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Vinylogous Mukaiyama–Michael Reactions of Dihydropyridinones

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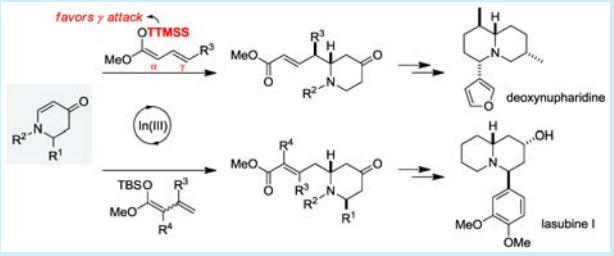
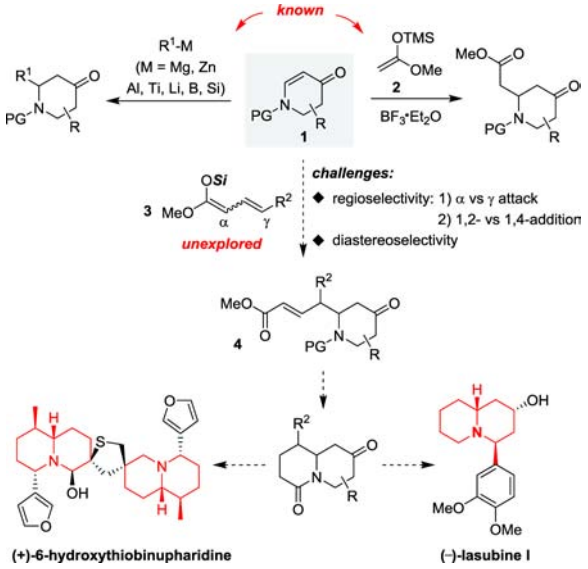
Supporting Information

ABSTRACT: An In(III)-catalyzed vinylogous addition of *O*-silyl vinylketene acetals to 2,3-dihydro-4-pyridinones has been developed. The method features the unprecedented employment of supersilyl groups to influence the γ versus α regiochemical control of vinylogous Mukaiyama–Michael (vM–Michael) reactions when γ-substituted *O*-silyl vinylketene acetals are used. We also demonstrate that these reactions allow facile access to quinolizidine-based alkaloids such as deoxynupharidine and well as lasubine I and II.



2,3-Dihydro-4-pyridinones **1** (Scheme 1) are versatile building blocks used to construct nitrogen-containing heterocyclic frameworks.[1] They have been described to undergo 1,4-conjugate addition with various aryl,[2] alkyl,[3] and alkenyl[4] nucleophiles. In addition, their capacity to participate in Mukaiyama–Michael reactions has been shown by Comins and co-workers using *O*-silyl ketene acetal **2**.[5]

Scheme 1. Michael Reactions of 2,3-Dihydro-4-pyridinone



Nonetheless, little is known about the reactivity of **1** with *vinylogous* silyl ketene acetals **3** although (1) the presence of an extra alkene in the products renders this type of reaction more efficient in increasing molecular complexity as compared to its Mukaiyama–Michael counterpart and (2) the resulting piperidines **4** may be transformed into highly functionalized quinolizidines (Scheme 1), thus providing potential approaches toward lasubine I and II,[6] and the dimeric nuphar alkaloids,[7] such as (+)-6-hydroxythiobinupharidine and others (recently synthesized by our group).[8] The lack of knowledge about this reaction type may be because the vinylogous process is a more challenging bond construction since synthetically useful vinylogous Mukaiyama–Michael (vM–Michael) reactions must simultaneously address both *regioselectivity* (i.e., α- vs γ-attack and 1,2- vs 1,4-addition) and *diastereoselectivity* during C–C bond construction.[9] In order to diminish the amount of α-alkylated products, nearly all of the previous reports elected to use cyclic vinylogous substrates (e.g., silyloxyfurans) with a strong inherent preference for γ-selectivity.[9d] In contrast, the use of linear substrates such as **3** remains elusive due to poor regioselectivity (α- vs γ-attack), reactivity, and diastereoselectivity. To the best of our knowledge, only limited reports have employed linear substrates in vM–Michael reactions.[9b−g]

