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Metal-Free Catalytic C−Si Bond Formation in an Aqueous Medium. Enantioselective NHC-Catalyzed Silyl Conjugate Additions to Cyclic and Acyclic α,*β*-Unsaturated Carbonyls

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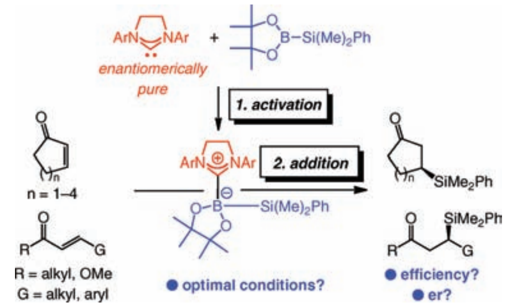
Supporting Information

ABSTRACT: A metal-free method for enantioselective conjugate addition of a dimethylphenylsilyl group to α,*β*-unsaturated carbonyls is reported. Transformations are catalyzed by a chiral N-heterocyclic carbene (NHC), performed in an aqueous solution (3:1 mixture of water and tetrahydrofuran) and are operationally simpler to perform than the NHC−Cu-catalyzed variant. The chiral catalyst is generated from an enantiomerically pure imidazolinium salt (prepared in three steps) and a common organic amine base (dbu). NHC-catalyzed processes proceed with 5.0−12.5 mol % catalyst loading at 22 °C within 1−12 h, affording the desired *β*-silyl carbonyls in 85:15 to >98:2 enantiomeric ratio and in 50% to >98% yield. Cyclic enones or lactones and acyclic α,*β*-unsaturated ketones, esters, and aldehydes can be used as substrates.

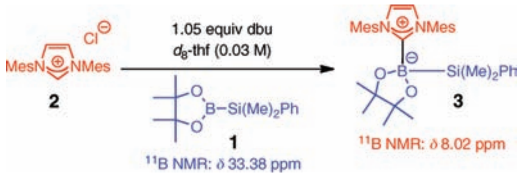
We recently discovered that achiral N-heterocyclic carbenes (NHCs), in the absence of a metal salt, activate the B−B bond of bis(pinacolato)diboron [$B_2(pin)_2$] and catalyze efficient (nonenantioselective) boronate conjugate additions to α,*β*-unsaturated carbonyls.[1] A related set of transformations corresponds to NHC-catalyzed silyl conjugate addition (SCA) reactions with commercially available dimethylphenylsilylpinacolatoboron [$Me_2PhSi-B(pin)$, **1**].[2] Notwithstanding the value of C−Si bond forming processes in chemical synthesis,[3] the basis for pursuing silyl conjugate additions[4] was twofold: First, we were interested in determining if, as outlined in Scheme 1, the unsymmetrical silylboronate can be activated to cause selective transfer of the $PhMe_2Si$ unit to a polarized olefin (vs (pin)B−C bond formation). Second, we were keen on investigating whether a chiral NHC can sufficiently influence the reaction course to render such metal-free catalytic processes highly enantioselective.[5] Herein, we report enantioselective SCA reactions involving cyclic and acyclic enones and α,*β*-unsaturated esters as well as various enals. Transformations are performed in the presence of **1** and promoted by 5.0−12.5 mol % of an NHC catalyst, which is prepared and used in situ from a readily accessible chiral imidazolinium salt and a common organic base. NHC-catalyzed processes are carried out at ambient temperature in a 3:1 mixture of water and tetrahydrofuran (thf).[6] The desired *β*-silylcarbonyls are isolated in up to >98% yield and >98:2 enantiomeric ratio (er). The method complements the related metal-catalyzed variants[4,7,8] and, to the best of our knowledge, represents the first examples of C−Si bond forming reactions that do not require an organometallic complex as the catalyst.

