DOI: 10.1002/cjoc.201400077

Enatioselective Chalcogeno-Baylis-Hillman Reaction of Arylaldehydes with MVK and Acrylates Catalyzed by Chiral Thiepin-$TiCl_4$ Complex

Yan Yin,*[a,b] Guofeng Sun,[a] Heng Zhang,[a] Hong Zhou,[a] and Fanhong Wu[a]

[a] *School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, China*
[b] *Key Laboratory of Synthetic Chemistry of Natural Substances, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

In a rational chiral molecular design of chalcogenides, optically active thiepin with C_2-symmetric chirality was synthesized from commercially available thiophene. Then enatioselective Chalcogeno-Baylis-Hillman reactions of arylaldehydes with methyl vinyl ketone (MVK) and acrylates were investigated in the presence of thiepin-Lewis acid complex. Finally, up to 64% *ee* was achieved in the presence of 0.2 equiv. of (*S*)-thiepin at 20 ℃.

Keywords 3,3'-bithienyls, chiral thiepin, Chalcogeno-Baylis-Hillman reaction, chalcogenides, $TiCl_4$

Introduction

Baylis-Hillman reaction has attracted a lot of interest in recent years.[1] Since Kataoka group[2] firstly reported Chalcogeno-Baylis-Hillman reaction between vinyl ketones and aldehydes catalyzed by chalcogenides in the presence of Lewis acids to provide allylic alcohols in moderate to good yields, a series of chiral organocatalysts were investigated for the catalytic asymmetric version of Chalcogeno-Baylis-Hillman reaction.[3] Hydroxyl chalcogenides such as 10-methylthioisoborneol exhibited modest asymmetric induction for this transformation and 72% *ee* was achieved in the treatment of *p*-nitrobenzaldehyde with MVK.[3a] C_2 symmetric bidentate ligands and bisoxazoline ligands showed low to zero enantiomeric excess.[3b] Goodman *et al*.[3c] reported chiral tetrahydrothiophenes-catalyzed asymmetric Chalcogeno-Baylis-Hillman reaction of MVK with various aldehydes and only up to 49% *ee* was achieved under −78 ℃.

3,3'-Bithiophenes including dithienothiophenes, cyclopentadithiophenones and dithienosiloles have attracted a lot of attention in resent years for the frequency applications in organic field effect transistors, organic light-emitting diodes and dye-sensitized solar cells,[4] but there were few reports in enatioselective synthesis catalyzed by 3,3'-bithiophenes[5] although molecules with 3,3'-bithiophene backbond were of chiroptical properties due to the restricted rotation around the thiophene-thiophene bond assisted by substitutents at α or β-positions.[6] As we all know, optically active biphenyls and 1,1'-binaphthalenyls were proved to be quite efficient catalysts in asymmetric transformations, we predict chiral 3,3'-bithiophenes with the same C_2-symmetic chirality and modifiable sites as biphenyls and 1,1'-binaphthalenyls will also be widely applied in chiral synthesis.

In this paper, thiepin and optically active thiepin with C_2-symmetric chirality were synthesized from commercially available thiophene (Scheme 1), and the enatioselectivities of chiral thiepin-catalyzed Chalcogeno-Baylis-Hillman reaction of arylaldehydes with MVK and acrylates were investigated in the presence of Lewis acids.

