Synthesis of Allenes via Nickel-Catalyzed Cross-Coupling Reaction of Propargylic Bromides with Grignard Reagents

Qinghan Li,*[a] Hanmou Gau[b]

[a] College of Chemistry and Environmental Proection Engineering, Southwest University for Nationalities, Chengdu, 610041, P. R. of China
Fax +86(28)85524382; E-mail: lqhchem@163.com

[b] Department of Chemistry, National Chung Hsing University, 250 Kuo-Kuang Road, Taichung 402, Taiwan

Received 11 November 2011

Abstract: We describe a convenient method for the synthesis of terminal allenes from cross-coupling of propargylic bromide with Grignard reagent. The reaction of propargylic bromide with 1.2 equivalents of Grignard reagent mediated by $Ni(acac)_2$ (2 mol%) and Ph_3P (4 mol%) in THF may produce terminal allenes in good yields and high regioselectivities at room temperature.

Key words: allenes, nickel, propargylic bromide, Grignard reagent, cross-coupling

Allenes are useful structural motifs in organic transformations[1] and have been found in many natural products as well as pharmaceutically related compounds.[2] As a result, allenes have inspired ample interest of organic and medical chemistry,[1b–1h,3] and numerous new synthetic methodologies to access such compounds have been developed,[4] for instance, the organocopper-catalyzed S_N2'-type displacement of propargyl alcohol derivatives,[5,6] the homologation of 1-alkynes,[7] asymmetric allylations,[8] the stereoselective reduction of alkynes,[9] β-eliminations by Horner–Emmons–Wadsworth[10] or sulfinyl radical[11] reactions, palladium-catalyzed hydrogenolysis[12] and hydride-transfer reaction,[13] coupling reactions of allenylstannanes[14] and allenylindiums,[15] indium-mediated reactions of propargylic bromides with aldehydes,[16] allene cross metathesis,[17] carbene/inylidene cross-coupling,[18] and cross-coupling of *N*-tosylhydrazone with terminal alkyne.[19] Among these methods hitherto developed, the organocopper-catalyzed S_N2'-type displacement of propargyl alcohol derivatives is one of the most generally useful ones.

The Grignard reagent is a reactive nucleophilic reagent and can easily be prepared from the corresponding halide. Although the synthesis of allene by cross-coupling of Grignard reagent with propargylic compounds has been described,[20] the synthesis based on direct coupling of propargylic halide with Grignard reagent is developed rarely. To the best of our knowledge, to date there are only a few reports in the literature, and copper is often used as catalyst in these methods.[20a,b,d,h] However, these methods still have some drawbacks, such as long reaction time, low temperature, low regioselectivity or large catalyst loading, and limited substrates. Recent investigations have demonstrated that the nickel is a good catalyst for many cross-coupling reactions.[21] Herein we report a novel nickel(II)-catalyzed cross-coupling of a propargylic halide with a Grignard reagent at ambient temperature in a short time with good yield for the synthesis of allenes.

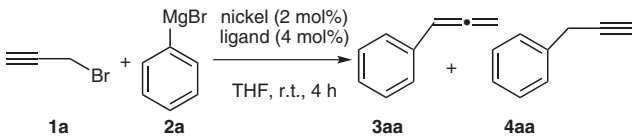
In a preliminary study, treatment of propargylic bromide (**1a**) with phenylmagnesium bromide (**2a**) in the absence of metal and ligand at ambient temperature in THF led to the formation of phenylallene (**3aa**) and 3-phenylprop-1-yne (**4aa**) in a moderate conversion of 74%, but with a low regioselectivity of **3aa/4aa** (63:37, Table 1, entry 1). To our delight, when $NiBr_2/Ph_3P$ was used, the reaction conversion was signally elevated to 98% with a good regioselectivity (**3aa/4aa** = 78:22, Table 1, entry 2). To further understand the essence of this catalysis, we tested the model reaction under various conditions. As shown in Table 1 (entries 3–5), $NiCl_2/Ph_3P$, $Ni(NO_3)_2/Ph_3P$, and $Ni(OAc)_2/Ph_3P$ were also effective for the conversion of the coupling between propargylic bromide (**1a**) and phenylmagnesium bromide (**2a**), but show some lower regioselectivity. Further screen of other nickel complex, $Ni(acac)_2/Ph_3P$ was found to be the most efficient catalyst for the coupling between propargylic bromide (**1a**) and phenylmagnesium bromide (**2a**) considering both the conversion and regioselectivity (Table 1, entry 6).

