

# Regio- and stereoselective functionalization of electron-deficient alkenes by organosilicon compounds via photoinduced electron transfer\*

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*Abstract:* Regio- and stereoselective photoallylation of electron-deficient alkenes by use of allylic silanes via photoinduced electron transfer has been described. Similar photoinduced functionalization reactions such as arylmethylation, alkylation, and silylation can be achieved by using a variety of organosilicon compounds. These photoreactions proceed via radical cations of organosilicon compounds and radical anions of electron-deficient alkenes as reactive intermediates. The key step of the photoreactions is the attack of carbon radicals, which are generated from the radical cations of organosilicon compounds, on the radical anions of alkenes. The mechanism of the regio- and stereoselective photofunctionalization is discussed.

## INTRODUCTION

Photoinduced electron transfer (PET) reactions of group 14 organometallic compounds in the presence of an appropriate electron acceptor (A) have been extensively investigated from synthetic and mechanistic viewpoints in the recent two decades [1,2]. Since Mariano and his coworkers first reported the photoallylation of iminium salts by allylic silanes [3], a variety of PET reactions have been reported by the use of organosilicon compounds as electron donors (D). We have previously reported the regioselective photosubstitution and/or photoaddition of dicyano-aromatic compounds by allylic silanes [4]. PET reactions can be readily predicted by the simple calculation of reaction free energies,  $\Delta G$ , using the Rehm–Weller equation [5]. The rapid decay of reactive species by back-electron transfer from radical anion ( $A^{\bullet-}$ ) to radical cation ( $D^{\bullet+}$ ) limits the efficiency of PET reactions. The efficiency can be improved by the selection of sensitizers and the effect of additives. The former is a redox photosensitization by using aromatic hydrocarbon (ArH) as sensitizer [6]; the latter is a salt effect [2,7,8]. In the case of organosilicon compounds, the cleavage of the carbon–silicon bond is assisted by nucleophiles (Nu), such as acetonitrile, or  $\pi$ -acceptors, such as benzene. The photoreaction usually proceeds in polar solvents to generate radical ion pairs, i.e.,  $A^{\bullet-}$  and  $D^{\bullet+}$ . The key process of these photoreactions is the cleavage of the C–Si bond, assisted by Nu, to generate a carbon radical. Then, C–C bonds are formed by the attack of the carbon radical on  $A^{\bullet-}$ . These processes are generally accepted based on detailed mechanistic studies on these PET reactions. However, the regio- and stereochemical aspects in the photoinduced carbon–carbon bond-forming reaction has received little attention. In this article, we describe the regio- and stereoselective carbon-functionalization of electron-deficient alkenes by organosilicon compounds. The pertinent mechanistic features will be discussed briefly.

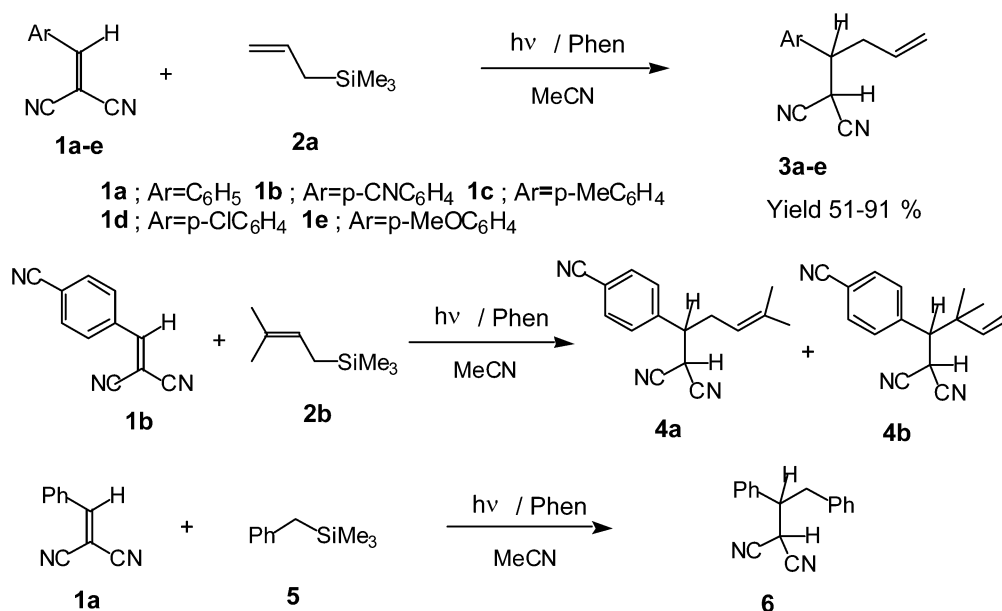
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## RESULTS AND DISCUSSION

