Organic LETTERS

Letter

pubs.acs.org/OrgLett

Ruthenium-Catalyzed Silylation of 1,3-Butadienes with Vinylsilanes

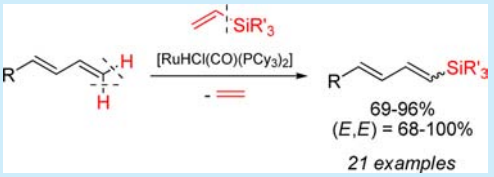
Justyna Szudkowska-Frątczak,[†] Bogdan Marciniec,[†,‡] Grzegorz Hreczycho,[†] Maciej Kubicki,[†] and Piotr Pawluć*[,†]

[†]Faculty of Chemistry, Adam Mickiewicz University in Poznan, Umultowska 89b, 61-614 Poznan, Poland

[‡]Center for Advanced Technologies, Adam Mickiewicz University in Poznan, Umultowska 89c, 61-614 Poznan, Poland

Supporting Information

ABSTRACT: A novel method for the synthesis of 1-silyl-substituted 1,3-butadienes, based on $[RuHCl(CO)(PCy_3)_2]$-catalyzed silylative coupling of terminal (*E*)-1,3-dienes with vinylsilanes, is reported. The reaction provides a facile and straightforward access to (*E*,*E*)-dienylsilanes in a highly stereoselective fashion (especially for aryl-substituted dienes) and opens a valuable and general synthetic route for the direct catalytic silylation of conjugated dienes with elimination of ethylene as a single byproduct. Preliminary results on synthetic application of the synthesized silylated 1,3-butadienes in desilylation reactions are described.



Silyl-substituted 1,3-dienes are versatile building blocks that have significant potential in stereoselective organic synthesis.[1] They can be used as substrates in enantioselective ruthenium catalyzed alcohol C−H crotylation via diene hydrohydroxyalkylation.[2] Silylated 1,3-butadienes have been demonstrated as useful building blocks to construct cyclic compounds through the Diels−Alder reaction and can be used for allylation and desilylation reactions.[1] Under different reaction conditions they can be converted to a variety of functional molecules, including a cyclohexene moiety or functionalized (halogen-, aryl-, acyl-substituted) diene fragment. The highly functionalized products of this type are difficult to obtain by other methods, which proves the importance of selective transformations of silyl-substituted 1,3-butadienes.

So far a large number of methods have been proposed to synthesize silylated 1,3-dienes, usually employing different organometallic reagents. Nevertheless, it is still a challenge to perform a highly selective and effective synthesis of stereodefined conjugated dienes. Conventional methods for preparing stereodefined dienylsilanes include a modified Peterson olefination[3] or Horner−Wadsworth−Emmons-type reactions.[4] An alternative approach to dienylsilanes relies on the palladium-catalyzed Heck coupling of vinylsilanes with vinyl halides or triflates[5] and silyl-substituted tosylates with olefins.[6] The cross-coupling of organometallic reagents, such as silyl-substituted stannanes[7] and organozinc[8] or organoaluminum derivatives with vinyl halides,[9] has been also applied in the synthesis of 1-silyl-1,3-butadienes. More recent approaches to silyl-substituted 1,3-butadienes involve reactions starting from alkyne derivatives.[1] Dixneuf and co-workers have reported ruthenium catalyzed double-addition of silyl-substituted diazo compounds to alkynes to give 1,4-bis(silyl)-substituted 1,3-dienes.[10] Hydrozirconation of silyl-substituted enynes followed by halogenation has been applied for the synthesis of halogen-containing silyl-substituted 1,3-dienes.[11] It has been established that it is possible to obtain 1-silyl-1,3-butadienes and 1,4-bis(silyl)-1,3-butadienes by hydrolysis of the corresponding metallacyclopentadienes (M = Zr, Ti), being derivatives of silyl-substituted diynes or alkynes.[12] The most popular approaches to 2-silicon substituted 1,3-butadienes involve ruthenium-catalyzed ene-yne cross-metathesis of silylacetylenes with olefins[13] and reaction of chlorosilanes with Grignard reagents derived from chloroprene.[14]

