Organic LETTERS

Letter

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Organocatalytic Enantioselective Synthesis of Tetrahydrofluoren-9-ones via Vinylogous Michael Addition/Henry Reaction Cascade of 1,3-Indandione-Derived Pronucleophiles

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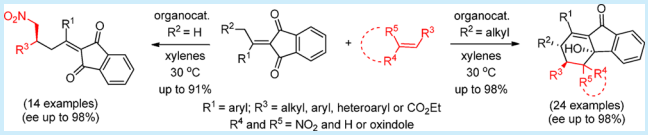
Supporting Information

ABSTRACT: An unprecedented organocatalytic enantioselective vinylogous Michael addition/Henry cyclization cascade is presented for the synthesis of highly substituted tetrahydrofluoren-9-ones **3** employing novel 1,3-indandione-derived pronucleophiles **1a−g** and nitroalkenes **2**. Following a very simple protocol, a wide range of products were obtained in good to excellent yields and with excellent enantioinduction (43−98% yield, up to 98% ee). The reaction proceeded with excellent diastereocontrol despite the simultaneous generation of four stereogenic centers. Surprisingly, when 2-(1-phenylethylidene)-1*H*-indandione (**1h**) was used as a pronucleophile, no cyclization was observed, and only Michael addition adducts **4a−x** were furnished in very good yields and excellent enantioselectivities.



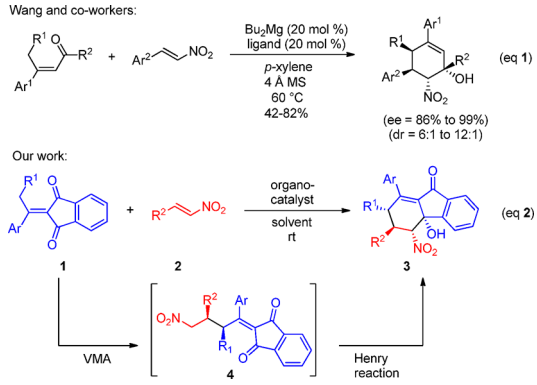
Asymmetric vinylogous Michael addition (VMA), which involves the enantioselective γ-addition of nucleophiles to the suitable Michael acceptors, has emerged as a versatile and powerful transformation in organic synthesis.[1] Although various metal-[2] and organocatalyzed[3] strategies have been reported, the enormous potential of this γ-addition reaction is often restricted to a single-step transformation. Until now, applications of asymmetric VMAs in tandem processes are uncommon, yet highly desired, since they enable a rapid synthesis of elaborated chemical structures starting from cheaper and easily available substrates.[4]

Furthermore, the development of an enantioselective Henry reaction with ketones is met with limited success[5] due to their inherently low reactivity when compared to aldehydes. The intramolecular versions of Henry cyclizations are seldom reported due to the difficulty in the synthesis of required nitrocarbonyl precursors bearing an electrophilic and a nucleophilic site in the same substrate.[6] However, this could be overcome by incorporating the Henry reaction in a cascade process where a more reactive transient intermediate could serve the purpose, resulting in efficient cyclizations. So far, only a few such tandem processes involving Henry reaction on ketones have been reported[7] and offer a large scope for exploration.

A very elegant VMA/Henry reaction cascade using a chiral magnesium complex has been reported by Wang and co-workers (Scheme 1, eq 1).[8] Following this method, substituted cyclohexene derivatives were obtained as products in moderate to good yields, good diastereoselectivities, and excellent enantioselectivities. However, to date, there are no reports on the organocatalytic enantioselective VMA/Henry reaction cascade involving ketones.

In the present work, we introduce a novel and versatile pronucleophile **1** which has never been explored for VMAs. We envisaged that due to the strong electron-withdrawing effect of the 1,3-indandione moiety, **1** would feature substantially high γ-acidity which is essential for its reactivity. Additionally, the carbonyl functionalities of the indandione moiety could be exploited for further tandem processes. Owing to the large planar structure, we presumed that it would be possible to achieve high levels of enantioinduction by employing a sterically bulky chiral organocatalyst. Hence, we expected that the treatment of **1** with a suitable Michael acceptor such as nitroalkene **2** in the presence of a chiral base catalyst would give a direct access to precious, highly complex tetrahydrofluoren-9-one derivatives[9] via a vinylogous Michael addition/Henry cyclization pathway.