## Regioselective carbon-functionalization

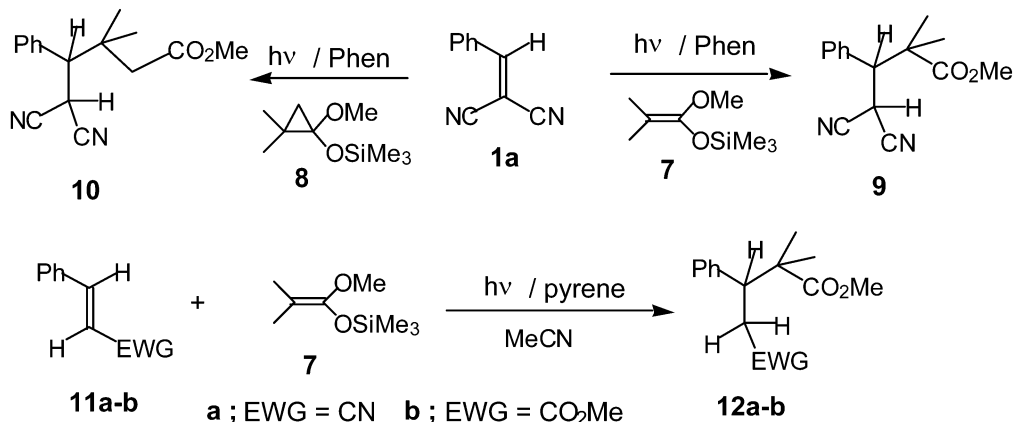
Irradiation of an acetonitrile solution containing 1,1-dicyano-2-phenylethene (**1a**) and allyltrimethylsilane (**2a**) in the presence of phenanthrene (Phen) as photosensitizer with a 300 W high-pressure Hg lamp through a Pyrex filter (>280 nm) under argon atmosphere regioselectively gave 5,5-dicyano-4-phenyl-1-pentene (**3a**) in 84 % yield [10]. Similarly, the photoallylation of 1-aryl-2,2-dicyanoethenes **1b–e** was achieved, giving the corresponding allylated products (**3b–e**); the yield of **3e** was low because of the high reduction potential of **1e**. The photoreaction of **1b** with 3-methyl-2-butenyltrimethylsilane (**2b**) afforded two allylated products (**4a** and **4b**) in a 5:1 ratio. In this reaction, the allylation occurred at both the 1- and 3-positions of the allylic moiety. The photoreaction of **1a** with benzyltrimethylsilane (**5**) in the presence of Phen proceeded as a regioselective photobenylation, giving 1,1-dicyano-2,3-diphenylpropane (**6**). These results clearly show the existence of allylic and benzylic radicals as key reactive species.



Ketene silyl acetals, cyclopropanone silyl acetals, and tetraalkylstannanes can also be utilized as electron-donating molecules: the ArH-sensitized photoreactions of **1** proceeded to give the corresponding alkylated products via a PET process. Irradiation of an acetonitrile solution containing a mixture of **1a** and 1-methoxy-2-methyl-1-trimethylsiloxy-1-propene (**7**) in the presence of Phen generated 4,4-dicyano-2,2-dimethyl-3-phenylbutyric acid methyl ester (**9**) in 95 % yield [10]. Similar irradiation of **1a–d** with ketene silyl acetal derivatives afforded the corresponding alkylated products. The photoreaction of **1a–d** with 1-methoxy-2,2-dimethyl-1-trimethylsiloxy-cyclopropane (**8**) and its derivatives in the presence of Phen afforded methyl 5,5-dicyano-3,3-dimethyl-4-phenylpentanoate (**10**) and its derivatives in excellent yields [11]. These ketene silyl acetal and cyclopropanone silyl acetal derivatives have been introduced to the electron-deficient alkenes as C2- and C3-carbon functional groups via the cleavage of Si–O bonds.