Next, the effect of other ligands on the conversion and regioselectivity of this reaction using $Ni(acac)_2$ were studied (Table 1, entries 6–9). When PCy_3, $(4\text{-MePh})_3P$ and $(C_6F_5)_3P$ were used, the conversion and the regioselectivity of the model reaction were not varied appreciably. In addition, only $Ni(acac)_2$ was used as catalyst, the conversion and the regioselectivity of this reaction were slightly decreased (Table 1, entry 6 vs. entry 10). Thus the $Ni(acac)_2/Ph_3P$ complex was identified as the most effective catalyst (Table 1, entry 6).

A study on the solvent effect showed that THF provided the best conversion and regioselectivity of the product **3aa** + **4aa** (Table 1, entry 6). In other solvent such as toluene, hexane, Et_2O, and CH_2Cl_2, good regioselectivity could not be observed (Table 2, entries 1–4). Changing the molar ratio between $Ni(acac)_2$/ Ph_3P led to a low regioselectivity (Table 2, entries 5 and 6). Unexpectedly, the highest conversion and regioselectivity was obtained when changing the molar ratio of substrates **1a/2a** from 1.0:1.1 to 1.0:1.2

SYNLETT 2012, 23, 747–750
Advanced online publication: 24.02.2012
DOI: 10.1055/s-0031-1290365; Art ID: W64011ST

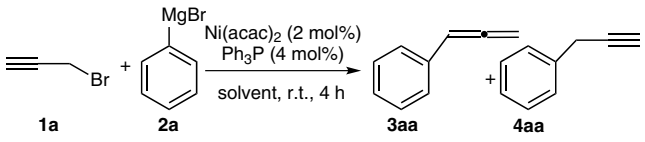
Table 1 Efffect of the Metal and Ligand in the Cross-Coupling of Propargylic Bromide with Phenylmagnesium Bromide[a]



Entry	Nickel source	Ligand	Conv. (%)[b]	Ratio **3aa/4aa**[c]
1	–	–	74	63:37
2	$NiBr_2$	Ph_3P	98	78:22
3	$NiCl_2$	Ph_3P	98	60:40
4	$Ni(NO_3)_2$	Ph_3P	97	72:28
5	$Ni(OAc)_2$	Ph_3P	96	66:34
6	$Ni(acac)_2$	Ph_3P	98	86:14
7	$Ni(acac)_2$	PCy_3	97	83:17
8	$Ni(acac)_2$	$(4\text{-MePh})_3P$	97	83:17
9	$Ni(acac)_2$	$(C_6F_5)_3P$	98	83:17
10	$Ni(acac)_2$	–	93	84:16

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (1.1 mmol), THF (2 mL), 4 h, r.t.
[b] Conversions of **3aa** and **4aa** were determined by ^{1}H NMR.
[c] The ratio of **3aa/4aa** was determined by ^{1}H NMR

Table 2 Efffect of the Solvent and the Molar Ratio of $Ni(acac)_2$/Ph_3P in the Cross-Coupling of Propargylic Bromide with Phenylmagnesium Bromide[a]



Entry	$Ni(acac)_2/Ph_3P$ (mol%)	Solvent	Conv. (%)[b]	Ratio **3aa/4aa**[c]
1	2:4	Et_2O	90	54:46
2	2:4	hexane	83	63:37
3	2:4	toluene	92	62:38
4	2:4	CH_2Cl_2	91	82:18
5	2:2	THF	92	80:20
6	2:6	THF	96	71:29
7[d]	2:4	THF	98	90:10
8[e]	2:4	THF	98	80:20
9[d]	1:2	THF	96	86:14