Experimental

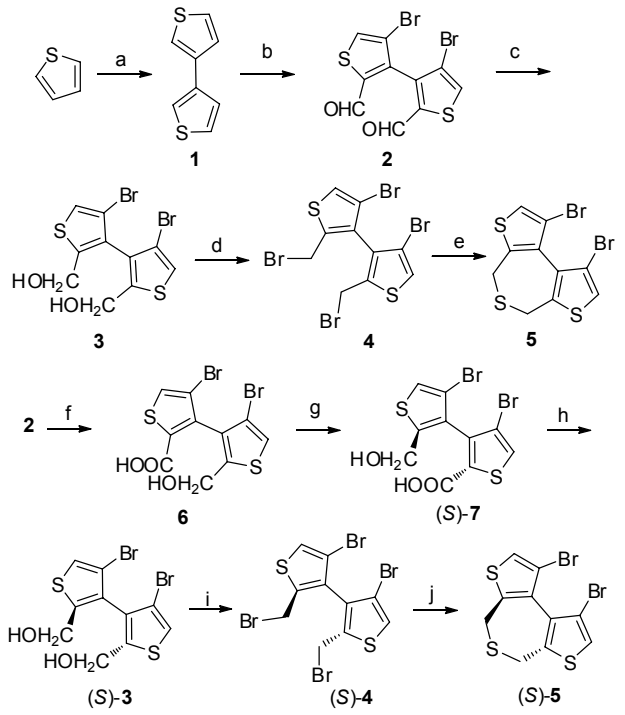
^{1}H NMR spetra were recorded at 300 MHz with TMS as an internal standard. IR spectra (KBr) were recorded on a FT-IR spectrometer in the range of 400−4000 cm^{-1}. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Substrates **8a**−**8d**, MVK, **11a**−**11c** were purchased from commercial sources and used as received. Substrate **11d** was prepared according to literature procedures. All products shown in this paper were known compounds and were characterized by ^{1}H NMR and IR spectrometer.

Preparation of thiepin 5 and optical active thiepin (*S*)-5

As shown in Scheme 1, thiepin **5** and optically active

* E-mail: yinyan@sit.edu.cn; Tel.: 0086-021-60877220; Fax: 0086-021-60877231
Received February 8, 2014; accepted March 28, 2014; published online April 22, 2014.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cjoc.201400077 or from the author.

Scheme 1 Synthesis of thiepin and (*S*)-thiepin



Reagents and conditions: (a) (i) Br_2, HBr, Et_2O; (ii) Zn, HOAc, Et_2O, reflux; (iii) *n*-BuLi, Et_2O, –78 ℃, then $CuCl_2$, Et_2O, r.t.; (b) (i) Br_2, (ii) *n*-C_4H_9Li, Et_2O, 0 ℃, then H_2O; (iii) *n*-C_4H_9Li, Et_2O, 0 ℃, then DMF; (c) $NaBH_4$, $(CH_3OCH_2CH_2)_2O$, r.t.; (d) PBr_3, benzene, reflux; (e) $Na_2S•H_2O$, ethanol, reflux; (f) KOH, reflux; (g) brucine, 95% ethanol, then 5 mol•L^{-1} HCl; (h) $LiAlH_4$, $AlCl_3$, Et_2O, reflux; (i) PBr_3, benzene, reflux; (j) $Na_2S•H_2O$, CH_3CN, reflux.

thiepin (*S*)-**5** were synthesized from commercially available thiophene according to reported procedures [4a]. Bromination of thiophene followed by reduction of 2,3,5-tribromothiophene and coupling reaction of 3-thiophen gave 3,3'-bithiophen (**1**) in large quantities. Bromination and twice transmetallations led to 4,4'-dibromo-2,2'-diformyl-3,3'-bithienyl (**2**). Reduction, bromination, and cyclization transferred **2** to thiepin **5**. Finally, thiepin **5** was obtained in 30% yields after 9 steps.

In alternative, **2** was transferred to (*S*)-(–)-thiepin through intramolecular Cammizzaro reaction, chiral separation with brucine, reduction, bromination and cyclization. Finally, optical active (*S*)-**5** was obtained in 17% yields after 11 steps.

(*S*)-1,9-Dibromo-4,6-dihydro-3,5,7-trithia-cyclopenta-[e]azulene [(*S*)-**5**]: $[\alpha]^{19}$ –62.6 (*c* 0.36, dioxane); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.20 (s, 2H), 3.80 (d, J= 13.8 Hz, 2H), 3.38 (d, J=13.8 Hz, 2H); IR v: 3107, 3099, 2912, 1210, 1089, 734 cm^{-1}.

