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Direct Organocatalytic Asymmetric Approach to Baylis–Hillman-Type Products Through a Push–Pull Dienamine Platform

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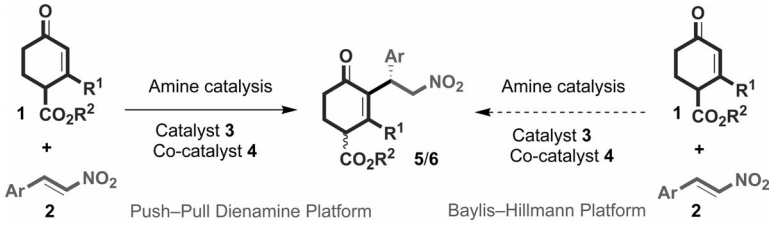
A general process for the asymmetric synthesis of highly substituted 3-alkyl-Hagemann's esters was achieved for the first time through organocatalytic Michael or Baylis–Hillman-type (BH-type) reaction of Hagemann's esters with β-nitrostyrenes in the presence of a catalytic amount of L-(3,5-Me_2)$_2$DPP/thiourea. We have discovered, for the first time, the chiral BH-type products from Hagemann's esters with β-nitrostyrenes by utilizing the push–pull dienamine platform.

Introduction

Asymmetric amino catalysis has become one of the most important and widespread areas of research through iminium or enamine activation of carbonyl compounds.[1] The direct Michael addition of saturated carbonyl compounds to β-nitrostyrenes through enamine activation by amino catalysis provides an expedient access for the development of functionalized molecules.[2] Recently Barbas[2a] and his coworkers discovered the novel technology for organocatalytic asymmetric Michael addition of aldehydes/ketones with nitroolefins that provides a general route to a variety of Michael adducts in good yields with high enantioselectivity, which is known as the "Barbas–Michael" reaction.[2] The advent of this enamine-based Barbas–Michael technology triggered a burst of activity towards the synthesis of a huge chiral pool of Michael adducts through biomimetic enamine chemistry.

Recently a very interesting dual catalytic system based on the combination of enamine and Lewis base catalysis for the Baylis–Hillman-type reaction between methyl vinyl ketone and benzaldehydes or α,β-unsaturated aldehydes and imines or β-nitrostyrenes was reported.[3] Interestingly, to the best of our knowledge, there is no asymmetric coupling between α,β-unsaturated ketones and β-nitrostyrenes at the α-position of enone through dienamine catalysis or zwitterionic catalysis [Equation (1)]. With these objectives, herein we have designed an asymmetric approach to the Baylis–Hillman-type (BH-type) products from commercially available Hagemann's esters (enones) and nitroolefins through push–pull dienamine catalysis as shown in Equation (1).[4]

However, the amine-catalyzed Michael reaction of enones **1** with nitroolefins **2** is not known, and the resulting products **5/6** will have a wide range of uses in synthetic chemistry [Equation (1)]. Herein, we report a metal-free and novel technology for the asymmetric synthesis of substituted alkyl 2-alkyl-3-(2-nitro-1-arylethyl)-4-oxo-cyclohex-2-enecarboxylates (BH-type products) **5/6** by using organocatalytic Michael or BH-type reactions from easily available Hagemann's esters **1**, nitroolefins **2** and amines **3** through push–pull dienamine catalysis [Equation (1) and Figure 1].[4]



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Results and Discussion

We initiated our preliminary studies of the BH-type reactions by screening a number of known and novel organocatalysts for the Michael addition of Hagemann's ester **1a**