In the case of less electron-deficient arylalkenes, e.g., *trans*-1-cyano-2-phenylethene (**11a**) and *trans*-1-methoxycarbonyl-2-phenylethene (**11b**), the Phen-sensitized photoreaction with **2a**, **5**, **7**, or **8** did not proceed. However, the photoalkylation of **11a–b** by **7** was efficiently sensitized by pyrene, giving **12a–b** in high yields. This photoreaction was also sensitized by other aromatic hydrocarbons hav-

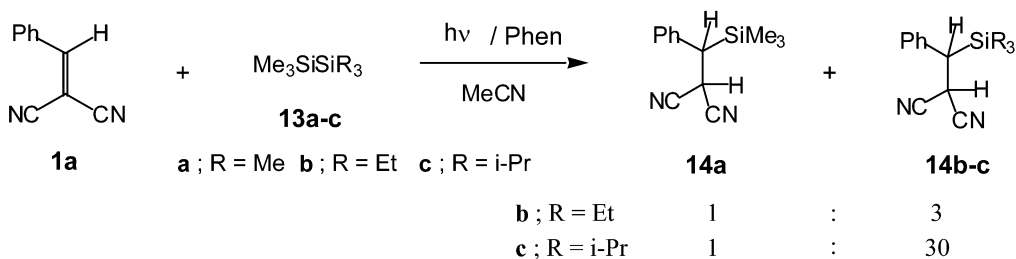
ing lower oxidation potentials such as chrysenes. Simple photoalkylation of **1a** by tetraalkylsilane did not occur even in the presence of Phen. However, the Phen-sensitized photobutylation of **1a–e** by tetra-butylstannane in propionitrile occurred to give 1,1-dicyano-2-phenylhexane derivatives in good yields [12].



In all these photoreactions, the addition of carbon-functional groups to the carbon–carbon double bonds occurred regioselectively at the position  $\beta$  to the cyano group of **1**. In the absence of ArH, the yields of carbon-functionalized products were significantly decreased.

### Regioselective photosilylation

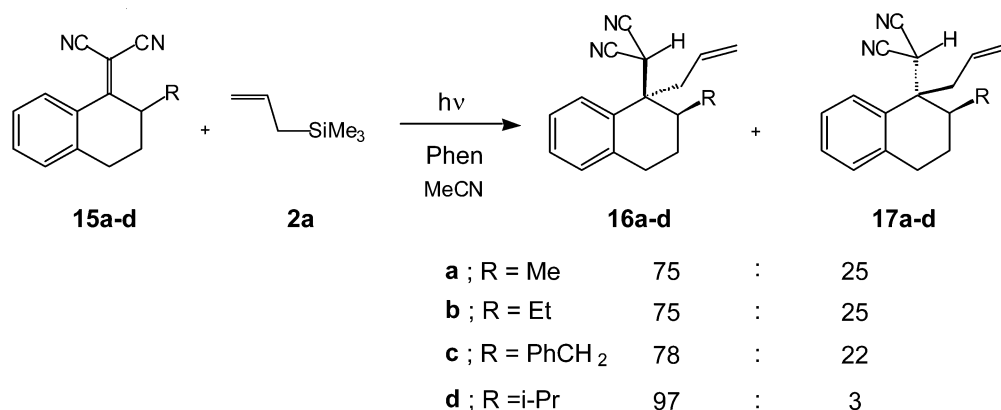
Photosilylation of **1a–e** was also achieved using disilanes (**13a–c**) under similar reaction conditions [13]. In this photoreaction, the silyl group was introduced in the position  $\beta$  to the cyano group of **1**. Silylated products were obtained in good yields accompanied by reduction products of **1**. With unsymmetrical disilanes as substrates, two kinds of silylated products were obtained in good yields; the more bulky silyl group was preferentially introduced to the alkenes. For example, irradiation of acetonitrile solutions of **1a** containing either 1,1,1-triethyl-2,2,2-trimethyldisilane (**13b**) or 1,1,1-triisopropyl-2,2,2-trimethylsilane (**13c**) afforded two kinds of silylated products, in ratios of 1:3 and 1:30, respectively.



