DOI: 10.1002/cjoc.201200910

Highly Enantioselective Michael Addition of Ketone to Alkylidene Malonates Catalyzed by Binaphthyl Sulfonimides in Water

Jia, Shengjian(贾胜见) Luo, Chunhua(罗春华) Du, Daming*(杜大明)

School of Chemical Engineering and Environment, *Beijing Institute of Technology*, *Beijing 100081*, *China*

Binaphthyl sulfonimides have been developed to catalyze the asymmetric Michael addition of ketone to alkylidene malonates, affording the corresponding Michael products in good to high yields (up to 98%) with good to excellent diastereoselectivity (up to 99∶1 *dr*) and enantioselectivity (up to 92% *ee*) under mild conditions using environmentally benign water as the solvent.

Keywords asymmetric catalysis, organocatalysis, Michael addition, malonates, sulfonimides

Introduction

In the past decades, the asymmetric Michael addition reaction as an important asymmetric carbon-carbon bond formation reaction obtained great development in organic synthesis of bifunctional products.[1] The direct organocatalytic asymmetric Michael addition of ketones or aldehydes to α,β-unsaturated compounds provides a particularly attractive atom-economical manner.[2] Although there are many types of substrates and donors for Michael reaction, many efforts have been made to achieve catalytic enantioselective conjugate addition and great progress can be seen. On one hand, the Michael acceptors have been extended from nitroalkenes[3] to α,β-unsaturated aldehydes,[4] ketones,[5] sulfones,[6] and phosphate[7] *etc*. electronic deficiency systems. On the other hand, many new types of catalysts have been developed, such as *L*-porline-based catalysts, primary amines, thioureas *etc*. The asymmetric Michael addition of ketones to alkylidene manolates has been reported only in a few case compared with other Michael donors, this was ascribed to the low reactivity of alkylidene manolates. The pioneering work of using pyrrolidine based diamine as highly efficient and stereoselective organocatalysts for the asymmetric Michael addition of ketones to alkylidene manolates was reported by Barbas and co-workers.[8] Although the catalytic effect was unsatisfactory, it provided a new idea for the chemical researchers to investigate those reactions and design new catalysts. In recent years, great efforts have been devoted to the *L*-porline-based catalysts or primary-secondary diamine catalysts for asymmetric Michael addition of ketones or aldehydes to α,β-unsaturated compounds by Tang, Wang, Feng and so on.[2,3,9]

Many chiral sulfonamide catalysts have been extensively applied in asymmetric catalysis. The strong electron withdrawing effect of sulfonyl can improve the acidity of sulfonamide, enhance hydrogen bond donor ability. Meanwhile, it also can provide lone pair of elections for coordination, which is conducive to raise enantioseletivity in asymmetric reactions. Sulfonamide organocatalysts are amazingly used in many asymmetric reaction such as asymmetric Michael addition, asymmetric Aldol reaction and asymmetric Mannich reaction. Wang *et al*.[3h,10] reported pyrrolidine-based sulfonamide organocatalyst in asymmetric Michael addition of aldehydes to nitroalkenes, asymmetric Aldol reaction of α,α-dialkyl substituted aldehydes with aromatic aldehydes, asymmetric Mannich reaction of ketones with α-imino esters. Tang *et al*.[2] devoted the same catalyst for the asymmetric Michael addition of ketones to alkylidene manolates with the additive *n*-butyric acid in organic solvent. Imai *et al*.[11] reported direct asymmetric Aldol reactions of aldehyde with ketones in brine using the novel sulfonamide catalysts, which give the desired adducts in high yields with modest enantioselectivities.

Recently, we have developed *L*-proline-based binaphthyl sulfonimides and sulfonamides **1** (Figure 1) as highly efficient and stereoselective organocatalysts for the asymmetric Michael addition of ketones to nitroalkenes with the additive $PhCO_2H$ in organic solvent or in water.[12] We assumed that catalysts **1** should be also a well organocatalyst and tried to apply them to catalyze the Michael addition reaction of ketones to alkylidene malonates. Herein, we present the application of *L*-proline-based binaphthyl sulfonimides and sulfona-

* E-mail: dudm@bit.edu.cn; Tel.: 0086-010-68914985; Fax: 0086-010-68914985
Received September 17, 2012; accepted November 1, 2012.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cjoc.201200910 or from the author.