We initiated our study by examining the reaction between dihydropyridinone **5a** and γ-substituted 3,4-*E* silyl vinylketene acetal **3a** (Table 1, entry 1). $In(OTf)_3$ is an air and moisture stable catalyst that we identified to be effective in promoting the vinylogous addition to form **6a** as the major product (see Supporting Information for a complete survey of Lewis acids). No 1,2-addition product was isolated. The reaction, however, only showed moderate regiochemical control with respect to the silyl ketene acetal (γ- vs α-attack). Performing the reaction at −20 °C resulted in diminished γ vs α regioselectivity but slightly increased diastereoselectivity (entry 2). Interestingly, the use of 3,4-*Z* silyl ketene acetal **3b** reversed the diastereoselectivity (entry 3), which suggested that the geometry of 3,4-double bond of **3** plays a role in the stereochemical outcome of the vinylogous addition.

To address the issue of α- vs γ-attack, we reasoned that differentiating the steric properties of chemical space around the α- and γ-positions of **3** may alter their inherent nucleophilicities. Inspired by the pioneering studies of Yamamoto with regards to using supersilyl groups to influence the chemo- and stereo-

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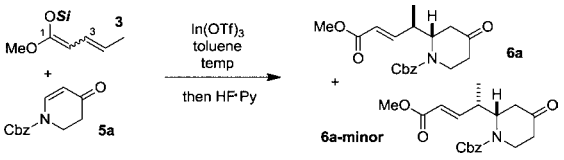
Table 1. Optimization of Reaction Conditions[a]



			3 (*E*:*Z*)				yield (%)		
entry	3	*Si*	1,2	3,4	temp (°C)	time (h)	γ[b]	α[c]	dr[d]
1	**3a**	TBS	1:2.7	>20:1	rt	0.5	46	43	5.2:1
2	**3a**	TBS	1:2.7	>20:1	−20	1.0	31	56	5.7:1
3	**3b**	TBS	1:8.0	<1:20	rt	0.5	60	29	1:6.8
4	**3c**	TTESS	1:5.0	>20:1	−30	2.0	83	<5	2.7:1
5	**3d**	TTMSS	<1:20	>20:1	rt	1.0	83	<5	5.8:1
6	**3d**	TTMSS	<1:20	>20:1	−20	2.0	81	<5	7.1:1

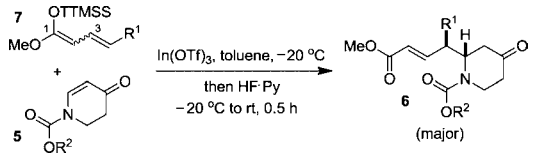
[a]**3** (2 equiv), **5a** (1 equiv), catalyst (5 mol %), reaction concentration 0.2 M. [b]Isolated yield for γ-alkylated 1,4-adducts. [c]Isolated yield for α-alkylated 1,4-adducts. [d]Ratio of **6a**:**6a-minor** as determined by ^{1}H NMR spectroscopy.

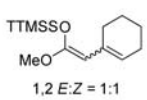
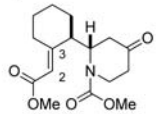
selectivity of various reactions,[10] we investigated the tris(triethylsilyl)silyl (TTESS) and tris(trimethylsilyl)silyl (TTMSS) groups (entries 4, 5) and discovered that their use substantially favors. Their use substantially favors the formation of γ-alkylated products. After surveying different temperatures (see Supporting Information), the best regio- and diastereoselectivity were obtained by conducting the reaction at −20 °C in toluene and using TTMSS as a protecting group (entry 6).

As shown in Table 2, the vinylogous addition of vinylketene acetals with diverse γ-substituents (alkyl, aryl, benzyl) proceeded smoothly. The employment of the TTMSS group greatly enhanced γ-regioselectivity (<5% of α-products were isolated in all cases). Notably, the use of a TBS group in place of TTMSS resulted in very poor α- vs γ-selectivity.[11] Smaller protecting groups at the nitrogen of dihydropyridinone **5** tended to give better stereochemical control (entry 1 vs 2). In some cases, a higher catalyst loading (10 mol %) was necessary to drive the reaction to completion (entries 3, 5−10). The reactions yielded a diverse range of piperidines **6b**−**k** with good diastereoselectivity. The relative stereochemical configurations of **6a**, minor diastereomer **6a-minor**, and **6c** were assigned by converting them to known quinolizidine compounds (*vide infra* and also see Supporting Information) while the relative stereochemical relationships of the remaining products were assigned by analogy.