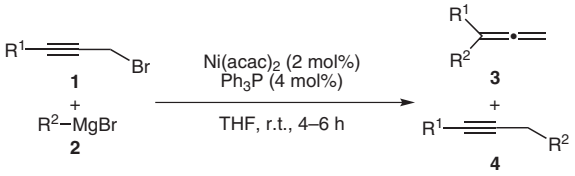
[a] Reaction conditions: **1a** (1.0 mmol), **2a** (1.1 mmol), THF (2 mL).
[b] Conversions of **3aa** and **4aa** were determined by ^{1}H NMR.
[c] The ratio of **3aa/4aa** was determined by ^{1}H NMR.
[d] Reaction conditions: **1a** (1.0 mmol), **2a** (1.2 mmol), THF (2 mL).
[e] Reaction conditions: **1a** (1.0 mmol), **2a** (1.3 mmol), THF (2 mL).

(Table 2, entry 7). Further studies indicated that the loading of catalyst exerted a slight influence upon the conversion and regioselectivity. The most favorable loading was 2 mol% $Ni(acac)_2$/4 mol% Ph_3P (Table 2, entry 7).

With the optimized reaction conditions in hand, the scope of this reaction was studied by using various Grignard reagent and propargylic bromide. The cross-coupling of propargylic bromide **1a** with Grignard reagent **2a–o** proceeded smoothly to provide the corresponding products **3aa–ao** in moderate to good yields (Table 3, entries 1–15). The reaction was not significantly affected by the substituents on the aromatic ring of the Grignard reagent. Both electron-rich (Table 3, entries 2–8) and electron-deficient substituent on the aromatic ring of the Grignard reagent were effective (Table 3, entries 9–11). Notably, alkoxy, methyl, chloro, fluoro, and trifluoromethyl groups are all tolerated under the given reaction conditions. The reaction also worked well with naphthyl Grignard reagent (Table 3, entries 12 and 13), alkyl Grignard reagent (Table 3, entries 14 and 15).

Then, the reaction was examined by using 1-bromopent-2-yne with Grignard reagent (Table 3, entries 16–18). However, whether electron-rich (Table 3, entry 17) or electron-deficient (Table 3, entry 18) substituent on the aromatic ring of the Grignard reagent gave only moderate yields.

Table 3 $Ni(acac)_2/Ph_3P$-Catalyzed Cross-Coupling Reaction of Propargylic Bromide with Grignard Reagent[a]



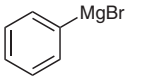
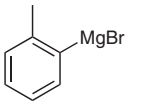
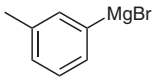
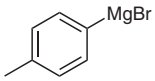
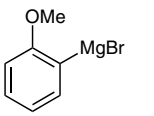
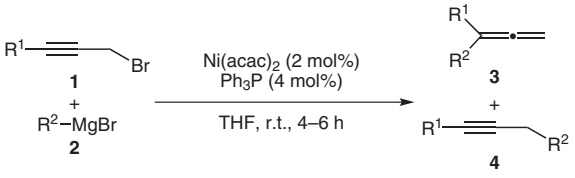
Entry	**1**	**2**	Yield of **3**[22] (%)[b]	Yield of **4** (%)[b]
1	**1a** R = H	 **2a**	**3aa** 78[a] **3aa** 50[c]	**4aa** 10[a] **4aa** 20[c]
2	**1a**	 **2b**	**3ab** 80	**4ab** 8
3	**1a**	 **2c**	**3ac** 74	**4ac** 14
4	**1a**	 **2d**	**3ad** 75	**4ad** 13
5	**1a**	 **2e**	**3ae** 70	**4ae** 11

Table 3 $Ni(acac)_2/Ph_3P$-Catalyzed Cross-Coupling Reaction of Propargylic Bromide with Grignard Reagent[a] (continued)