We first investigated the efficiency with which an NHC can associate with **1**, presumably at the more Lewis acidic boron site, and activate the B−Si bond. From the outset, we judged that a practical advantage of the metal-free protocol would be the procedural simplicity with which it can be performed. Thus, we decided to establish whether a relatively robust amine might be used to generate the requisite NHC instead of one of the moisture sensitive metal alkoxides employed with the Cu-catalyzed process (e.g., NaOMe or NaO*t*-Bu).[4a] Such considerations led us to determine that, as shown in Scheme 2, treatment of commercially available imidazolinium salt **2** with 1.05 equiv of 1,8-diazabicycloundec-7-ene (dbu) followed by the addition of **1** leads to complete consumption of the silylboron reagent within 5 min. Complexation was monitored by the appearance of a new signal at δ 8.02 ppm in the ^{11}B NMR spectrum, likely corresponding to **1**•NHC complex **3**; the signal for **1**, also a singlet, appears at δ 33.38 ppm.[9] Similar to the reaction of $B_2(pin)_2$,[1] such a significant shift is likely due to the associated electronic reorganization caused by the conversion of the sp^2-hybridized boron atom in **1** to one that

Scheme 1. NHC-Catalyzed Silyl Conjugate Addition to Unsaturated Carbonyls



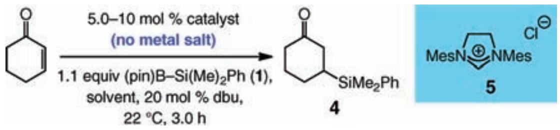
Scheme 2. Facile Formation of an NHC−B−Si Complex[a]



[a] Mes = 2,4,6-$(Me)_3C_6H_2$.

Received: April 6, 2011
Published: April 23, 2011

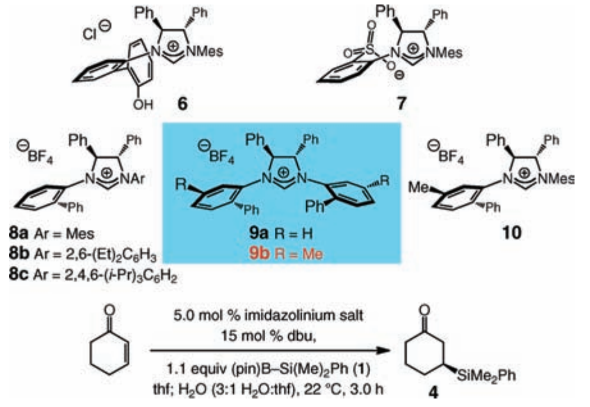
Table 1. Initial Studies on Catalytic Reaction of Cyclohexenone and Dimethylphenylsilylpinacolatoboron 1[a]



entry	heterocyclic salt or phosphine; mol %	additive; equiv	solvent	conv (%)[b]
1	**5**; 5.0	none	thf	<10
2	**5**; 5.0	MeOH; 20	thf	26
3	**5**; 5.0	none	1:1 thf:MeOH	34
4	**5**; 5.0	*none*	*1:1 thf:H_2O*	*95*
5	**5**; 5.0	*none*	*H_2O*	*>98*
6	**5**; 5.0	MeOH; 20	1:1 thf:H_2O	34
7	PPh_3; 10	none	1:1 thf:H_2O	<2
8	PCy_3; 10	none	1:1 thf:H_2O	30
9	$OPPh_3$; 10	none	1:1 thf:H_2O	<2

[a] Performed under N_2 atmosphere; with 15 mol % dbu for entries 1−6 and 20 mol % dbu for entries 7−9. [b] Conversion values determined by analysis of 400 MHz ^{1}H NMR spectra of unpurified mixtures.

Table 2. Evaluation of Various Chiral N-Heterocyclic Carbenes[a]



entry	imidazolinium salt	conv (%)[b]	er[c]
1	**6**	75	50:50
2	**7**	38	52:48
3	**8a**	>98	82:18
4	**8b**	44	84:16
5	**8c**	34	59:41
6	**9a**	87	86:14
7	**9b**	*>98*	*98:2*
8	**10**	72	83:17

[a] Performed under N_2 atmosphere. [b] Conversion values determined by analysis of 400 MHz ^{1}H NMR spectra of unpurified mixtures. [c] Enantiomeric ratio values determined by HPLC analysis (±2%); see the Supporting Information for details. Mes = 2,4,6-$Me_3C_6H_2$.

is sp^3-hybridized (**3**).[10] Treatment of **1** with dbu, under otherwise identical conditions, does not lead to a new entity.

