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COMMUNICATION

Chiral Crotyl Geminal Bis(silane): A Useful Reagent for Asymmetric Sakurai Allylation by Selective Desilylation-Enabled Chirality Transfer†

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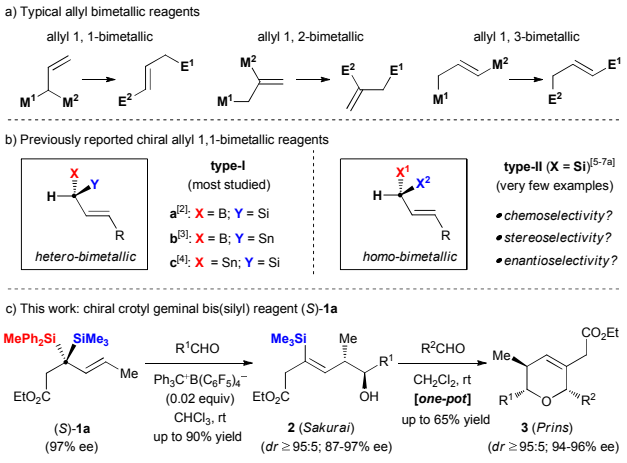
Zhiwen Chu,[a] Kai Wang,[a] Lu Gao,[a] and Zhenlei Song*[a, b]

Enantioselective synthesis of $SiMe_3$/$SiPh_2Me$-substituted crotyl geminal bis(silane) has been developed. This compound is a useful reagent for $Ph_3C^+B(C_6F_5)_4^-$-catalyzed asymmetric Sakurai allylation and one-pot Sakurai allylation/Prins cyclization process. Chemoselective desilylation of $SiPh_2Me$ leads to the efficient chirality transfer.

Allylboranes, silanes and stannanes are very important allyl metallic reagents in both academia and industry.[1] Allylation of aldehydes using these reagents has emerged as one of the most powerful methods for controlling the stereochemistry in acyclic structures. Compared with allyl mono-metallic reagents, bimetallic species appear to be more powerful for rapid increasing the structural complexity. These reagents typically play as a linchpin to assemble two electrophiles by sequential functionalization of C–M^1 and C–M^2 bonds. Based on the position of M^1 and M^2 on the allyl moiety, allyl bimetallic reagents can be divided into 1, 1-, 1, 2- and 1, 3-types (Scheme 1a). Among them, 1, 1-type is structurally distinct from other two, as two metals share with the same allylic double bond. When two metal moieties are different, the carbon they attached would be a chiral center. The efficiency of chirality transfer would largely depend on the chemoselectivity during the C–M bond cleavage. To this end, most studies have been mainly focused on hetero-bimetallic compounds containing two different metal centers (Scheme 1b, left). The representative combinations include B/Si,[2] B/Sn[3] and Sn/Si,[4] in which one of the C–M bonds (e.g. C–B bond) is weaker than another (e.g. C–Si bond). Thus, chemoselective eliminating the weaker C–M bond could be achieved, leading to effective enantioselective control in allylation.

Another type of chiral allyl 1, 1-bimetallic reagents is homo-bimetallic species (Scheme 1b, right). These reagents contain two identical metal centers such as silicon, but with different substituents on them. Imaginably, the chirality transfer would become more challenging than that using hetero-bimetallic reagent, because chemoselective cleaving one of the C–Si bonds is difficult by differentiation of the substituents on silicon. This is probably one of the reasons that little is known about the selectivity issues (i. e. *chemo-, stereo- and enantioselectivity*) in the allylation using allyl geminal bis(silanes), except for Wetter's (optically active, $SiMe_3$/$SiMe_2F$),[5] Lautens' (racemic, $SiMe_3$/$SiMe_2t$-Bu)[6] and our works (racemic, $SiMe_3$/$SiMe_2Ph$).[7a] Their potential values are still unexplored in organic synthesis.

Herein, we report enantioselective synthesis of crotyl geminal bis(silane) (*S*)-**1a** featuring a $SiMe_3$/$SiPh_2Me$-substituted quaternary carbon center. This compound proves to be a useful allylsilane reagent for $Ph_3C^+B(C_6F_5)_4^-$-catalyzed[8] Sakurai allylation[9] to give **2**, or one-pot Sakurai allylation/Prins cyclization process to give pyran **3** with excellent stereo- and enantioselectivity.



