12	13 ^[d]	> 99:1

[a] ¹H NMR yield. *E/Z* ratios of **6a** was over 99:1 unless otherwise noted. [b] Regioisomeric ratio determined by ¹H NMR spectroscopy. [c] *E/Z* ratio of **6a** was 93:7. [d] *E/Z* ratio of **6a** was 62:38.

entry 1). Interestingly, complexation of the zinc reagent with lithium halide resulted in perfect regioselectivity, albeit the yields of **6a** were low (Table 2, entries 2 and 3).^[12,13] The reaction with $\text{PhCH}_2\text{ZnBr}\cdot\text{MgClBr}$ (**2ac**), which was prepared from PhCH_2MgCl and ZnBr_2 , also afforded **6a** with perfect regioselectivity. Further investigation revealed that the use of dibenzylzinc reagent **5a** was effective and that the reaction proceeded at 25 °C to give **6a** in 54 % yield. Finally, we found that the addition of propionitrile was not crucial for the reaction of aryl-substituted alkynes. Hence, the reaction was carried out without propionitrile to give **6a** in 82 % yield (Table 2, entry 6). It is worth noting that benzylmetalation did not proceed when benzylmagnesium reagent was employed (Table 2, entry 7).

The scope of dibenzylzinc reagents and aryl-substituted alkynes is summarized in Table 3. The reaction of aryl-substituted alkynes bearing an electron-withdrawing group and

Table 3. Scope of dibenzylzinc reagents and aryl-substituted alkynes.^[a]

$$\begin{array}{c}
 \text{R}-\text{C}\equiv\text{C}-\text{Ar} \\
 \text{4} \\
 + \\
 (\text{ArCH}_2)_2\text{Zn}\cdot 2\text{MgClBr} \quad \text{5 (3 equiv)}
 \end{array}
 \xrightarrow[\text{then H}^+]{\begin{array}{c} 5 \text{ mol\% CoBr}_2 \\ 10 \text{ mol\% P(4-MeOC}_6\text{H}_4)_3 \\ \text{THF, 25 }^\circ\text{C, 12 h} \end{array}}
 \begin{array}{c}
 \text{R} \quad \text{Ar} \\
 \diagdown \quad \diagup \\
 \text{ArCH}_2 \quad \text{C} = \text{C} \\
 \quad \quad \diagup \quad \diagdown \\
 \quad \quad \text{H}
 \end{array}
 \quad \text{6}$$

4b : R = C₆H₁₃, Ar = 4-CF₃C₆H₄

5a : Ar = Ph

4c : R = C₆H₁₃, Ar = 4-MeOC₆H₄

5b : Ar = 4-MeC₆H₄

4d : R = C₆H₁₃, Ar = 2-MeC₆H₄

5c : Ar = 4-FC₆H₄

4e : R = EtO₂C(CH₂)₄, Ar = Ph

5d : Ar = 4-MeOC₆H₄

4f : R = C₆H₁₃, Ar = Ph

5e : Ar = 2-MeC₆H₄

	4	5	6	Yield [%] ^[b]	<i>E/Z</i> ^[c]	r.r. ^[d]
1	4b	5a	6b	71	> 99:1	> 99:1
2	4c	5a	6c	50	> 99:1	90:10
3	4d	5a	6d	96	> 99:1	> 99:1
4	4e	5a	6e	61	97:3	94:6
5	4f	5b	6f	66	97:3	95:5
6	4f	5c	6g	62	97:3	95:5
7	4f	5d	6h	63	97:3	95:5
8	4f	5e	6i	40	92:8	89:11