CHINESE JOURNAL OF CHEMISTRY

mides **1** in the asymmetric Michael addition of ketone to alkylidene malonates to give the desired products in good to high yields with good to excellent enantioselectivities and diastereoselectivities (up to 98% yield, 92% *ee*, 99∶1 *dr*) under mild conditions in water.

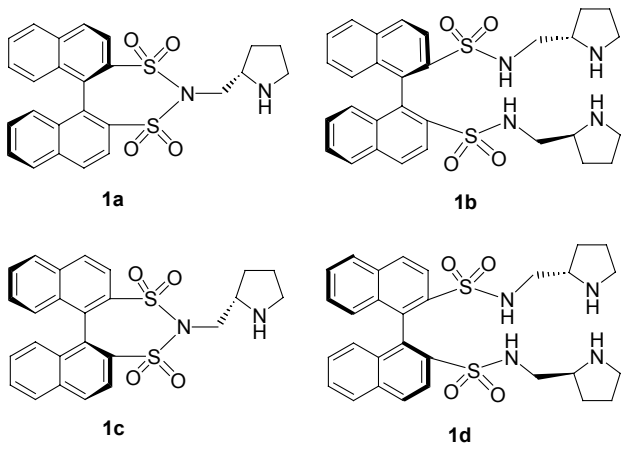


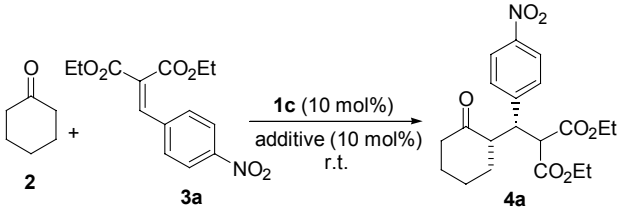
Figure 1 Binaphthyl sulfonimide and sulfonamide organocatalysts **1a**—**1d**.

Results and Discussion

Initially, the Michael reaction of cyclohexanone **2** with 2-(4-nitrobenzylidene)malonate (**3a**) catalyzed by catalyst **1c** (10 mol%) was selected as a model reaction at room temperature. The results are listed in Table 1. It was found that no desired product was observed under solvent-free reaction conditions without additive. To our delight, the reaction proceeded smoothly when $PhCO_2H$ was added as the additive; high diastereoselectivity (*dr*) and enantioselectivity were obtained (Table 1, Entry 2; 93% *ee*, 93∶7 *dr*). A series of solvents were then investigated, and the results are listed in Table 1. As expected, CH_2Cl_2, CH_3CN, THF, Et_2O, *i*-PrOH and DMF were employed as the solvent in the reaction, and the product was obtained in high diastereoselectivities and enantioselectivities but with poor yields (Table 1, Entries 3—8; 88%—90% *ee*, 25%—47% yield). Particularly, the optimal procedure was to perform the reaction in water (Table 1, Entry 16), which gave 88% yield with 97∶3 diastereoselectivity and 90% *ee* (major) in a shorter time. The reaction rate, yield, and enantioselectivity were decreased when acids $PhCO_2H$ (Table 1, Entry 9; 89% *ee*, 53% yield) and 2-$O_2NC_6H_4CO_2H$ (Table 1, Entry 10; 89% *ee*, 30% yield) were added in water. No product was observed in the presence of CF_3SO_3H and CF_3CO_2H (Table 1, Entries 11 and 12). Furthermore, the results of reaction were not better by using brine instead of water (Table 1, Entry 17). To our delight, increasing the catalyst loading increased the yield from 86% to 98% and enantioselectivity from 90% *ee* to 92% *ee* (Table 1, Entries 16 and 18).

Encouraged by these results, other chiral catalysts were screened by using water as solvent without additive, and the results are summarized in Table 2. The

Table 1 Optimization of solvents and additive[a]