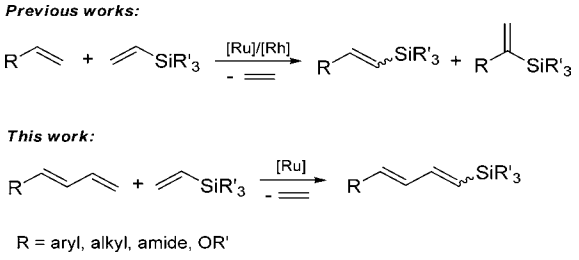
One of the most powerful methods for the synthesis of stereodefined alkenylsilanes yet proposed is the transition-metal-catalyzed silylative coupling of functionalized olefins with vinylsilanes.[15] The reaction of silylative coupling involves the cleavage of the C−H bond at the α and β carbon atoms from the vinyl group and activation of the C−Si bond in vinylsilane, accompanied by release of the ethylene molecule. This process is catalyzed by transition metal (M = Ru, Rh, Co, Ir) complexes either containing M−H and M−Si bonds or capable of their in situ generation. The mechanism of silylative coupling involves insertion of vinylsilane into the M−H bond and β-Si transfer to the metal, accompanied by release of ethylene so that the M−Si complex could be generated. This step is followed by insertion of alkene and β-H transfer to the metal with a simultaneous elimination of substituted vinylsilane.[16,17]

On the basis of our previous results on the highly stereoselective synthesis of substituted vinylsilanes from terminal alkenes,[15] we have envisaged that the transition-metal-catalyzed silylative coupling of olefins with vinyl-substituted organosilicon compounds can be successfully extended for systems based on conjugated dienes (Scheme 1). The silylative coupling of terminal 1,3-dienes with vinylsilanes opens a valuable and general synthetic route for the direct silylation of conjugated dienes at the terminal position with ethylene as a single byproduct.

Received: March 24, 2015
Published: April 27, 2015

DOI: 10.1021/acs.orglett.5b00865
Org. Lett. 2015, 17, 2366−2369

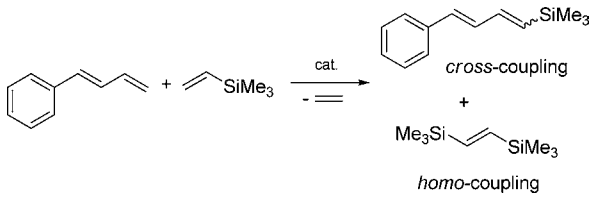
Scheme 1. Extension of Catalytic Silylative Coupling of Olefins with Vinylsilanes for 1,3-Dienes



In the letter we report a novel method to access functionalized 1-silyl-substituted 1,3-butadienes based on silylative coupling of terminal (*E*)-1,3-butadienes with vinylsilanes and vinylsiloxanes. To the best of our knowledge, the selective silylation of terminal dienes by silylative agents is extremely rare and there is only one report in the literature on effective silylation of terminal 1,3-dienes with benzene-fused silacyclobutane.[18] The catalytic silylation of conjugated butadienes by commercially available vinylsilanes opens a new, direct, and highly stereoselective route for the synthesis of 1-silylated 1,3-dienes from simple substrates.

We began the investigation with optimizing the reaction conditions. Catalytic screenings have been applied in the model catalytic process of (*E*)-1-phenylbuta-1,3-diene with vinyltrimethylsilane (Scheme 2). Selected ruthenium(II) and

Scheme 2. Silylation of (*E*)-1-Phenylbuta-1,3-diene with Vinyltrimethylsilane

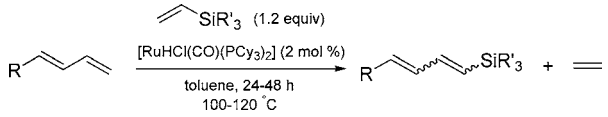


rhodium(I) complexes, i.e. $[RuHCl(CO)(PCy_3)_2]$ (**I**), $[RuHCl(CO)(PPh_3)_3]$ (**II**), $[RuCl_2(CO)_3]_2$ (**III**), $[Ru(SiMe_2Ph)Cl(CO)(PPh_3)_2]$ (**IV**), $[Rh(\mu\text{-}OSiMe_3)(cod)]_2$ (**V**), $[RhH(CO)(PPh_3)_3]$ (**VI**), and $[RhCl(cod)]_2$ (**VII**), known to be active in the silylative coupling of olefins with vinylsilanes have been tested in this process. Since the synthetic procedure requires the full conversion of 1,3-butadiene and small amounts of byproducts of the vinylsilane homocoupling, all the screening tests were performed with the 1:1.2 diene/vinylsilane ratio. In a typical procedure, the substrates and catalyst (2 mol %) were dissolved in toluene (0.1 M concentration to avoid competitive diene polymerization) and heated in a Schlenk bomb flask fitted with a plug valve at 100 °C for 24−48 h.

