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Facile Domino Access to Chiral Bicyclo[3.2.1]octanes and Discovery of a New Catalytic Activation Mode

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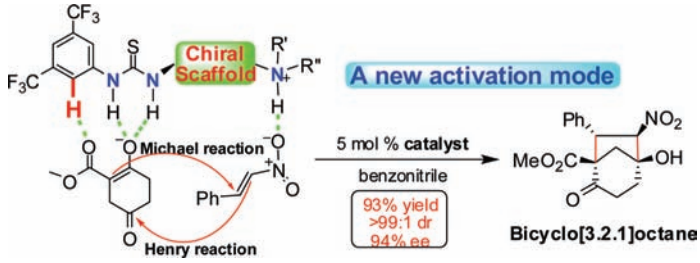
ABSTRACT



A highly enantio- and diastereoselective organocatalytic domino Michael−Henry process for the preparation of synthetically unique and medicinally important bicyclo[3.2.1]octane derivatives with four stereogenic centers including two quaternary stereocenters has been developed. Theoretical DFT calculations on the transition states have been carried out to reveal origins of the excellent stereoselectivities. A novel dual model was thus proposed.

Bicyclo[3.2.1]octane skeletons are found in a number of interesting natural products and pharmaceuticals[1] such as Trichorabdal B, Kadsurenin C and L, Piersformoside, Platensimysin, and Platencin (Figure 1). For example, Platencin which was isolated from *Streptomyces platensis* MA7339, can inhibit the biosynthesis of bacterial fatty acids through binding with the initiation condensing and elongation condensing enzymes FabH.[2] In 2008, Nicolaou[2b,c] and Rawal[2d] reported the total synthesis of this compound, involving a metal-catalyzed Diels−Alder reaction to construct the bicyclo[3.2.1]octane skeletons. The stereochemical importance of this structural motif in biological activity is significant, and it represents a considerable synthetic challenge that remained to be addressed in preparative studies.[3] It is therefore crucial to create an efficient synthetic route to this skeleton.

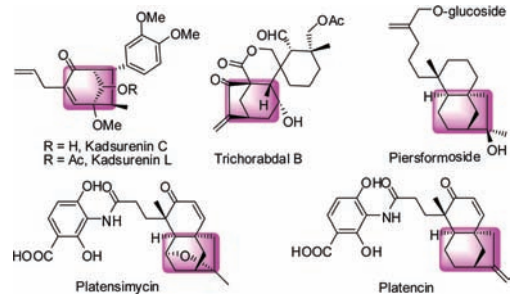


Figure 1. Natural products containing bicyclo[3.2.1]octanes.

Domino reactions serve as a powerful tool for the rapid and efficient assembly of complex structures from simple starting materials with minimized waste production.[4] Organocatalytic[5] enantioselective domino processes[6] are particu-

(1) (a) Fujita, K.; Node, M.; Sai, M.; Fujita, E.; Shingu, T.; Watson, W. H.; Grossie, D. A.; Zabel, V. *Chem. Pharm. Bull* **1989**, *37*, 1465. (b) Han, G.; Dai, P.; Xu, L.; Wang, S.; Zheng, Q. *Chin. Chem. Lett.* **1992**, *3*, 521. (c) Li, L.; Weng, Z.; Huang, S.; Pu, J.; Li, S.; Huang, H.; Yang, B.; Han, Y.; Xiao, W.; Li, M.; Han, Q.; Sun, H. *J. Nat. Prod.* **2007**, *70*, 1295. (d) Ma, Y.; Han, G.; Liu, Z. *Yaoxue Xuebao* **1993**, *28*, 307. (e) Filippini, M. H.; Rodriguez, J. *Chem. Rev.* **1999**, *99*, 27.

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larly appealing because of their operational simplicity and environmental friendliness. Although much progress has been made in the organocatalytic domino reactions,[7] the construction of bicyclo[3.2.1]octane skeletons still remains elusive, and the development of new methodologies for the generation of molecules with multiple stereogenic carbons including quaternary centers[8] in a cascade manner remains a big challenge at the forefront of synthetic organic chemistry.