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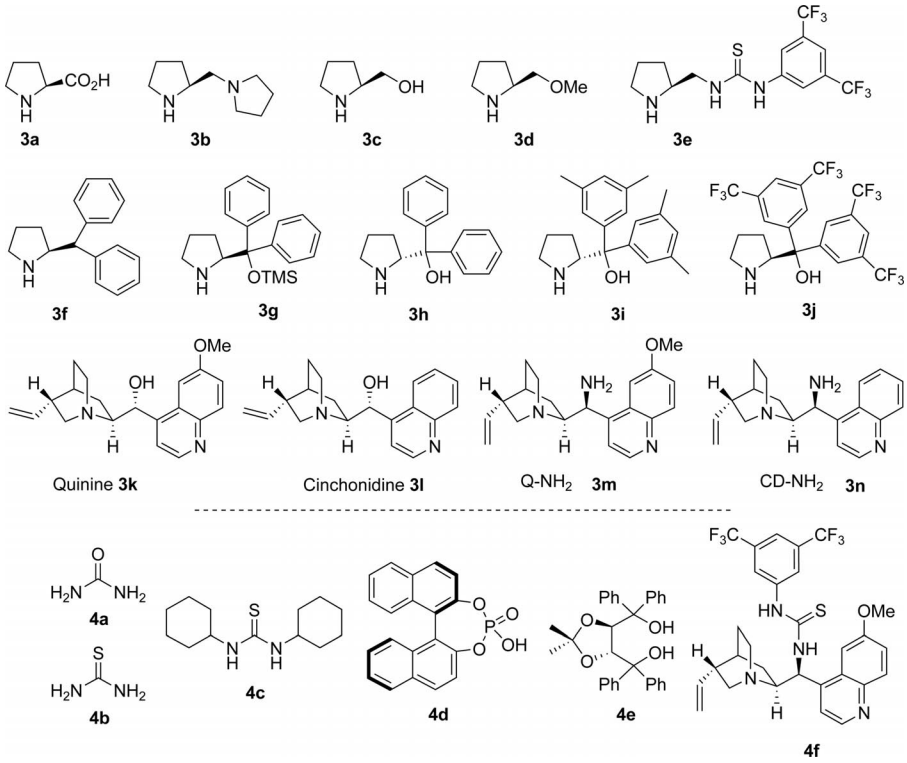
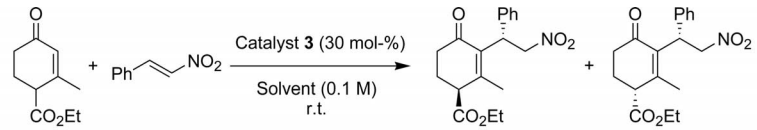


Figure 1. Library of catalysts and co-catalysts screened for the direct asymmetric BH-type reactions through a push–pull dienamine platform.

