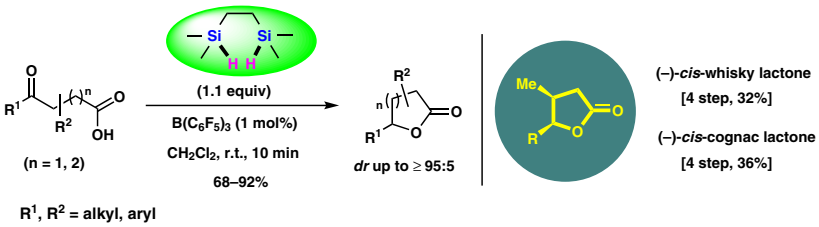
Synlett H. Xie et al. Cluster

$(HMe_2SiCH_2)_2$: A Useful Reagent for $B(C_6F_5)_3$-Catalyzed Reduction–Lactonization of Keto Acids: Concise Syntheses of (–)-*cis*-Whisky and (–)-*cis*-Cognac Lactones

Hengmu Xie[a]
Ji Lu[a]
Yingying Gui[a]
Lu Gao[a]
Zhenlei Song*[a,b]

[a] Key Laboratory of Drug-Targeting and Drug Delivery System of the Education Ministry, West China School of Pharmacy, Sichuan University, Chengdu, 610041,, P. R. of China
zhenleisong@scu.edu.cn
[b] State Key Laboratory of Elemento-organic Chemistry, Nankai University, Tianjin, 300071, P. R. of China

Published as part of the Cluster *Silicon in Synthesis and Catalysis*



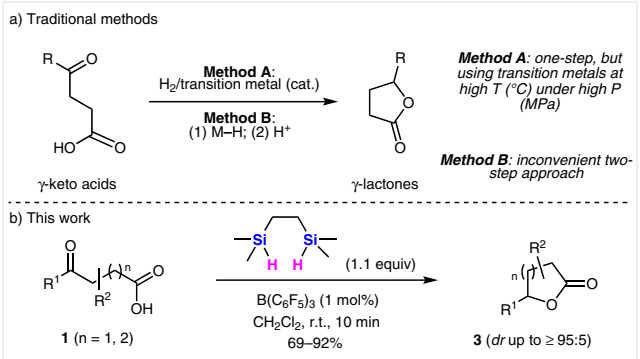
Received: 23.04.2017
Accepted after revision: 10.06.2017
Published online: 19.07.2017
DOI: 10.1055/s-0036-1588488; Art ID: st-2017-b0284-c

Abstract $(HMe_2SiCH_2)_2$ has been utilized as a useful reagent for $B(C_6F_5)_3$-catalyzed reduction–lactonization of keto acids to synthesize γ- and δ-lactones. The process led concisely to (–)-*cis*-whisky and (–)-*cis*-cognac lactones in respective overall yields of 32% and 36%.

Key words lactonization, reduction, silanes, $B(C_6F_5)_3$, keto acids

The γ-lactone and its variants are important core structures that occur often in a broad range of natural products and biologically active compounds.[1] Therefore, it is highly demanded to develop efficient methods for constructing γ-lactones.[2] The simple substrates γ-keto acids are easily accessible and so are one of the most practical starting points to generate γ-lactones, usually via a sequential hydrogenation–lactonization process (Scheme 1, a, method A).[3] The synthesis occurs in one step, but it requires a homo- or heterogeneous transition-metal catalyst as well as high temperature, high pressure and reaction time of several hours. An alternative approach is to first reduce the ketone using various hydride reagents, followed by an acid-promoted lactonization (Scheme 1, a, method B), but this two-step process is inconvenient.[4] Therefore, one of the major challenges in this field is to develop a one-step synthesis of γ-lactones from γ-keto acids under mild reaction conditions.

