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Enantioselective Organocatalytic Michael−Wittig−Michael−Michael Reaction: Dichotomous Construction of Pentasubstituted Cyclopentanecarbaldehydes and Pentasubstituted Cyclohexanecarbaldehydes

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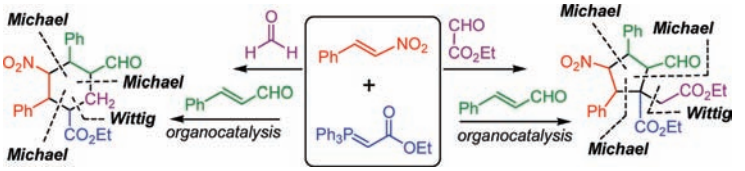
ABSTRACT



Michael addition of carbethoxymethylenetriphenylphosphorane (a Wittig reagent) to nitroalkenes, followed by a reaction with ethyl formylformate and cinnamaldehydes, or formaldehyde and cinnamaldehydes, provided the respective pentasubstituted cyclopentanecarbaldehydes bearing a quaternary carbon center and pentasubstituted cyclohexanecarbaldehydes having five contiguous stereocenters with excellent enantioselectivities (up to >99% ee).

The recent impressive progress made in organocatalysis via cascade, tandem, domino,[1,2] or sequential reaction sequences has driven synthetic chemists to develop new procedures and methodologies for producing diverse arrays of compounds in an enantioselective and efficient manner. Among the strategies demonstrated, several are noteworthy, including multicomponent reactions,[3] stereoselective synthesis of quaternary carbons, and the construction of poly contiguous stereocenters in a stereoselective manner,[4] especially of those bearing a quaternary carbon center.[5] Moreover, polysubstituted cyclopentanes and cyclohexanes are prevalent in natural products that display biological activities, and their derivatives have long served as important intermediates in organic synthesis.[6] Despite the successes in the approaches to these systems, a diverse synthesis providing the cyclopentane and cyclohexane derivatives with multifunctionality, quaternary carbon centers, and poly contiguous stereocenters with excellent enantioselectivities remains a compelling area of investigation. As an extension of our efforts in developing organocatalytic annulations,[7] we envisaged a strategy that involved an enantioselective organocatalytic Michael−Wittig−Michael−Michael reaction, Scheme 1, which in turn would afford pentasubstituted cyclopentanecarbaldehydes bearing a quaternary carbon center and pentasubstituted cyclohexanecarbaldehydes having five

(1) For recent reviews see: (a) Alba, A.-N.; Companyo, X.; Viciano, M.; Rios, R. *Curr. Org. Chem.* **2009**, *13*, 1432. (b) Enders, D.; Grondal, C.; Hüttl, M. R. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 1570. (c) Poisson, T. *Synlett* **2008**, 147. (d) Walji, A. M.; MacMillan, D. W. C. *Synlett* **2007**, 1477.

(2) For selected recent examples of organocatalytic cascade/domino reactions, see: (a) Wang, C.; Han, Z.-Y.; Luo, H.-W.; Gong, L.-Z. *Org. Lett.* **2010**, *12*, 2266. (b) Zhang, F.-L.; Xu, A.-W.; Gong, Y.-F.; Wei, M.-H.; Yang, X.-L. *Chem.—Eur. J.* **2009**, *15*, 6815. (c) Franzeén, J.; Fisher, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 787. (d) Zhao, G.-L.; Vesely, J.; Rios, R.; Ibrahem, I.; Sunden, H.; Cordova, A. *Adv. Synth. Catal.* **2008**, *350*, 237. (e) Hazelard, D.; Ishikawa, H.; Hashizume, D.; Koshino, H.; Hayashi, Y. *Org. Lett.* **2008**, *10*, 1445. (f) Penon, O.; Carlone, A.; Mazzanti, A.; Locatelli, M.; Sambri, L.; Bartoli, G.; Melchiorre, P. *Chem.—Eur. J.* **2008**, *14*, 4788. (g) Carlone, A.; Cabrera, S.; Marigo, M.; Jørgenson, K. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 1101. (h) Enders, D.; Hüttl, M. R. M.; Runsink, J.; Raabe, G.; Wendt, B. *Angew. Chem., Int. Ed.* **2007**, *46*, 467. (i) Zhou, J.; List, B. *J. Am. Chem. Soc.* **2007**, *129*, 7498. (j) Beeson, T. D.; Mastracchio, A.; Hong, J.-B.; Ashton, K.; MacMillan, D. W. C. *Science* **2007**, *316*, 582.