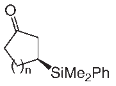
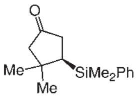
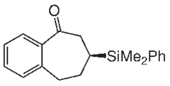
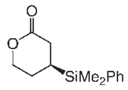
Next, we evaluated the ability of the carbene derived from imidazolinium salt **5** to promote silyl conjugate addition to cyclohexenone (Table 1); the selection of this particular NHC precursor was based on its structural similarity to the chiral variants developed in these laboratories[4a,11] (versus unsaturated imidazolium salts). As illustrated in entry 1, with 5.0 mol % **5** and 15 mol % dbu, a minimal amount of the desired β-silylcarbonyl **4** is generated (<10%). To facilitate SCA, the effect of methanol as an additive was examined; we surmised that such modification might facilitate formation of the charged intermediates likely involved in the catalytic process. The presence of the alcohol additive indeed results in a more efficient silyl conjugate addition (22−34%) without any C−B bond formation (<2%, ^{1}H NMR analysis; entries 2−3, Table 1). In light of the positive effect of MeOH, we chose to examine the influence of a more polar medium, leading us to the finding that when the catalytic SCA is performed in an equal mixture of thf and water, there is 95% conversion to the desired **4** within three hours at 22 °C (entry 4, Table 1); when pure water is used as solvent, SCA is complete (>98% conv, entry 5).[12] In the absence of **5**, under otherwise identical conditions to entry 4, there is <2% conversion to the desired **4**. As the representative data in entry 6 of Table 1 point out, the addition of MeOH to the aqueous solution does not improve efficiency (vs entry 3). Moreover, an aryl and an alkyl phosphine or a phosphine oxide, in spite of higher catalyst loadings (10 mol %), either do not promote any reaction or are far less effective catalysts (entries 7−10, Table 1).

With conditions for effective NHC-catalyzed SCA outlined, we focused on identifying an effective chiral carbene for the enantioselective version of the process. Cyclohexenone continued to serve as the model substrate; transformations were performed at 22 °C in a solution that largely consists of water (3:1 H_2O/thf)[13] and were analyzed after 3 h. Bidentate imidazolinium salts **6** and **7**, used as ligands in various metal-catalyzed enantioselective transformations,[4a,11] promote C−Si bond formation with moderate efficiency, but **4** is obtained in negligible enantiomeric purity (entries 1−2, Table 2). With **8a**, which, similar to **6** and **7**, is C_1-symmetric, but lacks the hydroxyl or the sulfonate unit (entry 3, Table 2), SCA is more efficient (>98% conv) and the desired product is formed in 82:18 er. Increasing the size of the symmetrical N−Ar moiety of the catalyst (i.e., **8b**−**c**, entries 4−5) leads to diminution in efficiency and/or enantioselectivity. When C_2-symmetric imidazolinium salt **9a** is used (entry 6), lower conversion but similarly high er values are attained (compared to **8a**, entry 3). Further catalyst screening led us to establish that incorporation of a *m*-Me unit within the N−Ar moieties furnishes an NHC catalyst that affords β-silylketone **4** efficiently (>98% conv) and in 98:2 er. The low selectivity observed with **10** underlines the significance of the C_2-symmetric structure of the optimal **9b** in this application.

A range of cyclic enones, including cyclopentenones as well as seven- and eight-membered ring α,β-unsaturated ketones, undergoes enantioselective NHC-catalyzed SCA to afford the β-silyl ketones in 50% to >98% yield and in 90:10 to >98:2 er (entries 1−6 of Table 3). There is complete consumption of the starting materials in the transformations shown in entries 1−4 (Table 3). However, catalytic additions that furnish sterically demanding cyclopentenone **14** and bicyclic cycloheptenone **15** proceed less readily (83% and 60% conv in 3 h, respectively); longer reaction times do not result in further conversion, suggesting that the NHC catalyst is perhaps undergoing competitive decomposition.[14] As the example in entry 7 of Table 3 indicates, unsaturated cyclic esters can be used to access the derived β-silyl lactones (**16** in 71% yield and 85:15 er); as was also observed in studies regarding the NHC−Cu-catalyzed version of this process, such additions are less efficient and enantioselective than with the corresponding cyclic enones (compare entries 2 and 7, Table 3).[4a]