The Lewis acid tris(pentafluorophenyl)borane $[B(C_6F_5)_3]$[5] has recently emerged as an attractive catalyst because of its ability to activate H–H and Si–H bonds through η^1coordination.[6] This unique activation mechanism allows several transformations involving hydrosilane, such as C=X bond reduction (X = O, N, S, and C) [5n,7] and C–O

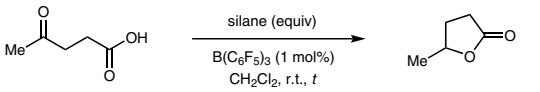


Scheme 1 (a) Traditional methods to synthesize γ-lactones from γ-keto acids; (b) $(HMe_2SiCH_2)_2$ as a useful reagent for $B(C_6F_5)_3$-catalyzed one-step reduction–lactonization of keto acids

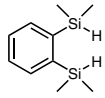
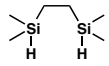
bond cleavage.[8] The $B(C_6F_5)_3$-catalyzed reaction has substantially expanded possibilities for transition-metal-free catalysis,[9] making it compatible with both sustainable chemistry and pharmaceutical synthesis. Moreover, the approach using hydrosilanes is a safer and easier-to-handle process compared with traditional methods using H_2 or M–H reagents. Hydrosilanes exploited in this approach have so far been limited to those with only one silicon center (R_nSiH_{4-n}). Little attention has been paid to bis(silyl) species such as $(HMe_2SiCH_2)_2$[10] or its analogues. As part of our continuing interest in bis(silyl) chemistry,[11] we are intrigued by the bifunctionality of $(HMe_2SiCH_2)_2$ and its potential in the discovery of unique transformations. Herein, we report a $B(C_6F_5)_3$-catalyzed reduction–lactonization process of keto acids **1** using $(HMe_2SiCH_2)_2$ (Scheme 1, b, 2) . The approach leads to an one-step synthesis of diverse γ- and δ-lactones **3**

in good yield at room temperature.[12] It also allowed us to synthesize (–)-*cis*-whisky and (–)-*cis*-cognac lactones in four steps.

Table 1 Screening of Reduction–Lactonization Conditions[a]



levulinic acid (**LA**) γ-valerolactone (**GVL**)

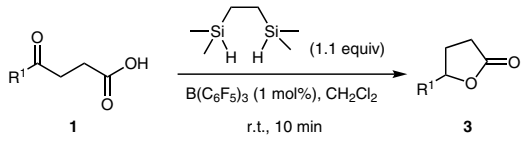
Entry	Silane (equiv)	Time (min)	GVL (conv., %)[c]
1	Ph_3SiH (2.1)	60	N.R.
2[b]	Et_3SiH (2.1)	60	34 (78)
3[b]	Ph_2SiH_2 (1.1)	60	44 (68)
4[b]	Et_2SiH_2 (1.1)	60	34 (88)
5	$PhSiH_3$ (0.7)	300	N.R.
6	$HMe_2SiSiMe_2H$ (1.1)	300	N.R.
7	$HMe_2SiOSiMe_2H$ (1.1)	20	67 (100)
8	 (1.1)	300	N.R.
9[d]	 (1.1)	10	86 (100)

[a] Reaction conditions: 0.34 mmol of LA, $B(C_6F_5)_3$ (1 mol%), and hydrosilane in dry CH_2Cl_2 at r.t.
[b] 15–20% of the hydroxyl product was obtained in these cases, indicating that the reaction stopped at the reduction step without further lactonization.
[c] Isolated yields after purification by silica gel column chromatography.
[d] 2,2,5,5-Tetramethyl-1-oxa-2,5-disilacyclopentane was isolated in 56% yields as byproduct.