The Michael and Henry reactions are widely recognized as among the most important C−C bond-formation processes in organic chemistry, as they are versatile tools to assemble multisubstituted carbon skeletons[9] and transform nitroaldol products into a number of nitrogen- and oxygen-containing derivatives.[10] However, to our knowledge, there is no report describing the formation of two quaternary centers in the asymmetric synthesis of the bicyclo[3.2.1] motif using a domino Michael−Henry reaction strategy with good results. Herein, we discovered an organocatalytic enantioselective domino Michael−Henry reaction to afford highly functionalized bicyclo[3.2.1]octanes with four stereogenic centers including two quaternary carbons.

Readily accessible cinchona alkaloids and derivatives, which were developed recently in several research groups, have been identified as efficient bifunctional organocatalysts in an asymmetric Michael reaction,[11] Henry reactions,[12] and domino Michael−Henry reactions.[13] These results prompted us to explore the feasibility of employing quinine amine catalyst **I** to catalyze the domino Michael−Henry reaction involving a nitroolefin and a designed carbon nucleophiles **1a**. To our delight, the desired product was obtained in good yield and with moderate enantioselectivity (40% ee). Encouraged by this initial results, several cinchona alkaloid derived catalysts (Figure 2) were investigated and displayed noteworthy effects on the outcome of the domino reaction. Thiourea catalysts generally afforded better results in yields and stereoselectivities. Various solvents were screened, and it was found that the more polar solvent benzonitrile resulted in a higher enantioselectivity while maintaining the activity of the catalyst. We next investigated the influence of the reaction temperature and catalyst loading. It was observed that the reactions were not affected by changing reaction temperatures, unlike most reactions where lower temperatures usually led to higher enantioselectivies and lower reaction rates (Table 1, entries 11 and 12). However, lower catalyst

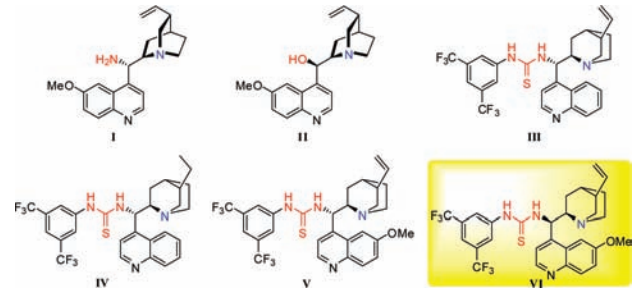


Figure 2. Structures of cinchona alkaloid derived catalysts.

(2) (a) Jayasuriya, H.; Herath, K. B.; Zhang, C.; Zink, D. L.; Basilio, A.; Genilloud, O.; Teresa Diez, M.; Vicente, F.; Gonzalez, I.; Salazar, O.; Pelaez, F.; Cummings, R.; Ha, S.; Wang, J.; Singh, S. B. *Angew. Chem., Int. Ed.* **2007**, *46*, 4684. (b) Nicolaou, K. C.; Pappo, D.; Tsang, K. Y.; Gibe, R.; Chen, D. Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 944. (c) Nicolaou, K. C.; Toh, Q.; Chen, D. Y. *J. Am. Chem. Soc.* **2008**, *130*, 11292. (d) Hayashida, J.; Rawal, V. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 4373. (e) Kim, C. H.; Jang, K. P.; Choi, S. Y.; Chung, Y. K.; Lee, E. *Angew. Chem., Int. Ed.* **2008**, *47*, 4009. (f) Li, P.; Payette, J. N.; Yamamoto, H. *J. Am. Chem. Soc.* **2007**, *129*, 9534.

(3) (a) Buchi, G.; Mak, C. P. *J. Am. Chem. Soc.* **1977**, *99*, 8073. (b) Engler, T. A.; Wei, D.; Letavic, M. A. *Tetrahedron Lett.* **1993**, *34*, 1429. (c) Wang, M.; Wu, A.; Pan, X.; Yang, H. *J. Org. Chem.* **2002**, *67*, 5405.