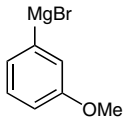
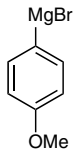
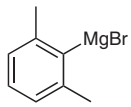
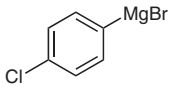
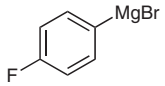
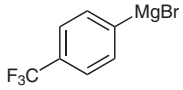
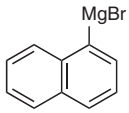
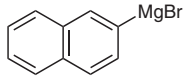
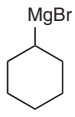
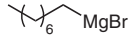
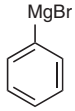
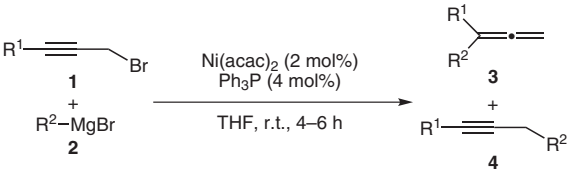
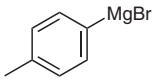
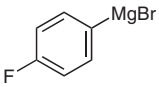
Entry	1	2	Yield of **3**[22] (%)[b]	Yield of **4** (%)[b]
6	**1a**	 **2f**	**3af** 72	**4af** 15
7	**1a**	 **2g**	**3ag** 74	**4ag** 12
8	**1a**	 **2h**	**3ah** 78	**4ah** 9
9	**1a**	 **2i**	**3ai** 83	**4ai** 8
10	**1a**	 **2j**	**3aj** 73	**4aj** 15
11	**1a**	 **2k**	**3ak** 78	**4ak** 12
12	**1a**	 **2l**	**3al** 76	**4al** trace
13	**1a**	 **2m**	**3am** 80	**4am** 9
14	**1a**	 **2n**	**3an** 77	**4an** 10
15	**1a**	 **2o**	**3ao** 74	**4ao** trace
16	**1b** R = Et	 **2a**	**3ba** 54	**4ba** 34

Table 3 $Ni(acac)_2/Ph_3P$-Catalyzed Cross-Coupling Reaction of Propargylic Bromide with Grignard Reagent[a] (continued)



Entry	1	2	Yield of **3**[22] (%)[b]	Yield of **4** (%)[b]
17	**1b**	 **2d**	**3bd** 56	**4bd** 33
18	**1b**	 **2j**	**3bj** 53	**4bj** 33

[a] Reaction conditions: **1** (1.0 mmol), **2** (1.2 mmol), $Ni(acac)_2$ (2 mol%), Ph_3P (4 mol%), THF (2 mL).
[b] Isolated yield.
[c] Ref. 20d: **1** (0.12 mmol), **2** (0.1 mmol), CuBr (7 mol%), LiBr (23 mol%), THF (14.0 mL), the reaction mixture was stirred at –50 °C for 45 min, then the reaction mixture was stirred at 10 °C.

On comparing the cross-coupling of propargylic bromide with Grignard reagent by the nickel-catalyzed method with that by the copper-catalyzed method (Table 3, entry 1), we found that the former proceeded with comparably high yields and regioselectivity, low catalyst loading, and easy manipulation.

In conclusion, an improved procedure for the nickel-catalyzed cross-coupling of propargylic bromide with Grignard reagent has been developed, and it is demonstrated that this methodology is a simple and efficient method for the preparation of various monosubstituted arylallenes and alkylallenes with high regioselectivity. Further application of these allenes in organic synthesis and detailed mechanistic studies are in progress.

Acknowledgment

We thank the Fundamental Research Funds for the Central Universities, Southwest University for Nationalities (No. 11NZYTD01) and the Natural Science Foundation of Southwest University for Nationalities (No. 381010).

References and Notes

(1) (a) *Modern Allene Chemistry*, Vol. 1 and 2; Krause, N.; Hashmi, A. S. K., Eds.; Wiley-VCH: Weinheim, **2004**. (b) Ma, S. M. *Acc. Chem. Res.* **2009**, *42*, 1679. (c) Brasholz, M.; Reissig, H. U.; Zimmer, R. *Acc. Chem. Res.* **2009**, *42*, 45. (d) Ma, S. M. *Chem. Rev.* **2005**, *105*, 2829. (e) Brandsma, L.; Nedolya, N. A. *Synthesis* **2004**, 735. (f) Ma, S. M. *Acc. Chem. Res.* **2003**, *36*, 701. (g) Tius, M. A. *Acc. Chem. Res.* **2003**, *36*, 284. (h) Wei, L. L.; Xiong, H.; Hsung, R. P. *Acc. Chem. Res.* **2003**, *36*, 773. (i) Han, X. Y.; Wang, Y. Q.; Zhong, F. R.; Lu, Y. X. *J. Am. Chem. Soc.* **2011**, *133*, 1726. (j) Bolte, B.; Gagosz, F. *J. Am. Chem. Soc.*

2011, *133*, 7696. (k) Minkler, S. R. K.; Lipshutz, B. H.; Krause, N. *Angew. Chem. Int. Ed.* **2011**, *50*, 1..