Our model scaffold was levulinic acid (LA), an important platform molecule among lignocellulosic biomass-based chemicals.[13] Reduction–lactonization of LA would generate γ-valerolactone (GVL), which has been proposed as feedstock for producing alkenes and transportation fuels.[14] The reaction was initially examined using monohydrosilane and 1 mol % of $B(C_6F_5)_3$ as catalyst in CH_2Cl_2 at room temperature. Et_3SiH proved more efficient than Ph_3SiH in the reduction–lactonization, yet GVL was still obtained in only 34% yield after one hour (Table 1, entries 1 and 2). In addition, a substantial amount of hydroxyl product formed from the reduction (17% yield), without undergoing subsequent lactonization. Since the ketone moiety in the reduction is activated by silicon rather than boron,[6] we reasoned that the reaction with a monohydrosilane could only proceed via an intermolecular silicon–ketone coordination. This mechanistic consideration led us to envision that switching to intramolecular silicon–ketone coordination might improve the reduction, and that the switch could occur if the initially formed silyl ester served as a linkage. To this end, we tested a range of dihydro- and trihydrosilanes containing one silicon center (Table 1, entries 3–5). Unfortunately, these reactions led to yields that were comparable or even lower than those obtained using Et_3SiH. While no reaction occurred using disilane $HMe_2SiSiMe_2H$ (Table 1, entry 6), $HMe_2SiOSiMe_2H$ was partially effective to generate GVL in 67% yield (Table 1, entry 7). Next we tested disilanes, respectively, containing a phenyl ring (Table 1, entry 8) and a $–CH_2CH_2–$ group (Table 1, entry 9) as linkage. To our delight, the conformationally more flexible $(HMe_2SiCH_2)_2$ led to complete consumption of LA within ten minutes and generated GVL in 86% yield.

With the optimal reaction conditions in hand, the scope of our approach was explored. The reaction tolerated γ-keto acid **1a** with a branched *i*-Pr group and **1b** with a cyclohexyl ring (Table 2, entries 1 and 2). However, substitution with the sterically more hindered *t*-Bu group completely inhibited reduction of ketone and the subsequent formation of **3c** (Table 2, entry 3). Lewis basic functionalities, such as Br and PhO groups, were tolerated. No debromination or deoxygenation occurred during formation of the desired γ-lactones **3d** and **3e** (Table 2 entries 4 and 5). The reaction of 1,4-diketo acid **1f** generated **3f** in 83% yield as an 8:1 mixture of two diastereomers, and competitive eight-membered lactonization was not observed (Table 2, entry 6). The approach was also suitable for keto acids **1g–i** containing a phenyl group or an electron-deficient or electron-rich phenyl ring (Table 2, entries 7–9). It is noteworthy that Lewis basic MeO group, which generally undergoes facile Me–O bond cleavage,[7j] did not interfere with the reaction, giving **3i** in 68% yield (Table 2, entry 9). For α,β-unsaturated keto acids, 1,2-reduction proceeded regioselectively to afford **3j** and **3k** in good yields (Table 2, entries 10 and 11). In addition, reaction of γ-keto acid **1l**, in which the ketone and carboxyl groups are tethered to a phenyl ring, gave bicyclic lactone **3l** in 75% yield (Table 2, entry 12).

Table 2 Scope of γ-Keto Acids with Terminal Substituents[a]



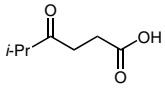
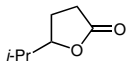
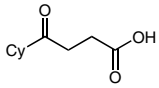
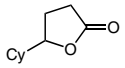
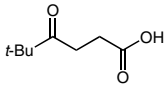
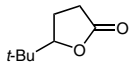
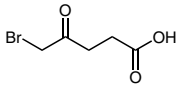
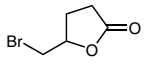
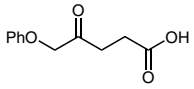
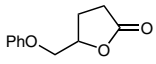
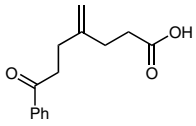
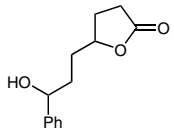
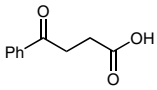
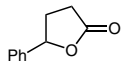
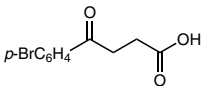
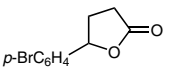
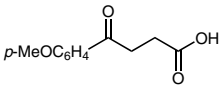
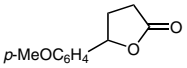
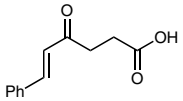
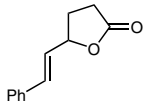
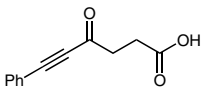
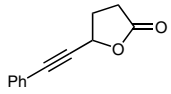
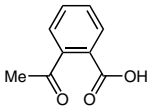
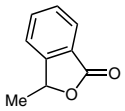
Entry	γ-Keto acid		γ-Lactone		Yield (%)[b]
1		**1a**		**3a**	82
2		**1b**		**3b**	90
3		**1c**		**3c**	–[f]
4		**1d**		**3d**	80
5		**1e**		**3e**[c]	80
6		**1f**		**3f**[d]	83
7		**1g**		**3g**	92
8		**1h**		**3h**	71
9		**1i**		**3i**[e]	68
10		**1j**		**3j**	70