Scheme 1. a) Typical allyl bimetallic reagents; b) previously reported chiral allyl 1, 1-bimetallic reagents; c) chiral crotyl geminal bis(silyl) reagent (*S*)-**1a**.

The racemic **1a** was initially synthesized by the protocol shown in Scheme 2. Reduction of propargyl alcohol **4** with Red-Al followed by trapping with iodine[10] and silylation of the hydroxyl group afforded vinyl iodide **5** in 85% overall yield. *t*-BuLi-promoted lithium-iodide exchange provided the corresponding vinyl anion, which underwent

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† Electronic supplementary information (ESI) available: Experimental procedures, characterisation data for new compounds. See DOI: 10.1039/x0xx00000x

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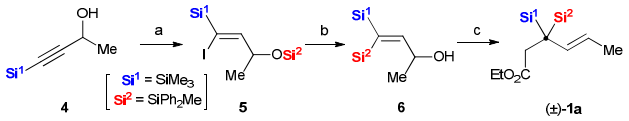
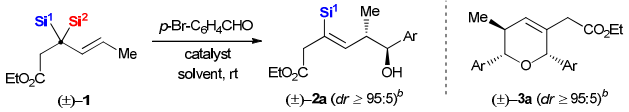


Scheme 2. Reaction conditions of synthesizing racemic (±)-**1a**: a. i) Red-Al, Et_2O, then I_2; ii) $Ph_2MeSiCl$, DMAP, Et_3N, CH_2Cl_2, 0 °C to rt, 85% (2 steps). b. *t*-BuLi, THF, 95%. c) $CH_3C(OEt)_3$, $CH_3CH_2CO_2H$, toluene, 140 °C, 15 h, 95%.

retro-[1, 4]-Brook rearrangement to deliver allylic alcohol **6** in 95% yield.[11] The subsequent Johson-Claisen rearrangement of **6** with $CH_3C(OEt)_3$ gave rise to **1a** cleanly in 95% yield.[12] This procedure was also applied successfully to synthesizing analogous crotyl silanes **1b**-**1e**, which were used for screening the Sakurai allylation conditions (Table 1).

Sakurai allylation of (±)-**1a** with *p*-Br-C_6H_4CHO was first examined in CH_2Cl_2 using stoichiometric amount of Lewis acids such as TMSOTf and $SnCl_4$, or Brønsted acids such as HBF_4. Unfortunately, no desired allylation occurred even at room temperature (Table 1, entry 1). However, we were delighted to find that 0.02 equiv of $Ph_3C^+B(C_6F_5)_4^-$ appeared to be an effective catalyst. Interestingly, chemoselective desilylation of $SiPh_2Me$ rather than the generally more reactive $SiMe_3$ was observed to give *Z*-*anti*-homoallylic alcohol (±)-**2a** in 36% yield as a single isomer. The major by-product was pyran (±)-**3a**, which was generated by sequential Prins cyclization of (±)-**2a** with the second aldehyde (entry 2). This side pathway could be inhibited by decreasing the loading of aldehyde from 1.2 to 1.0 equiv, and switching the solvent from CH_2Cl_2 to $CHCl_3$. The yield of (±)-**2a** was improved to 75% (entry 3). In contrast to $Ph_3C^+B(C_6F_5)_4^-$, trityl cation catalyst $Ph_3C^+PF_6^-$ or $Ph_3C^+SbCl_6^-$ was either ineffective or partially effective to form (±)-**2a** (entries 4 and 5). The combination mode of silyl groups also has great impact on the allylation efficiency. As shown in entry 6, a lower yield of 46% was obtained in the reaction of silane **1b** featuring a $SiMe_3$/$SiMe_2Ph$ combination. In addition, no reaction

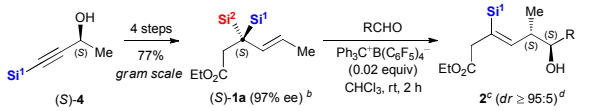
Table 1 Screening of Sakurai Allylation Conditions and Silyl Combinations. [a]