Scheme 1. Vinylogous Michael Addition/Henry Reaction Cascade

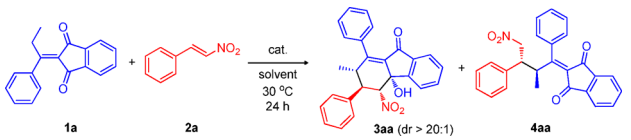


Received: December 25, 2015

DOI: 10.1021/acs.orglett.5b03663
Org. Lett. XXXX, XXX, XXX−XXX

We started our investigations using **1a** and **2a** as model substrates in the presence of DABCO as catalyst in xylenes. The reaction proceeded smoothly, and the expected product *rac*-**3aa** was obtained in moderate yield (Table 1, entry 1). A

Table 1. Optimization of the Reaction Conditions[a]



entry	cat.	solvent	**3aa**[b] (%)	**4aa**[b] (%)	ee[c] (%)
1	DABCO	xylenes	41[d]	30[d]	
2[e]	DABCO	xylenes	11	71	
3	**5a**	xylenes	55	<5	40
4	**5b**	xylenes	84	<5	87[f]
5	**5c**	xylenes	77	<5	90
6	**5d**	xylenes	91	<5	90
7	**5e**	xylenes	93	<5	95
8	**5f**	xylenes	87	<5	93[f]
9	**5g**	xylenes	81	<5	96
10	**5e**	toluene	81	8	95
11	**5e**	DCM	70	14	95
12	**5e**	THF	65	14	93
13[e]	**5e**	xylenes	15	52	99[g]
14[h]	**5e**	xylenes	35	24	nd

[a]Reaction conditions: 0.055 mmol of **1a**, 0.05 mmol of **2a**, 0.5 mL of solvent, 10 mol % of catalyst at 30 °C. [b]Yields as determined by ^{1}H NMR analysis of crude reaction mixture using Ph_3CH as internal standard. [c]ee of **3aa** was determined by HPLC analysis on a chiral stationary phase. [d]*rac*-**3aa** and *rac*-**4aa** were obtained. [e]5 mol % of catalyst was used. [f]Opposite enantiomer (*ent*-**3aa**) was in excess. [g]ee of **4aa**. [h]Reaction was carried out at −10 °C.

significant amount of *rac*-**4aa** was also initially observed, which later transformed into the cyclized product *rac*-**3aa**, affirming the expected two-step VMA/Henry reaction pathway.[10]

Despite the fact that four stereogenic centers are formed simultaneously, tetrahydrofluoren-9-one *rac*-**3aa** was obtained as a single diastereomer, making this protocol highly efficient. After the successful proof of principal, a selection of chiral organocatalysts **5a−g** (Figure 1) were evaluated for the VMA/

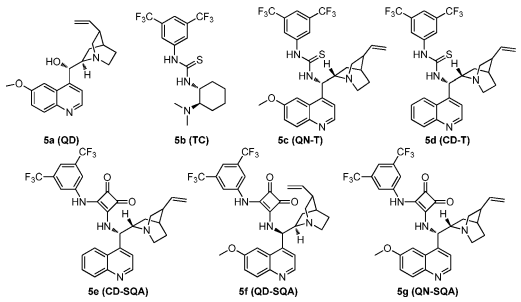


Figure 1. Chiral catalysts screened during optimization.

Henry cyclization cascade. Reducing the catalyst loading to 5 mol % resulted in the intermediate *rac*-**4aa** as the major product, which was isolated and characterized (Table 1, entry 2). This further confirmed that the reaction followed a stepwise VMA/Henry cyclization rather than a concerted pathway. Quinidine **5a** could result in the product **3aa** in only moderate yield and enantioselectivity (Table 1, entry 3). Takemoto's catalyst **5b** could enhance the yield and enantiomeric excess of the product *ent*-**3aa** to 84% and 87%, respectively (Table 1, entry 4).[11] When thiourea catalyst **5c** was used, the enantioselectivity increased, while the yield dropped slightly (Table 1, entry 5).[12] By changing the catalyst to **5d**, the yield of **3aa** could be further enhanced, retaining the similar enantioselectivity (Table 1, entry 6). Finally, different squaramide catalysts **5e−g** were tested (Table 1, entries 7−9).[13] To our delight, when the catalyst **5e** was used, the yield and enantiomeric excess of **3aa** could be enhanced to 93% and 95%, respectively (Table 1, entry 7).