with 1.5 equiv. β-nitrostyrene **2a**. Some representative results are shown in Table 1. Interestingly, reaction of **1a** with 1.5 equiv. β-nitrostyrene **2a** in DMSO without a catalyst furnished a 1:1 diastereomeric ratio of BH-type products **5aa/6aa** in 61% yield (Table 1, Entry 1). Further, we tested the catalyst-free, solvent-induced reaction in other solvents such as $C_6H_5CH_3$, DCM, THF, $CHCl_3$, CH_3CN, EtOH, MeOH, CH_3COCH_3, H_2O, 1,4-dioxane and *i*PrOH, but we did not observe the formation of BH-type products **5aa/6aa** (results not presented in Table 1). We then screened various natural and unnatural amino acids [(*S*)-indoline-2-carboxylic acid, hydroxy L-proline, L-phenylalanine, L-tyrosine, L-serine, L-threonine, L-leucine, *o*-*tert*-butyl-L-threonine and L-proline (**3a**)] as catalysts for the Michael addition of Hagemann's ester **1a** with β-nitrostyrene **2a** in toluene, but these amino acids did not furnish the products **5aa/6aa** (results not presented in Table 1). Reaction of **1a** with 1.5 equiv. **2a** with diamine **3b** as catalyst in toluene furnishes a 1.3:1 *dr* of products **5aa/6aa** in 30% yield with 2/0% *ee*, respectively (Table 1, Entry 3). (*S*)-Prolinol **3c** also catalyzes the reaction of **1a** with **2a** in $CHCl_3$ at 25 °C and 0 °C to furnish a 1.5:1 and 1.8:1 ratio of products **5aa/6aa** in 75 and 40% yields with 0/3% *ee* and 31/0% *ee*, respectively (Table 1, Entries 4,5). The same reaction under catalysis by **3c** in toluene furnishes a 1:1.6 ratio of products **5aa/6aa** in 60% yield with 11/2% *ee*. The reaction with (*S*)-2-(methoxymethyl)pyrrolidine (**3d**) furnishes the Michael products **5aa/6aa** with improved yield and moderate *de*/*ee* values (Table 1, Entry 7). We also tested a number of primary and secondary amines such as chiral thiourea (**3e**), L-2-benzhydryl-pyrrolidine (**3f**), L-DPPOTMS (**3g**), L-[3,5-$(CF_3)_2$]$_2$DPP (**3j**), Q-NH_2 (**3m**) and CD-NH_2 (**3n**) as catalysts for the BH-type reaction of **1a** with **2a** in toluene, although they did not furnish Michael products **5aa/6aa** (Table 1, Entries 8–10, 13, 16, 17). Interestingly, the reaction of **1a** and **2a** with D-DPP (**3h**) as catalyst in toluene at 25 °C for 24 h furnishes the Michael products **5aa/6aa** in 35% yield with 1.1:1 *dr* and –49/–8% *ee*, respectively (Table 1, Entry 11). The reaction with D-(3,5-Me_2)$_2$DPP (**3i**) in toluene at 25 °C for 72 h furnishes the Michael products **5aa/6aa** in 45% yield with 1.2:1 *dr* and –55/–11% *ee*, respectively (Table 1, Entry 12). Quinine **3k** catalyzed the BH-type reaction to furnish the products in 66% yield with 1:1.2 *dr* and 42/40% *ee*, respectively (Table 1, Entry 14).

To further improve the asymmetric BH-type reaction, with regard to decreasing the reaction time and increasing the *ee*/*de* and yields, we tested the Michael reaction of **1a** and **2a** catalyzed by **3h** and **3i** with different amines/acids **3e** and **4a**–**f** as co-catalysts in toluene at 25 °C (Table 2, Entries 1–12). After many experiments, we were happy to find that the BH-type reaction of **1a** with **2a** in toluene under catalysis by 30 mol-% L-(3,5-Me_2)$_2$DPP/thiourea (**3i/4b**) at 25 °C for 72 h furnished the products **5aa/6aa** in 70% yield with 70/7% *ee* and 13% *de*, respectively (Table 2, Entry 8). After successful results with thiourea **4b** as catalyst, we screened D-(3,5-Me_2)$_2$DPP **3i** as catalyst for BH-type reaction to monitor the outcome of selectivity (Table 2, Entry 10). The BH-type reaction of **1a** with **2a** in toluene with 30 mol-% D-(3,5-Me_2)$_2$DPP/thiourea (**3i/4b**) at 25 °C for 72 h furnished the products **5aa/6aa** in 80% yield with 69/15% *ee*

Table 1. Effect of solvent and catalyst on the direct asymmetric BH-type reaction of **1a** with **2a**.[a]