General procedures of Chalcogenide-Baylis-Hillman reaction

Thiepin **5** or (*S*)-**5** (0.02 mmol), dry DCM (2 mL), Lewis acid (0.2 mmol) and aldehyde (0.2 mmol) in dry DCM (2 mL) were frequently added to a dry vial under argon. Then active alkene (0.24 mmol) was added after the reaction mixture was stirred for 15 min. At the end of the reaction, water (2 mL) was added to quench the reaction, and the organic phase was extracted with ethyl ether, washed with saturated brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give a residue.

A mixture of Et_3N (0.5 mL) in DCM (2 mL) was added to the obtained residue and the mixture was stirred for another 0.5 h at room temperature, then the mixture was concentrated under reduced pressure and purified on silica gel with hexane/EtOAc (V∶V=2∶1) as eluent to give normal Baylis-Hillman products.

3-[Hydroxy-(4-nitro-phenyl)-methyl]-but-3-en-2-one (**9a**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.16 (d, J=8.7 Hz, 2H), 7.53 (d, J=8.7 Hz, 2H), 6.26 (s, 1H), 6.04 (s, 1H), 5.66 (s, 1H), 3.42 (br, 1H, OH), 2.33 (s, 3H); IR v: 3480, 3076, 1662, 1523, 1346, 1049 cm^{-1}.

3-[(4-Chloro-phenyl)-hydroxy-methyl]-but-3-en-2-one (**9b**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.32—7.28 (m, 5H), 6.21 (s, 1H), 5.99 (s, 1H), 5.59 (s, 1H), 3.21 (br, 1H, OH), 2.34 (s, 3H); IR v: 3420, 1675, 1491, 1367, 1092 cm^{-1}.

3-(Hydroxy-phenyl-methyl)-but-3-en-2-one (**9c**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.34—7.30 (m, 5H), 6.19 (s, 1H), 5.99 (s, 1H), 5.61 (s, 1H), 3.0 (br, 1H, OH), 2.33 (s, 3H); IR v: 3444, 3061, 3031, 1674, 1628, 1454, 1020 cm^{-1}.

3-[Hydroxy-(4-methoxy-phenyl)-methyl]-but-3-en-2-one (**9d**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.22 (d, J= 9.2 Hz, 2H), 6.80 (d, J=9.2 Hz, 2H), 6.12 (s, 1H), 5.93 (d, J=1.1 Hz, 1H), 5.51 (d, J=1.1 Hz, 1H), 3.73 (s, 3H), 2.94 (br, 1H, OH), 2.27 (s, 3H); IR v: 3451, 2933, 1673, 1464, 1031 cm^{-1}.

3-Chloromethyl-4-(4-nitro-phenyl)-but-3-en-2-one (**10a**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.35 (d, J=8.8 Hz, 2H), 7.75 (d, J=8.8 Hz, 2H), 7.70 (s, 1H), 4.38 (s, 2H), 2.55 (s, 3H); IR v: 2919, 2849, 1668, 1519, 1347, 1271, 739, 694 cm^{-1}.

3-Chloromethyl-4-(4-chloro-phenyl)-but-3-en-2-one (**10b**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.64 (s, 1H), 7.60 (d, J=8.5 Hz, 2H), 7.46 (d, J=8.5 Hz, 2H), 4.42 (s, 2H), 2.6 (s, 3H); IR v: 3075, 2983, 1668, 1494, 719 cm^{-1}.

3-Chloromethyl-4-phenyl-but-3-en-2-one (**10c**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.71 (s, 1H), 7.56—7.50 (m, 5H), 4.46 (s, 2H), 2.51 (s, 3H); IR v: 3056, 1668, 1431, 1388, 700 cm^{-1}.

3-Chloromethyl-4-(4-methoxy-phenyl)-but-3-en-2-one (**10d**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.66 (s, 1H), 7.61 (d, J=8.6 Hz, 2H), 7.01 (d, J=8.6 Hz, 2H), 4.50 (s, 2H), 3.88 (s, 3H), 2.50 (s, 3H); IR v: 3003, 2837, 1659, 1604, 1509, 1483, 1177, 1030, 721 cm^{-1}.