(4) (a) Wasilke, J. C.; Obrey, S. J.; Baker, R. T.; Bazan, G. C. *Chem. Rev.* **2005**, *105*, 1001. (b) Tietze, L. F. *Chem. Rev.* **1996**, *96*, 115. (c) Nicolaou, K. C.; Edmonds, D. J.; Bulger, P. G. *Angew. Chem., Int. Ed.* **2006**, *45*, 7134.

(5) (a) List, B. *Chem. Commun.* **2006**, 819. (b) Gaunt, M. J.; Johnsson, C. C.; McNally, A.; Vo, N. T. *Drug Discovery Today* **2007**, *12*, 8. (c) Barbas, C. F., III *Angew. Chem., Int. Ed.* **2008**, *47*, 42. (d) Dondoni, A.; Massi, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 4638. (e) Melchiorre, P.; Marigo, M.; Carlone, A.; Bartoli, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 6138. (f) Kano, T.; Maruoka, K. *Chem. Commun.* **2008**, 5465.

(6) (a) Tietze, L. F.; Brasche, G.; Gericke, K. *Domino Reactions in Organic Synthesis*; Wiley-VCH: Weinheim, 2006. For reviews, see: (b) Enders, D.; Grondal, C.; Huttl, M. R. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 1570. (c) Yu, X.; Wang, W. *Org. Biomol. Chem.* **2008**, *6*, 2037.

(7) For selected examples of organocatalytic asymmetric domino reactions, see: (a) Ramachary, D. B.; Chowdari, N. S.; Barbas, C. F., III *Angew. Chem., Int. Ed.* **2003**, *42*, 4233. (b) Yang, J. W.; Fonseca, M. T. H.; List, B. *J. Am. Chem. Soc.* **2005**, *127*, 15036. (c) Huang, Y.; Walji, A. M.; Larsen, C. H.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2005**, *127*, 15051. (d) Marigo, M.; Schulte, T.; Franzen, J.; Jørgensen, K. A. *J. Am. Chem. Soc.* **2005**, *127*, 15710. (e) Enders, D.; Hüttl, M. R. M.; Grondal, C.; Raabe, G. *Nature* **2006**, *441*, 861. (f) Wang, W.; Li, H.; Wang, J.; Zu, L. *J. Am. Chem. Soc.* **2006**, *128*, 10354. (g) Carlone, A.; Cabrera, S.; Marigo, M.; Jørgensen, K. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 1101. (h) Li, H.; Wang, J.; Xie, H.; Zu, L.; Jiang, W.; Duesler, E. N.; Wang, W. *Org. Lett.* **2007**, *9*, 965. (i) Hayashi, Y.; Okano, T.; Aratake, S.; Hazelard, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 4922. (j) Reyes, E.; Jiang, H.; Milelli, A.; Elsner, P.; Hazell, R. G.; Jørgensen, K. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 9202. (k) Zu, L.; Wang, J.; Li, H.; Xie, H.; Jiang, W.; Wang, W. *J. Am. Chem. Soc.* **2007**, *129*, 1036. (l) Momiyama, N.; Yamamoto, Y.; Yamamoto, H. *J. Am. Chem. Soc.* **2007**, *129*, 1190. (m) Zhu, D.; Lu, M.; Chua, P. J.; Tan, B.; Wang, F.; Yang, X.; Zhong, G. *Org. Lett.* **2008**, *10*, 4585. (n) Lu, M.; Zhu, D.; Lu, Y.; Hou, Y.; Tan, B.; Zhong, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 10187. (o) Tan, B.; Shi, Z.; Chua, P. J.; Li, Y.; Zhong, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 758. (p) Liu, Y.; Ma, C.; Jiang, K.; Liu, T.; Chen, Y. *Org. Lett.* **2009**, *11*, 2848. (q) Sun, F.; Zeng, M.; Gu, Q.; You, S.-L. *Chem.—Eur. J.* **2009**, *15*, 8709.