Scheme 2 illustrates our proposed transition-state model to rationalize the observed stereochemical outcome. We assume

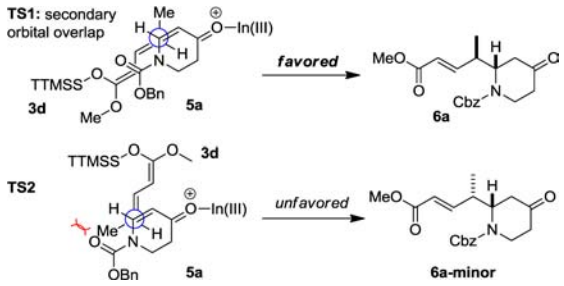
Table 2. vM−Michael Reactions of Dihydropyridinones with γ-Substituted Vinylketene Acetals[a]



		7 (*E*:*Z*)						
entry	R^1	1,2	3,4	R^2	In(OTf)$_3$ (mol %)	product	yield (%)[b]	dr[c]
1	Me	< 1:20	> 20:1	*t*-Bu	5	**6b**	73	5.8:1
2	Me	< 1:20	> 20:1	Me	5	**6c**	80	11.7:1
3	Et	< 1:20	> 20:1	Me	10	**6d**	79	15.9:1
4[d]	*i*-Pr	< 1:20	> 20:1	Me	5	**6e**	62	20.7:1
5	*n*-Pr	1:8	> 20:1	Me	10	**6f**	74	8.0:1
6	*n*-Bu	1:11	> 20:1	Me	10	**6g**	76	9.1:1
7	Ph	1:2.6	> 20:1	Me	10	**6h**	59	10.2:1
8	Bn	1:10	> 20:1	Me	10	**6i**	68	7.4:1
9	2-thienyl	1:1	> 20:1	Me	10	**6j**	56	8.6:1
10				Me	10		82	13.1:1

[a]**5** (1 equiv), **7** (2 equiv), reaction concentration 0.2 M. [b]Isolated yield for γ-alkylated 1,4-adducts. [c]Determined by ^{1}H NMR spectroscopy. [d]−20 to 0 °C. [e]2,3-*E*/*Z* > 20:1.

Scheme 2. Stereochemical Models for 3d + 5a



that the reaction between **3d** and **5a** may preferentially adopt an antiperiplanar transition state **TS1**,[12] which could be stabilized by secondary orbital overlap (i.e., π−π stacking interactions)[13] between the vinylketene moiety of **3d** and the carbamate of **5a**. The model **TS2**, which proceeds through a synclinal transition state, could be unfavored because the tetrahedral methyl group on **3d** may experience strong nonbonding interactions with the carbamate of **5a**.

With regard to the vinylogous addition of γ-*un*substituted *O*-TBS vinylketene acetals **9**[14] to various 2-substituted dihydropyridinones (Table 3; see Supporting Information for optimization details), a range of *trans*-disubstituted 4-piperidinones were derived with high γ-selectivity without the need for employing a supersilyl group (<5% of α-products were isolated in all cases). This is likely because the absence of a substituent on the γ-position of **9** renders it more nucleophilic than the α-position toward Michael addition. Moreover, larger C2-substituents on **8** resulted in relatively higher diastereoselectivity (e.g., entry 1 vs 6). The catalyst loading may be lowered to 2.5 mol % in the

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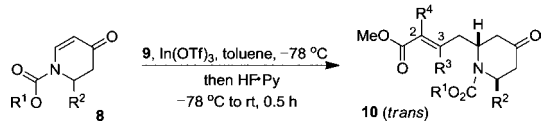
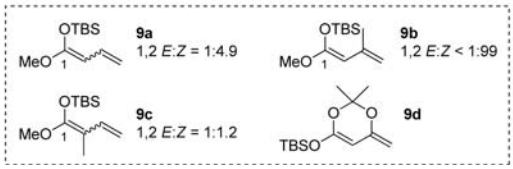
Table 3. vM−Michael Reactions of 2-Substituted Dihydropyridinone with γ-Unsubstituted Vinylketene Acetals[a]