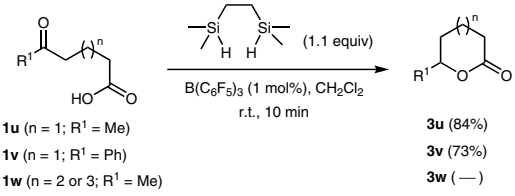
Table 2 (continued)

Entry	γ-Keto acid		γ-Lactone		Yield (%)[b]
11		**1k**		**3k**	75
12		**1l**		**3l**	75

[a] Reaction conditions: 0.34 mmol of keto acid, 0.38 mmol of $(HMe_2SiCH_2)_2$, and $B(C_6F_5)_3$ (1 mol%) in 4 mL of dry CH_2Cl_2 at r.t. for 10 min.
[b] Isolated yields after purification by silica gel column chromatography.
[c] 0.58 mmol of $(HMe_2SiCH_2)_2$.
[d] 0.61 mmol of $(HMe_2SiCH_2)_2$. **3f** was an 8:1 mixture of two diastereomers.
[e] 0.34 mmol of $(HMe_2SiCH_2)_2$ and $B(C_6F_5)_3$ (3 mol%).
[f] The initially formed γ-keto silyl ester of **1c** is easy to hydrolyze. Thus, **1c** was recovered nearly completely based on the crude ^1H NMR analysis.

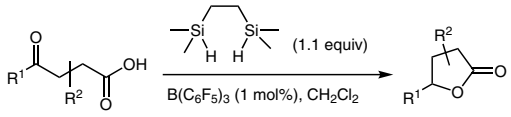
Next we tested γ-keto acids substituted with a range of internal R^2 groups. Substitution such as Me, Ph, allyl, or propargyl group at the α-position of the ketone led to complete 1,2-*cis* diastereoselectivity in the formation of **3m–p** (Table 3, entries 1–4). Moreover, the reaction of **1q** and **1r** efficiently generated *cis*-fused 5,5- and 5,6-bicyclic lactones **3q** and **3r** (Table 3, entries 5 and 6). In a similar manner, substitution of R^2 group at the β-position of ketone resulted in 1,3-*cis* selectivity, although *cis*/*trans* ratios were moderate (Table 3, entries 7 and 8). This lower diastereoselectivity of the reduction probably reflects that 1,3-induction is generally less effective than 1,2-induction.

We attempted to use our approach to synthesize lactones with larger rings (Scheme 2). The δ-lactones **3u** and **3v** formed readily in good yields within ten minutes, but the reaction of **1w** led only to slow ketone reduction, with no subsequent lactonization to **3w** observed. The failure to form **3w** probably reflects the greater strain in seven- or eight-membered rings, which are therefore more difficult to construct than five- and six-membered rings.



Scheme 2 Synthesis of δ-lactones **3u** and **3v**

Table 3 Scope of γ-Keto Acids with Internal Substituents[a]