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contiguous stereocenters, both with excellent enantioselectivities.

We began by embarking on the asymmetric domino-Michael reactions toward racemic **7a**, prepared from the reaction of (±)-**3a** and formylformate with cinnamaldehyde. To our delight, the reaction with the Jørgensen−Hayashi catalyst **I** and HOAc in $CHCl_3$ at ambient temperature for 48 h provided a 1:1 diastereomeric ratio of *anti*-**8a** and *syn*-**8a** in 94% yield, both with 99% ee (Table 1, entry 1). To optimize the reaction, we screened various organocatalysts, solvents, additives, and reaction conditions. The reaction in CH_2Cl_2 gave similar yield (91%) and enantioselectivity (99% ee) but was somewhat slower to reach completion (Table 1, entry 2). Conducting the same reaction in other solvents (e.g., CH_3CN, THF, EtOH, DMF, and EtOAc) afforded lower yields and required longer reaction times (Table 1, entries 3−8). Notably, the reaction in EtOH did not need an acid additive (HOAc) for the reaction and was completed in 83 h, however, with somewhat lower yield (59%) (Table 1, entry 8). Furthermore, the reactions with catalyst **III** in the presence or the absence of additive TEA afforded very low yields (Table 1, entries 9 and 10). Reaction with pyrrolidine (**II**)-HOAc gave lower yields (33%) but provided the racemic products that served as suitable standards for HPLC analysis in determining the ee values. Apparently, the original procedure provides the best conditions for the reaction (Table 1, entry 1). The structure of *anti*-**8a** was assigned by the single-crystal X-ray analysis of the corresponding alcohol (+)-**9** (Figure 1), obtained by the treatment of *anti*-**8a** with $NaBH_4$ (0 °C to rt, 6 h, 68% yield).

Scheme 1. Plan for the Dichotomous Synthesis

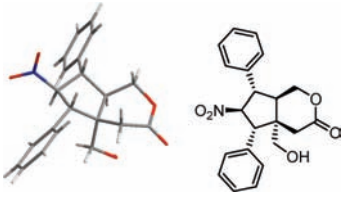
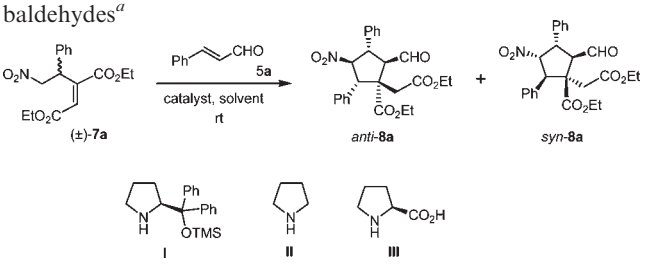


Figure 1. Stereo plots of the X-ray crystal structures of (+)-**9**: C, gray; N, blue; O, red.