entry	9	R^1	R^2	In(OTf)$_3$ (mol %)	product[f]	yield[b] (%)	dr[c] (*trans*:*cis*)
1	**9a**	*t*-Bu	Ph	5.0	**10a**	86	11.3:1
2	**9a**	*t*-Bu	4-ClPh	5.0	**10b**	78	13.6:1
3	**9a**	*t*-Bu	4-FPh	5.0	**10c**	71	12.2:1
4	**9a**	*t*-Bu	vinyl	2.5	**10d**	70	7.0:1
5	**9a**	*t*-Bu	PhC≡C-	5.0	**10e**	88	5.7:1
6	**9a**	*t*-Bu	ethynyl	5.0	**10f**	85	4.3:1
7	**9a**	Bn	Ph	5.0	**10g**	79	8.4:1
8	**9a**	Me	Ph	5.0	**10h**	74	5.1:1
9[d]	**9a**	Bn	3,4-(MeO)$_2$Ph	5.0	**10i**	81	4.5:1
10	**9b**	*t*-Bu	Ph	5.0	**10j**	71	6.0:1[e]
11	**9c**	*t*-Bu	Ph	5.0	**10k**	81	5.6:1[e]
12	**9d**	*t*-Bu	Ph	10	**10l**	77	6.8:1

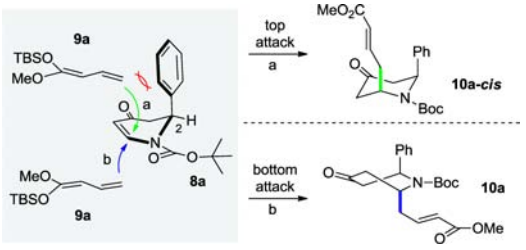


[a]**9** (2 equiv), **8** (1 equiv), reaction concentration was 0.2 M. [b]Isolated yield for γ-alkylated products. [c]Determined by ^{1}H NMR spectroscopy. [d]Solvent: toluene/DCM (v/v = 9:1). [e]**10**: 2,3-*E*:*Z* > 20:1. [f]The relative stereochemical configuration of all the products were established by NOESY experiments (see Supporting Information).

reaction starting from 2-vinyl dihydropyridinone (entry 4), while 10 mol % was necessary to drive the reaction to completion when using **9d** as a nucleophile (entry 12).

We hypothesize that the observed *anti*-facial selectivity arises from a combination of stereoelectronic and steric control. Based on the reported X-ray crystal structure of *N*-Cbz-2- phenyl-3,4-dihydro-4-pyridinone,[15] we propose that **8a** exists in a half-boat conformation (Scheme 3), with the C2 phenyl group adopting a

Scheme 3. Stereochemical Models for 8a + 9a

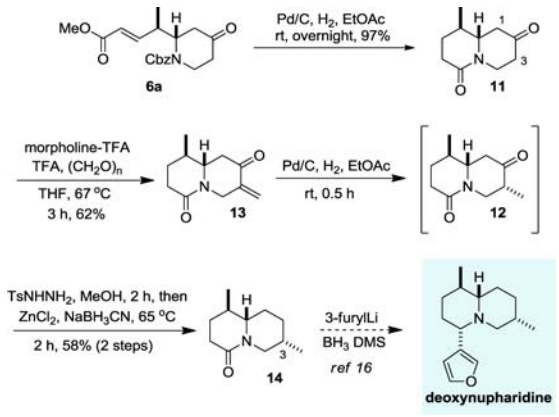


pseudoaxial position to avoid $A_{(1,3)}$ interactions with the *N*-Boc group. Axial attack of vinylketene acetal **9a** from either top or bottom would generate, respectively, the chairlike *syn*-adduct **10a-*cis*** or the higher energy twist boat-like *anti*-adduct **10a**.[16] But although the delivery of **9a** from the top is predicted to be favored based on stereoelectronic considerations, it may experience greater steric repulsion from the C2 phenyl group of **8a**, thus making bottom-face attack energetically more favorable. This is consistent with the model proposed previously of *trans*-addition of aryl cuprates to dihydropyridinones.[15]

Having developed the vM−Michael reaction of 2,3-dihydro-4-pyridinones with vinylogous silyl ketene acetals, we turned our attention to its incorporation in the syntheses of related quinolizidine alkaloids, including deoxynupharidine, lasubine I and II.