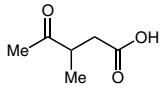
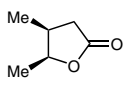
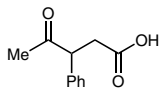
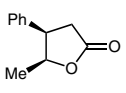
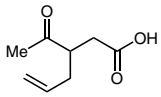
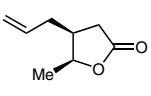
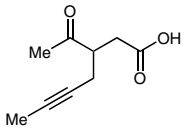
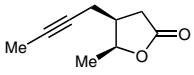
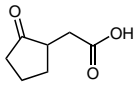
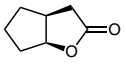
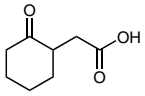
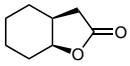
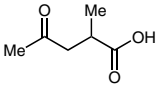
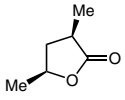
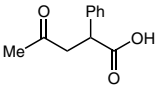
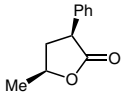
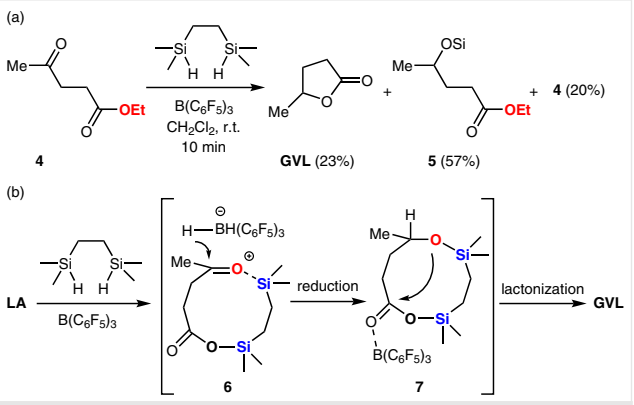
Entry	γ-Keto acid		γ-Lactone[b]		Yield (%)[c]	dr[d]
1		**1m**		**3m**	83	≥95:5
2		**1n**		**3n**	68	≥95:5
3		**1o**		**3o**	77	≥95:5

Table 3 (continued)

Entry	γ-Keto acid		γ-Lactone[b]		Yield (%)[c]	dr[d]
4		**1p**		**3p**	79	≥95:5
5		**1q**		**3q**	81	≥95:5
6		**1r**		**3r**	80	≥95:5
7		**1s**		**3s**	78	75:25
8		**1t**		**3t**	75	80:20

[a] Reaction conditions: 0.34 mmol of keto acid, 0.38 mmol of $(HMe_2SiCH_2)_2$, and $B(C_6F_5)_3$ (1 mol%) in 4 mL of dry CH_2Cl_2 at r.t. for 10 min.
[b] The compounds **3m**,[15d] **3n**,[15b] **3q**,[15b] **3r**,[15c] and **3s**[15a] with *cis* stereochemistry are known, and the spectroscopic data of our samples were in accordance with the data reported in ref. 15a–d.
[c] Isolated yields after purification by silica gel column chromatography.
[d] The ratios were determined based on crude ^1H NMR analysis of the products.

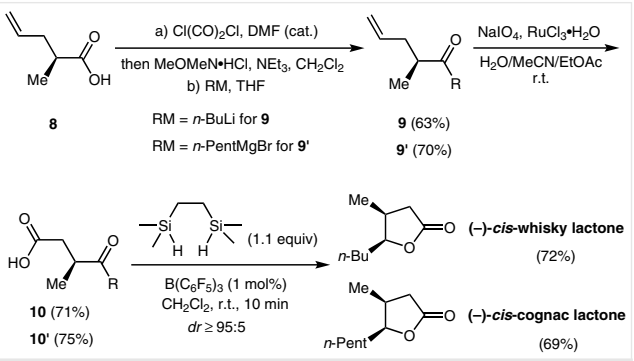


Scheme 3 (a) Reaction of keto ester **4** with $(HMe_2SiCH_2)_2$, the ratios were determined by the ^1H NMR spectroscopy of the crude products; (b) proposed intramolecular silicon activation in the reaction of LA with $(HMe_2SiCH_2)_2$.

To gain a deeper insight into the mechanism of the approach, we performed a control experiment using **4**, in which the carboxyl group was masked as an ethyl ester (Scheme 3, a). In sharp contrast to that of LA, reaction of **4** afforded 23% of GVL together with 57% of the reduced product **5** and 20% of unreacted **4**. These contrasting results suggest that in the reaction of LA with $(HMe_2SiCH_2)_2$, while the intermolecular silicon–ketone coordination is still involved, the initially formed silyl ester **6** might serve as a linkage, allowing an intramolecular silicon–ketone coordination to promote the reduction step (Scheme 3, b). It is also possible that this intramolecular silicon–ketone coordination benefits subsequent lactonization, since in the predicted cyclic intermediate **7**, the carboxyl and hydroxyl groups, tethered to a bis(silyl) moiety, lie close to each other. Lactonization by transannular nucleophilic attack should therefore proceed smoothly to give GVL.