On the other hand, the approach to the cyclohexanecarboxylates from racemic **4a**, prepared from (±)-**3a** and formaldehyde with cinnamaldehyde via double Michael reactions, was conducted with catalyst **I**−HOAc in $CHCl_3$ at ambient temperature for 56 h, followed by the reduction with $NaBH_4$ in EtOH to give a 1:2 ratio of *syn*-**6a** and *anti*-**6a** in 74% yields with 95% ee (Table 2, entry 1). Owing to the 1:2 ratio of the diastereoisomeric products, a moderate kinetic asymmetric transformation (KAT) took place in this reaction. In fact, the occurrence of KAT was further supported by the fact that an enantiomeric excess of 79% for the recovered (*R*)-**4a** was observed after the reaction of (±)-**4a** with 0.7 equiv of (*E*)-3-(4-bromophenyl)acrylaldehyde (**5b**).[8] The originally formed cyclohexanecarbaldehydes were somewhat unstable during the isolation and purification process; therefore, the reaction adducts were immediately reduced by $NaBH_4$ to the corresponding alcohol, and the ee values were determined on the major isomeric alcohol (*anti*-**6a**). The reaction in CH_3CN was completed in a short period of time (48 h) and with higher yields (79%) with the same 1:2 isomeric ratio of the alcohol products (Table 2, entry 2). The reactions in other solvents (e.g., toluene, CH_2Cl_2, THF, DMF, and EtOH) afforded lower yields and/or lower stereoselectivities (Table 2, entries 3−7). Replacement of HOAc by another acid (e.g., PNBA) gave a lower yield (Table 2, entry 8).

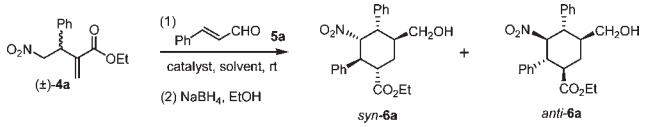
Table 1. Screening of Catalyst, Solvent, and Reaction Conditions for the Synthesis of Pentasubstituted Cyclopentanecarbaldehydes[a]



entry	catalyst−additive	solvent	time (h)	yield (%)[b]	ee (%)[c]
1	**I**−AcOH	$CHCl_3$	48	94	99, (99)[d]
2	**I**−AcOH	CH_2Cl_2	54	91	99
3	**I**−AcOH	toluene	72	83	nd
4	**I**−AcOH	CH_3CN	96	51	nd
5	**I**−AcOH	THF	96	32	nd
6	**I**−AcOH	DMF	96	8	nd
7	**I**−AcOH	EtOAc	96	15	nd
8	**I**	EtOH	83	59	nd
9	**III**	CH_3CN	96	5	nd
10	**III**−TEA	CH_3CN	96	10	nd
11	**II**−AcOH	$CHCl_3$	60	33	0

[a] Unless otherwise noted, the reactions were performed in 0.5 M (±)-**7a** at 25 °C. [b] A 1:1 ratio of *anti*-**8a**:*syn*-**8b** was obtained in all cases, as determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Unless otherwise noted, the ee of *anti*-**8a** was determined by HPLC with a chiral column (Chiralpak IC). [d] The ee of *syn*-***8a*** in parentheses was determined by HPLC with a chiral column (Chiralpak IC). nd: not determined.

Table 2. Screening of Catalyst, Solvent, and Reaction Conditions for the Synthesis of Pentasubstituted Cyclohexanecarboxylates[a]



entry	catalyst−additive	solvent	time (h)	yield[b] (%)	dr[c]	ee (%)[d]
1	**I**−AcOH	$CHCl_3$	56	74	1:2	95
2	**I**−AcOH	CH_3CN	48	79	1:2	96
3	**I**−AcOH	toluene	60	57	1:3	nd
4	**I**−AcOH	CH_2Cl_2	50	78	1:2	84
5	**I**−AcOH	THF	60	58	1:1	nd
6	**I**−AcOH	DMF	72	9	nd	nd
7	**I**	EtOH	72	64	1:1	nd
8	**I**−PNAB	CH_3CN	72	8	nd	nd
9	**I**−DABCO	$CHCl_3$	56	66	1:3.5	63
10	**I**−DBU	CH_3CN	72	5	nd	nd
11	**I**−sparteine	CH_3CN	72	23	nd	nd
12	**II**−AcOH	CH_3CN	48	76	1:9	0
13	**III**	CH_3CN	96	5	nd	nd
14	**III**−Et_3N	CH_3CN	96	11	nd	nd

[a] Unless otherwise noted, the reactions were performed in 0.5 M (±)-**4a** at 25 °C. [b] Total yields for the double Michael reactions and $NaBH_4$ reduction. [c] *syn:anti*. Determined by ^1H NMR analysis of the crude reaction mixture. [d] The ee of *anti*-**6a**, determined by chiral column (Chiralpak IC) of their corresponding alcohol. nd: not determined; na: not available; DABCO: 1,4-diazabicyclo[2.2.2]octane; DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene; PNBA: 4-nitrobenzoic acid.