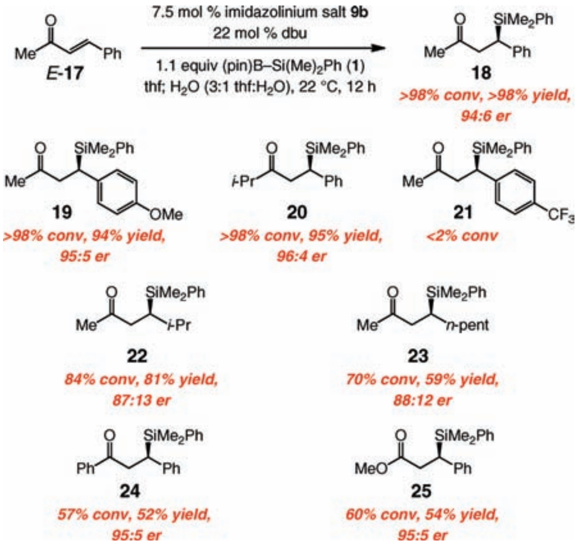
Acyclic α,β-unsaturated ketones can be used in NHC-catalyzed SCA (Scheme 3). Generally, reactions proceed less readily than the cyclic unsaturated carbonyls and require a slightly higher

Table 3. NHC-Catalyzed Enantioselective Silyl Conjugate Addition (SCA) Reaction with Cyclic α,*β*-Unsaturated Carbonyls[a]

entry	product		time (h)	conv (%);[b] yield (%)[c]	er[d]
1		n = 1 (**11**)	3.0	>98; >98	90:10
2		n = 2 (**4**)	1.0	>98; 97	98:2
3		n = 3 (**12**)	3.0	>98; 95	98:2
4		n = 4 (**13**)	1.0	>98; 74	>98:2
5	 **14**		3.0	83; 73	94.5:4.5
6	 **15**		3.0	60; 50	90:10
7	 **16**		3.0	82; 71	85:15

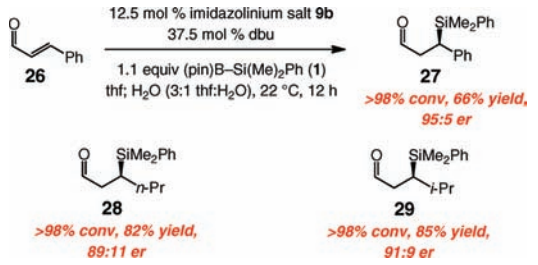
[a] Reactions performed in 3:1 H_2O/thf under the conditions shown in Table 1 and with imidazolinium salt **9b** as the catalyst precursor. [b] Conversion values determined by analysis of 400 MHz ^1H NMR spectra of unpurified mixtures. [c] Yields of isolated products after purificaton (±5%). [d] Enantiomeric ratio values determined by HPLC analysis (±2%); see the Supporting Information for details.

Scheme 3. NHC-Catalyzed Enantioselective Silyl Conjugate Addition (SCA) Reactions with Acyclic α,*β*-Unsaturated Carbonyls[a]



[a] All reactions performed under identical conditions as those shown for synthesis of **18**, except for **24** and **25** (12.5 and 10 mol % **9b**, and 37.5 and 30 mol % dbu, respectively). For determination of conversions and er values, see Table 3. Yields relate to isolated and purified products (±5%).