This methodology allowed us to achieve a concise synthesis of (–)-*cis*-whisky lactone and (–)-*cis*-cognac lactone from the known acid **8**[16] (Scheme 4). Although many syntheses of *trans* isomers have been achieved,[17] far fewer reports of enantioselective syntheses of *cis* isomers have been published.[18] Transformation of **8** into the corresponding Weinreb amide[19] followed by addition with *n*-BuLi or *n*-PentMgBr led, respectively, to **9** in 63% yield or **9′** in 70% yield. Direct cleavage of the terminal alkene using $NaIO_4/RuCl_3{\cdot}3H_2O$[20] generated the key precursor acids **10** and **10′** in respective yields of 71% and 75%. Finally, reduction–lactonization mediated by $B(C_6F_5)_3/(HMe_2SiCH_2)_2$ generated (–)-*cis*-whisky lactone in 72% yield, and (–)-*cis*-cognac lactone in 69% yield with complete *cis* stereocontrol.

Spectroscopic data of our synthetic samples were in full accordance with those reported[18] for the naturally occurring compounds.



Scheme 4 Total syntheses of (–)-*cis*-whisky and (–)-*cis*-cognac lactones

In summary, $(HMe_2SiCH_2)_2$ has been explored as a useful reagent for $B(C_6F_5)_3$-catalyzed reduction–lactonization of keto acids to synthesize γ- and δ-lactones. $(HMe_2SiCH_2)_2$-assisted intramolecular silicone–ketone coordination of ketone was proposed to facilitate both the reduction and lactonization steps. This one-step approach also led to a concise synthesis of (–)-*cis*-whisky and (–)-*cis*-cognac lactones in respective overall yields of 32% and 36%. More detailed studies and applications of this approach are currently under way.

Funding Information

We are grateful for financial support from the National Natural Science Foundation of China (21290180, 21622202, 21502125).

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1588488.

References and Notes

(1) For selected reviews, see: (a) Alonso, D. M.; Wettstein, S. G.; Dumesic, J. A. *Green Chem.* **2013**, *15*, 584. (b) Lorente, A.; Merketegi, J. L.; Albericio, F.; Álvarez, M. *Chem. Rev.* **2013**, *113*, 4567.

(2) For selected reviews, see: (a) Kitson, R. R. A.; Millemaggi, A.; Taylor, R. J. K. *Angew. Chem. Int. Ed.* **2009**, *48*, 9426. (b) Salvador, G.; Margarita, P.; Pablo, R.; Jose, S. *Mini-Rev. Org. Chem.* **2009**, *6*, 345.

(3) (a) Fábos, V.; Mika, L. T.; Horváth, I. T. *Organometallics* **2014**, *33*, 181. (b) Shimizu, K.-I.; Kanno, S.; Kon, K. *Green Chem.* **2014**, *16*, 3899. (c) Yang, Z.; Huang, Y.-B.; Guo, Q.-X.; Fu, Y. *Chem. Commun.* **2013**, *49*, 5328.

(4) (a) Ramachandran, P. V.; Pitre, S.; Brown, H. C. *J. Org. Chem.* **2002**, *67*, 5315. (b) Frenette, R.; Kakushima, M.; Zamboni, R.; Young, R. N.; Verhoeven, T. R. *J. Org. Chem.* **1987**, *52*, 304.