A quick solvent screening was then performed that confirmed xylenes as the best choice (Table 1, entries 10−12). It is worth mentioning that there was no difference in the outcome of the reaction when it was conducted in either *o*-, *m*- or *p*-xylene. Furthermore, both moisture and air were tolerated well and did not affect the reaction result, making this protocol very simple and easy to reproduce. Finally, a low temperature experiment (−10 °C) (Table 1, entry 14) and a reduced catalyst loading (5 mol %) (Table 1, entry 13) were examined. In both cases, the reaction failed to accomplish full conversion within 24 h, and **3aa** was obtained in poor yields. Therefore, we decided to set the conditions in entry 7 as our optimal reaction conditions and started with the exploration of the substrate scope.

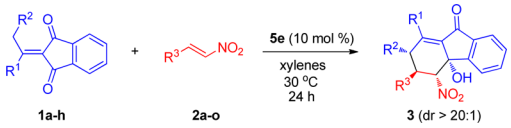
First, differently substituted nitroalkenes **2a−o** were examined (Table 2, entries 1−15). In each case, the product **3** could be obtained as a single diastereomer. Various functionalities could be tolerated well under the reaction conditions. Halogen-substituted nitrostyrenes gave the desired products in excellent yields and enantioselectivities (Table 2, entries 2−5). The position of the functionality did not have a strong influence on the reaction outcome, and comparable results were obtained (Table 2, entries 2 and 3). Interestingly, in the case of the *o*-Br-substituted electrophile **2c**, the appearance of two rotamers (1:1) was evident from NMR-spectroscopic analysis. The absolute configuration could be identified as (2*S*,3*R*,4*R*,4*αS*) by X-ray analysis of **3ac** (CCDC 1449770). Other strong electron-withdrawing groups, such as nitro and cyano, were also compatible with good to excellent yields and enantioselectivities (Table 2, entries 6 and 7). Surprisingly, *p*-trifluoromethyl nitrostyrene (**2h**) showed reduced reactivity, and it is necessary to increase the catalyst loading to 15 mol % in order to achieve full consumption of **2h** (Table 2, entry 8).

As compared to electron-withdrawing substituents, electron-donating groups displayed slightly diminished reactivities (Table 2, entries 9−12). Hence, in some cases it was necessary to increase the catalyst loading to 15 mol % (Table 2, entries 10 and 11). Heteroaryl-substituted nitroolefins **2m,n** were also compatible with this protocol (Table 2, entries 13 and 14), and satisfactory results were obtained. In case of the aliphatic substitution, the reaction had to be prolonged for 36 h (Table 2, entry 15) because of its lower reactivity. The desired product **3ao** was obtained with excellent enantioselectivity, albiet in moderate yield. However, the reaction did not work with other aliphatic substituents.

We then examined a variety of 1,3-indandione-derived pronucleophiles **1b−h**. Bromo substitution on the aryl group was tolerated, although its location had an obvious influence on the reaction outcome. Usage of (*p*-bromophenyl)propylidene indandione (**1b**) resulted in the formation of **3ba** and **3bb** with excellent yields and enantioselectivities (Table 2, entries 16 and