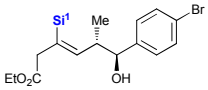
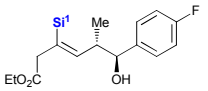
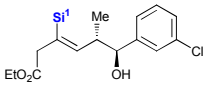
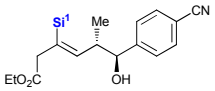
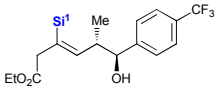
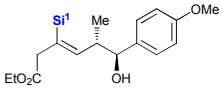
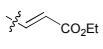
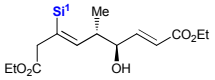
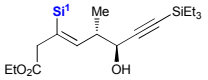
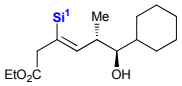
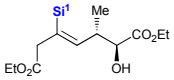


Entry	(±)-**1** (Si^1/Si^2)	ArCHO (equiv)	catalyst (equiv)	solvent	(±)-**2a**[d]	(±)-**3a**[d]
1	**1a** ($SiMe_3$/ $SiPh_2Me$)	1.2	L.A. or H^+	CH_2Cl_2	N.D.	N.D.
2	**1a** ($SiMe_3$/ $SiPh_2Me$)	1.2	$[C^+]$-1 (0.02)	CH_2Cl_2	36%	36%
3	**1a** ($SiMe_3$/ $SiPh_2Me$)	1.0	$[C^+]$-1[c] (0.02)	$CHCl_3$	75%	0%
4	**1a** ($SiMe_3$/ $SiPh_2Me$)	1.0	$[C^+]$-2[c] (0.02)	$CHCl_3$	N.R	N.R.
5	**1a** ($SiMe_3$/ $SiPh_2Me$)	1.0	$[C^+]$-3[c] (0.02)	$CHCl_3$	31%	0%
6	**1b** ($SiMe_3$/ $SiMe_2Ph$)	1.0	$[C^+]$-1 (0.02)	$CHCl_3$	46%	0%
7	**1c** ($SiMe_3$/ $SiEt_3$)	1.0	$[C^+]$-1 (0.02)	$CHCl_3$	N.R	N.R.
8	**1d** ($SiMe_3$/ $SiMe_2t$-Bu)	1.0	$[C^+]$-1 (0.02)	$CHCl_3$	N.R	N.R.
9	**1e** ($SiEt_3$/ $SiPh_2Me$)	1.0	$[C^+]$-1 (0.02)	$CHCl_3$	N.R	N.R.

[a] Reaction conditions: **1a** (0.05 mmol), *p*-Br-C_6H_4CHO (0.05mmol) and $Ph_3C^+B(C_6F_5)_4^-$ (0.02 equiv). [b] The stereochemistry was assigned using optically pure compounds in Tables 2 and 3. The ratios were determined by ^1H NMR spectroscopy of the crude products. [c] $[C^+]$-1: $Ph_3C^+B(C_6F_5)_4^-$; $[C^+]$-2: $Ph_3C^+PF_6^-$; $[C^+]$-3: $Ph_3C^+SbCl_6^-$. [d] Isolated yields after purification by silica gel column chromatography.

Table 2 Scope of Asymmetric Sakurai Allylation of (*S*)-**1a** with Aldehydes. [a]



Entry	R	Product		Yield [e]	ee [f]
1	-C_6H_4-Br-*p*		**2a**	75%	97%
2	-C_6H_4-F-*p*		**2b**	59%	95%
3	-C_6H_4-Cl-*m*		**2c**	70%	97%
4	-C_6H_4-CN-*p*		**2d**	90%	96%
5	-C_6H_4-CF_3-*p*		**2e**	70%	94%
6	-C_6H_4-OMe-*p*		**2f**	N.R.	N.D.
7			**2g**	72%	96%
8			**2h**	71%	87%
9	-Cy		**2i**	60%	93%
10	-CO_2Et		**2j**	60%	96%

[a] Reaction conditions: (*S*)-**1a** (0.05 mmol), aldehdye (0.05 mmol) and $Ph_3C^+B(C_6F_5)_4^-$ (0.02 equiv) in $CHCl_3$ (0.5 mL) at room temperature for 2 h. [b] The (*S*)-configuration was determined by circular dichroism spectroscopy. [c] The *Z*-(*S*, *S*)-stereochemistry was assigned by *X*-ray analysis of the diol of **2a**.[16] [d] The ratios were determined by ^1H NMR spectroscopy of the crude products. [e] Isolated yields after purification by silica gel column chromatography. [f] The ee values were determined by HPLC analysis using a chiral stationary phase.

occurred when using other analogous crotyl silanes **1c** ($SiMe_3$/$SiEt_3$), **1d** ($SiMe_3$/$SiMe_2t$-Bu) or **1e** ($SiEt_3$/$SiPh_2Me$).