(5) For selected reviews, see: (a) Nikolaos, D.; Erhan, O.; Bill, M. *Synlett* **2016**, *27*, 1760. (b) Oestreich, M.; Hermeke, J.; Mohr, J. *Chem. Soc. Rev.* **2015**, *44*, 2202. (c) Robert, T.; Oestreich, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 5216. (d) Hatano, M.; Ishihara, K. *Chem. Commun.* **2012**, *48*, 4273. (e) Erker, G. *Chem. Commun.* **2003**, *13*, 1469. (f) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391. (g) Ishihara, K.; Yamamoto, H. *Eur. J. Org. Chem.* **1999**, 527. (h) Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, *26*, 345. For selected seminal works on $B(C_6F_5)_3$, see: (i) Massey, A. G.; Park, A. J.; Stone, F. G. A. *Proc. Chem. Soc.* **1963**, 212. (j) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623. (k) Ishihara, K.; Hananki, N.; Yamamoto, H. *Synlett* **1993**, 577. (l) Ishihara, K.; Hananki, N.; Yamamoto, H. *Synlett* **1995**, 721. (m) Temme, B.; Erker, G.; Karl, J.; Luftmann, H.; Fröhlich, R.; Kotila, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1755. (n) Parks, D. J.; Piers, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 9440. (o) Welch, G. C.; Juan, R. R. S.; Masuda, J. D.; Stephan, D. W. *Science* **2006**, *314*, 1124. (p) Spies, P.; Erker, G.; Kehr, G.; Bergander, K.; Fröhlich, R.; Grimme, S.; Stephan, D. W. *Chem. Commun.* **2007**, 5072.

(6) (a) Houghton, A. Y.; Hurmalainen, J.; Mansikkamäki, A.; Piers, W. E.; Tuononen, H. M. *Nat. Chem.* **2014**, *6*, 983. (b) Hermeke, J.; Mewald, M.; Oestreich, M. *J. Am. Chem. Soc.* **2013**, *135*, 17537. (c) Sakata, K.; Fujimoto, H. *J. Org. Chem.* **2013**, *78*, 12505. (d) Piers, W. E.; Marwitz, A. J. V.; Mercier, L. G. *Inorg. Chem.* **2011**, *50*, 12252. (e) Rendler, S.; Oestreich, M. *Angew. Chem. Int. Ed.* **2008**, *47*, 5997. (f) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090.

(7) (a) Kim, Y. C.; Chang, S. *Angew. Chem. Int. Ed.* **2016**, *55*, 218. (b) Ma, Y. H.; Wang, B. L.; Zhang, L.; Hou, Z. M. *J. Am. Chem. Soc.* **2016**, *138*, 3663. (c) Wübbolt, S.; Oestreich, M. *Angew. Chem. Int. Ed.* **2015**, *54*, 15876. (d) Kim, D. W.; Joung, S.; Kim, J. G.; Chang, S. *Angew. Chem. Int. Ed.* **2015**, *54*, 14805. (e) Chatterjee, I.; Oestreich, M. *Angew. Chem. Int. Ed.* **2015**, *54*, 1965. (f) Gandhamsetty, N.; Park, S.; Chang, S. *J. Am. Chem. Soc.* **2015**, *137*, 15176. (g) Zhang, Z.; Du, H. *Angew. Chem. Int. Ed.* **2015**, *54*, 623. (h) Gandhamsetty, N.; Joung, S.; Park, S.-W.; Park, S.; Chang, S. *J. Am. Chem. Soc.* **2014**, *136*, 16780. (i) Liu, Y.; Du, H. *J. Am. Chem. Soc.* **2013**, *135*, 6810. (j) Bézier, D.; Park, S.; Brookhart, M. *Org. Lett.* **2013**, *15*, 496. (k) Mewald, M.; Oestreich, M. *Chem. Eur. J.* **2012**, *18*, 14079. (l) Geier, S. J.; Chase, P. A.; Stephan, D. W. *Chem. Commun.* **2010**, *46*, 4884. (m) Shchepin, R.; Xu, C.; Dussault, P. *Org. Lett.* **2010**, *12*, 4772. (n) Harrison, D. J.; McDonald, R.; Rosenberg, L. *Organometallics* **2005**, *24*, 1398. (o) Chandrasekhar, S.; Reddy, C. R.; Babu, B. N. *J. Org. Chem.* **2002**, *67*, 9080. (p) Rubin, M.; Schwier, T.; Gevorgyan, V. *J. Org. Chem.* **2002**, *67*, 1936. (q) Blackwell, J. M.; Morrison, D. J.; Piers, W. E. *Tetrahedron* **2002**, *58*, 8247. (r) Blackwell, J. M.; Sonmor, E. R.; Scoccitti, T.; Piers, W. E. *Org. Lett.* **2000**, *2*, 3921.