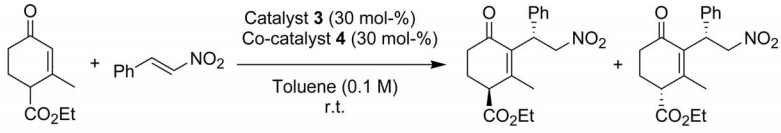


1a **2a** **5aa** **6aa**

Entry	Catalyst	Solvent	Time [h]	Yield [%][b]	*dr*[c] **5aa/6aa**	*ee*[c] **5aa/6aa**
1	–	DMSO	28	61	1:1	0/0
2	**3a**	Toluene	72	–	–	–
3	**3b**	Toluene	96	30	1.3:1	2/0
4	**3c**	$CHCl_3$	4	75	1.5:1	0/3
5[d]	**3c**	$CHCl_3$	48	40	1.8:1	31/0
6	**3c**	Toluene	5	60	1:1.6	11/2
7	**3d**	Toluene	60	60	1:1.6	26/24
8	**3e**	Toluene	48	–	–	–
9	**3f**	Toluene	120	–	–	–
10	**3g**	Toluene	72	–	–	–
11[e]	**3h**	**Toluene**	**24**	**35**	**1.1:1**	**–49/–8**
12	**3i**	**Toluene**	**72**	**45**	**1.2:1**	**–55/–11**
13	**3j**	Toluene	48	–	–	–
14	**3k**	Toluene	60	66	1:1.2	42/40
15	**3l**	Toluene	60	70	1:1.2	19/13
16	**3m**	Toluene	96	–	–	–
17	**3n**	Toluene	96	–	–	–

[a] Reactions were carried out in 0.1 M solvent with 1.5 equiv. nitrostyrene (**2a**) relative to Hagemann's ester **1a** in the presence of 30 mol-% of catalyst **3**. [b] Yield refers to the column purified product. [c] *dr* and *ee* were determined by HPLC analysis. [d] Reaction performed at 0 °C. [e] Reaction was carried out in 0.15 M solvent.

Table 2. Effect of co-catalyst on the direct asymmetric BH-type reaction of **1a** with **2a**.[a]



1a **2a** **5aa** **6aa**

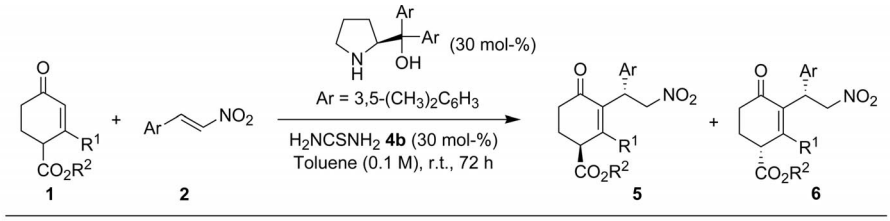
Entry	Catalyst	Co-catalyst	Time [h]	Yield [%][b]	*dr*[c] **5aa/6aa**	*ee*[c] **5aa/6aa**
1	**3h**	**4a**	72	50	1:1.3	–38/–31
2	**3h**	**4b**	48	70	1:1.0	–52/–31
3	**3h**	**4c**	36	44	1:1.4	–34/–30
4[d]	**3h**	**3e**	72	69	1.3:1	–66/2
5[d]	**3h**	**4d**	96	54	1.2:1	–57/7
6[e]	**3h**	**4b**	72	76	1:1.1	–42/–30
7	(*S*)-**3i**	**4e**	120	30	1:1.2	59/4
8	(*S*)-**3i**	**4b**	**72**	**70**	**1.3:1**	**70/7**
9[d]	**3i**	**3e**	72	66	1.2:1	–68/–12
10	**3i**	**4b**	**72**	**80**	**1.1:1**	**–69/–15**
11	(*S*)-**3h**	**3e**	36	66	1.9:1	11/20
12[d]	(*S*)-**3h**	**4f**	72	65	1.4:1	3/20

[a] Reactions were carried out in solvent (0.1 M) with 1.5 equiv. β-nitrostyrene **2a** relative to Hagemann's ester **1a** in the presence of 30 mol-% catalyst **3** and 30 mol-% co-catalyst. [b] Yield refers to the column purified product. [c] *dr* and *ee* were determined by HPLC analysis. [d] 10 mol-% co-catalyst was used. [e] Reaction performed at 50 °C.

and 5% *de*, respectively (Table 2, Entry 10). Unfortunately we were not so successful in achieving high yields and *ee*/*de* with chiral thiourea-based catalysts **3e/4f** as co-catalysts relative to thiourea **4b** as shown in Table 2, Entries 4, 9, and 11–12. Finally, The optimized conditions were found to be 25 °C in toluene with 30 mol-% L-(3,5-Me_2)$_2$DPP/thiourea (**3i/4b**) as catalysts, which furnished the highly substituted products **5aa/6aa** in 70% yield with 70/7% *ee* and 13% *de* (Table 2, Entry 8). The structure and absolute stereochemistry of the BH-type products **5aa/6aa** were confirmed by NMR analysis and also by correlation with amine-catalyzed Barbas–Michael reactions.[2]