(8) (a) Rios, R.; Sundln, H.; Vesely, J.; Zhao, G.; Dziedzic, P.; Cordova, A. *Adv. Synth. Catal.* **2007**, *349*, 1028. (b) Penon, O.; Carlone, A.; Mazzanti, A.; Locatelli, M.; Sambri, L.; Bartoli, G.; Melchiorre, P. *Chem.—Eur. J.* **2008**, *14*, 4788. (c) Enders, D.; Wang, C.; Bats, J. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 7539.

(9) For selected reviews, see: (a) Koichi, M.; Terada, M.; Hiroshi, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3554. (b) Tsogoeva, S. B. *Eur. J. Org. Chem.* **2007**, 1701. (c) Almasi, D.; Alonso, D. A.; Najera, C. *Tetrahedron: Asymmetry* **2007**, *18*, 299.

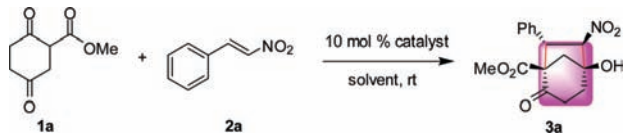
(10) (a) Ono, N. *The Nitro Group in Organic Synthesis*; Wiley-VCH: Weiheim, Germany, 2001. (b) Palomo, C.; Oiarbide, M.; Laso, A. *Eur. J. Org. Chem.* **2007**, 2561.

(11) For cinchona-derived catalysts, see: (a) Tian, S.; Chen, Y.; Hang, J.; Tang, L.; McDaid, P.; Deng, L. *Acc. Chem. Res.* **2004**, *37*, 621. (b) Ye, J.; Dixon, D. J.; Hynes, P. S. *Chem. Commun.* **2005**, 4481. (c) Vakulya, B.; Varga, S.; Csampai, A.; Soos, T. *Org. Lett.* **2005**, *7*, 1967. (d) Tillman, A. L.; Ye, J.; Dixon, D. J. *Chem. Commun.* **2006**, 1191. (e) Mattson, A. E.; Zuhl, A. M.; Reynolds, T. E.; Scheidt, K. A. *J. Am. Chem. Soc.* **2006**, *128*, 4932. (f) McCooey, S. H.; Connon, S. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6367. (g) France, S.; Shah, M. H.; Weatherwax, A.; Wack, H.; Roth, J. P.; Lectka, T. *J. Am. Chem. Soc.* **2005**, *127*, 1206. (h) Taggi, A. E.; Hafez, A. M.; Wack, H.; Young, B.; Drury, W. J., III; Lectka, T. *J. Am. Chem. Soc.* **2000**, *122*, 7831.

(12) (a) Marcelli, T.; van der Haas, R. N. S.; van Maarseveen, J. H.; Hiemstra, H. *Angew. Chem., Int. Ed.* **2006**, *45*, 929. (b) Li, H.; Wang, B.; Deng, L. *J. Am. Chem. Soc.* **2006**, *128*, 732.

(13) (a) Tan, B.; Chua, P. J.; Li, Y.; Zhong, G. *Org. Lett.* **2008**, *10*, 2437. (b) Tan, B.; Chua, P. J.; Zeng, X.; Lu, M.; Zhong, G. *Org. Lett.* **2008**, *10*, 3489.

Table 1. Organocatalytic Domino Michael−Henry Reactions of Trisubstituted Carbon Nucleophiles and *trans*-β-Nitrostyrene[a]