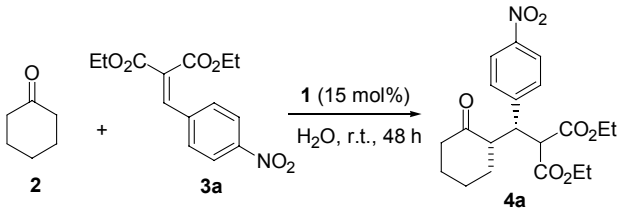
Entry	Additive	Solvent	Time/h	Yield[b]/%	*dr* (*syn*/*anti*)[c]	*ee*[d]/%
1	—	—	72	0	—	—
2	$PhCO_2H$	—	72	50	93∶7	93
3	$PhCO_2H$	CH_2Cl_2	72	35	93∶7	88
4	$PhCO_2H$	CH_3CN	72	47	92∶8	90
5	$PhCO_2H$	THF	72	25	91∶9	90
6	$PhCO_2H$	Et_2O	72	30	91∶9	89
7	$PhCO_2H$	*i*-PrOH	72	37	92∶8	90
8	$PhCO_2H$	DMF	72	35	91∶9	90
9	$PhCO_2H$	H_2O	48	53	96∶4	89
10	2-$O_2NC_6H_4$-CO_2H	H_2O	48	30	90∶10	89
11	CF_3SO_3H	H_2O	48	0	—	—
12	CF_3CO_2H	H_2O	48	0	—	—
13	CF_3CO_2H	Brine	48	0	—	—
14	DMAP	H_2O	48	35	94∶6	89
15	DMAP	Brine	48	40	95∶5	88
16	—	H_2O	48	88	97∶3	90
17	—	Brine	48	86	97∶3	90
18[e]	—	H_2O	48	98	97∶3	92

[a] All reactions were carried out using cyclohexanone (**2**, 196 mg, 2.0 mmol), additive (10 mol%) and catalyst **1c** (10 mol%) in solvent (0.2 mL) with stirring at room temperature for 15 min. Then 2-(4-nitrobenzylidene) malonate (33 mg, 0.125 mmol) was added. [b] Yield of the isolated product after chromatography on silica gel. [c] Determined by chiral HPLC on Chiracel IA column with *n*-hexane and 2-propanol as eluents. [d] Determined by chiral HPLC analysis. [e] The catalyst was loading at 15 mol%.

catalyst **1c** gave the best result: 98% yield and 92% *ee* (Table 2, Entry 3) for the *syn* diastereomer (97∶3 *dr*). It was observed that, by changing the chirality of the binaphthyl part as in **1a**, the results were equally good with enantioselectivity of 91% *ee* (Table 2, Entry 1). Slight higher yields and enantioselectivities catalyzed by sulfonimides **1a** and **1c** were observed than sulfonamides **1b** and **1d**.

Under the optimized conditions, a variety of alkylidene malonate substrates were investigated to test the generality of the present reaction and the results are summarized in Table 3. Various alkylidene malonates can react smoothly with cyclohexanone in the presence of the catalyst **1c** (15 mol%), leading to the corresponding adducts in moderate to high yields and with good to excellent diastereoselectivities and high enantioselectivities in water (Table 3, Entries 1—9, 11 and 12). It was observed that substituents on aryl groups had no obvious influence on the diastereoselectivities and

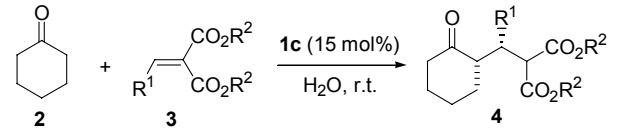
Table 2 Screening of catalysts[a]



Entry	Catalyst	Yield[b]/%	*dr* (*syn*/*anti*)[c]	*ee*[d]/%
1	**1a**	91	96∶4	91
2	**1b**	88	93∶7	86
3	**1c**	98	97∶3	92
4	**1d**	87	90∶10	85

[a] All reactions were carried out using cyclohexanone (**2**, 196 mg, 2.0 mmol) and catalyst **1** (15 mol%) in water (0.2 mL) with stirring at room temperature for 15 min. Then 2-(4-nitrobenzylidene) malonate (33 mg, 0.125 mmol) was added. [b] Yield of the isolated product after chromatography on silica gel. [c] Determined by chiral HPLC on Chiracel IA column with *n*-hexane and 2-propanol as eluents. [d] Determined by chiral HPLC analysis.

Table 3 Catalytic asymmetric Michael addition of cyclohexanone to alkylidene malonates[a]



Entry	R^1	R^2	Product	Yield[b]/%	*dr*[c]	*ee*[d]/%
1	4-$NO_2C_6H_4$	Et	**4a**	98	97∶3	92
2	4-$NO_2C_6H_4$	Me	**4b**	97	96∶4	91
3	3-$NO_2C_6H_4$	Et	**4c**	95	96∶4	90
4	3-$NO_2C_6H_4$	Me	**4d**	88	98∶2	88
5	2-$NO_2C_6H_4$	Et	**4e**	80	99∶1	91
6	2-$NO_2C_6H_4$	Me	**4f**	85	>99∶1	92
7[e]	4-FC_6H_4	Me	**4g**	69	97∶3	88
8[e]	4-ClC_6H_4	Me	**4h**	64	97∶3	88
9[e]	4-BrC_6H_4	Me	**4i**	68	97∶3	88
10[e]	4-MeC_6H_4	Me	**4j**	—	—	—
11[e]	4-$CH_3OC_6H_4$	Me	**4k**	49	86∶14	92
12[f]	3-Pyridineyl	Me	**4l**	61	80∶20	87
13[f]	Cyclohexyl	Me	**4n**	—	—	—
14[f]	Ph	Me	**4o**	—	—	—
15[f]	Ph	*i*-Pr	**4p**	—	—	—
16[f]	Ph	Ph	**4q**	—	—	—
17[f]	Ph	Bn	**4r**		—	—