Enantioselective synthesis of (*S*)-**1a** (97% ee)[13, 14] was achieved on gram scale from optically pure (*S*)-**4**[15] using the same procedure as that used for racemic **1a**. $Ph_3C^+B(C_6F_5)_4^-$-catalyzed Sakurai allylation of (*S*)-**1a** was tested next with a range of aldehydes. The approach was suitable for electron-withdrawing group-substituted aryl

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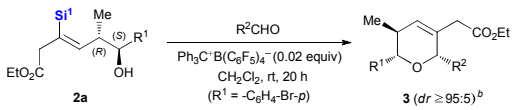
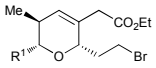
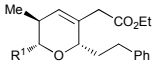
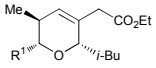
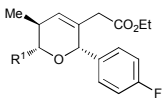
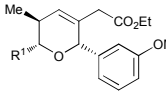
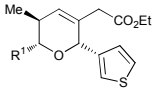
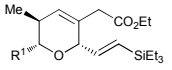
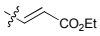
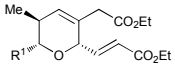
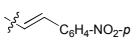
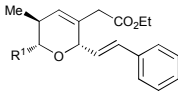
aldehydes (Table 2). Chemoselective desilylation of $SiPh_2Me$ was observed in all cases, leading to reliable chirality transfer from geminal bis(silyl) moiety to the products. **2a**-**2e** were obtained in good yield as a single *Z*-*anti*-isomer with (*S*, *S*)-enantioselectivity (entries 1-5). However, no reaction occurred with *p*-anisaldehyde containing an electron-donating MeO group (entry 6). Reaction of enal provided a higher ee (**2g**, 96% ee) than that (**2h**, 87% ee) obtained using less sterically demanding propargyl aldehyde (entries 7 and 8). While allylation of cyclohexyl aldehyde and ethyl glyoxylate gave **2i** and **2j**, respectively, in good yield with high ee, using unbranched alkyl aldehydes led to pyran as the major product (not shown).

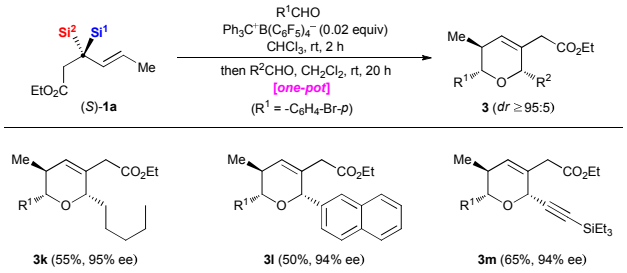
Table 3 Scope of Prins Cyclization of **2a** with Aldehdyes.[a]



Entry	R^2	Product		Yield [c]	ee [d]
1	$-C_2H_4Br$		**3b**	92%	94%
2	$-C_2H_4Ph$		**3c**	70%	95%
3	*i*-Bu		**3d**	98%	95%
4	$-C_6H_4-F-p$		**3e**	90%	96%
5	$-C_6H_4-OMe-m$		**3f**	95%	95%
6	3-thienyl		**3g**	98%	94%
7			**3h**	90%	96%
8			**3i**	80%	95%
9			**3j**	90%	96%

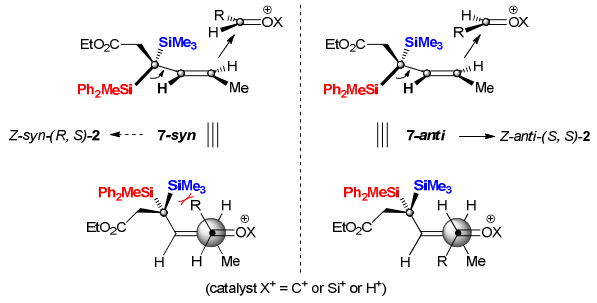
[a] Reaction conditions: **2a** (0.05 mmol), aldehyde (0.05 mmol) and $Ph_3C^+B(C_6F_5)_4^-$ (0.02 equiv) in $CHCl_3$ (0.5 mL) at room temperature for 20 h. [b] The stereochemistry was determined based on NOE experiments of **3d**. The ratios were determined by ^1H NMR spectroscopy of the crude products. [c] Isolated yields after purification by silica gel column chromatography. [d] The ee values were determined by HPLC analysis using a chiral stationary phase.