Substitution of HOAc with base (e.g., DABCO and DBU) in the reaction preferentially provided the product *anti*-**6a**, although with lower yields and ee value (for DABCO) or much lower yields (for DBU and sparteine) (Table 2, entries 9−11). Reaction with pyrrolidine (**II**)-AcOH afforded the products with excellent diastereoselectivity (9:1), (Table 2, entry 12). As noted previously, the reactions with catalyst **III** afforded very low yields (Table 2, entries 13 and 14).

Although the optimal reaction conditions for higher yields and enantioselectivities for this dichotomous reaction have been determined, we wanted to achieve better diastereoselectivities to improve this asymmetric synthesis. Accordingly, use of the optically enriched **3a** appeared to be a solution. Enantioselective conjugate addition of stabilized phosphorus ylides to nitroalkenes followed by proton transfer to give chiral functionalized P-ylides had not been previously disclosed until our recent observation in the study of organocatalytic [1 + 2 + 3] annulation.[9] After extensive screening a series of organocatalysts in the enantioselective addition reaction, we observed the successful reaction with catalyst **IV** (20 mol %, CH_3CN, −40 °C, 4 d) to afford 51% ee of (*R*)-**3a**.[10] To our surprise, the reaction with the monosubstituted thiourea catalyst **V** not only provided the enantioselective **3a**, but the product displayed inverse enantioselectivity to give (*S*)-**3a**, as opposed to the disubstituted thiourea catalyst **IV**.[11] Various reaction conditions were screened, and the best result was obtained with 60% ee by slow addition of the stabilized phosphorus ylides **2** to a mixture of nitroalkene **1a** and catalyst **VI** (20 mol %) in $CHCl_3$ over 8 h at −40 °C, followed by the reaction at the same temperature for an additional 72 h. Treatment of (*R*)-**3a** (60% ee), prepared using the monothiourea catalyst **VI**, with formylformate, followed by the addition of cinnamaldehyde (**5a**) and catalyst **I**−HOAc (20 mol %) in $CHCl_3$, provided *anti*-**8a** and *syn*-**8a** with much better dr (*anti*:*syn* = 3.7:1) in 94% total yields, (Table 3, entry 1). Having established the optimal reaction conditions, we studied the use of different α,β-unsaturated aldehydes to synthesize a variety of pentasubstituted cyclopentanecarbaldehydes (Table 3, entries 2−9). These adducts were in all cases isolated in good yields (more than 90% yields in many cyclopentanecarbaldehyde examples), good dr, and with high enantioselectivities (>99% ee).[12] On the other hand,

(3) For a review of natural product synthesis using multicomponent reaction strategies, see: (a) Touré, B. B.; Hall, D. G. *Chem. Rev.* **2009**, *109*, 4439. Select examples: (b) Enders, D.; Narine, A. A. *J. Org. Chem.* **2008**, *73*, 7857. (c) Jiang, H.; Nielsen, J. B.; Nielsen, M.; Jørgensen, K. A. *Chem.—Eur. J.* **2007**, *13*, 9068. (d) Zou, Y.; Wang, Q. R.; Goeke, A. *Chem.—Eur. J.* **2008**, *14*, 5335. (e) Ramachary, D. B.; Reddy, Y. V. *J. Org. Chem.* **2010**, *75*, 74.

(4) For recent examples of the construction of five contiguous stereocenters via organocatalysis, see: (a) Reyes, E.; Jiang, H.; Milelli, A.; Elsner, P.; Hazell, R. G.; Jørgensen, K. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 9202. (b) Urushima, T.; Sakamoto, D.; Ishikawa, H.; Hayashi, Y. *Org. Lett.* **2010**, *12*, 4588. (c) Imashiro, R.; Uehara, H.; Barbas, C. *F. Org. Lett.* **2010**, *12*, 5250.