[a] Unless otherwise noted, the reactions were carried out using cyclohexanone **2** (196 mg , 2.0 mmol) and catalyst **1c** (15 mol%) in water (0.2 mL). The mixture was stirred at room temperature for 15 min, then alkylidene malonate **3** (0.20 mmol) was added and stirred at room temperature for 72 h. [b] Yield of the isolated product after chromatography on silica gel. [c] Determined by chiral HPLC. [d] Determined by chiral HPLC analysis, the configuration was assigned according to literature. [e] The reaction time was 8 d. [f] The reaction time was 12 d.

enantioselectivities but affected strongly the yields (Table 3, Entries 1—12). Alkylidene malonates with electron-donating groups gave poor yields than those with electron-withdrawing groups (Table 3, Entries 1—9 vs. 10, 11). 4-Methylphenyl or phenyl substituted substrate has very low reactivity, no reaction was occurred at all (Table 3, Entries 10 and 14—17).

Furthermore, the asymmetric Michael addition of other ketones such as cyclopentanone, cycloheptanone, acetone were also carried out in the presence of catalyst **1c**. Unfortunately, the reactions for cyclopentanone, cycloheptanone or acetone with alkylidene malonates in water did not afford corresponding product.

Based on the configuration of the product, we propose the putative transition state for the **1c**-catalyzed asymmetric Michael addition of cyclohexanone to alkylidene malonates as shown in Figure 2. The pyrrolidine ring first reacts with the carbonyl compound to form the enamine. The oxygen atom of the sulfonimides group, via a H-bond with water, directs the alkyliene manolates so that the enamine will attack the alkyliene manolates from the *Re* face to give product with high enantio- and diastereoselectivity.

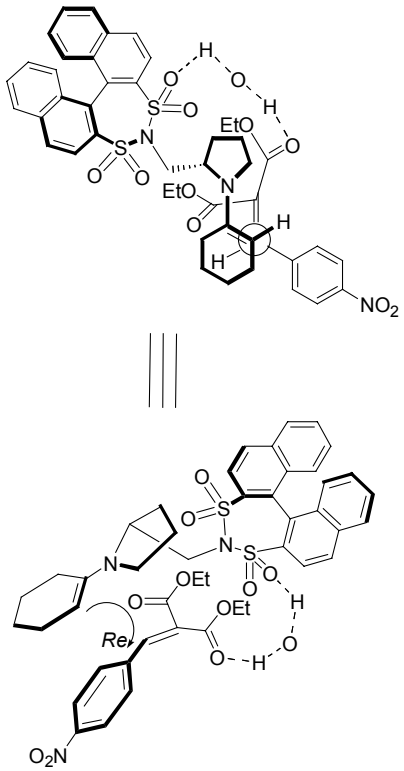


Figure 2 A proposed transition state.

Conclusions

In summary, we have developed an *L*-proline-based binaphthyl sulfonamide-catalyzed asymmetric Michael addition of cyclohexanone to alkylidene malonates, and the corresponding products were obtained in good to high yields (up to 98%) with good to excellent diastereoselectivity (up to 99∶1 *dr*) and high enantio-

selectivity (up to 92% *ee*) under mild conditions in water. Meanwhile, the putative transition state for the **1c**-catalyzed asymmetric Michael addition of cyclohexanone to alkylidene malonates was proposed.