(2) For reviews, see: (a) Hoffmann-Röder, A.; Krause, N. *Angew. Chem. Int. Ed.* **2004**, *43*, 1196. (b) Kim, H.; Williams, L. J. *Curr. Opin. Drug Discovery Dev.* **2008**, *11*, 891.

(3) For recent reviews, see: (a) Bates, R.; Satcharoen, V. *Chem. Soc. Rev.* **2002**, *31*, 12. (b) Zimmer, R.; Dinesh, C.; Nandanan, E.; Khan, F. A. *Chem. Rev.* **2000**, *100*, 3067. (c) Hashmi, A. S. K. *Angew. Chem. Int. Ed.* **2000**, *39*, 3590. (d) Lu, X.; Zhang, C.; Xu, Z. *Acc. Chem. Res.* **2001**, *34*, 535. (e) Marshall, J. A. *Chem. Rev.* **2000**, *100*, 3163. (f) Sydnes, L. *Chem. Rev.* **2003**, *103*, 1133. (g) Ma, S. M. *Aldrichimica Acta* **2007**, *40*, 91.

(4) For recent reviews on the synthesis of allenes, see: (a) Krause, N.; Hoffmann-Röder, A. *Tetrahedron* **2004**, *60*, 11671. (b) Brummond, K. M.; Deforrest, J. E. *Synthesis* **2007**, 795. (c) Ogasawara, M. *Tetrahedron: Asymmetry* **2009**, *20*, 259. (d) Yu, S. C.; Ma, S. M. *Chem. Commun.* **2011**, *47*, 5384.

(5) (a) Pona, P.; Crabbé, P. J. *J. Am. Chem. Soc.* **1968**, *90*, 4733. (b) Rona, P.; Crabbé, P. *J. Am. Chem. Soc.* **1969**, *91*, 3289. (c) Gaudemar, M. J. *J. Organomet. Chem.* **1976**, *108*, 159. (d) Daeuble, J. F.; McGettigan, C.; Dollat, J. M.; Luche, J. L.; Crabbé, P. J. *J. Chem. Soc., Chem. Commun.* **1977**, 761. (e) Coppola, G. M.; Schuster, H. F. *Allenes in Organic Synthesis*; Wiley: New York, **1984**. (f) Alexakis, A.; Marek, I.; Mangeney, P.; Normant, J. F. *J. Am. Chem. Soc.* **1990**, *112*, 8042. (g) Daeuble, J. F.; McGettigan, C.; Stryker, J. M. *Tetrahedron Lett.* **1990**, *31*, 2397. (h) Myers, A. G.; Zheng, B. *J. Am. Chem. Soc.* **1996**, *118*, 4492. (i) Brummond, K. M.; Lu, J. *J. Am. Chem. Soc.* **1999**, *121*, 5087. (j) Deutsch, C.; Lipshutz, B. H.; Krause, N. *Angew. Chem. Int. Ed.* **2007**, *46*, 1650.