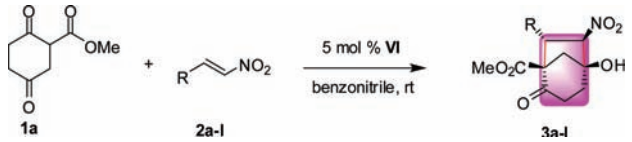
entry	catalyst	solvent	time (h)	yield (%)[b]	dr[c]	ee (%)[d]
1	**I**	toluene	12	73	>99:1	−40
2	**II**	toluene	12	78	>99:1	50
3	**III**	toluene	4	85	>99:1	−80
4	**IV**	toluene	4	90	>99:1	−89
5	**V**	toluene	4	87	>99:1	−89
6	**VI**	toluene	6	86	>99:1	92
7	**VI**	Et_2O	4	89	>99:1	92
8	**VI**	*m*-xylene	4	88	>99:1	90
9	**VI**	nitrobenzene	4	91	>99:1	90
10	**VI**	benzonitrile	4	91	>99:1	94
11[e]	**VI**	benzonitrile	8	89	>99:1	94
12[e]	**V**	benzonitrile	8	86	>99:1	−92
13[f]	**VI**	benzonitrile	6	91	>99:1	94
14[g]	**VI**	benzonitrile	10	83	>99:1	93

[a] Unless otherwise specified, the reactions were carried out using **1a** (0.2 mmol, 2.0 equiv) and **2a** (0.1 mmol, 1.0 equiv) with 10 mol % of catalysts in 0.5 mL of solvent at room temperature (23 °C). [b] Isolated yields. [c] Determined by NMR and HPLC analysis. [d] Determined by chiral HPLC analysis. [e] Reaction at 4 °C. [f] 5 mol % catalyst. [g] 3 mol % catalyst.

loadings did lead to longer reaction times (Table 1, entries 13 and 14), and using **V** or **VI** could produce both enantiomers.

In our exploratory effort, this new methodology not only provides a facile access to a range of multisubstituted bicyclo[3.2.1]octane derivatives but also serves as a facile approach for the preparation of a range of substituted bicycles containing four chiral centers in excellent enantiomeric exesses (90−96% ee) and diastereoselectivities (>99:1 dr in all cases) (Table 2). The **VI**-promoted domino Michael−Henry process takes place with a variety of nitroolefin Michael acceptors, which possess neutral, electron-donating, electron-withdrawing groups in the phenyl ring (Table 2, entries 1−8 and 11−12). It appeared that substituents' electronic and steric natures have minimal impact on efficiencies, enantioselectivities, and diastereoselectivities of the Michael−Henry reactions. Not only aromatic groups but also heteroaromatic groups such as furyl and thienyl could be successfully employed to afford the respective cyclopentane rings with excellent stereoselectivities (Table 2, entries 9 and 10). Notably, only one Michael−Henry adduct was obtained from the reaction of nitrodiene **2m** in 86% ee (Scheme 1).

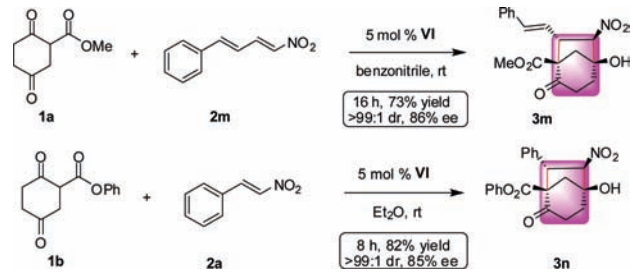
Table 2. Domino Michael−Henry Reactions of **1a** and Nitroolefins **2** Catalyzed by Catalyst **VI**[a]



entry	R	**3**	time (h)	yield (%)[b]	dr[c]	ee (%)[d]
1	Ph	**3a**	6	93	>99:1	94
2	3-OMe-Ph	**3b**	10	84	>99:1	95
3	4-OMe-Ph	**3c**	10	79	>99:1	90
4	4-Me-Ph	**3d**	8	91	>99:1	93
5	4-Br-Ph	**3e**	6	87	>99:1	94
6	2-Cl-Ph	**3f**	6	86	>99:1	96
7	4-Cl-Ph	**3g**	6	93	>99:1	95
8	4-F-Ph	**3h**	6	88	>99:1	94
9	2-thienyl	**3i**	8	80	>99:1	92
10	2-furyl	**3j**	6	84	>99:1	92
11	1-naphthyl	**3k**	12	85	>99:1	94
12	4-NO_2-Ph	**3l**	12	77	>99:1	93

[a] All the reactions were carried out using **1a** (0.2 mmol, 2 equiv) and **2** (0.1 mmol, 1.0 equiv) in the presence of 5 mol % of **VI** at rt with benzonitrile (0.5 mL). [b] Isolated yields. [c] Determined by NMR and HPLC analysis. [d] Determined by chiral HPLC analysis.