Experimental

Materials

Commercially available compounds were used without further purification. Column chromatography was carried out using silica gel (200—300 mesh). Melting points were measured with an XT-4 melting point apparatus. The NMR spectra were recorded with Varian Mercury-plus 400 MHz or Bruker Avance III 400 MHz spectrometer. Optical rotations were measured with a WZZ-3 polarimeter. The enatiomeric excesses (*ee* values) of the products were determined by chiral HPLC analysis using an Aglient HP 1200 instrument (*n*-hexane/2-propanol as eluent). High resolution mass spectra (HRMS) were recorded on a Bruker PEX IV Fourier-Transform mass spectrometer with electrospray ionization (ESI). *L*-Proline-based binaphthyl sulfonimides and sulfonamides **1** were prepared according to our previous report.[12]

General procedure for asymmetric Michael addition of hexanone to alkylidene malonates

The organocatalyst **1c** (14.7 mg, 0.03 mmol) was added to cyclohexanone **2** (196 mg, 2.0 mmol) in H_2O (0.2 mL) and stirred for 15 min. Then alkylidene malonates **3** (0.2 mmol) was added, and the resulting mixture was stirred at room temperature for indicated time until the reaction was complete (monitered by TLC). The corresponding Michael addition product was isolated by flash chromatography on silica gel using petroleum ether-ethyl acetate (10∶1 to 5∶1) as eluent.

2-[(2-Oxocyclohexyl)-4-nitrophenylmethyl]malonic acid diethyl ester (**4a**)[9b]: The product **4a** was obtained as a white solid (76.6 mg, 98% yield) according to the general procedure after reacted for 72 h. HPLC (Chiralpak IA, hexane/*i*-PrOH, $V∶V$=70∶30, flow rate 0.80 mL/min, detection at 230 nm): *syn* diastereomer t_R(minor)=13.5 min, t_R(major)=22.9 min; *syn*/*ant*=97/3, 92% *ee*.

2-[(2-Oxocyclohexyl)-4-nitrophenylmethyl]malonic acid dimethyl ester (**4b**)[9b]: The product **4b** was obtained as a white solid (70.0 mg, 97% yield) according to the general procedure after reacted for 72 h. HPLC analysis (Chiralpak AS-H column, *n*-hexane/ 2-propanol, $V∶V$=96∶4, flow rate 1 mL/min, detection at 254 nm): *syn* diastereomer t_R(minor)=46.1 min, t_R(major)=58.9 min; *syn*/*anti*=96/4, 91% *ee*.

2-[(2-Oxocyclohexyl)-3-nitrophenylmethyl]malonic acid diethyl ester (**4c**)[9b]: The product **4c** was obtained as a colorless oil (75.0 mg, 95% yield) according to the general procedure after reacted for 72 h. HPLC analysis (Chiralpak IA column, *n*-hexane/2-propanol, $V∶V$=90∶10, flow rate 0.80 mL/min, detection at 254 nm): *syn* diastereomer t_R(minor)=17.6 min, t_R(major)=24.9 min; *syn*/*anti*=96/4, 90% *ee*.

2-[(2-Oxocyclohexyl)-3-nitrophenylmethyl]malonic acid dimethyl ester (**4d**)[9b]: The product **4d** was obtained as a white solid (69.0 mg, 96% yield) according to the general procedure after reacted for 72 h. HPLC analysis (Chiralpak IA column, *n*-hexane/ 2-propanol, $V∶V$=70∶30, flow rate 0.80 mL/min, detection at 254 nm): *syn* diastereomer t_R(minor)=9.4 min, t_R(major)=11.1 min; *syn*/*anti*=98/2, 88% *ee*.

2-[(2-Oxocyclohexyl)-2-nitrophenylmethyl]malonic acid diethyl ester (**4e**): The product **4e** was obtained as a brown oil (54.0 mg, 69% yield) according to the general procedure after reacted for 72 h. $[\alpha]_D^{20}$ −32.7 (*c* 0.51, CH_2Cl_2); ^{1}HNMR (400 MHz, $CDCl_3$) δ: 7.75 (d, J=8.4 Hz, 1H, ArH), 7.52—7.50 (m, 2H, ArH), 7.37—7.33 (m, 1H, ArH), 4.06 (t, J=8.4 Hz, 1H, CH), 4.16—3.91 (m, 5H, CH+2CH_2), 3.18—3.12 (m, 1H, CH), 2.48—2.34 (m, 2H, CH_2), 2.05—2.02 (m, 1H, CH_2), 1.82—1.78 (m, 2H, CH_2), 1.74—1.66 (m, 2H, CH_2), 1.60—1.53 (m, 1H, CH_2), 1.50—1.43 (m, 1H, CH_2), 1.19 (t, J=7.2 Hz, 3H, CH_3), 1.07 (t, J=7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 211.4, 168.2, 168.0, 134.3, 132.1, 130.9, 128.8, 127.7, 124.3, 61.7, 61.3, 55.3, 53.1, 42.5, 32.7, 29.6, 28.3, 25.3, 13.8, 13.7; IR (KBr) *v*: 2939, 2866, 1728, 1530, 1448, 1358, 1243, 1178, 1032, 854, 788 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{25}NaO_7$ $[M+Na]^+$ 414.15232, found 414.15303. HPLC analysis (Chiralpak IA column, *n*-hexane/2-propanol, $V∶V$=70∶30, flow rate 0.80 mL/min, detection at 254 nm): *syn* diastereomer t_R(minor)=9.1 min, t_R(major)=16.6 min; *syn*/*ant*>99/1, 90% *ee*.