A formal synthesis of deoxynupharidine is shown in Scheme 4, which began with the hydrogenation/hydrogenolysis of **6a** to

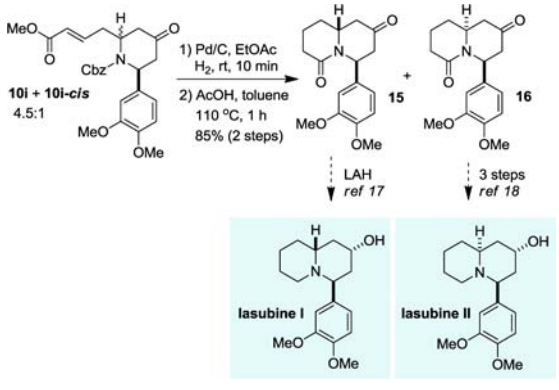
Scheme 4. Formal Synthesis of Deoxynupharidine



simultaneously reduce the alkene and remove the Cbz group. This was followed by spontaneous lactam formation to give quinolizidine **11** in a single step from **6a**. Our initial attempt to obtain compound **12** via direct α-methylation of the C3 position of **11** was unsuccessful as the reactions gave complex mixtures. We then elected to pursue an alternative route by first installing a methylene group at C3 of **11**. After screening various reaction conditions, morpholine-TFA salt was identified as an effective catalyst to promote regioselective C3-methylenation to give enone **13**.[17] Its C1-methylenated isomer was not observed based on ^{1}H NMR spectroscopic analysis. Compound **13** then underwent diastereoselective hydrogenation to give intermediate **12**, which was followed by modified Wolff−Kishner reduction to yield a mixture of **14** and a minimal amount of its C3-epimer (15.6:1). Quinolizidine **14** can be converted to deoxynupharidine in one step as described by Harrity and others.[18]

To achieve the synthesis of lasubine I and II (Scheme 5), a mixture of disubstituted piperidinones **10i** and its *cis*-diastereomer (**10i**:**10i-*cis*** = 4.5:1) was subjected to simultaneous hydrogenation and hydrogenolysis, followed by acid-mediated

Scheme 5. Formal Synthesis of Lasubine I and II



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lactam formation to give **15** and **16**, respectively, which are easily separable using silica gel chromatography. The conversion of quinolizidine **15** to lasubine I through LAH reduction,[19] and **16** to lasubine II, has been previously reported.[20]

In conclusion, we have developed In(III)-catalyzed stereoselective vM−Michael reactions with 2,3-dihydro-4-pyridinones, which provide diversified synthetic approaches to access quinolizidine alkaloids. We have also demonstrated the first use of the supersilyl group to govern the γ-vs-α regiochemical outcome of vM−Michael reactions. This "supersilyl" strategy may be extended to analogous processes in which γ-substituted silyl vinylketene acetals are utilized.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02778.

Experimental details and characterization of all new compounds, including ^{1}H, ^{13}C, and selected 2D-NOESY, 2D-COSY, HMBC, and HMQC data (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For selected references, see: (a) Comins, D. L.; Zhang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 12248−12249. (b) Kuethe, J. T.; Comins, D. L. *Org. Lett.* **2000**, *2*, 855−857. (c) Comins, D. L.; Huang, S.; McArdle, C. L.; Ingalls, C. L. *Org. Lett.* **2001**, *3*, 469−471. (d) Comins, D. L.; Zheng, X.; Goehring, R. R. *Org. Lett.* **2002**, *4*, 1611−1613. (e) Comins, D. L.; Sahn, J. J. *Org. Lett.* **2005**, *7*, 5227−5228. (f) Wolfe, B. H.; Libby, A. H.; Al-awar, R. S.; Foti, C. J.; Comins, D. L. *J. Org. Chem.* **2010**, *75*, 8564−8570. (g) Tsukanov, S. V.; Comins, D. L. *Angew. Chem., Int. Ed.* **2011**, *50*, 8626−8628. (h) Tsukanov, S. V.; Comins, D. L. *J. Org. Chem.* **2014**, *79*, 9074−9085.

(2) For selected references, see: (a) Shintani, R.; Tokunaga, N.; Doi, H.; Hayashi, T. *J. Am. Chem. Soc.* **2004**, *126*, 6240−6241. (b) Gini, F.; Hessen, B.; Minnaard, A. J. *Org. Lett.* **2005**, *7*, 5309−5312. (c) Xu, Q.; Zhang, R.; Zhang, T.; Shi, M. *J. Org. Chem.* **2010**, *75*, 3935−3937. (d) Gao, X.; Singh, R. P.; Corey, E. J. *Org. Lett.* **2010**, *12*, 1812−1814. (e) Kim, Y. W.; Georg, G. *Org. Lett.* **2014**, *16*, 1574−1577.