### Diastereoselective photofunctionalization

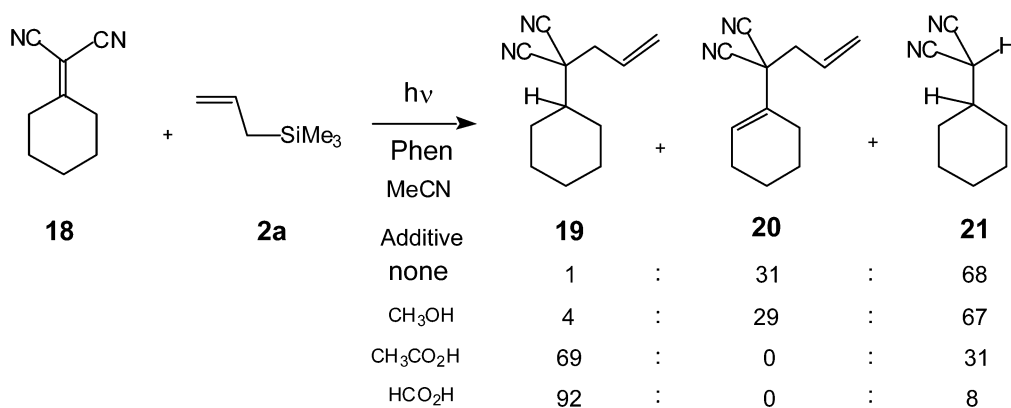
The stereoselectivity in the photoallylation and photobenzoylation under PET reaction conditions was also examined. Phen-sensitized photoreaction of 1-dicyanomethylene-2-methyl-1,2,3,4-tetrahydronaphthalene (**15a**) in the presence of **2a** in acetonitrile resulted in two kinds of allylated products, *r*-1-allyl-1-dicyanomethyl-2-methyl-1,2,3,4-tetrahydronaphthalene, **16a**, and the *cis*-isomer, **17a**, in 87 % yield [14]. Similar irradiation of the 2-ethyl and 2-benzyl derivatives, **15b–c**, gave the corresponding allylated products, **16b–c** and **17b–c**, in high yields. The photoinduced reaction of **15a–c** with **5**

afforded the corresponding benzylated products. In these photoreactions, the *trans*-isomers were obtained predominantly, and the product ratios (3:1) were not affected by the substituents in the 2-position and the C-functional groups. However, the photoreaction of the 2-isopropyl derivative **15d** with **2a** and **5** in the presence of Phen afforded the *trans*-allylated product, **16d**, and the corresponding *trans*-benzylated one in highly diastereoselective manner (*trans*:*cis* = 97:3). Some of these structures were confirmed by their X-ray analyses.



### Different regioselectivity in the photoallylation of alkylidenepropanedinitrile

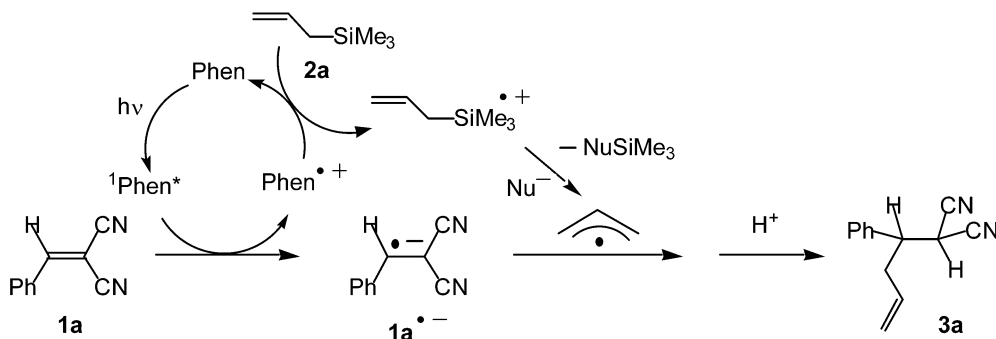
The Phen-sensitized photoreaction of cyclohexylidenepropanedinitrile (**18**) with **2a** gave two allylated products **19** and **20** and the reduction product, **21**, depending on the acidity (*pK*<sub>a</sub>) of the additives [9,15]. The addition of organic acids such as acetic acid and formic acid predominantly gave **19** in good yields. However, in the absence of acids **20** and **21** were obtained predominantly. It is notable here that the allylation of **18** occurs at the position  $\alpha$  to the cyano group.