(8) (a) Hazra, C. K.; Gandhamsetty, N.; Park, S.; Chang, S. *Nat. Commun.* **2016**, *7*, 13431. (b) Bender, T. A.; Dabrowski, J. A.; Zhong, H. Y.; Gagne, M. R. *Org. Lett.* **2016**, *18*, 4120. (c) Adduci, L. L.; Bender, T. A.; Dabrowski, J. A.; Gagné, M. R. *Nat. Chem.* **2015**, *7*, 576. (d) Drosos, N.; Morandi, B. *Angew. Chem. Int. Ed.* **2015**, *54*, 8814. (e) Mack, D. J.; Guo, B.; Njardarson, J. T. *Chem. Commun.* **2012**, *48*, 7844. (f) Chojnowski, J.; Rubinsztajn, S.; Cella, J. A.; Fortuniak, W.; Cypryk, M.; Kurjata, J.; Kaźmierski, K.

Organometallics **2005**, *24*, 6077. (g) Gevorgyan, V.; Liu, J.-X.; Rubin, M.; Benson, S.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 8919.
(9) Sun, C.-L.; Shi, Z.-J. *Chem. Rev.* **2014**, *114*, 9219.
(10) (a) Hreczycho, G. *Eur. J. Inorg. Chem.* **2015**, 67. (b) Hanada, S.; Motoyama, Y.; Nagashima, H. *Eur. J. Org. Chem.* **2008**, 4097.
(11) Liu, Z. J.; Lin, X. L.; Yang, N.; Su, Z. S.; Hu, C. W.; Xiao, P. H.; He, Y. Y.; Song, Z. L. *J. Am. Chem. Soc.* **2016**, *138*, 1877; and references cited therein.
(12) For related works, see: (a) Sakai, N.; Horikawa, S.; Ogiwara, Y. *RSC Adv.* **2016**, *6*, 81763. (b) Bercot, E. A.; Kindrachuk, D. E.; Rovis, T. *Org. Lett.* **2005**, *7*, 107. (c) Mukaiyama, T.; Izumi, J.; Shiina, I. *Chem. Lett.* **1997**, 187.
(13) Corma, A.; Iborra, S.; Velty, A. *Chem. Rev.* **2007**, *107*, 2411.
(14) Horváth, I. T.; Mehdi, H.; Fábos, V.; Boda, L.; Mika, L. T. *Green Chem.* **2008**, *10*, 238.
(15) (a) Korpaka, M.; Pietruszkaa, J. *Adv. Synth. Catal.* **2011**, *353*, 1420. (b) Adrio, L. A.; Quek, L. S.; Taylor, J. G.; Hii, K. K. (M.). *Tetrahedron* **2009**, *65*, 10334. (c) Müller, P.; Lacrampe, F.; Bernardinelli, G. *Tetrahedron: Asymmetry* **2003**, *14*, 1503. (d) Fang, J.-M.; Hong, B.-C.; Liao, L.-F. *J. Org. Chem.* **1987**, *52*, 855.
(16) Chatterjee, B.; Mondal, D.; Bera, S. *Tetrahedron: Asymmetry* **2012**, *23*, 1170.
(17) Koschker, P.; Kähny, M.; Breit, B. *J. Am. Chem. Soc.* **2015**, *137*, 3131; and references cited therein.
(18) (a) Pisani, L.; Superchi, S.; D'Elia, A.; Scafato, P.; Rosini, C. *Tetrahedron* **2012**, *68*, 5779. (b) Ghosh, M.; Bose, S.; Ghosh, S. *Tetrahedron Lett.* **2008**, *49*, 5424. (c) Zhang, Y.; Wang, Y.-Q.; Dai, W.-M. *J. Org. Chem.* **2006**, *71*, 2445. (d) Ozeki, M.; Hashimoto, D.; Nishide, K.; Kajimoto, T.; Node, M. *Tetrahedron: Asymmetry* **2005**, *16*, 1663.
(19) Nahm, S.; Weinreb, S. M. *Tetrahedron Lett.* **1981**, *22*, 3815.
(20) Craig, R. A. II; Loskot, S. A.; Mohr, J. T.; Behenna, D. C.; Harned, A. M.; Stoltz, B. M. *Org. Lett.* **2015**, *17*, 5160.