DOI: 10.1021/acs.orglett.5b03663
Org. Lett. XXXX, XXX, XXX−XXX

Table 2. Substrate Scope for the Enantioselective VMA/Henry Reaction Cascade[a]



entry	R^1/R^2	R^3	3, yield[b] (%)	ee[c] (%)
1	Ph/Me	Ph	**3aa** (91)	97
2	Ph/Me	*p*-BrPh	**3ab** (89)	95
3	Ph/Me	*o*-BrPh	**3ac**[d] (98)	95
4	Ph/Me	*p*-ClPh	**3ad** (94)	92
5	Ph/Me	*p*-FPh	**3ae** (96)	94
6	Ph/Me	*p*-NO_2Ph	**3af** (91)	93
7	Ph/Me	*p*-CNPh	**3ag** (83)	94
8[e]	Ph/Me	*p*-CF_3Ph	**3ah** (80)	98
9	Ph/Me	*p*-MePh	**3ai** (76)	95
10[e]	Ph/Me	*p*-OMePh	**3aj** (85)	94
11[e]	Ph/Me	*m*-OMePh	**3ak** (93)	91
12	Ph/Me	3,4-OMePh	**3al** (76)	94
13	Ph/Me	2-furyl	**3am** (80)	93
14	Ph/Me	2-thienyl	**3an** (92)	94
15[e,f]	Ph/Me	Cy	**3ao** (43)	95
16	*p*-BrPh/Me	Ph	**3ba** (91)	93
17	*p*-BrPh/Me	*p*-BrPh	**3bb** (91)	92
18	*o*-BrPh/Me	Ph	**3ca**[d] (77)	95
19[e,f]	*p*-OMePh/Me	Ph	**3da** (78)	93
20	3,4-ClPh/Me	Ph	**3ea** (83)	90
21	2-thienyl/Me	Ph	**3fa** (70)	94
22	Ph/*n*-Pr	Ph	**3ga** (79)	94
23	Ph/H	Ph	**3ha**[g] (12)	nd

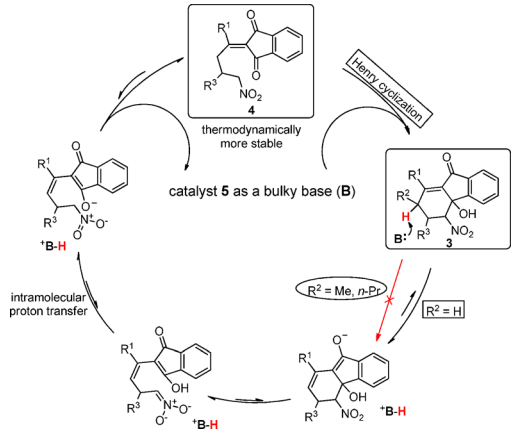
[a]Reaction conditions: 0.11 mmol of **1**, 0.1 mmol of **2**, 1.0 mL of xylenes, 10 mol % of **5e** at 30 °C. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]The product appears as a mixture of two atropisomers. [e]15 mol % of **5e** was used. [f]Reaction time was 36 h. [g]33% of the corresponding acyclic product **4ha** was formed.

17). For the *o*-Br-substituted pronucleophile **1c**, the yield of **3ca** decreased significantly to 77%, although the enantioselectivity remained excellent (Table 2, entry 18). Even in this case, characterization of **3ca** via NMR analysis revealed the appearance of two rotamers in a ratio of 2:1. For pronucleophile **1d** bearing an electron-donating methoxy group, 15 mol % of **5e** and a prolonged reaction time had to be employed to afford **3da** in 78% yield and 94% ee (Table 2, entry 19).

The strongly electron-deficient dichloroaryl-substituted pronucleophile **1e** also performed well in this cascade reaction (Table 2, entry 20). The thienyl-substituted pronucleophile **1f** resulted in slightly diminished yield of the product **3fa**, while the excellent enantioselectivity was retained (Table 2, entry 21).

Finally, the variation of the R^2 substitution was investigated. When a longer alkyl chain was presented, the corresponding product **3ga** was obtained in good yield with excellent enantioselectivity (Table 2, entry 22). However, when methyl-substituted pronucleophile **1h** (R^2 = H) was used, only a small amount of **3ha** was obtained while the intermediate **4ha** appeared as the major product (Table 2, entry 23). The strikingly different results with R^2 = H and R^2 = alkyl made us wonder about the possible reasons for such outcome. It would be expected that the remote R^2 group would have no role to play in assisting the cyclization of **4**, and the Henry reaction would be equally feasible irrespective of whether R^2 = H or R^2 = alkyl. Hence, we believe that even when R^2 = H, the cyclization is indeed taking place (Scheme 2).