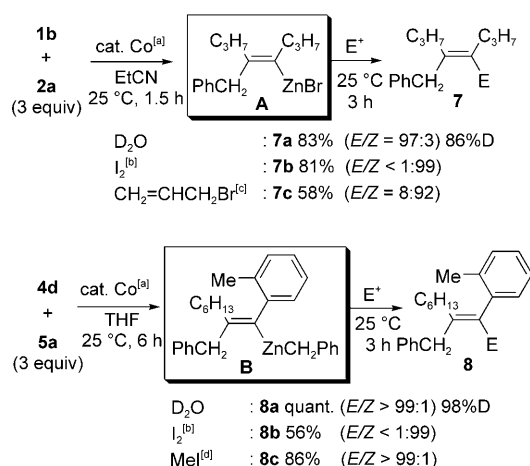
[a] Performed on a 0.3 mmol scale. [b] Isolated yield. [c] *E/Z* ratio of the major regioisomer **6** determined by ¹H NMR spectroscopy. [d] Regioisomeric ratio determined by ¹H NMR spectroscopy.

an electron-donating group reacted smoothly (Table 3, entries 1 and 2). The reaction of sterically hindered 1-(2-methylphenyl)-1-octyne (**4d**) provided the benzylated product **6d** in high yield. The ester group of **4e** survived and **6e** was obtained in 61 % yield (Table 3, entry 4). The reaction with 4-methyl-, 4-fluoro-, and 4-methoxybenzylzinc reagents proceeded smoothly to give the corresponding benzylated products (Table 3, entries 5–7). The sterically hindered 2-methylbenzylzinc reagents reacted in moderate yield (Table 3, entry 8).

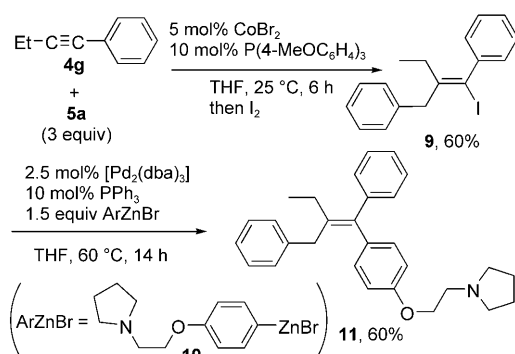
Having the efficient protocols for the benzylzincation reaction in hand, we examined the reaction of alkenylzinc intermediates with various electrophiles. The alkenylzinc intermediate **A**, which was prepared by the reaction of **1b** with **2a**, reacted with D_2O and I_2 to afford **7a** and **7b**, respectively (Scheme 2, top). As for the reaction of allyl bromide, the addition of $i\text{PrMgCl}\cdot\text{LiCl}$ ^[12a] to the alkenylzinc intermediate **A** was necessary due to the low reactivity of **A**. The alkenylzinc intermediate **B** also reacted smoothly to afford tetra-substituted alkenes **8a–8c** regio- and stereoselectively in good yields (Scheme 2, bottom).

Finally, we attempted to synthesize estrogen receptor antagonist **11** (Scheme 3). Benzylzincation of **4g** followed by an addition of iodine gave the corresponding vinyl iodide **9** in 60 % yield. Then, Negishi coupling of **9** with arylzinc reagent **10** afforded **11** in 60 % yield. The efficient two-step synthesis highlights the synthetic advantage of the benzylzincation.

In conclusion, we have developed cobalt-catalyzed benzylzincation reaction of alkynes. The reaction proceeded



Scheme 2. Reactions of alkenylzinc intermediates with electrophiles. Reagents and conditions: [a] $CoBr_2$ (5 mol %), $P(4-MeOC_6H_4)_3$ (10 mol %). [b] 0°C , 5 h. [c] i) $iPrMgCl \cdot LiCl/THF$ (3 equiv), 0°C , 0.5 h; ii) $CuCN \cdot 2LiCl$ (20 mol %), allyl bromide. [d] $CuCN \cdot 2LiCl$ (20 mol %), MeI.



Scheme 3. Regio- and diastereoselective synthesis of estrogen receptor antagonist.

smoothly at ambient temperature to afford tri- and tetrasubstituted benzylated alkenes regio- and stereoselectively.