Scheme 4. NHC-Catalyzed Enantioselective Silyl Conjugate Addition (SCA) Reactions with α,*β*-Unsaturated Aldehydes[a]



[a] All reactions performed under identical conditions as those shown for synthesis of **27**.

catalyst loading for achieving complete conversion.[15] Formation of *β*-silyl methyl ketones bearing an aryl substituent (cf. **18**–**20**) is relatively more facile and enantioselective than those that carry an alkyl unit (cf. **22**–**23**). NHC-catalyzed SCA reactions involving chalcone (cf. **24**) and an acyclic ester (cf. **25**) are highly enantioselective but less efficient than the corresponding methyl ketones. Diminished efficiency and substantially lower enantioselectivity are observed with a corresponding *cis* isomer: when *Z*-**17** is used, **18** is generated in nearly racemic form (54:46 vs 94:6 er). Considering that cyclic *β*-silylketones are obtained in high enantiomeric purity (entries 1–4, Table 3), the aforementioned variation in selectivity is striking. Furthermore, in contrast to substrates bearing a phenyl or an electron-rich *p*-methoxyphenyl substituent (cf. **18** and **19**), there is <2% conversion to **21**, which contains the electron-deficient *p*-trifluoromethylphenyl moiety. The above trends might shed light on the inner workings of the NHC-catalyzed process and are the subject of ongoing investigations.

A particularly noteworthy type of NHC-catalyzed SCA involves α,*β*-unsaturated aldehydes;[8f] three cases are illustrated in Scheme 4. *β*-Silyl aldehydes are formed in similarly high levels of enantiomeric purity as observed with acyclic ketones. What renders the transformations in Scheme 4 intriguing is that unsaturated aldehydes have been utilized extensively in NHC-catalyzed coupling reactions, which proceed via Breslow-type intermediates,[16] generated by the addition of the carbene to the relatively uncongested carbonyl. That the SCA products, represented by **27**–**29**, can be isolated in 66–85% yields implies that the silylboron reagent competes effectively with the aldehyde site for reaction with the nucleophilic catalyst. Initial studies indicate that NHC-catalyzed silyl 1,2-additions (vs 1,4-) to aldehydes are feasible;[17] thus, the transformations shown in Scheme 4 illustrate notable chemoselectivity in favor of conjugate addition. It is also worthy of note that the NHC-catalyzed SCAs with unsaturated aldehydes require higher catalyst loadings compared to the corresponding methyl ketones (e.g., reaction of **17** vs **26**); the reason for such differences in reactivity is a topic that is being probed as part of our mechanistic explorations.

The metal-free protocol offers a complementary catalytic approach to the SCA promoted by chiral metal-based complexes, where the more costly Pd or Rh salts might be needed.[8a–e] With the chiral NHC–Cu-catalyzed system,[4a] lower catalyst loadings are sufficient (1.0–2.0 mol % vs 5.0–12.5 mol %), at times higher enantioselectivities are observed with acyclic substrates, and electron-deficient *β*-silylketone **21** (Scheme 3) can be accessed. On the other hand, the NHC-catalyzed transformations are more attractive as there is no need for the use of an air- and moisture-sensitive Cu salt (CuCl), and dbu can be employed in lieu of the more sensitive metal alkoxides. The above factors and the availability of the requisite chiral imidazolinium salt, which can be prepared by a three-step operation, together with the demonstrated utility of *β*-silyl carbonyls,[3,18] render the present strategy of value.

The enantioselectivities observed indicate that an NHC catalyst is intimately involved in the formation of the C–Si bond (cf. Scheme 1) and that the role of the heterocyclic carbene is not limited to activation of the silylboron reagent. Design and development of catalytic reactions that involve NHC-activation of other B-based reagents may thus be feasible; investigations along these lines are in progress. Moreover, study of the mechanism of the metal-free transformations, including identification of the origins of enantioselectivity, the reactivity differences among various substrate classes, and the critical role of water, is underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures and spectral, analytical data for all reaction products. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

Financial support was provided by the NIH (GM-57212) and the NSF (CHE-0715138). We are grateful to Maitane Fernandez for valuable experimental assistance and to Dr. Kang-sang Lee, Hao Wu, Dr. Adil R. Zhugralin, and Dr. Simon J. Meek for helpful discussions. Mass spectrometry facilities at Boston College are supported by the NSF (DBI-0619576).