Scheme 2. Ring Opening of 3 Resulting in the Retro-Henry Product 4



However, as a consequence of the sufficiently high γ-acidity imparted to the carbon bearing R^2 group in **3**, there is a subsequent ring-opening occurring, and the intermediate **4** is being regenerated, which seems to be thermodynamically more stable than **3**. However, when R^2 = alkyl, deprotonation of the sterically congested acidic γ-site by the bulky catalyst **5** would be difficult, preventing the ring opening and thereby resulting in the retention of the cyclized product **3**. This also explains the result in entry 1 of Table 1, where a considerable amount of intermediate **4aa** is retained as a consequence of ring-opening of initially formed product **3aa**.

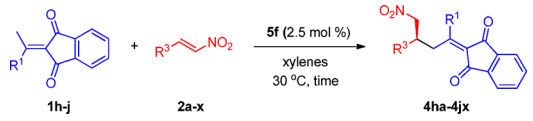
Hence, we focused on the synthesis of thermodynamically more stable intermediate **4** with R^2 = H. After an additional tuning of the reaction parameters, the yield of the product **4ha** could be greatly enhanced (Table 3, entry 1), while the enantioselectivity was retained. Subsequently, the substrate scope of this transformation was examined by employing various substrates, and the results are summarized in Table 3. When **1h** or **1i** was used as the pronucleophile, good to excellent yields and enatioselectivities were achieved for all nitroalkenes in short reaction times (Table 3, entries 1−13). However, when the symmetric pronucleophile **1j** bearing two methyl groups was tested, the yield of the product **4ja** dropped significantly while the excellent enantioselectivity still remained (Table 3, entry 14).

To demonstrate the generality of the indandione-derived pronucleophiles, we then tested the other Michael acceptor, such as **6a** derived from oxindole, in our preliminary study. When **1a** or **1f** was treated with **6a** under the slightly modified reaction conditions using the catalyst **5d**, the reactions proceeded well and the products were obtained in excellent yields and enantioselectivities (Scheme 3). However, the formation of two diastereomers could be observed in these cases. The relative configuration of **7fa** was established by X-ray crystallography (CCDC no. 1436597).

In summary, we have established indandione derivatives **1a−j** as novel, highly efficient pronucleophiles for the enantioselective VMAs. We can successfully obtain the subsequent cyclization products **3** via a Henry reaction which is an infrequently used transformation involving a ketone. The

DOI: 10.1021/acs.orglett.5b03663
Org. Lett. XXXX, XXX, XXX−XXX

Table 3. Substrate Scope for the Enantioselective VMA[a]

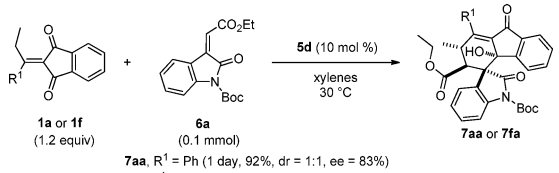


1h-j 2a-x 4ha-4jx

entry	R^1/R^3	time (h)	4, yield[b] (%)	ee[c] (%)
1[d]	Ph/Ph	2	**4ha** (84)	92
2	Ph/*p*-BrPh	1.5	**4hb**[e] (78)	90
3	Ph/*p*-ClPh	1.5	**4hd** (77)	94
4	Ph/*p*-FPh	1.5	**4he** (82)	93
5	Ph/*p*-NO_2Ph	3	**4hf** (86)	90
6	Ph/*p*-CNPh	2	**4hg** (81)	90
7	Ph/*p*-CF_3Ph	2	**4hh** (91)	98
8	Ph/*p*-MePh	2	**4hi** (83)	93
9[d]	Ph/*m*-FPh	5	**4hj** (72)	95
10[d]	Ph/*m*-OMePh	2	**4hk** (80)	95
11[d]	Ph/3,4-OMePh	2	**4hl** (77)	95
12	Ph/2-thienyl	1.5	**4hn** (68)	94
13[d]	*p*-BrPh/Ph	2	**4ia** (80)	83
14[f]	Me/Ph	24	**4ja** (45%)	93

[a]Reaction conditions: 0.11 mmol **1**, 0.1 mmol **2**, 1.0 mL of xylenes, 2.5 mol % of **5f** at 30 °C. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]5 mol % of catalyst was used. [e]The absolute configuration of **4hb** was established by X-ray crystallography (CCDC No. 1429354). [f]20 mol % of catalyst was used.