Experimental Section

Typical procedure for the preparation of benzylzinc reagents: Zn powder (13 mmol) was placed in a 50 mL reaction flask. THF (10 mL) was added. TMSCl (0.01 mmol) and 1,2-dibromoethane (0.05 mmol) were added subsequently. The mixture was stirred for 10 min at room temperature. Then, the corresponding benzyl bromide (10 mmol) was added slowly to keep the solvent gently refluxed. After addition, the mixture was stirred for 3 h at room temperature.

Typical procedure for cobalt-catalyzed benzylzincation of dialkylacetylenes and terminal acetylenes: The reaction of 6-dodecyne with benzylzinc bromide is representative (Scheme 1). $CoBr_2$ (3.3 mg, 0.015 mmol) and $P(4-MeOC_6H_4)_3$ (10.7 mg, 0.03 mmol) were placed in a 20 mL reaction flask under argon. Propionitrile (1 mL) and benzylzinc bromide (0.90 mmol, 0.90 mL, 1 M solution in THF) were added. Then, 6-dodecyne (**1a**, 50 mg, 0.30 mmol) was added. The mixture was stirred at 25°C for 1.5 h. A saturated aqueous solution of NH_4Cl (2 mL) was added. The organic compounds were extracted with ethyl acetate three times. The combined organic part was dried over Na_2SO_4 and concentrated in vacuo. Chromatographic purification on silica gel by using hexane as an eluent

afforded (*E*)-6-phenylmethyl-6-dodecene (**3a**, 70 mg, 0.27 mmol) in 90% yield.

Typical procedure for the preparation of dibenzylzinc reagents: Anhydrous $ZnBr_2$ (10 mmol) was placed in a 50 mL reaction flask and dried for 20 min at $150\text{--}170^\circ\text{C}$ under high vacuum. The flask was refilled with argon and cooled to 0°C . The corresponding benzylmagnesium chloride (20 mmol, 20 mL, 1 M in THF) was slowly added to the flask and the mixture was stirred for 10 min. Then, the mixture was warmed to room temperature.

Typical procedure for cobalt-catalyzed benzylzincation of arylacetylenes: The reaction of 1-(2-methylphenyl)-1-octyne with dibenzylzinc reagent is representative (Table 3, entry 3). $CoBr_2$ (3.3 mg, 0.015 mmol) and $P(4-MeOC_6H_4)_3$ (10.7 mg, 0.03 mmol) were placed in a 20 mL reaction flask under argon. Compound **4d** (60 mg, 0.30 mmol) was added. Then, dibenzylzinc reagent **5a** (0.90 mmol, 1.8 mL, 0.5 M in THF) was added. The mixture was stirred at 25°C for 12 h. A saturated aqueous solution of NH_4Cl (2 mL) was added. The organic compounds were extracted with ethyl acetate three times. The combined organic part was dried over Na_2SO_4 and concentrated in vacuo. Chromatographic purification on silica gel by using hexane as an eluent afforded (*E*)-1-(2-methylphenyl)-2-phenylmethyl-1-octene (**6d**, 84 mg, 0.29 mmol) in 96% yield.

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Keywords: alkenes • benzylation • carbometallation • cobalt • zinc