(5) (a) Wu, L. Y.; Bencivenni, G.; Mancinelli, M.; Mazzanti, A.; Bartoli, G.; Melchiorre, P. *Angew. Chem., Int. Ed.* **2009**, *48*, 7196. (b) Tan, B.; Shi, Z.; Chua, P. J.; Zhong, G. *Org. Lett.* **2008**, *10*, 3425. (c) Tan, B.; Chua, P. J.; Zeng, X.; Lu, M.; Zhong, G. *Org. Lett.* **2008**, *10*, 3489. (d) Tan, B.; Chu, J.; Li, Y.; Zhong, G. *Org. Lett.* **2008**, *10*, 2437. (e) Chen, X. H.; Zhang, W. Q.; Gong, L. Z. *J. Am. Chem. Soc.* **2008**, *130*, 5652. (f) Ishihara, K.; Nakano, K. *J. Am. Chem. Soc.* **2007**, *129*, 8930. (g) Bencivenni, G.; Wu, L. Y.; Mazzanti, A.; Giannichi, B.; Pesciaioli, F.; Song, M. P.; Bartoli, G.; Melchiorre, P. *Angew. Chem., Int. Ed.* **2009**, *48*, 7200.

(6) For reviews, see: (a) Heasley, B. *Eur. J. Org. Chem.* **2009**, 1477. (b) Schultz, A. G. *Acc. Chem. Res.* **1990**, *23*, 207.

(7) For our recent efforts in exploring new organocatalytic annulations, see: (a) Hong, B.-C.; Kotame, P.; Liao, J.-H. *Org. Biomol. Chem.* **2011**, *9*, 382. (b) Hong, B.-C.; Dange, N. S.; Hsu, C.-S.; Liao, J.-H. *Org. Lett.* **2010**, *12*, 4812. (c) Hong, B.-C.; Kotame, P.; Tsai, C.-W.; Liao, J.-H. *Org. Lett.* **2010**, *12*, 776. (d) Hong, B.-C.; Jan, R.-H.; Tsai, C.-W.; Nimje, R. Y.; Liao, J.-H.; Lee, G.-H. *Org. Lett.* **2009**, *11*, 5246. (e) Hong, B.-C.; Nimje, R. Y.; Liao, J.-H. *Org. Biomol. Chem.* **2009**, *7*, 3095. (f) Kotame, P.; Hong, B.-C.; Liao, J.-H. *Tetrahedron Lett.* **2009**, *50*, 704. (g) Hong, B.-C.; Nimje, R. Y.; Sadani, A. A.; Liao, J.-H. *Org. Lett.* **2008**, *10*, 2345 and references cited therein.

(8) 65% ee for the recovered (*R*)-**4a** in the reaction of (±)-**4a** with 0.6 equiv of **5b** and cat. **I**−HOAc (20 mol %), and 45% ee for the recovered (*R*)-**4a** when (±)-**4a** was reacted with 0.4 equiv of **5b** and cat. **I**−HOAc (20 mol %).

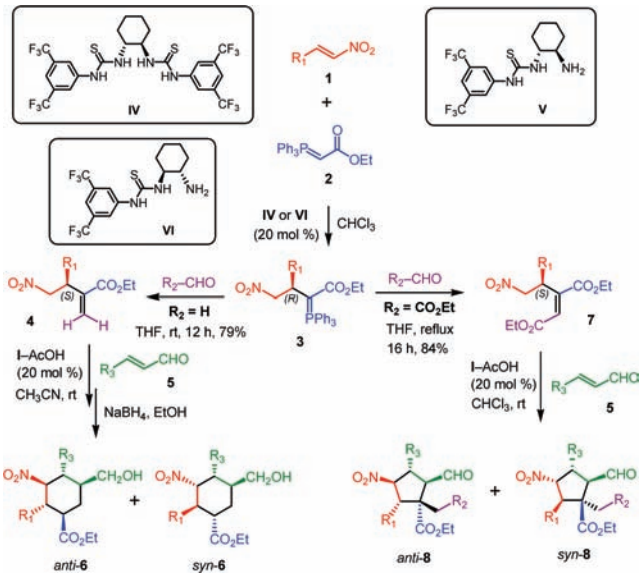
(9) (a) See ref 7c. (b) Soon after our publication, a similar study of the conjugate addition of the Wittig reagent to nitroalkenes was reported that also afforded moderate ee; see: Allu, S.; Selvakumar, S.; Singh, V. K. *Tetrahedron Lett.* **2010**, *51*, 446. (c) For an organocatalytic enantioselective Mannich-type reaction of phosphorus ylides, see: Zhang, Y.; Liu, Y.-K.; Kang, T.-R.; Hu, Z.-K.; Chen, Y.-C. *J. Am. Chem. Soc.* **2008**, *130*, 2456.