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(8) For catalytic enantioselective silyl conjugate addition methods with metal-containing catalysts, see: (a) Hayashi, T.; Matsumoto, Y.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 5579. (b) Matsumoto, Y.; Hayashi, T.; Ito, Y. *Tetrahedron* **1994**, *50*, 335. (c) Walter, C.; Auer, G.; Oestreich, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 5675. (d) Walter, C.; Oestreich, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3818. (e) Walter, C.; Fröhlich, R.; Oestreich, M. *Tetrahedron* **2009**, *65*, 5513.(f) Ibrahem, I.; Santoro, S.; Himo, F.; Córdova, A. *Adv. Synth. Catal.* 2011, *353*, 245. The last four studies involve the use of **1** as a reagent.

(9) See the Supporting Information for details.

(10) For an in-depth analysis of the concept of Lewis base activation and its use in chemical synthesis, see: Denmark, S. E.; Beutner, G. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 1560.

(11) For example, see: (a) Van Veldhuizen, J. J.; Campbell, J. E.; Giudici, R. E.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2005**, *127*, 6877. (b) Gillingham, D. G.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 3860. (c) Brown, M. K.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2008**, *130*, 12904. (d) Lee, Y.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 3160. (e) O'Brien, J. M.; Lee, K-s.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2010**, *132*, 10630. (f) Dabrowski, J. A.; Gao, F.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2011**, *133*, 4778.

(12) Control experiments indicate that the more facile β-silylketone formation is not due to involvement of the corresponding silyl hydride that might be generated through reaction of **1** with water.

(13) Subsequent optimization studies indicated that use of 3:1 H_2O/thf, versus an equal mixture, as used in the studies summarized in Table 1, affords improved efficiency and enantioselectivity. For example, reaction in 100% water results in 96% conversion but affords **4** in 75:25 er in the presence of the NHC catalyst derived from **9b**. Solutions appear as emulsions while stirring continues but become biphasic while standing.

(14) Initial mechanistic studies indicate that indeed NHCs undergo decomposition under the reaction conditions and the resulting products promote nonselective conjugate additions albeit at a slower rate (vs NHC-catalyzed). Details of these investigations will be disclosed in the full account of this work.

(15) The reason for the higher catalyst loadings might partly be because, with slower SCA reactions, decomposition of the imidazolinium salt/NHC through reaction with water becomes more competitive. Initial mechanistic studies indicate that the derived products promote reactions with little or no enantioselectivity. Details will be disclosed in the full account of this work. For detailed studies on hydrolysis of imidazolium salts, see: Hollóczki, O.; Terleczky, P.; Szieberth, D.; Mourgas, G.; Gudat, D.; Nyulászi, L. *J. Am. Chem. Soc.* **2011**, *133*, 780.

(16) (a) Breslow, R. *J. Am. Chem. Soc.* **1958**, *80*, 3719. (b) Stetter, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 639. For recent applications of catalysts that likely proceed through Breslow-type intermediates, see: (c) Jiang, H.; Gschwend, B.; Albrecht, L.; Jørgensen, K. A. *Org. Lett.* **2010**, *12*, 5052 and references cited therein.

(17) For example, treatment of benzaldehyde with 5.0 mol % **5** and 15 mol % dbu and 1.1 equiv of **1** (3:1 H_2O/thf, 22 °C, 12 h) leads to the formation of the corresponding silylcarbinol (73% conv by ^{1}H NMR analysis).

(18) Enantiomerically enriched β-silylcarbonyls have been prepared by methods other than silyl conjugate additions. Through catalytic enantioselective conjugate hydride additions to trisubstituted Si-substituted enones: (a) Lipshutz, B. H.; Tanaka, N.; Taft, B. R.; Lee, C.-T. *Org. Lett.* **2006**, *8*, 1963. Through catalytic conjugate additions of alkyl, aryl, or vinyl groups, respectively, to silyl-substituted enones: (b) Shintani, R.; Okamoto, K.; Hayashi, T. *Org. Lett.* **2005**, *7*, 4757. (c) Balskus, E. P.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2006**, *128*, 6810. (d) Kacprzynski, M. A.; Kazane, S. A.; May, T. L.; Hoveyda, A. H. *Org. Lett.* **2007**, *9*, 3187. (e) Shintani, R.; Ichikawa, Y.; Hayashi, T.; Chen, J.; Nakao, Y.; Hiyama, T. *Org. Lett.* **2007**, *9*, 4643.