Formation of the by-product (±)-**3a** implies that $Ph_3C^+B(C_6F_5)_4^-$ should be also capable to catalyze the Prins cyclization[17] of **2a** with aldehydes if using CH_2Cl_2 as solvent. As expected, the approach tolerated to alkyl, aryl, and α, β-unsaturated aldehydes (Table 3). Pyrans **3** were obtained as a single diastereomer in high yields and enantioselectivity. This clean Prins cyclizaton allowed us to realize a one-pot Sakurai allylation/Prins cyclization process (Scheme 3). Once the Sakurai allylation of (*S*)-**1a** with R^1CHO was complete and had formed **2a**, a solution of the second aldehdye R^2CHO in CH_2Cl_2 was added to the same reaction tube. In this way, a range of pyrans **3k**-**3m** were generated in 50-65% yields with high *dr* and ee.



Scheme 3. One-pot Sakurai allylation/Prins cyclization to form **3k**-**3m**.

Sakurai allylation of (*S*)-**1a** with aldehydes shows four different selectivities in a single transformation: chemoselective desilylation of $SiMe_2Ph$ over $SiMe_3$, forming *Z*- over *E*-vinyl silane, *anti* over *syn*-diastereoselectivity and *S*/*S* over *R*/*S*-enantioselectivity. We proposed a model in Scheme 5 to rationalize the above selectivity outcomes. The reactive conformation of (*S*)-**1a** should be that, in which the most sterically demanding $SiPh_2Me$ group is positioned perpendicular to the alkene and the CH_2CO_2Et group adopts an *exo*-orientation at the allylic position. This conformation would minimize the allylic strain, and also benefits from a hyperconjugation effect between the C–$SiPh_2Me$ bond and alkene. Thus, chemoselective elimination of $SiPh_2Me$ would generate $SiMe_3$-substituted *Z*-vinyl silane. Despite the real catalyst (C^+, Si^+ or H^+) is not clear currently,[18] the classical *anti*-S_E' mechanism[19] could apply to each of them, giving a unified allylation model: antiperiplanar transition states ***7-syn*** and ***7-anti***. ***7-anti*** appears being more favorable than ***7-syn***, which suffers from a severe gauche interaction between R and $SiMe_3$ groups. Thus, reaction would proceed through ***7-anti*** to generate *Z*-*anti*-(*S, S*)-**2** diastereo- and enantioselectively.



Scheme 5. Model analysis to explain *Z*-*anti*-(*S, S*)-selectivity outcome.

Functionalization of the *endo*-cyclic olefin in **3** allowed us to

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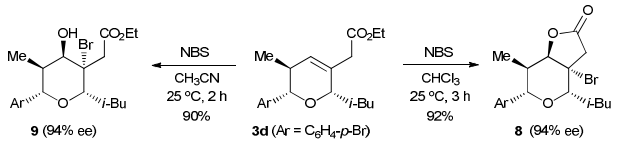
obtain fully substituted pyran with defined stereochemistry. As shown in Scheme 6, treatment of **3d** with NBS in $CHCl_3$ led to a sequential bromination/lactonization. Pyran **8** was generated in 92% yield with excellent stereochemical control. Interestingly, switching the solvent from $CHCl_3$ to CH_3CN favored a bromination/hydroxylation process, giving **9** in 90% yield as a single diastereoisomer.



Scheme 6. Bromination of **3d** to form fully substituted pyrans **8** and **9**.

In summary, we have achieved an enantioselective synthesis of $SiMe_3$/$SiPh_2Me$-substituted crotyl geminal bis(silane). This compound is a useful reagent for $Ph_3C^+B(C_6F_5)_4^-$-catalyzed asymmetric Sakurai allylation and one-pot Sakurai allylation/Prins cyclization process. Chemoselective desilylation of $SiPh_2Me$ leads to the efficient chirality transfer, giving *Z-anti*-(*S, S*)-selectivity. Applications of this methodology in organic synthesis are underway.

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