2-[(2-Oxocyclohexyl)-2-nitrophenylmethyl]malonic acid dimethyl ester (**4f**)[9c]: The product **4f** was obtained as a light yellow solid (61.0 mg, 85% yield) according to the general procedure after reacted for 72 h. HPLC analysis (Chiralpak IA column, *n*-hexane/2-propanol, $V∶V$=90∶10, flow rate 1.0 mL/min, detection at 254 nm): *syn* diastereomer t_R(minor)=15.1, t_R(major)=24.3 min; *syn*/*ant*>99/1, 92% *ee*.

2-[(2-Oxocyclohexyl)-4-fluorophenylmethyl]malonic acid dimethyl ester (**4g**): The product **4g** was obtained as a white solid (46.0 mg, 69% yield) according to the general procedure after reacted for 8 d. m.p. 91—93 ℃; $[\alpha]_D^{20}$ −17.5 (*c* 0.80, CH_2Cl_2); ^{1}HNMR (400 MHz, $CDCl_3$) δ: 7.25—7.21 (m, 2H, ArH), 6.98—6.94 (m, 2H, ArH), 4.00—3.95 (m, 2H, 2CH), 3.67 (s, 3H, CH_3), 3.49 (s, 3H, CH_3), 2.94—2.88 (m, 1H, CH), 2.48—2.43 (m, 1H, CH_2), 2.40—2.32 (m, 1H, CH_2), 2.01—1.98 (m, 1H, CH_2), 1.78—1.73 (m, 2H, CH_2), 1.65—1.58 (m, 2H, CH_2), 1.20—1.10 (m, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 211.9, 168.8, 168.4, 161.7 (d, $^1J_{C\text{-}F}$=244.2 Hz), 134.3, 130.9 (d, $^3J_{C\text{-}F}$=7.8 Hz), 115.0 (d, $^2J_{C\text{-}F}$=21.2 Hz), 55.5, 53.0, 52.5, 52.2, 43.1, 42.1, 31.9, 27.9, 24.6; IR(KBr) *v*: 3040, 3000, 2950, 2863, 1756, 1702, 1603, 1512, 1456, 1435, 1310, 1266, 1224, 1150, 1015, 979, 848, 788 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{21}FNaO_5$ $[M+Na]^+$ 359.12652, found 359.12725.

HPLC analysis (Chiralpak IA column, *n*-hexane/ 2-propanol, $V:V=90:10$, flow rate=0.80 mL/min, detection at 254 nm): *syn* diastereomer t_R(minor)=12.7, t_R(major)=13.8 min; *syn*/*ant*=97/3, 88% *ee*.

2-[(2-Oxocyclohexyl)-4-chlorophenylmethyl]malonic acid dimethyl ester (**4h**)[9c]: The product **4h** was obtained as a white solid (45.0 mg, 64% yield) according to the general procedure after reacted for 8 d. HPLC analysis (Chiralpak IA column, *n*-hexane/ 2-propanol, $V:V=90:10$, flow rate=0.80 mL/min, detection at 230 nm): *syn* diastereomer t_R(minor)=13.7, t_R(major)=14.9 min; *syn*/*anti*=97/3, 88% *ee*.

2-[(2-Oxocyclohexyl)-4-bromophenylmethyl]malonic acid dimethyl ester (**4i**)[9c]: The product **4i** was obtained as a white solid (54.0 mg, 68% yield) according to the general procedure after reacted for 8 d. HPLC analysis (Chiralpak IA column, *n*-hexane/2-propanol, $V:V=95:5$, flow rate 0.80 mL/min, detection at 230 nm): *syn* diastereomer t_R(minor)=21.7, t_R(major)=23.8 min; *syn*/*anti*=97/3, 88% *ee*.