From among the tested catalysts, ruthenium-hydride monocarbonyl complexes $[RuHCl(CO)(PCy_3)_2]$ (**I**) and $[RuHCl(CO)(PPh_3)_3]$ (**II**) clearly showed higher catalytic activity (99% yield of silylated diene after 24 h) than other ruthenium(II) as well as rhodium(I) derivatives. The ruthenium-hydride complex **I** showed the highest selectivity (*E*/*Z* = 93/7) under the conditions applied and was selected for further synthetic procedures. Despite the use of a slight excess of vinylsilane, only trace amounts of the competitive homocoupling product, 1,2-bis(silyl)ethene, were detected in the presence of catalyst **I** and **II**. The reaction proceeded with moderate yield (~40%) and selectivity (*E*/*Z* = 8/2) when a ruthenium-silyl complex (**IV**) was used; however, the reaction required a longer time and even after 48 h the substrates did not reach full conversion. Rhodium-siloxide (**V**) and rhodium-hydride (**VI**) complexes showed significantly lower catalytic activity in the silylation reaction of (*E*)-1-phenylbuta-1,3-diene with vinyltrimethylsilane (10−20% yield of silylated diene after 48 h), whereas $[RuCl_2(CO)_3]_2$ (**III**) and $[RhCl(cod)]_2$ (**VII**) proved to be inactive in this process.

Given our optimized conditions, we investigated the scope of this reaction, using selected commercially available or synthesized 1-substituted (*E*)-1,3-butadienes.[19] The silylation of terminal (*E*)-1,3-butadienes by various vinylsilanes and vinylsiloxanes of general formula $CH_2{=}CHSiR_3$ (where SiR_3 = $SiMe_3$, $SiMe_2Ph$, $Si(OEt)_3$, $Si(OEt)_2Me$, $SiMe_2OEt$, $Si(OSiMe_3)_2Me$, $Si(OSiMe_3)Me_2$) proceeded efficiently in the presence of 2 mol % catalyst (**I**) to give 1,3-butadienes silylated at the terminal position (Scheme 3). In a typical procedure, the

Scheme 3. Silylation of (*E*)-1,3-Butadienes with Vinylsilanes



substrates and catalyst were dissolved in toluene (0.1 M concentration) and heated in a Schlenk bomb flask fitted with a plug valve at 100 °C (for aryl-substituted 1,3-butadienes) or 120 °C (for methyl- and methoxy-substituted 1,3-butadienes) for 24−48 h. The results are presented in Table 1.

All of the silylated 1,3-butadienes were isolated and characterized spectroscopically. The stereoselectivity of the overall transformation was good. In all cases, the (*E*,*E*)-double bond geometry was favored (68−100%) as measured by ^1H NMR; however, the isomer ratio depended on the substituents in the butadiene molecule and vinylsilane used. DEPT analysis of the 1-phenyl-4-(trimethylsilyl)-1,3-butadiene **1** obtained (Table 1, entry 1) excluded the presence of the geminally substituted dienylsilane. The stereochemical assignments for products **1**−**21** confirmed that most of the reactions yielded a mixture of (*E*,*E*) and (*E*,*Z*) isomers; however, in some cases during the reaction, partial *E* → *Z* isomerization of double bonds (2−13%) took place which resulted in the formation of the (*Z*,*Z*) isomer (Table 1, entries 5, 10, and 14−20).