2-[Hydroxy-(4-nitro-phenyl)-methyl]-acrylonitrile (**12a**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.26 (d, J=8.7 Hz, 2H), 7.62 (d, J=8.7 Hz, 2H), 6.20 (s, 1H), 6.12 (s, 1H), 5.46 (s, 1H), 2.95 (br, 1H, OH); IR v: 3448, 3116, 3082, 2229, 1607, 1521, 1409, 1342, 1058 cm^{-1}.

2-[Hydroxy-(4-nitro-phenyl)-methyl]-acrylic acid

CHINESE JOURNAL OF CHEMISTRY

methyl ester (**12b**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.58 (d, J=9.0 Hz, 2H), 7.27 (d, J=9.0 Hz, 2H), 6.41 (s, 1H), 5.89 (s, 1H), 5.64 (d, J=6 Hz, 1H), 3.76 (s, 3H), 3.35 (br, 1H, OH); IR v: 3512, 3107, 1699, 1602, 1519, 1445, 1349, 1045 cm^{-1}.

2-[Hydroxy-(4-nitro-phenyl)-methyl]-acrylic acid ethyl ester (**12c**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.21 (d, J=8.2 Hz, 2H), 7.58 (d, J=8.2 Hz, 2H), 6.40 (s, 1H), 5.86 (s, 1H), 5.63 (d, J=6.0 Hz, 1H), 4.19 (q, J=8.0 Hz, 2H), 3.40 (d, J=6.0 Hz, OH), 1.27 (t, J=8.0 Hz, 3H); IR v: 3477, 3079, 2982, 1712, 1607, 1521, 1402, 1350, 1059 cm^{-1}.

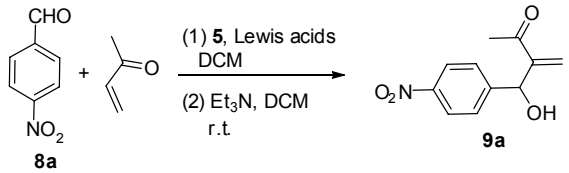
2-[Hydroxy-(4-nitro-phenyl)-methyl]-acrylic acid naphthalen-1-yl ester (**12d**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.13 (d, J=8.9 Hz, 2H), 7.56 (d, J=8.9 Hz, 2H), 7.80−7.78 (m, 1H), 7.70−7.64 (m, 1H), 7.38−7.34 (m, 4H), 7.10−7.06 (m, 1H), 6.75 (s, 1H), 6.12 (s, 1H), 5.72 (d, J=5.6 Hz, 1H), 3.18 (d, J=5.6 Hz, OH); IR v: 3522, 3065, 1732, 1599, 1520, 1345, 1044 cm^{-1}.

Results and Discussion

Lewis acids, temperatures, solvents, reaction substrates, catalysts and quenchers exhibited great influences on Chalcogenide-Baylis-Hillman reaction. Reaction conditions including Lewis acids, temperatures and quenchers were initially screened with *p*-nitrobenzaldehyde and methyl vinyl ketone as reaction substrates, DCM as solvent, and thiepin **5** as catalyst. The results are shown in Table 1. With water as quencher, only chlorinated product was obtained in the presence of $TiCl_4$ as Lewis acid at –20 ℃. If reaction mixture was further treated with Et_3N in DCM for another 0.5 h, chlorinated product would disappear and normal Baylis-Hillman product **9a** was separated in 89% yield through column chromatography on silica gel (Entry 1). While reaction temperature was increased from –20 to 20 ℃, reaction rate was greatly accelerated and 92% yield was obtained after 0.1 h (Entry 2). Changing Lewis acid from $TiCl_4$ to BBr_3 led to lower reaction rate (Entry 3 vs. Entry 1), and 13% yield based on *p*-nitrobenzaldehyde and 87% yield based on consumed *p*-nitrobenzaldehyde were obtained after 4 h, respectively (Entry 3). In the presence of 1 equiv. of BF_3•OEt_2 which was of weaker acidity compared to $TiCl_4$ and BBr_3, very low to zero yields were obtained even with longer reaction time (Entries 4 and 5 vs. Entries 1−3). Without Lewis acids, the intermolecular Baylis-Hillman reaction did not take place (Entry 6) because the carbonyl group in MVK was not activated by acids, which were mentioned by Kataoka[3d] and Shi[7] before. $TiCl_4$ as Lewis acid exhibited highest reaction rate and reaction yields among the screened Lewis acids, so $TiCl_4$ was chosen for further explorations of Chalcogenide-Baylis-Hillman reaction between benzaldehydes and active alkenes.