- [1] a) M. H. Gezinci, B. N. Timmermann, *Tetrahedron Lett.* **2001**, 42, 6083; b) G. D. Brown, H.-F. Wong, *Tetrahedron* **2004**, 60, 5439; c) R. S. Ward, A. Pelter, M. I. Edwards, J. Gilmore, *Tetrahedron* **1996**, 52, 12799; d) T. Takeya, S. Yamaki, T. Itoh, H. Hosogai, S. Tobinaga, *Chem. Pharm. Bull.* **1998**, 44, 909; e) P. Sellès, *Org. Lett.* **2005**, 7, 605.
- [2] M. J. Meegan, R. B. Hughes, D. G. Lloyd, D. C. Williams, D. M. Zisster, *J. Med. Chem.* **2001**, 44, 1072.
- [3] Recent reviews for cobalt-catalyzed reactions, see: a) H. Yorimitsu, K. Oshima, *Pure Appl. Chem.* **2006**, 78, 441; b) H. Shinokubo, K. Oshima, *Eur. J. Org. Chem.* **2004**, 2081; c) K. Oshima, *Bull. Chem. Soc. Jpn.* **2008**, 81, 1; d) C. Gosmini, J.-M. Bégouin, A. Moncomble, *Chem. Commun.* **2008**, 3221; e) A. Rudolph, M. Lautens, *Angew. Chem.* **2009**, 121, 2694; *Angew. Chem. Int. Ed.* **2009**, 48, 2656; f) M. Jeganmohan, C.-H. Cheng, *Chem. Eur. J.* **2008**, 14, 10876; g) W. Hess, J. Treutwein, G. Hilt, *Synthesis* **2008**, 3537; h) G. Cahiez, A. Moyeux, *Chem. Rev.* **2010**, 110, 1435.
- [4] Recent reviews for carbometallation reactions, see: a) P. Knochel in *Comprehensive Organic Synthesis*, Vol. 4 (Eds.: B. M. Trost, I. Fleming, M. F. Semmelhack), Pergamon Press, New York, **1991**, pp. 865–911; b) I. Marek, J.-F. Normant in *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinheim, **1998**, pp. 271–337; c) E. Negishi, Z. Huang, G. Wang, S. Mohan, C. Wang, H. Hattori, *Acc. Chem. Res.* **2008**, 41, 1474; d) A. B. Flynn, W. W. Ogilvie, *Chem. Rev.* **2007**, 107, 4698; e) A. G. Fallis, P. Forgone, *Tetrahedron* **2001**, 57, 5899; f) K. Itami, J. Yoshida in *The Chemistry of Organomagnesium Compounds* (Eds.: Z. Rappoport, I. Marek), Wiley, New York, **2008**, Chapter 18.
- [5] There are few reports on transition metal-catalyzed benzylzincation of limited alkynes. Ynamide: a) B. Gourdet, M. E. Rudkin, C. A. Watts, H. W. Lam, *J. Org. Chem.* **2009**, 74, 7849; b) B. Gourdet, H. W. Lam, *J. Am. Chem. Soc.* **2009**, 131, 3802; 1-alkynyl sulfoxides: c) N. Maezaki, H. Sawamoto, R. Yoshigami, T. Suzuki, T. Tanaka, *Org. Lett.* **2003**, 5, 1345.