The (*E*,*E*)-configuration of the double bond of the compounds **12** and **13** was further confirmed by single-crystal X-ray diffraction analysis.[20]

Under the conditions applied, 1-substituted (*E*)-1,3-butadienes bearing aryl groups reacted successfully to give the corresponding 1-aryl-4-silyl-1,3-butadienes in high isolated yields (80−96%), irrespective of the substituent's electronic character (Table 1, entries 1−13). Both alkyl- and alkoxy-substituted vinylsilanes as well as vinylsiloxanes can be employed for the silylation of aryl-substituted 1,3-butadienes to give corresponding 1-aryl-4-silyl-1,3-butadienes. However, the silylation of aryl-substituted (*E*)-1,3-butadienes by trialkyl-substituted vinylsilanes seems to be more selective than that using alkoxy-substituted vinylsilanes or vinylsiloxanes. Despite the use of a slight excess of vinylsilane, only trace amounts of the competitive homocoupling products, 1,2-bis(silyl)ethenes, were detected. Detailed monitoring of the reaction of (*E*)-1-

DOI: 10.1021/acs.orglett.5b00865
Org. Lett. 2015, 17, 2366−2369

Table 1. Silylation of (*E*)-1,3-Butadienes with Vinylsilanes[a]

entry (product no.)	R	SiR_3'	time [h]	isolated yield	selectivity (*E,E*)/(*E,Z*)/(*Z,Z*)[b]
1.	Ph	$SiMe_3$	24	89	93:7:0
2.	Ph	$SiMe_2Ph$	24	80	93:7:0
3.	Ph	$SiMe_2OEt$	24	86	94:6:0
4.	Ph	$Si(OEt)_2Me$	24	87	98:2:0
5.	Ph	$Si(OEt)_3$	24	89	83:15:2
6.	Ph	$SiEt_3$	24	90	99:1:0
7.	Ph	$Si(OSiMe_3)_2Me$	24	87	90:10:0
8.	Ph	$Si(OSiMe_3)Me_2$	24	96	96:4:0
9.	4-$MeOC_6H_4$	$SiMe_3$	24	85	94:6:0
10.	4-$MeOC_6H_4$	$Si(OEt)_2Me$	24	90	80:10:10
11.	4-$MeOC_6H_4$	$Si(OSiMe_3)_2Me$	24	94	88:12:0
12.	4-ClC_6H_4	$SiMe_3$	24	89	93:7:0
13.	4-BrC_6H_4	$SiMe_3$	24	90	100:0:0
14.	MeO	$SiMe_2Ph$	48	78	75:23:2
15.	MeO	$Si(OEt)_3$	48	79	68:20:12
16.	MeO	$Si(OEt)_2Me$	48	75	70:20:10
17.	MeO	$Si(OSiMe_3)_2Me$	48	76	70:21:9
18.	Me	$SiMe_2Ph$	48	80	71:27:3
19.	Me	$Si(OEt)_3$	48	82	71:16:13
20.	Me	$Si(OEt)_2Me$	48	69	75:14:11
21.	*N*-phthalimide	$SiMe_3$	24	89	90:10:0

[a]Reaction conditions [diene]/[vinylsilane]/[$RuHCl(CO)(PCy_3)_2$] = 1:1.2:0.02; toluene, 100 °C (entries 1−13, 21) or 120 °C (entries 14−20). [b]*EE/EZ/ZZ* ratio determined by ^1H NMR and GC-MS.

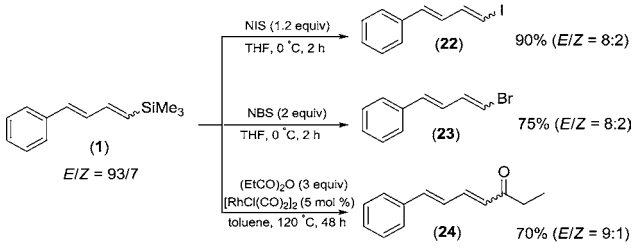
phenylbuta-1,3-diene with vinyltrimethylsilane (Table 1, entry 1) by GC-MS analysis allowed the detection of small amounts of byproducts (less than 5%) which were assigned as a Diels−Alder cycloaddition product and desilylated cycloaddition product (3-phenylcyclohexene).