### MECHANISM

Considering the mechanism of these reactions, we note the following. All these photoreactions occurred in poor yields or not at all in less-polar solvents, such as benzene or dichloromethane. The fluorescence of ArH, such as Phen or pyrene, in acetonitrile was efficiently quenched by electron-deficient alkenes, but was not quenched by organosilicon compounds. The free-energy change ( $\Delta G$ ) for the one-electron transfer process from the excited singlet state of ArH to the electron-deficient alkenes was estimated to be negative.

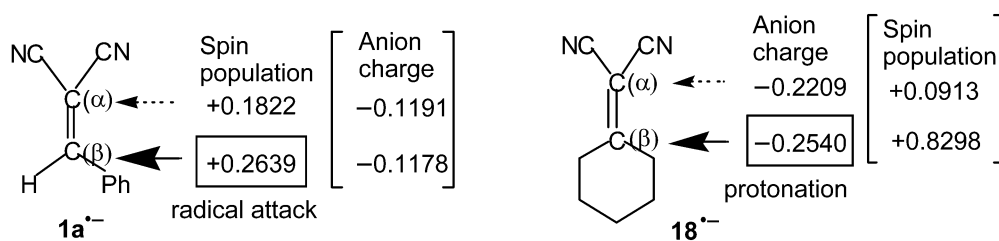
Based on these results, we propose a simple redox photosensitization mechanism for the Phen-sensitized photoallylation of **1a** by **2a** as a representative example (Scheme 1). The first step is one-electron transfer from  $^1\text{Phen}^*$  to **1a** to give the radical cation of Phen ( $\text{Phen}^{\bullet+}$ ) and the radical anions of **1a** ( $\mathbf{1a}^{\bullet-}$ ). A secondary electron transfer from **2a** to  $\text{Phen}^{\bullet+}$  then produces the radical cation of **2a** ( $\mathbf{2a}^{\bullet+}$ ). The key step of photo-functionalization of **1a** is the generation of the allyl radical from  $\mathbf{2a}^{\bullet+}$ . The cleavage of the C–Si bond is assisted by nucleophiles (Nu) such as acetonitrile.



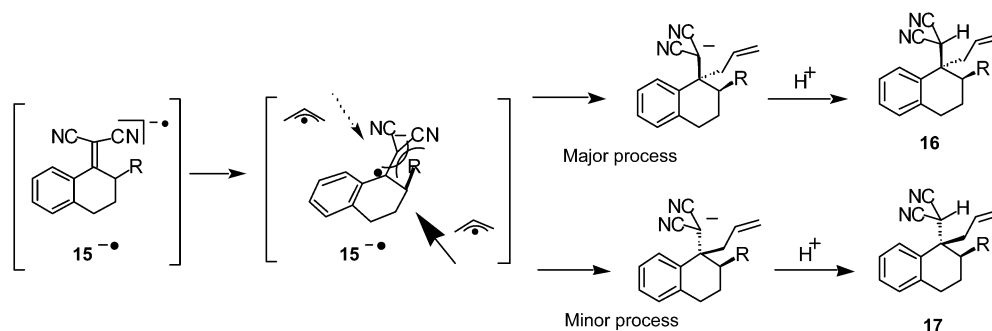
Scheme 1

The difference in regioselectivity between the aryl- and alkyl-substituted dicyanoethenes may be explained in terms of spin population and anion charge of their radical anions such as  $\mathbf{1a}^{\bullet-}$  and  $\mathbf{18}^{\bullet-}$ . In the case of **1a**, the benzylic position of  $\mathbf{1a}^{\bullet-}$ , which has a higher spin population, is attacked regioselectively by the allyl radical generated from  $\mathbf{2a}^{\bullet+}$ . The cleavage of C–Si bond may be assisted by the attack of Nu such as acetonitrile on trimethylsilyl group. In fact, in photosilylations using unsymmetrical disilanes the more bulky silyl radical is predominantly generated and introduced by attack of Nu on the less-hindered silicon.

On the other hand,  $\mathbf{18}^{\bullet-}$  might be unstable. Therefore, three competitive processes occur from the cluster  $[\text{Phen} - \mathbf{18}^{\bullet-} - \mathbf{2a}^{\bullet+}]$ : protonation, hydrogen abstraction, and hydride elimination. The final products depend on the  $pK_a$  values of the additives. In the presence of acids, protonation of  $\mathbf{18}^{\bullet-}$  at  $\beta$ -position to the cyano groups generates dicyanocyclohexylmethyl radical regioselectively, which then couples with the allyl radical to give **19**.