After successful demonstration and understanding of the BH-type reaction of **1a** with **2a** under amine catalysis, the scope and generality of the BH-type reaction was investigated with functionalized Hagemann's esters **1a**–**d** and β-nitrostyrenes **2a**–**i**. Although there is no methodology available to prepare achiral Michael products **5/6**, herein we have been able to prepare a library of achiral Michael products **5/6** in good yields under pyrrolidine catalysis through a

Table 3. Synthesis of chiral BH-type products **5/6**.[a,b]



70% (**5aa/6aa**)
dr = 1.3:1
ee = 70%, 7%

60% (**5ba/6ba**)
dr = 1:1.6
ee = 61%, 11%

61% (**5ca/6ca**)
dr = 2.1:1
ee = 84%, 40%

35% (**5cb/6cb**)
dr = 1.5:1
ee = 83%, 33%

66% (**5cc/6cc**)[c]
dr = 5.2:1
ee = 69%, 11%

36% (**5da/6da**)
dr = 2.0:1
ee = 77%, 3%

45% (**5ad/6a**d)
dr = 1.2:1
ee = 78%, 17%

61% (**5ae/6ae**)
dr = 1.2:1
ee = 26%, 21%

60% (**5af/6af**)
dr = 1:1.4
ee = 44%, 15%

63% (**5ab/6ab**)
dr = 1.1:1
ee = 60%, 4%

50% (**5ag/6ag**)
dr = 1:1.7
ee = 29%, 27%

74% (**5ah/6ah**)
dr = 1:1.7
ee = 42%, 27%

60% (**5ai/6ai**)
dr = 1.1:1
ee = 47%, 6%

60% (**5ac/6ac**)
dr = 1.5:1
ee = 41%, 12%

73% (+)-**5aa/6aa**[d]
dr = 1.2:1
ee = –70%, –14%

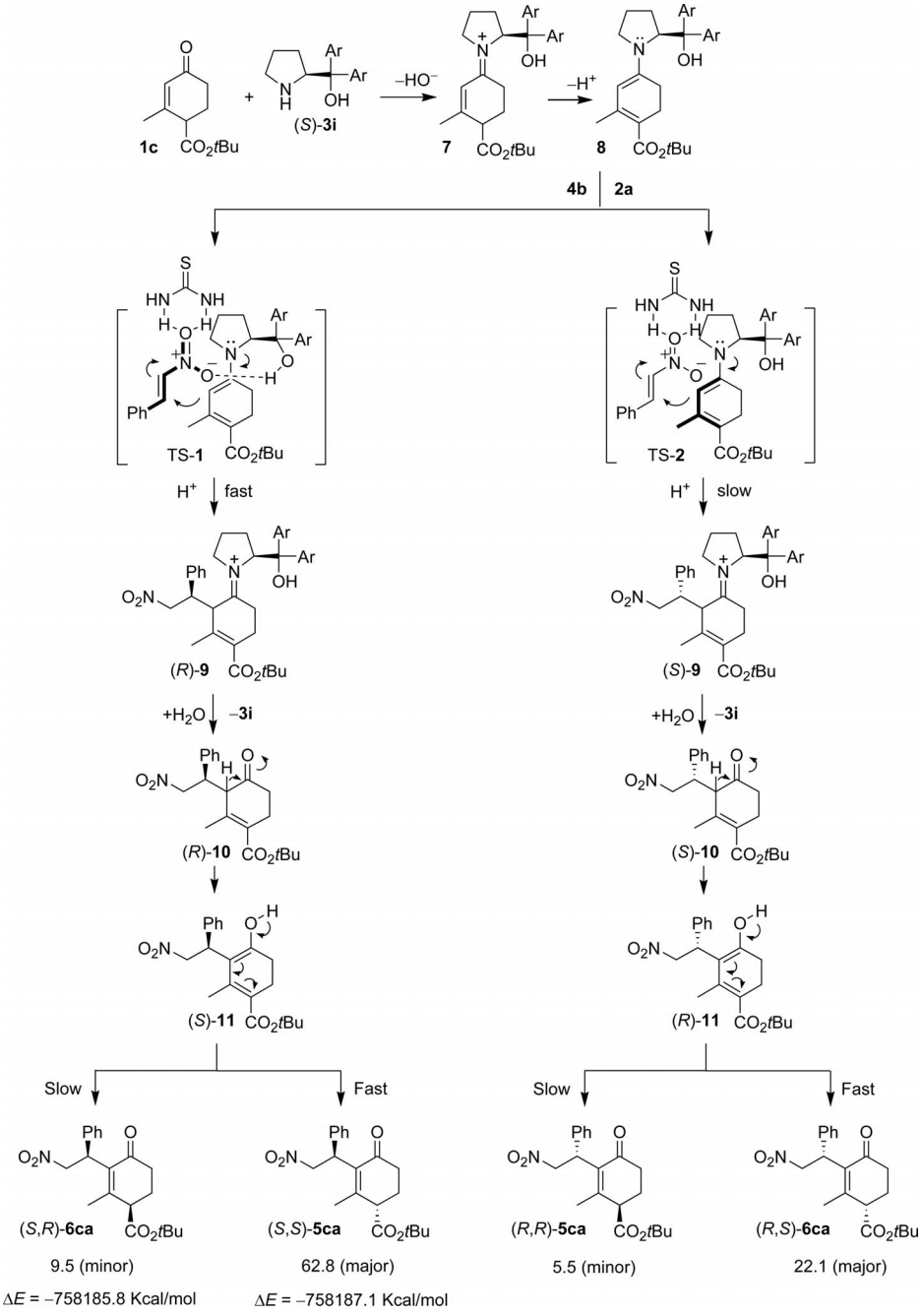
52% (–)-**5ca/6ca**[d]
dr = 2.6:1
ee = –85%, –8%