(6) For selected examples of allene synthesis with related methods, see: (a) Fürstner, A.; Mendez, M. *Angew. Chem. Int. Ed.* **2003**, *42*, 5355. (b) Pu, X.; Ready, J. M. *J. Am. Chem. Soc.* **2008**, *130*, 10874. (c) Lo, V. K.-Y.; Wong, M.-K.; Che, C.-M. *Org. Lett.* **2008**, *10*, 517. (d) Tang, M.; Fan, C.-A.; Zhang, F.-M.; Tu, Y.-Q.; Zhang, W.-X.; Wang, A.-X. *Org. Lett.* **2008**, *10*, 5585. (e) Ogasawara, M.; Okada, A.; Nakajima, K.; Takahashi, T. *Org. Lett.* **2009**, *11*, 177. (f) Zhao, X.; Zhong, Z.; Peng, L.; Zhang, W.; Wang, J. *Chem. Commun.* **2009**, 2535. (g) Liu, H.; Leow, D.; Huang, K.-W.; Tan, C.-H. *J. Am. Chem. Soc.* **2009**, *131*, 7212. (h) Kolakowski, R. V.; Manpadi, M.; Zhang, Y.; Emge, T. J.; Williams, L. J. *J. Am. Chem. Soc.* **2009**, *131*, 12910. (i) Lo, V. K.-Y.; Zhou, C.-Y.; Wong, M.-K.; Che, C.-M. *Chem. Commun.* **2010**, *46*, 213.

(7) (a) Searles, S.; Li, Y.; Nassim, B.; Robert Lopes, M.-T.; Tran, P. T.; Crabbé, P. *J. Chem. Soc., Perkin Trans. 1* **1984**, 747. (b) Kuang, J. Q.; Ma, S. M. *J. Org. Chem.* **2009**, *74*, 1763. (c) Kuang, J.; Ma, S. M. *J. Am. Chem. Soc.* **2010**, *132*, 1786. (d) Kitagaki, S.; Komizu, M.; Mukai, C. *Synlett* **2011**, 1129.

(8) (a) Ogasawara, M.; Ikeda, H.; Nagano, T.; Hayashi, T. *J. Am. Chem. Soc.* **2001**, *123*, 2089. (b) Fukuhara, K.; Okamoto, S.; Sato, F. *Org. Lett.* **2003**, *5*, 2145.

(9) Myers, A. G.; Zheng, B. *J. Am. Chem. Soc.* **1996**, *118*, 4492.

(10) (a) Tanaka, K.; Otsubo, K.; Fuji, K. *Synlett* **1995**, 993. (b) Brummond, K. M.; Dingess, E. A.; Kent, J. L. *J. Org. Chem.* **1996**, *61*, 6096.

(11) Delouvrie, B.; Lacote, E.; Fensterbank, L.; Malacria, M. *Tetrahedron Lett.* **1996**, *40*, 3565.

(12) (a) Tsuji, J.; Sugiura, T.; Yuhara, M.; Minami, I. *Chem. Commun.* **1986**, 922. (b) Tsuji, J.; Sugiura, T.; Minami, I. *Synthesis* **1987**, 603.

(13) (a) Nakamura, H.; Kamakura, T.; Ishikura, M.; Biellmann, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 5958. (b) Nakamura, H.; Onagi, S. *Tetrahedron Lett.* **2006**, *47*, 2539. (c) Nakamura, H.; Kamakura, T.; Onagi, S. *Org. Lett.* **2006**, *8*, 2095. (d) Nakamura, H.; Ishikura, M.; Sugiishi, T.; Kamakura, T.; Biellmann, J. F. *Org. Biomol. Chem.* **2008**, *6*, 1471. (e) Bolte, B.; Odabachian, Y.; Gagosz, F. *J. Am. Chem. Soc.* **2010**, *132*, 7294.

(14) (a) Badone, D.; Cardamone, R.; Guzzi, U. *Tetrahedron Lett.* **1994**, *35*, 5477. (b) Huang, C. W.; Shanmugasundaram, M.; Chang, H. M.; Cheng, C. H. *Tetrahedron* **2003**, *59*, 3635.

(15) Lee, K.; Seomon, D.; Lee, P. H. *Angew. Chem. Int. Ed.* **2002**, *41*, 3901.

(16) (a) Lin, M. J.; Loh, T. P. *J. Am. Chem. Soc.* **2003**, *125*, 13042. (b) Lee, P. H.; Kim, H.; Lee, K. *Adv. Synth. Catal.* **2005**, *347*, 1219.

(17) Ahmed, M.; Arnauld, T.; Barrett, A. G. M.; Braddock, D. C.; Flack, K.; Procopiou, P. A. *Org. Lett.* **2000**, *2*, 551.