- [6] For examples of benzylmetalation of alkynes, see: a) J. G. Duboudin, B. Jousseume, A. Saux, *J. Organomet. Chem.* **1979**, 168, 1; b) H. Nishiyama, M. Sasaki, K. Itoh, *Chem. Lett.* **1981**, 10, 905; c) Y. Ishino, K. Wakamoto, T. Hirashima, *Chem. Lett.* **1984**, 13, 765; d) N. Fujiwara, Y. Yamamoto, *J. Org. Chem.* **1999**, 64, 4095; e) M. P. Jennings, K. B. Sawant, *Eur. J. Org. Chem.* **2004**, 3201; f) T. Konno, T. Daitoh, A. Noiri, J. Chae, T. Ishihara, H. Yamanaka, *Org. Lett.* **2004**, 6, 933; g) T. Konno, T. Daitoh, A. Noiri, J. Chae, T. Ishihara, H. Yamanaka, *Tetrahedron* **2005**, 61, 9391; h) G. S. Kauffman, P. S. Watson, W. A. Nugent, *J. Org. Chem.* **2006**, 71, 8975; i) P. Sellès, *Org. Lett.* **2005**, 7, 605.
- [7] Recent examples of transition metal-catalyzed carbozincation of alkynes: a) R. Shintani, T. Yamagami, T. Hayashi, *Org. Lett.* **2006**, 8, 4799; b) R. Shintani, T. Hayashi, *Org. Lett.* **2005**, 7, 2071; c) S. Xue, L. He, Y.-K. Liu, K.-Z. Han, Q.-X. Guo, *Synthesis* **2006**, 666; d) G. Sklute, C. Bolm, I. Marek, *Org. Lett.* **2007**, 9, 1259; e) T. Stüdemann, M. Ibrahim-Ouali, P. Knochel, *Tetrahedron* **1998**, 54, 1299; f) H. Yasui, T. Nishikawa, H. Yorimitsu, K. Oshima, *Bull. Chem. Soc. Jpn.* **2006**, 79, 1271; g) K. Murakami, H. Yorimitsu, K. Oshima, *Org. Lett.* **2009**, 11, 2373.
- [8] Carbometalation of unfunctionalized alkynes is difficult and there are few examples of carbometalation of dialkylacetylenes. Carbomagnesiation: a) E. Shirakawa, T. Yamagami, T. Kimura, S. Yamaguchi, T. Hayashi, *J. Am. Chem. Soc.* **2005**, 127, 17164; b) K. Murakami, H. Ohmiya, H. Yorimitsu, K. Oshima, *Org. Lett.* **2007**, 9, 1569; carboboration: c) M. Suginome, M. Shirakura, A. Yamamoto, *J. Am. Chem. Soc.* **2006**, 128, 14438; d) M. Daini, M. Suginome, *Chem. Commun.* **2008**, 5224; carbostannylation: e) E. Shirakawa, K. Yamasaki, H. Yoshida, T. Hiyama, *J. Am. Chem. Soc.* **1999**, 121, 10221; carbozincation: reference [6g].
- [9] Optimization of the reaction was noted in the Supporting Information.
- [10] Three equivalents of benzylzinc reagents were necessary. Using fewer amounts of benzylzinc reagents resulted in lower yields and slower conversions.
- [11] Usually, cobalt-catalyzed cyclotrimerization of alkyne requires high temperature, see: a) J. A. Varela, C. Saá, *J. Organomet. Chem.* **2009**, 694, 143; b) L. V. R. Boñaga, H.-C. Zhang, A. F. Moretto, H. Ye, D. A. Gauthier, J. Li, G. C. Leo, B. E. Maryanoff, *J. Am. Chem. Soc.* **2005**, 127, 3473.
- [12] For examples of acceleration of reaction by adding Li salt, see: a) A. Krasovskiy, P. Knochel, *Angew. Chem.* **2004**, 116, 3396; *Angew. Chem. Int. Ed.* **2004**, 43, 3333; b) A. Krasovskiy, V. Malakhov, A. Gavryushin, P. Knochel, *Angew. Chem.* **2006**, 118, 6186; *Angew. Chem. Int. Ed.* **2006**, 45, 6040; c) F. M. Pillar, P. Appukkuttan, A. Gavryushin, M. Helm, P. Knochel, *Angew. Chem.* **2008**, 120, 6907; *Angew. Chem. Int. Ed.* **2008**, 47, 6802; d) N. Fujii, K. Nakai, H. Habashita, H. Yoshizawa, T. Ibuka, F. Gerrido, A. Mann, Y. Chounan, Y. Yamamoto, *Tetrahedron Lett.* **1993**, 34, 4227; e) H. Ochiai, M. Jang, K. Hirano, H. Yorimitsu, K. Oshima, *Org. Lett.* **2008**, 10, 2681; f) G. T. Achonduh, N. Hadei, C. Valente, S. Avola, C. J. O'Brien, M. G. Organ, *Chem. Commun.* **2010**, DOI: 10.1039/c002759f.
- [13] The reason for the dramatic effect of the addition of the lithium and magnesium salts is not clear at this stage.

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