[a] Reactions were carried out in toluene (0.1 M) with 1.5 equiv. **2** relative to Hagemann's ester **1** in the presence of 30 mol-% catalyst (*S*)-**3i** and 30 mol-% co-catalyst **4b**. [b] Yield refers to the column purified product and *dr*/*ee* was determined by HPLC analysis. [c] Reaction time is 96 h. [d] 30 mol-% (*R*)-**3i** used as catalyst.

push–pull dienamine platform (Table S1, see Supporting Information). By BH-type reaction of Hagemann's esters **1a**–**d** with a structurally diverse group of electron-donating, electron-withdrawing, halogenated and heterocyclic-substituted β-nitrostyrenes **2a**–**i**, the expected products **5/6** were generated in good to excellent yields with 1:1 to 6.6:1 *dr* as shown in Table S1. The structure and regiochemistry of achiral Michael products **5/6** were confirmed by NMR spectroscopy and mass analysis.

With the optimized reaction conditions in hand, we decided to investigate the asymmetric BH-type reaction between functionalized Hagemann's esters **1b**–**d** and β-nitrostyrenes **2b**–**i** in toluene at 25 °C to study the asymmetric induction in the products **5/6**. A series of β-nitrostyrenes **2** containing different functional groups were treated with Hagemann's esters catalyzed by 30 mol-% L-(3,5-Me_2)$_2$DPP with 30 mol-% thiourea **4b** as co-catalyst at 25 °C for 72 h in toluene to furnish asymmetric BH-type products **5/6** in good yields with good to moderate *ee*/*de* values as shown in Table 3.