(10) The absolute stereochemistry of (*R*)-**3a** was further elucidated via the subsequent hydrogenation of (*S*)-**4a**, providing (2*S*,3*R*)-2-methyl-4-nitro-3-phenylbutan-1-ol, and compared with the optical rotation data of (2*R*,3*S*)-2-methyl-4-nitro-3-phenylbutanal, obtained from the reaction of propionaldehyde and nitrostyrene catalyzed by **I**−HOAc, via the literature procedure, see: Hayashi, Y.; Gotoh, H.; Hayashi, T.; Shoji, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4212.

(11) For a recent review of unexpected inversions in asymmetric reactions, see: Bartók, M. *Chem. Rev.* **2010**, *110*, 1663.

(12) Reaction of (±)-**7a** with **5** gave 1:1 ratio of *anti*-**8** and *syn*-**8** with the same high yields and enantioselectivities. The structure of *syn*-**8** was assigned on the basis of ^1H and ^{13}C NMR, COSY, DEPT, HMQC, and NOESY analysis.

Table 3. Scope of the Organocatalytic Michael−Wittig−Michael−Michael Reaction



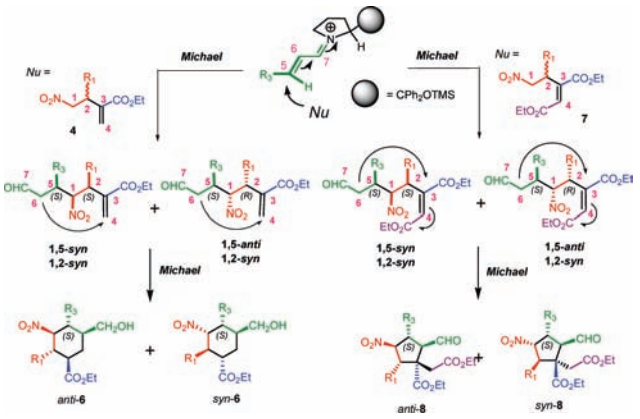
entry	product	time (h)[a]	yield (%)[b]	dr[c]	ee (%)[d]
1	**8a** R_1 = Ph; R_2 = CO_2Et; R_3 = Ph	48	94	3.7:1	99, (99)[e]
2	**8b** R_1 = Ph; R_2 = CO_2Et; R_3 = 4-BrC_6H_4	53	95	3.0:1	99
3	**8c** R_1 = Ph; R_2 = CO_2Et; R_3 = 4-$OMeC_6H_4$	61	93	3.0:1	99
4	**8d** R_1 = Ph; R_2 = CO_2Et; R_3 = 4-$NO_2C_6H_4$	55	84	3.0:1	99[f]
5	**8e** R_1 = Ph; R_2 = CO_2Et; R_3 = 4-MeC_6H_4	60	89	2.7:1	95
6	**8f** R_1 = Ph; R_2 = CO_2Et; R_3 = 4-ClC_6H_4	56	92	3.0:1	99
7	**8g** R_1 = 4-BrC_6H_4; R_2 = CO_2Et; R_3 = Ph	55	94	3.2:1	97
8	**8h** R_1 = 4-$OMeC_6H_4$; R_2 = CO_2Et; R_3 = Ph	60	93	2.8:1	99
9	**8i** R_1 = 4-FC_6H_4; R_2 = CO_2Et; R_3 = Ph	51	91	3.1:1	99
10	**6a** R_1 = Ph; R_2 = H; R_3 = Ph	48	79	6.3:1	96[g]
11	**6b** R_1 = Ph; R_2 = H; R_3 = 4-BrC_6H_4	51	73	6.5:1	97[g,h]
12	**6c** R_1 = Ph; R_2 = H; R_3 = 4-$OMeC_6H_4$	59	76	5.4:1	93[g,h]
13	**6d** R_1 = Ph; R_2 = H; R_3 = 4-$NO_2C_6H_4$	53	83	5.5:1	94[g,h]