Scheme 3. Scope of the Enantioselective VMA/Aldol Reaction Cascade with Oxindole Derivative



1a or **1f** (1.2 equiv) **6a** (0.1 mmol) **7aa** or **7fa**

7aa, R^1 = Ph (1 day, 92%, dr = 1:1, ee = 83%)
7fa, R^1 = 2-thienyl (1.5 day, 98%, dr = 2:1, ee = 81%)

largely planar conformation of the nucleophile makes it possible for the catalyst to induce high levels of enantioselectivities. Surprisingly, when 2-(1-phenylethylidene)-1*H*-indandione (**1h**) was used as pronucleophile, only the initial Michael addition adducts **4** were furnished in good yields and with excellent enantiomeric induction. A study is in progress to demonstrate the generality of pronucleophile **1** using other electrophiles, and the results will be published in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b03663.

Experimental procedures, characterization data, and spectra for all compounds (PDF)
Crystallographic data for **3ac** (CIF)
Crystallographic data for **4hb** (CIF)
Crystallographic data for **7fa** (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Ministry of Science and Technology of the Republic of China (MOST 103-2113-M-003-009-MY3) for financial support.

■ REFERENCES

(1) (a) Schneider, C.; Abels, F. *Org. Biomol. Chem.* **2014**, *12*, 3531. (b) Casiraghi, G.; Battistini, L.; Curti, C.; Rassu, G.; Zanardi, F. *Chem. Rev.* **2011**, *111*, 3076. (c) Jusseau, X.; Chabaud, L.; Guillou, C. *Tetrahedron* **2014**, *70*, 2595.

(2) (a) Xiao, X.; Mei, H.; Chen, Q.; Zhao, X.; Lin, L.; Liu, X.; Feng, X. *Chem. Commun.* **2015**, *51*, 580. (b) Yang, D.; Wang, L.; Zhao, D.; Han, F.; Zhang, B.; Wang, R. *Chem. - Eur. J.* **2013**, *19*, 4691. (c) Lin, L.; Zhang, J.; Ma, X.; Fu, X.; Wang, R. *Org. Lett.* **2011**, *13*, 6410. (d) Shepherd, N. E.; Tanabe, H.; Xu, Y.; Matsunaga, S.; Shibasaki, M. *J. Am. Chem. Soc.* **2010**, *132*, 3666.

(3) (a) Zhang, W.; Tan, D.; Lee, R.; Tong, G.; Chen, W.; Qi, B.; Huang, K.-W.; Tan, C.-H.; Jiang, Z. *Angew. Chem., Int. Ed.* **2012**, *51*, 10069. (b) Sekikawa, T.; Kitaguchi, T.; Kitaura, H.; Minami, T.; Hatanaka, Y. *Org. Lett.* **2015**, *17*, 3026. (c) Das, U.; Chen, Y.-R.; Tsai, Y.-L.; Lin, W. *Chem. - Eur. J.* **2013**, *19*, 7713. (d) Chen, Y.-R.; Das, U.; Liu, M.-H.; Lin, W. *J. Org. Chem.* **2015**, *80*, 1985. (e) Huang, H.; Jin, Z.; Zhu, K.; Liang, X.; Ye, J. *Angew. Chem., Int. Ed.* **2011**, *50*, 3232. (f) Rout, S.; Ray, S. K.; Unhale, R. A.; Singh, V. K. *Org. Lett.* **2014**, *16*, 5568. (g) Zhang, J.; Liu, X.; Ma, X.; Wang, R. *Chem. Commun.* **2013**, *49*, 9329. (h) Curti, C.; Rassu, G.; Zambrano, V.; Pinna, L.; Pelosi, G.; Sartori, A.; Battistini, L.; Zanardi, F.; Casiraghi, G. *Angew. Chem., Int. Ed.* **2012**, *51*, 6200. (i) Chen, Q.; Wang, G.; Jiang, X.; Xu, Z.; Lin, L.; Wang, R. *Org. Lett.* **2014**, *16*, 1394.