(18) Lavallo, V.; Frey, G. D.; Kousar, S.; Donnadieu, B.; Bertrand, G. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 13569.

(19) Xiao, Q.; Xia, Y.; Li, H.; Zhang, Y.; Wang, J. B. *Angew. Chem. Int. Ed.* **2011**, *50*, 1114.

(20) (a) Toshikazu, H.; Daisuke, M.; Koichi, Y.; Toshio, A. *Tetrahedron Lett.* **1986**, *27*, 929. (b) Macdonald, T. L.; Reagan, D. R. *J. Org. Chem.* **1990**, *55*, 4740. (c) Ma, S. M.; Negishi, E. *J. Am. Chem. Soc.* **1995**, *117*, 6345. (d) Taherirastgar, F.; Brandsma, L. *Synth. Commun.* **1997**, *27*, 4035. (e) Llerena, D.; Buisine, O.; Aubert, C.; Malacria, M. *Tetrahedron* **1998**, *54*, 9373. (f) Satoh, T.; Kurihara, T.; Fujita, K. *Tetrahedron* **2001**, *57*, 5369. (g) Krause, N.; Hoffmann-Röder, A.; Canisius, J. *Synthesis* **2002**, 1759. (h) Li, J.; Kong, W.; Fu, C.; Ma, S. M. *J. Org. Chem.* **2009**, *74*, 5104. (i) Li, J.; Zhou, C.; Fu, C.; Ma, S. *Tetrahedron* **2009**, *65*, 3695. (j) Poonoth, M.; Krause, N. *Adv. Synth. Catal.* **2009**, *351*, 117. (k) Tang, X.; Woodward, S.; Krause, N. *Eur. J. Org. Chem.* **2009**, 2836. (l) Ma, Z.; Zeng, R.; Yu, Y.; Ma, S. *Tetrahedron Lett.* **2009**, *50*, 6472. (m) Pu, X.; Qi, X.; Ready, J. M. *J. Am. Chem. Soc.* **2009**, *131*, 10364.

(21) (a) Ng, S.-S.; Jamison, T. F. *Tetrahedron* **2006**, *62*, 11350. (b) Caeiro, J.; Sestelo, J. P.; Sarandeses, L. A. *Chem. Eur. J.* **2008**, *14*, 741. (c) Koyama, I.; Kurahashi, T.; Matsubara, S. *J. Am. Chem. Soc.* **2009**, *131*, 1350. (d) Shi, Y.; Huang, J.; Yang, Y.-F.; Wu, L.-Y.; Niu, Y.-N.; Huo, P.-F.; Liu, X.-Y.; Liang, Y.-M. *Adv. Synth. Catal.* **2009**, *351*, 141. (e) Terao, J.; Bando, F.; Kambe, N. *Chem. Commun.* **2009**, 7336. (f) Sako, S.; Kurahashi, T.; Matsubara, S. *Chem. Commun.* **2011**, *47*, 6150.

(22) **General Procedure for the Cross-Coupling of Propargylic Bromide with Grignard Reagent**

Under an atmosphere of nitrogen, $Ni(acac)_2$ (5.12 mg, 0.02 mmol), Ph_3P (0.04 mmol), and THF (2 mL) were mixed in a Schlenk flask. Shortly afterwards, aryl or alkyl Grignard reagent (1.2 mmol) was added, and subsequently the properglic bromide was added. Then the reaction mixture was stirred at r.t. for 4–6 h. After completion of the reaction, the mixture was diluted with H_2O (15 mL) and extracted with Et_2O (3 × 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated in vacuum. The residue was subjected to flash column chromatography on silica gel (hexane or EtOAc–hexane, 100:1) to afford the corresponding allene products **3**.

Allenylbenzene (3aa):[13e] colorless oil; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.19 (m, 5 H), 6.17 (t, J = 6.8 Hz, 1 H), 5.16 (d, J = 6.8 Hz, 2 H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ = 209.8, 133.9, 128.6, 126.9, 126.7, 93.9, 78.7. HRMS: m/z calcd for C_9H_8: 116.0626; found: 116.0637 $[M]^+$.