[a] Reaction time for the double-Michael reaction step. [b] Combined isolated yields of the isomers in the double-Michael reaction step. [c] Determined by ^1H NMR analysis of the crude reaction mixture. [d] Unless otherwise noted, ee of the major stereoisomer (*anti*-isomer), determined by HPLC with chiral column (Chiralpak IC). [e] The ee of the minor stereoisomer is given in parentheses (*syn*-isomer). [f] Determined by HPLC with chiral column (Chiralpak IA). [g] The ee of the corresponding alcohol. [h] Determined by HPLC with chiral column (Chiralcel OD-H).

treatment of (*R*)-**3a** (60% ee), prepared with monothiourea catalyst **VI**, with formaldehyde, followed by the addition of α,β-unsaturated aldehydes **5** and catalyst **I**-HOAc (20 mol %) in CH_3CN, provided *anti*-**6** and *syn*-**6** with good dr (e.g., *anti*-**6a**:*syn*-**6a** = 6.3:1) and with high enantioselectivities, (Table 3, entries 10−13).

To explain the stereochemistry of this transformation, we propose a plausible mechanism, as shown in Scheme 2. The reaction was initiated from the iminium activation of the α,β-unsaturated aldehyde by catalyst **I**, followed by the nitro-Michael addition of the nitroalkane nucleophile, resulting from the aforementioned Michael-Wittig reaction, from the *Re* face under the control of the catalyst to give an intermediate with a 5-*S* configuration (irregular

Scheme 2. Plausible Dichotomous Reaction Mechanism of the Succeeding Double-Michael Reaction with the Michael−Wittig Adduct



number system, noted in Scheme 2).[13] The relative topicities were further demonstrated by the reaction with (*S*)-enriched **7** to give *anti*-**8**, and by reaction with (*S*)-enriched **4** to give *anti*-**6**, respectively, as the major products.

In conclusion, we have discovered a sequential enantioselective organocatalytic Michael−Wittig−Michael−Michael reaction. Remarkably, with the subtle variations in the ester substituents on the enolates, this methodology provides dichotomous construction of pentasubstituted cyclopentanecarbaldehydes bearing a quaternary carbon center and pentasubstituted cyclohexanecarbaldehydes having five contiguous stereocenters with excellent enantioselectivities (up to >99% ee). The production of five contiguous chiral centers with high enantioselectivity is especially noteworthy. An increase in diastereoselectivity was achieved by the first organocatalytic asymmetric conjugate addition of a phosphonium ylide to nitrostyrenes with the noncovalent thiourea catalyst **VI**. The unexpected inversion in the asymmetric reactions obtained with monothiourea **V** and dithiourea **IV** organocatalysts in the Michael reaction of the naked nucleophile (nonenolizable) **2** to **1a** is notable. This observation may provide a useful clue in the search for better organocatalysts for these types of asymmetric conjugate addition reactions.

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Supporting Information Available. Experimental procedures and characterization data for the new compounds and X-ray crystallographic data for compound (+)-**9** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

(13) Thus, the stereoselectivity was similar to that observed in other examples of organocatalysis; for examples, see: (a) Gotoh, H.; Okamura, D.; Ishikawa, H.; Hayashi, Y. *Org. Lett.* **2009**, *11*, 4056. (b) Han, B.; Xiao, Y.-C.; He, Z.-Q.; Chen, Y.-C. *Org. Lett.* **2009**, *11*, 4660. (c) Enders, D.; Wang, C.; Bats, J. W. *Synlett* **2009**, 1777.