Treatment of methyl keto-ester **1b** with β-nitrostyrene **2a** in toluene at 25 °C for 72 h with 30 mol-% L-(3,5-Me_2)$_2$-DPP/thiourea (L-**3i**/**4b**) furnished a 1:1.6 *dr* of products **5ba**/**6ba** in 60% yield with 61% and 11% *ee*, respectively



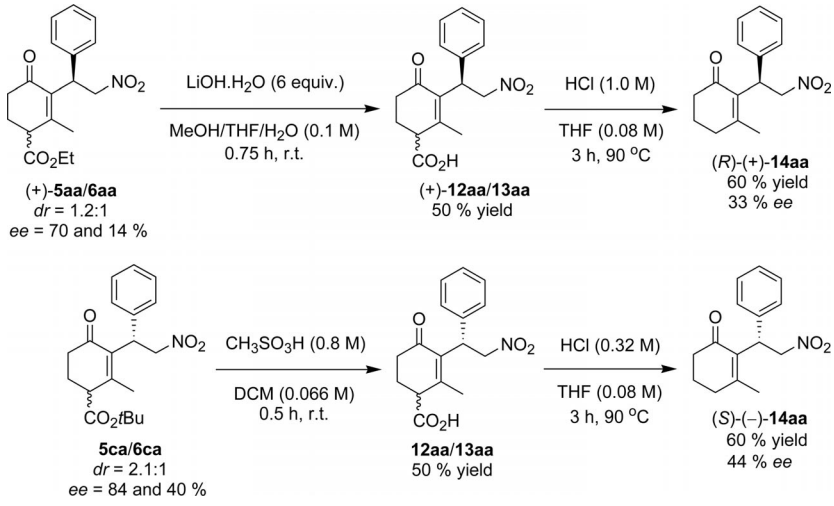
Scheme 1. Proposed reaction mechanism.

(Table 3, Entry 2). Interestingly, asymmetric BH-type reaction of β-nitrostyrene **2a** with *tert*-butyl keto-ester **1c** catalyzed by L-**3i/4b** in toluene at 25 °C for 3 d furnished a 2.1:1 ratio of **5ca/6ca** in 61% yield with 84% and 40% *ee*, respectively (Table 3, Entry 3). In a similar manner, high asymmetric induction was observed with *tert*-butyl keto-ester **1c** as substrate with two more β-nitrostyrenes **2b**,**c** catalyzed by L-**3i/4b** in toluene at 25 °C for 3–4 d as shown in Table 3, Entries 4,5. Reaction of higher alkyl-substituted ethyl keto-ester **1d** with **2a** also furnished the expected BH-type products **5da/6da** in 36% yield with 77/3% *ee* and 2:1 *dr*, respectively (Table 3, Entry 6). Asymmetric BH-type reaction of Hagemann's ester **1a** with functionalized β-nitrostyrenes **2d**–**i** catalyzed by L-**3i/4b** gave the products **5ad/6ad**–**5ai/6ai** in 45–74% yields with moderate to good *ee*/*de* values, respectively as shown in Table 3, Entries 7–14. These results clearly suggest that the electronic nature of the functional groups on β-nitrostyrenes **2d**–**i** may control the asymmetric induction in BH-type reactions by decreasing the nitro group intereactions with thiourea (see, for example, **2e**/**2g**). Further, to demonstrate the broad scope of this novel methodology for generating an opposite enantiomer of BH-type products **5**/**6**, we used D-**3i/4b** as catalyst to furnish products (+)-**5aa/6aa** in 73% yield with –70/–14% *ee* and (–)-**5ca/6ca** in 52% yield with –85/–8% *ee* (Table 3, Entries 15,16). Interestingly, we did not observe the formation of BH-type products from ethyl keto-ester **1e**,**f** [R^1 = H and Ph, see Equation (1)] with **2a** under the optimized conditions, may be because of electronic and steric factors (results not shown in Table 3). The structures and regiochemistry of the BH-type products were confirmed by NMR spectroscopy and mass analysis. The absolute configuration of products were established by correlation with Barbas–Michael reactions.[2]