The ruthenium-catalyzed silylative coupling proceeded efficiently also for other dienes such as (*E*)-1,3-pentadiene (Table 1, entries 18−20) as well as conjugated dienes containing heteroatoms, (*E*)-1-methoxy-1,3-butadiene and (*E*)-2-(buta-1,3-dien-1-yl)isoindoline-1,3-dione (Table 1, entries 14−17, 21). The silylation of (*E*)-1-methoxy-1,3-butadiene and (*E*)-1,3-pentadiene proceeded with lower selectivity, irrespective of the vinylsilane used, to give a mixture of (*E,E*), (*E,Z*), and (*Z,Z*) isomers, with (*E,E*)-dienylsilane as the predominant product (68−75%). The lower selectivity of the reaction with methoxy-substituted diene is consistent with previous data on the silylative coupling of vinylsilanes with alkyl vinyl ethers.[21] The reaction of (*E*)-2-(buta-1,3-dien-1-yl)-isoindoline-1,3-dione with $CH_2{=}CHSiMe_3$ proceeded with high yield and selectivity.

The reactivity of 2-substituted dienes in the reaction with vinylsilanes has been also tested. Unfortunately, the reaction of isoprene or myrcene with vinyltriethoxysilane or vinyldimethylphenylsilane in the presence of catalyst **I** occurs to a low degree, to give monosilylated products corresponding to up to 25% conversion of diene, after 48 h under the conditions given.

To demonstrate the potential applications of silylated 1,3-butadienes, we pursued transformation of the obtained 1-phenyl-4-(trimethylsilyl)-1,3-butadiene **1** into halogeno and ketone derivatives of 1,3-butadiene via halodesilylation or desilylative acylation reactions. Treatment of the silylative coupling product **1** with NIS (1.2 equiv) or NBS (2 equiv) caused iodo-[22] or bromodesilylation[23] in a highly stereospecific manner, giving (*E,E*)-(4-iodobuta-1,3-dien-1-yl)benzene **22** or (*E,E*)-(4-bromobuta-1,3-dien-1-yl)benzene **23** as predominant products in good geometrical purity (*E*/*Z* = 8/2) within 2 h (Scheme 4). The reaction of **1** with 3 equiv of propionic anhydride in the presence of rhodium catalyst $[RhCl(CO)_2]_2$ (5 mol %) in dry toluene at 120 °C for 48 h under an Ar atmosphere according to the method described by Narasaka and co-workers[24] allowed isolation of 6-phenylhexa-3,5-dien-2-one **24** in 70% yield (Scheme 4).

Scheme 4. Synthetic Application of 1-Phenyl-4-(trimethylsilyl)-1,3-butadiene in Desilylation Reactions



In summary, a novel type of ruthenium-catalyzed silylation of 1,3-dienes with vinylsilanes has been developed. This unconventional way of introducing a silyl substituent at a diene terminus extends the synthetic application of classical silylative coupling of olefins with vinylsilicon compounds and complements the conventional methodologies for the synthesis of functionalized 1-silyl-1,3-butadienes.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, NMR spectra, and compound characterization data as well as X-ray analysis details. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b00865.

DOI: 10.1021/acs.orglett.5b00865
Org. Lett. 2015, 17, 2366−2369

AUTHOR INFORMATION

Corresponding Author

*E-mail: piotrpaw@amu.edu.pl.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support from the National Science Centre (Poland), Grant No. Opus 2011/03/B/ST5/01034 and Maestro 2011/02/ST5/00472 are gratefully acknowledged.