The diastereoselective allylation can be explained by the bulkiness of the substituents in the 2-position of **15**. The allylic radical attacks the benzylic position of  $\mathbf{15}^{\bullet-}$  from the less-hindered side as shown in Scheme 2; protonation then gives **16** and **17**. Substrate **15d** undergoes a highly diastereoselective photofunctionalization by organosilicon compounds via a PET reaction, producing the quaternary carbon stereocenters.



Scheme 2

## ACKNOWLEDGMENTS

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## REFERENCES

1. K. Mizuno, T. Tamai, A. Sugimoto, H. Maeda. In *Advances in Electron-Transfer Chemistry*, P. S. Mariano (Ed.), Vol. 6, pp. 131–165, JAI Press, New York (1999).
2. K. Mizuno and Y. Otsuji. *Top. Curr. Chem.* **169**, 301 (1994).
3. K. Ohga and P. S. Mariano. *J. Am. Chem. Soc.* **104**, 617 (1982); U. C. Yoon and P. S. Mariano. *Acc. Chem. Res.* **25**, 233 (1992).
4. K. Mizuno, M. Ikeda, Y. Otsuji. *Tetrahedron Lett.* **26**, 461 (1985); K. Mizuno, K. Terasaka, M. Ikeda, Y. Otsuji. *Tetrahedron Lett.* **26**, 5819 (1985); K. Mizuno, K. Terasaka, M. Yasueda, Y. Otsuji. *Chem. Lett.* 145 (1988); K. Mizuno, K. Nakanishi, Y. Otsuji. *Chem. Lett.* 1833 (1988); K. Mizuno, T. Nishiyama, K. Terasaka, M. Yasuda, K. Shima, Y. Otsuji. *Tetrahedron* **48**, 9673 (1992); K. Nakanishi, K. Mizuno, Y. Otsuji. *Bull. Chem. Soc. Jpn.* **66**, 2371 (1993); T. Tamai, K. Mizuno, I. Hashida, Y. Otsuji. *Bull. Chem. Soc. Jpn.* **66**, 3747 (1993); T. Nishiyama, K. Mizuno, Y. Otsuji, H. Inoue. *Tetrahedron* **51**, 6695 (1995).
5. D. Rehm and A. Weller. *Isr. J. Chem.* **8**, 259 (1970).
6. T. Majima, C. Pac, H. Sakurai. *J. Am. Chem. Soc.* **102**, 5265 (1980); T. Majima, C. Pac, A. Nakasone, H. Sakurai. *J. Am. Chem. Soc.* **103**, 4499 (1981).
7. J. Santamaria. In *Photoinduced Electron Transfer*, Part B, M. A. Fox and M. Chanon (Eds.), pp. 483–540, Elsevier, New York (1988).
8. K. Mizuno, N. Ichinose, Y. Otsuji. *Chem. Lett.* 455 (1985); *J. Org. Chem.* **57**, 1855 (1992); K. Mizuno, N. Ichinose, T. Tamai, Y. Otsuji. *Tetrahedron Lett.* **26**, 5823 (1985); T. Tamai, K. Mizuno, I. Hashida, Y. Otsuji. *Photochem. Photobiol.* **54**, 23 (1991).
9. K. Mizuno, M. Ikeda, Y. Otsuji. *Chem. Lett.* 1507 (1988).
10. K. Mizuno, N. Takahashi, T. Nishiyama, H. Inoue. *Tetrahedron Lett.* **36**, 7463 (1995).
11. K. Mizuno, T. Nishiyama, N. Takahashi, H. Inoue. *Tetrahedron Lett.* **37**, 2955 (1996).
12. K. Mizuno, K. Nakanishi, A. Tachibana, Y. Otsuji. *J. Chem. Soc., Chem. Commun.* 344 (1991).
13. K. Mizuno, K. Nakanishi, J. Chosa, T. Nguyen, Y. Otsuji. *Tetrahedron Lett.* **28**, 3689 (1989); K. Mizuno, K. Nakanishi, J. Chosa, Y. Otsuji. *J. Organomet. Chem.* **473**, 35 (1994).
14. T. Hayamizu, H. Maeda, M. Ikeda, K. Mizuno. *Tetrahedron Lett.* **42**, 2361 (2001).
15. T. Hayamizu, M. Ikeda, H. Maeda, K. Mizuno. *Org. Lett.* **3**, 1277 (2001).