2-[(2-Oxocyclohexyl)-4-methoxyphenylmethyl]-malonic acid dimethyl ester (**4k**)[9b]: The product **4k** was obtained as a white solid (34.0 mg, 49% yield) according to the general procedure after reacted for 8 d. HPLC analysis (Chiralpak AS-H column, *n*-hexane/ 2-propanol, $V:V=95:5$, flow rate 0.50 mL/min, detection at 230 nm): *syn* diastereomer t_R(minor)=40.4 min, t_R(major)=46.0 min; *syn*/*anti*=86/14, 92% *ee*.

2-[(2-Oxocyclohexyl)-3-pyridinylmethyl]malonic acid dimethyl ester (**4l**): The product **4l** was obtained as a red oil (39.0 mg, 69% yield) according to the general procedure after reacted for 12 d. $[\alpha]_D^{20}$ −80.2 (*c* 1.95, CH_2Cl_2); ^{1}HNMR (400 MHz, $CDCl_3$-d_6) δ: 8.52 (br s, 2H, ArH), 7.69 (d, J=8.0 Hz, 1H, ArH), 7.25 (s, 1H, ArH), 4.07 (d, J=8.4 Hz, 1H, CH), 4.01 (t, J=8.0 Hz, 1H, CH), 3.68 (s, 3H, CH_3), 3.52 (s, 3H, CH_3), 3.01—2.95 (m, 1H, CH), 2.46—2.33 (m, 2H, CH_2), 2.04—2.01 (m, 1H, CH_2), 1.83—1.76 (m, 2H, CH_2), 1.65—1.55 (m, 2H, CH_2), 1.21—1.12 (m, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$-d_6) δ: 211.3, 168.6, 168.2, 150.6, 148.3, 137.1, 130.8, 128.7, 54.7, 52.6, 52.30, 52.29, 42.2, 41.5, 31.8, 27.6, 24.8; IR (KBr) *v*: 2951, 2862, 1732, 1435, 1147, 1012, 738 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{22}NO_5$ $[M+H]^+$ 320.14925, found 320.14954. HPLC analysis (Chiralpak AD-H column, *n*-hexane/ 2-propanol, $V:V=90:10$, flow rate=0.80 mL/min, detection at 254 nm): *syn* diastereomer t_R(minor)=28.7, t_R(major)=29.7 min; *syn*/*anti*=80/20, 87% *ee*.

Acknowledgment

We are grateful for financial support from the National Natural Science Foundation of China (No. 21072020), the Science and Technology Innovation Program of Beijing Institute of Technology (No. 2011CX01008) and the Development Program for Distinguished Young and Middle-aged Teachers of Beijing Institute of Technology.

References

[1] For selected reviews, see (a) Berner, O. M.; Tedeschi, L.; Enders, D. *Eur. J. Org. Chem.* **2002**, 1877; (b) Du, D. M.; Hua, W. T. *Chin. J. Org. Chem.* **2002**, *22*, 164 (in Chinese); (c) Dalko, P. I.; Moisan, L. *Angew Chem., Int. Ed.* **2004**, *43*, 5138; (d) Tsogoeva, S. B. *Eur. J. Org. Chem.* **2007**, 1701; (e) Christoffers, J.; Koripelly, G.; Rosiak, A.; Rössle, M. *Synthesis* **2007**, 1279; (f) Vicario, J. L.; Badía, D.; Carrillo, L. *Synthesis* **2007**, 2065; (g) Almaşi, D.; Alonso, D. A.; Nájera, C. *Tetrahedron*: *Asymmetry* **2007**, *18*, 299; (h) Hawner, C.; Alexakis, A. *Chem. Commun.* **2010**, *46*, 7295.

[2] Cao, C. L.; Sun, X. L.; Zhou, J. L.; Tang, Y. *J. Org. Chem.* **2007**, *72*, 4073.