(3) For selected references, see: (a) Brown, J. D.; Foley, M. A.; Comins, D. L. *J. Am. Chem. Soc.* **1988**, *110*, 7445−7447. (b) Comins, D. L. *J. Am. Chem. Soc.* **1993**, *115*, 8851−8852. (c) Sato, M.; Aoyagi, S.; Yago, S.; Kibayashi, C. *Tetrahedron Lett.* **1996**, *37*, 9063−9066. (d) Sebesta, R.; Pizzuti, M. G.; Boersma, A. J.; Minnaard, A. J.; Feringa, B. L. *Chem. Commun.* **2005**, 1711−1713. (e) McCall, W. S.; Grillo, T. A.; Comins, D. L. *Org. Lett.* **2008**, *10*, 3255−3257. (f) McCall, W. S.; Comins, D. L. *Org. Lett.* **2009**, *11*, 2940−2942. (g) Endo, K.; Ogawa, M.; Shibata, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 2410−2413.

(4) For selected references, see: (a) Xie, C.; Runnegar, M. T. C.; Snider, B. B. *J. Am. Chem. Soc.* **2000**, *122*, 5017−5024. (b) Heintzelman, G. R.; Fang, W.; Keen, S. P.; Wallace, G. A.; Weinreb, S. M. *J. Am. Chem. Soc.* **2002**, *124*, 3939−3945. (c) Maloney, D. J.; Danishefsky, S. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 7789−7792. (d) Muller, D.; Alexakis, A. *Org. Lett.* **2012**, *14*, 1842−1845.

(5) (a) Kuethe, J. T.; Comins, D. L. *Org. Lett.* **1999**, *1*, 1031−1033. (b) Kuethe, J. T.; Comins, D. L. *J. Org. Chem.* **2004**, *69*, 5219−5231. (c) Kuethe, J. T.; Comins, D. L. *Org. Lett.* **2000**, *2*, 855−857.

(6) Comins, D. L.; LaMunyon, D. H. *J. Org. Chem.* **1992**, *57*, 5807−5809.

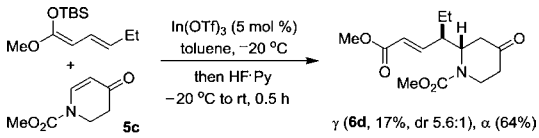
(7) Jansen, D. J.; Shenvi, R. A. *J. Am. Chem. Soc.* **2013**, *135*, 1209−1212.

(8) Korotkov, A.; Li, H.; Chapman, C. W.; Xue, H.; MacMillan, J. B.; Eastman, A.; Wu, J. *Angew. Chem., Int. Ed.* **2015**, *54*, 10604−10607.

(9) For a recent review and example of a diastereoselective vinylogous Mukaiyama−Michael reaction, see: (a) Schneider, C.; Abels, F. *Org. Biomol. Chem.* **2014**, *12*, 3531−3543. (b) Basu, S.; Gupta, V.; Nickel, J.; Schneider, C. *Org. Lett.* **2014**, *16*, 274−277. (c) Gupta, V.; Sudhir, S.; Mandal, T.; Schneider, C. *Angew. Chem., Int. Ed.* **2012**, *51*, 12609−12612. (d) Gu, Y.; Wang, Y.; Yu, T.; Liang, Y.; Xu, P. *Angew. Chem., Int. Ed.* **2014**, *53*, 14128−14131. (e) Scettri, A.; Sio, V.; Villano, R.; Manzo, P.; Acocella, M. R. *Tetrahedron Lett.* **2010**, *51*, 3658−3661. (f) Casamitjana, H.; Jorge, A.; Pérez, C. G.; Bosch, J.; Espinosa, E.; Molins, E. *Tetrahedron Lett.* **1997**, *38*, 2295−2298. (g) Chan, T. H.; Prasad, C. V. C. *J. Org. Chem.* **1987**, *52*, 110−119.