Scheme 1. Domino Michael−Henry Reactions of **1a** with **2m** and **1b** with **2a**



Although both β- and δ-positions of **2m** can possibly be theoretically attacked because of the two congruous double bonds, the formation of only one adduct showed the great regioselectivity and stereoselectivity of this methodology. Furthermore, the domino reaction also proceeded smoothly when **1a** was replaced by **1b**, giving good enantio- (85% ee) and diastereoselectivities (>99:1 dr) as displayed in Scheme 1.

According to the dual activation model, the two substrates involved in the reaction are activated simultaneously by catalyst[14] as shown in Figure 3a. Nitroolefins have been assumed to interact with the amine moiety of the thiourea

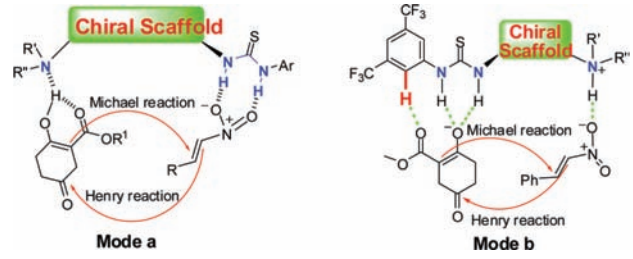


Figure 3. Proposed activation modes of the catalyst and substrates before (a) and after (b) the DFT calculations.

on the catalyst via multiple H-bondings, thus enhancing the electrophilic character of the reacting carbon center. However, the enolic form is assumed to interact with the tertiary amine group, and a subsequent Henry reaction results in a stereocontolled product. The absolute configuration of **3f** was determined by X-ray analysis (see Supporting Information), presenting in accordance with our prediction the relative structure anticipated from the catalytic mechanism.

To provide theoretical insight on the high diastereo- and enantioselectivity of this reaction, a systematic conformational analysis of transition states were investigated with density functional theory (DFT) calculations. The relative energies of the different transition state were then used to predict the product ratios (see Supporting Information).[15]

There should be many possible conformational isomers for the transition state due to its flexibility. Based on a systematic conformational search (see Figure in Supporting Information), eight possible transition states have been optimized for the Michael addition catalyzed by the catalyst **VI**. The best transition state is **TS-6** (Figure 4 right), which

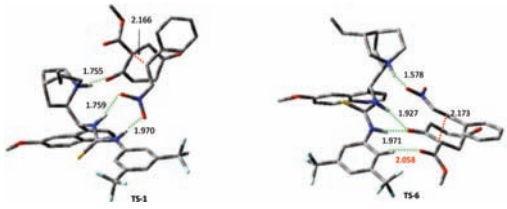


Figure 4. Typical transition states (**TS-1** and **TS-6**) using thiourea catalyst **VI** by DFT calculation.