(4) (a) Li, X.; Lu, M.; Dong, Y.; Wu, W.; Qian, Q.; Ye, J.; Dixon, D. J. *Nat. Commun.* **2014**, *5*, 4479. (b) Joie, C.; Deckers, K.; Raabe, G.; Enders, D. *Synthesis* **2014**, *46*, 1539. (c) Shi, X.-M.; Dong, W.-P.; Zhu, L.-P.; Jiang, X.-X.; Wang, R. *Adv. Synth. Catal.* **2013**, *355*, 3119. (d) Jiang, X.; Liu, L.; Zhang, P.; Zhong, Y.; Wang, R. *Angew. Chem., Int. Ed.* **2013**, *52*, 11329. (e) Xie, J.-W.; Chen, W.; Li, R.; Zeng, M.; Du, W.; Yue, L.; Chen, Y.-C.; Wu, Y.; Zhu, J.; Deng, J.-G. *Angew. Chem., Int. Ed.* **2007**, *46*, 389.

(5) (a) Li, H.; Wang, B.; Deng, L. *J. Am. Chem. Soc.* **2006**, *128*, 732. (b) Christensen, C.; Juhl, K.; Jorgensen, K. A. *Chem. Commun.* **2001**, *21*, 2222. (c) Christensen, C.; Juhl, K.; Hazell, R. G.; Jorgensen, K. A. *J. Org. Chem.* **2002**, *67*, 4875. (d) Matsumoto, K.; Misumi, Y.; Bulman, R. A. *Heterocycles* **2002**, *56*, 599. (e) Du, D.-M; Lu, S.-F.; Fang, T.; Xu, J. *J. Org. Chem.* **2005**, *70*, 3712. (f) Holmquist, M.; Blay, G.; Munoz, M. C.; Pedro, J. R. *Org. Lett.* **2014**, *16*, 1204. (g) Sasai, H. The Henry (Nitroaldol) Reaction. In *Comprehensive Organic Synthesis II*; Knochel, P., Molander, G. A., Eds.; Elsevier: Amsterdam, 2014; p 543.

(6) Luzzio, F. A. *Tetrahedron* **2001**, *57*, 915.

(7) (a) Volla, C. M. R.; Atodiresei, I.; Rueping, M. *Chem. Rev.* **2014**, *114*, 2390. and references therein (b) Tan, B.; Lu, Y.; Zeng, X.; Chua, P. J.; Zhong, G. *Org. Lett.* **2010**, *12*, 2682. (c) Tan, B.; Chua, P. J.; Zeng, X.; Lu, M.; Zhong, G. *Org. Lett.* **2008**, *10*, 3489. (d) Tan, B.; Chua, P. J.; Li, Y.; Zhong, G. *Org. Lett.* **2008**, *10*, 2437. (e) Boyce, G. R.; Johnson, J. S. *Angew. Chem., Int. Ed.* **2010**, *49*, 8930.

(8) Yang, D.; Wang, L.; Han, F.; Zhao, D.; Zhang, B.; Wang, R. *Angew. Chem., Int. Ed.* **2013**, *52*, 6739.

(9) Ramazani, A.; Noshiranzadeh, N.; Mohammadi, B. *Phosphorus, Sulfur Silicon Relat. Elem.* **2003**, *178*, 761.

(10) Following the reaction progress by NMR analysis revealed that **4aa** is converted to **3aa** over time.

(11) Okino, T.; Hoashi, Y.; Takemoto, Y. *J. Am. Chem. Soc.* **2003**, *125*, 12672.

(12) McCooey, S. H.; Connon, S. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6367.

(13) Malerich, J. P.; Hagihara, K.; Rawal, V. H. *J. Am. Chem. Soc.* **2008**, *130*, 14416.

DOI: 10.1021/acs.orglett.5b03663
Org. Lett. XXXX, XXX, XXX−XXX