(10) (a) Boxer, M. B.; Yamamoto, H. *J. Am. Chem. Soc.* **2006**, *128*, 48−49. (b) Boxer, M. B.; Yamamoto, H. *J. Am. Chem. Soc.* **2007**, *129*, 2762−2763. (c) Kawasaki, M.; Li, P.; Yamamoto, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 3795−3797. (d) Boxer, M. B.; Yamamoto, H. *J. Am. Chem. Soc.* **2007**, *129*, 2762−2763. (e) Yamaoka, Y.; Yamamoto, H. *J. Am. Chem. Soc.* **2010**, *132*, 5354−5356. (f) Albert, B. J.; Yamamoto, H. *Angew. Chem., Int. Ed.* **2010**, *49*, 2747−2749. (g) Saadi, J.; Akakura, M.; Yamamoto, H. *J. Am. Chem. Soc.* **2011**, *133*, 14248−14251. (h) Albert, B. J.; Yamaoka, Y.; Yamamoto, H. *Angew. Chem., Int. Ed.* **2011**, *50*, 2610−2612. (i) Brady, P. B.; Yamamoto, H. *Angew. Chem., Int. Ed.* **2012**, *51*, 1942−1946. (j) Tan, J.; Akakura, M.; Yamamoto, H. *Angew. Chem., Int. Ed.* **2013**, *52*, 7198−7202. (k) Izumiseki, A.; Yamamoto, H. *J. Am. Chem. Soc.* **2014**, *136*, 1308−1311. (l) Izumiseki, A.; Yamamoto, H. *Angew. Chem., Int. Ed.* **2015**, *54*, 8697−8699.

(11)



(12) For representative discussions on antiperiplanar and synclinal transition states, see: (a) Keck, G. E.; Savin, K. A.; Cressman, E. N.; Abbott, D. E. *J. Org. Chem.* **1994**, *59*, 7889−7896. (b) Denmark, S. E.; Beutner, G. L.; Wynn, T.; Eastgate, M. D. *J. Am. Chem. Soc.* **2005**, *127*, 3774−3789. (c) Denmark, S. E.; Lee, W. *Chem. - Asian J.* **2008**, *3*, 327−341. (d) Beutner, G. L.; Denmark, S. E. *Angew. Chem., Int. Ed.* **2013**, *52*, 9086−9096. For representative discussions on the transition states of Mukaiyama−Aldol reactions, see: (e) Kalesse, M.; Cordes, M.; Symkenberg, G.; Lu, H. *Nat. Prod. Rep.* **2014**, *31*, 563−594. (f) Hassfeld, J.; Christmann, M.; Kalesse, M. *Org. Lett.* **2001**, *3*, 3561−3564.

(13) For representative discussions on secondary orbital interactions, see: Lu, H.-H.; Martinez, M. D.; Shenvi, R. A. *Nat. Chem.* **2015**, *7*, 604−607.

(14) Preparation of *O*-silyl ketene acteal using TTMSS as a protecting group was unsuccessful.

(15) Hamblett, C. L.; Sloman, D. L.; Kliman, L. T.; Adams, B.; Ball, R. G.; Stanton, M. G. *Tetrahedron Lett.* **2007**, *48*, 2079−2082.

(16) (a) Fürst, A.; Plattner, P. A. *Helv. Chim. Acta* **1949**, *32*, 275−283. (b) Kirby, A. J. *Stereoelectronic Effects*; Oxford Science Publications: New York, 2002; p 54.

(17) Bugarin, A.; Jones, K. D.; Connell, B. T. *Chem. Commun.* **2010**, *46*, 1715−1717.

(18) (a) Hwang, Y. C.; Fowler, F. W. *J. Org. Chem.* **1985**, *50*, 2719−2726. (b) Moran, W. J.; Goodenough, K. M.; Raubo, P.; Harrity, J. P. A. *Org. Lett.* **2003**, *5*, 3427−3429.

(19) Bardot, V.; Gardette, D.; Gelas-Mialhe, Y.; Gramain, J.; Remuson, R. *Heterocycles* **1998**, *48*, 507−518.

(20) Verkade, J. M. M.; van der Pijl, F.; Willems, M. M. J. H. P.; Quaedflieg, F. L. D.; Rutjes, F. J. T. *J. Org. Chem.* **2009**, *74*, 3207−3210.

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Org. Lett. 2015, 17, 5424−5427