[3] (a) Ishii, T.; Fujioka, S.; Kotsuki, H. *J. Am. Chem. Soc.* **2004**, *126*, 9558; (b) List, B.; Pojarlier, P.; Martin, H. J. *Org. Lett.* **2001**, *3*, 2423; (c) Wang, W.; Wang, J.; Li, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 1369; (d) Hayashi, Y.; Gotoh, H.; Hayashi, T.; Shoji, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4212; (e) Luo, S. Z.; Mi, X. L.; Zhang, L.; Liu, S.; Xu, H.; Cheng, J. P. *Angew. Chem., Int. Ed.* **2006**, *45*, 3093; (f) Pansare, S. V.; Pandya, K. *J. Am. Chem. Soc.* **2006**, *128*, 9624; (g) Cao, C. L.; Ye, M. C.; Sun, X. L.; Tang, Y. *Org. Lett.* **2006**, *8*, 2901; (h) Zu, L. S.; Wang, J.; Li, H.; Wang, W. *Org. Lett.* **2006**, *8*, 3077; (i) Wang, J.; Li, H.; Lou, B.; Zu, L.; Guo, H.; Wang, W. *Chem. Eur. J.* **2006**, *12*, 4321; (j) Andrey, O.; Alexakis, A. *Org. Lett.* **2003**, *5*, 2559; (k) Alexakis, A.; Andrey, O. *Org. Lett.* **2002**, *4*, 3611; (l) Sakthivel, K.; Notz, W.; Bui, T.; Barbas, III. C. F. *J. Am. Chem. Soc.* **2001**, *123*, 5260; (m) Li, H.; Wang, Y.; Tang, L.; Wu, F.; Liu, X. F.; Guo, C. Y.; Foxman, B. M.; Deng, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 105; (n) Terada, M.; Ube, H.; Yaguchi, Y. *J. Am. Chem. Soc.* **2006**, *128*, 1454.

[4] (a) Hong, B. C.; Wu, M. F.; Tseng, H. C.; Liao, J. H. *Org. Lett.* **2006**, *8*, 2217; (b) Marigo, M.; Bertelsen, S.; Jørgensen, K. A. *J. Am. Chem. Soc.* **2006**, *128*, 5475.

[5] (a) Melchiorre, P.; Jørgensen, K. A. *J. Org. Chem.* **2003**, *68*, 4151; (b) Hechavarria Fonseca, M. T.; List, B. *Angew. Chem., Int. Ed.* **2004**, *43*, 3958; (c) Peelen, T. J.; Chi, Y. G.; Gellman, S. H. *J. Am. Chem. Soc.* **2005**, *127*, 11598; (d) Wang, J.; Li, H.; Zu, L. S.; Wang, W. *Adv. Synth. Catal.* **2006**, *348*, 425.

[6] Mossé, S.; Alexakis, A. *Org. Lett.* **2005**, *7*, 4361.

[7] Sulzer-Mossé, S.; Tissot, M.; Alexakis, A. *Org. Lett.* **2007**, *9*, 3749.

[8] (a) Betancort, J. M.; Sakthivel, K.; Thayumanavan, R.; Barbas, III. C. F. *Tetrahedron Lett.* **2001**, *42*, 4441; (b) Betancort, J. M.; Sakthivel, K.; Thayuman-avan, R.; Tanaka, F.; Barbas, III. C. F. *Synthesis* **2004**, *9*, 1509.

[9] (a) Zhao, G. L.; Vesely, J.; Sun, J. L.; Christensen, K. E.; Bonneau, C.; Córdova, A. *Adv. Synth. Catal.* **2008**, *350*, 657; (b) Liu, J.; Yang, Z. G.; Liu, X. H.; Weng, Z.; Liu, Y. L.; Bai, S.; Lin, L. L.; Feng, X. M. *Org. Biomol. Chem.* **2009**, *7*, 4120; (c) Magar, D. R.; Chang, C.; Ting, Y. F.; Chen, K. *Eur. Org. Chem.* **2010**, *11*, 2062.

[10] (a) Wang, W.; Wang, J.; Li, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 1369; (b) Wang, W.; Li, H.; Wang, J. *Tetrahedron Lett.* **2005**, *46*, 5077; (c) Wei, K.; Zhang, S.; He, S.; Li, P.; Jin, M.; Xue, F.; Luo, G.; Zhang, H.; Song, L.; Duan, W.; Wang, W. *Tetrahedron Lett.* **2008**, *49*, 2681; (d) Zu, L. S.; Xie, H. X.; Li, H.; Wang, J.; Wang, W. *Org. Lett.* **2008**, *10*, 1211; (e) Wang, W.; Wang, J.; Li, H. *Tetrahedron Lett.* **2004**, *45*, 7243.

[11] Miura, T.; Yasaku, Y.; Koyata, N.; Murakami, Y.; Imai, N. *Tetrahedron Lett.* **2009**, *50*, 2632.

[12] (a) Ban, S. R.; Du, D. M.; Liu, H.; Yang, W. *Eur. J. Org. Chem.* **2010**, 5160; (b) Luo, C. H.; Du, D. M. *Synthesis* **2011**, 1968.

(Zhao, C.)