is in accordance with the major product isolated during the experiment. In **TS-6**, both the 1,3-dicarbonyl group and nitroolefin were bonded to the catalyst **VI** simultaneously through hydrogen bondings. However, unlike the "dual activation model" in Figure 3a, the nitro group was activated by the tertiary amine group, and the enolic ester part was activated by the thiourea group. The enolic ester part and the thiourea unit showed an almost coplanar structure, and this gave rise to a concerted hydrogen bonding network where the steric hindrance is minimized. This was also consistent with the previous theoretical calculation results.[16] More importantly, there was a hydrogen bond between hydrogen in the phenyl group and ester group (O···H 2.058 Å). Because of the existence of the two CF_3 groups, the acidity of the hydrogen atom in the phenyl group was increased significantly, and they were keener to form hydrogen bonds with nucleophilic atoms, such as oxygen. We found out that in the **TS-6** enolic ester substrate was firmly bound to catalyst **VI** and the proton in the tertiary amine was largely transferred to the nitro group as is shown by the N−H bond distance (1.070 Å). The formation of the (*R*,*S*)- enantiomer was favored by 5.71 kcal/mol (Table 3 in Supporting Information) when compared to the (*S*,*R*)-enantiomer, which supported the high stereoselectivity observed in the experiment. Transition state **TS-1** (Figure 4 left) was coincided with the "dual activation model",[17] as the enolic ester part was bound to the tertiary amine group and the nitro group was bound to the thiourea unit. However, **TS-6** not only has the most number of hydrogen bonding between the thiourea moiety and the enolic ester part when compared to the other transition states, it also exhibits hydrogen bonding between hydrogen in the phenyl group and ester group that plays a crucial role in determining the stereoselectivities of the Michael adduct. In addition, we find that a proton transfer from the coordinated enol to the amine group of the catalyst can easily take place, which is displayed clearly in Figure 4.

We thus proposed a new catalytic model for this domino Michael−Henry reaction (Figure 3b). In this model, the thiourea group and an acidic proton in the phenyl ring activates the 1,3-dicarbonyl substrates together, and at the same time a tertiary amine activates the nitro group, which promotes the domino reaction smoothly with excellent stereoselectivity. The novel model may direct the future design of bifunctional catalysts.

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Supporting Information Available: Experimental procedures, characterization, spectra, chiral HPLC conditions and X-ray crystallographic data (CIF file of **3f**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Okino, T.; Hoashi, Y.; Furukawa, T.; Xu, X.; Takemoto, Y. *J. Am. Chem. Soc.* **2005**, *127*, 119.

(15) For recent reports involving theoretical calculations on organocatalysis, see: (a) Bahmanyar, S.; Houk, K. N. *J. Am. Chem. Soc.* **2001**, *123*, 11273. (b) Bahmanyar, S.; Houk, K. N.; Martin, H. J.; List, B. *J. Am. Chem. Soc.* **2003**, *125*, 2475. (c) Bahmanyar, S.; Houk, K. N. *Org. Lett.* **2003**, *5*, 1249. (d) Iwamura, H.; Wells, D. H., Jr.; Mathew, S. P.; Klussmann, M.; Armstrong, A.; Blackmond, D. G. *J. Am. Chem. Soc.* **2004**, *126*, 116312. (e) Cheong, P. H.-Y.; Zhang, H.; Thayumanavan, R.; Tanaka, F.; Houk, K. N.; Barbas, C. F., III *Org. Lett.* **2006**, *8*, 811. (f) Cabrera, S.; Reyes, E.; Aleman, J.; Milelli, A.; Kobbelgaard, S.; Jørgensen, K. A. *J. Am. Chem. Soc.* **2008**, *130*, 12031. (g) Chen, X.; Wei, Q.; Luo, S.; Xiao, H.; Gong, L. *J. Am. Chem. Soc.* **2009**, *131*, 13819. (h) Cao, C.; Zhou, Y.; Zhou, J.; Sun, X.; Tang, Y.; Li, Y.; Li, G.; Sun, J. *Chem.—Eur. J.* **2009**, *15*, 11384. (i) Xia, Y.; Liang, Y.; Chen, Y.; Wang, M.; Jiao, L.; Huang, F.; Liu, S.; Li, Y.; Yu, Z.-X. *J. Am. Chem. Soc.* **2007**, *129*, 3470. (j) Liang, Y.; Liu, S.; Xia, Y.; Li, Y.; Yu, Z.-X. *Eur. J. Chem.* **2008**, *14*, 4361.

(16) Hamza, A.; Schubert, G.; Soos, T.; Papai, I. *J. Am. Chem. Soc.* **2006**, *128*, 13151.

(17) (a) Tan, B.; Zhang, X.; Chua, P. J.; Zhong, G. *Chem. Commun.* **2009**, 779. (b) Tan, B.; Shi, Z.; Chua, P. J.; Zhong, G. *Org. Lett.* **2008**, *10*, 3425.