Although further studies are needed to firmly elucidate the mechanism of asymmetric BH-type reactions through push–pull dienamine catalysis, the possible reaction mechanism for stereoselective synthesis of products **5ca/6ca** through the reaction of *tert*-butyl Hagemann's ester **1c** and β-nitrostyrene **2a** catalyzed by L-**3i/4b** is illustrated in Scheme 1. First, reaction of L-**3i** with **1c** generates the imine cation **7**, which transforms into chiral push–pull dienamine **8** through proton elimination. Formation of the Michael product (*R*)-**9** over (*S*)-**9** through *re*-face attack of β-nitrostyrene **2a** with chiral push–pull dienamine **8** will be faster than that with *si*-face attack as shown in TS-**1** and TS-**2**, on the basis of hydrogen-bonding interactions with OH. In situ hydrolysis followed by keto-enol tautomerism of Michael products (*R*)-**9** and (*S*)-**9** leads to highly substituted (*S*)-**11** and (*R*)-**11**. Formation of the thermodynamically stable (*S*, *S*)-**5ca** occurs faster than that of the kinetically stable (*S*, *R*)-**6ca** product from (*S*)-**11**. The calculated heat of formation (ΔE) for the (*S*, *S*)-**5ca** product is 1.3 kcal/mol more than that of the (*S*, *R*)-**6ca** product as revealed by DFT calculations (see Supporting Information). Interestingly, the reverse trend in case of (*R*)-**11**, as shown in Scheme 1, may be because of the weak CH–π interactions between the phenyl ring and olefinic methyl group.

Strong support for our proposed dienamine catalysis was obtained through performing the BH-type reaction on simple cyclohexenone **1g** with **2a** catalyzed by **3a**, **3b**, **3c** and **3i/4b** (results not shown in Table 3). Interestingly, as we expected, we did not observe the formation of the BH-type product from the above reactions, and this gives support to the formation of dienamines as intermediates from **1a**–**d** with **3**/**4**.

The proposed transition states and also the ratio of enantiomers were confirmed by converting the products (+)-**5aa/6aa** and (+)-**5ca/6ca** into (*R*)-(+)-**14aa** and (*S*)-(–)-**14aa**, respectively, by using hydrolysis and the decarboxylation sequence, as shown in Scheme 2. Reaction of BH-type product (+)-**5aa/6aa** [*dr* 1.2:1 and *ee* 70 and 14%] with $LiOH{\cdot}H_2O$ in MeOH/THF/H_2O at 25 °C for 0.75 h furnished the keto acid (+)-**12aa/13aa** in 50% yield, which upon treatment with acid in THF gave the decarboxylated product (*R*)-(+)-**14aa** in 60% yield with 33% *ee*, as shown in Scheme 2. In a similar manner, (*S*)-(–)-**14aa** was synthesized from (+)-**5ca/6ca** [*dr* 2.1:1 and *ee* 84 and 40%] in 50% yield



Scheme 2. Synthesis of functionalized chiral cyclohexenones **14aa**.

with –44% *ee*, as shown in Scheme 2. Obtaining lower *ee* values for (*R*)-/(*S*)-**14aa** through the hydrolysis–decarboxylation sequence on (+)-**5aa/6aa** and (+)-**5ca/6ca** can be explained by the conversion of diastereomers into enantiomers instead of epimerization, as shown in Schemes 1 and 2 (see HPLC data).

Conclusions

In summary, we have described a chemo-, regio- and enantioselective process for the synthesis of highly substituted alkyl 2-alkyl-3-(2-nitro-1-arylethyl)-4-oxocyclohex-2-enecarboxylates **5/6** by amine catalysis. Herein, we described the L-(3,5-Me_2)$_2$DPP/thiourea-catalyzed asymmetric BH-type reactions from Hagemann's esters **1** with nitroolefins **2** at ambient conditions. This novel asymmetric BH-type reaction proceeds in good yields with high enantioselectivity through a push–pull dienamine platform. Furthermore, we demonstrated the application of chiral BH-type products in the synthesis of highly functionalized cyclohexenones.

Experimental Section

Supporting Information (see footnote on the first page of this article): Experimental procedures, characterization data for new products, and complete details about the synthesis of new products are available.

Acknowledgments

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