REFERENCES

(1) (a) Zhao, F.; Zhang, S.; Xi, Z. *Chem. Commun.* **2011**, *47*, 4348. (b) Welker, M. E. *Tetrahedron* **2008**, *64*, 11529.
(2) (a) Zbieg, J. R.; Moran, J.; Krische, M. J. *J. Am. Chem. Soc.* **2011**, *133*, 10582. (b) Itoh, T.; Montgomery, T. P.; Recio, A., III; Krische, M. J. *Org. Lett.* **2014**, *16*, 820.
(3) (a) Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780. (b) McNulty, J.; Das, P. *Chem. Commun.* **2008**, 1244.
(4) Lee, B. S.; Gil, J. M.; Oh, D. Y. *Tetrahedron Lett.* **2001**, *42*, 2345.
(5) Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1988**, *53*, 4909.
(6) Hansen, A. L.; Ebran, J.-P.; Ahlquist, M.; Norrby, P.-O.; Skrydstrup, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 3349.
(7) Stille, J. K.; Groht, B. L. *J. Am. Chem. Soc.* **1987**, *109*, 813.
(8) Matsubara, S.; Otake, Y.; Morikawa, T.; Utimoto, K. *Synlett* **1998**, 1315.
(9) Andreini, B. P.; Carpita, A.; Rossi, R. *Tetrahedron Lett.* **1988**, *29*, 2239.
(10) (a) Paih, J. L.; Bray, C. V.-L.; Derien, S.; Dixneuf, P. H. *J. Am. Chem. Soc.* **2010**, *132*, 7391. (b) Le Paih, J.; Derien, S.; Özdemir, I.; Dixneuf, P. H. *J. Am. Chem. Soc.* **2000**, *122*, 7400.
(11) Cai, M. Z.; Zhou, Z.; Wang, P. P. *Synthesis* **2006**, 789.
(12) (a) Urabe, H.; Sato, F. *J. Org. Chem.* **1996**, *61*, 6756. (b) Delas, C.; Urabe, H.; Sato, F. *Chem. Commun.* **2002**, 820. (c) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336. (d) Xi, Z.; Liu, X.; Lu, J.; Bao, F.; Fan, H.; Li, Z.; Takahashi, T. *J. Org. Chem.* **2004**, *69*, 8547. (e) Xi, Z.; Song, Z.; Liu, G.; Liu, X.; Takahashi, T. *J. Org. Chem.* **2006**, *71*, 3154.
(13) (a) Junker, C. S.; Welker, M. E.; Day, C. S. *J. Org. Chem.* **2010**, *75*, 8155. (b) Ostrowska, S.; Powała, B.; Jankowska-Wajda, M.; Żak, P.; Rogalski, S.; Wyrzykiewicz, B.; Pietraszuk, C. *J. Organomet. Chem.* **2015**, *783*, 135.
(14) Pidaparthi, R. R.; Junker, C. S.; Welker, M. E.; Day, C. S.; Wright, M. W. *J. Org. Chem.* **2009**, *74*, 8290.
(15) (a) Marciniec, B. *Acc. Chem. Res.* **2007**, *40*, 943. (b) Marciniec, B. *Coord. Chem. Rev.* **2005**, *249*, 2374.
(16) Wakatsuki, Y.; Yamazaki, H.; Nakano, N.; Yamamoto, Y. *J. Chem. Soc. Chem. Commun.* **1991**, 703.
(17) (a) Marciniec, B.; Pietraszuk, C. *J. Chem. Soc. Chem. Commun.* **1995**, 2003. (b) Marciniec, B.; Pietraszuk, C. *Organometallics* **1997**, *16*, 4320.
(18) Hirano, K.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2007**, *129*, 6094.
(19) Szudkowska-Fratczak, J.; Ryba, A.; Franczyk, A.; Walkowiak, J.; Kubicki, M.; Pawluc, P. *Appl. Organomet. Chem.* **2014**, *28*, 137.
(20) Please see Supporting Information for details
(21) Marciniec, B.; Kujawa, M.; Pietraszuk, C. *Organometallics* **2000**, *19*, 1677.
(22) Recent applications of the NIS-mediated iododesilylation of substituted vinylsilanes: (a) Ilardi, E. A.; Stivala, C. E.; Zakarian, A. *Org. Lett.* **2008**, *10*, 1727. (b) Sidera, M.; Costa, A. M.; Vilarrasa, J. *Org. Lett.* **2011**, *13*, 4934. (c) Xie, Q.; Denton, R. W.; Parker, K. A. *Org. Lett.* **2008**, *10*, 5345. (d) Herrmann, A. T.; Martinez, S. R.; Zakarian, A. *Org. Lett.* **2011**, *13*, 3636.
(23) Recent applications of the NBS-mediated bromodesilylation of substituted vinylsilanes: (a) Nagao, M.; Asano, K.; Umeda, K.; Katayama, H.; Ozawa, F. *J. Org. Chem.* **2005**, *70*, 10511. (b) Smith, A. B., III; Razler, T. M.; Ciavarri, J. P.; Hirose, T.; Ishikawa, T.; Meis, R. M. *J. Org. Chem.* **2008**, *73*, 1192. (c) Fuwa, H.; Yamagata, N.; Saito, A.; Sasaki, M. *Org. Lett.* **2013**, *15*, 1630.
(24) Yamane, M.; Uera, K.; Narasaka, K. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 477.

DOI: 10.1021/acs.orglett.5b00865
Org. Lett. 2015, 17, 2366−2369