Next, we explored the scope of the intermolecular Chalcogenide-Baylis-Hillman reaction with MVK as nucleophilic reagent. After screening a series of benzaldehydes with different substitutions *para* to carbonyl group, we found both substituent groups and reaction time had obvious effects on the reaction products, and the results are shown in Table 2. Prolonging the reaction time of *p*-nitrobenzaldehyde with MVK from 0.1 to 0.5 h led to 11% elimination product **10a** in 20 ℃ (Entries 2 and 3). The results would be explained that normal Baylis-Hillman product **9a** was kinetical control and elimination product **10a** was thermodynamic control

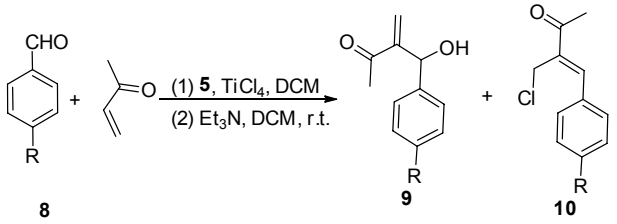
Table 1 Effect of temperatures and Lewis acids on Chalcogeno-Baylis-Hillman reactions[a]



Entry	Lewis acid	Temp./℃	Time/h	Yield[b]/%
1	$TiCl_4$	–20	1.5	89
2	$TiCl_4$	20	0.1	92
3	BBr_3	–20	4	13 (87)[c]
4	BF_3•OEt_2	–20	48	NR[d]
5	BF_3•OEt_2	20	48	Trace[d]
6	—	20	48	NR[d]

[a] Conditions: *p*-nitrobenzaldehyde (0.2 mmol), MVK (0.24 mmol), thiepin **5** (0.02 mmol), Lewis acid (0.2 mmol), DCM (2 mL), then Et_3N (0.5 mL), DCM (2 mL). [b] Isolated yield based on *p*-nitrobenzaldehyde. [c] Isolated yield based on consumed *p*-nitrobenzaldehyde. [d] Detected by TLC plate.

Table 2 Effect of substitutions and reaction time on Chalcogeno-Baylis-Hillman reactions[a]



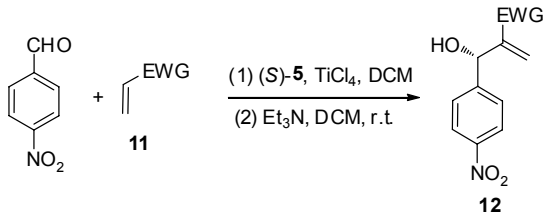
Entry	R	Temp./℃	Time/h	Yield of **9**[b]/%	Yield of **10**[b]/%
1	NO_2 (**8a**)	–20	1.5	89	NR[c]
2	NO_2 (**8a**)	20	0.1	92	NR[c]
3	NO_2 (**8a**)	20	0.5	80	11
4	Cl (**8b**)	20	48	Trace[c]	65 (87)[d]
5	H (**8c**)	20	48	Trace[c]	50 (84)[d]
6	CH_3O[e] (**8d**)	20	48	38	33

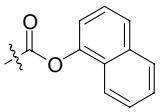
[a] Conditions: benzaldehyde (0.2 mmol), MVK (0.24 mmol), thiepin **5** (0.02 mmol), $TiCl_4$ (0.2 mmol), DCM (2 mL), then Et_3N (0.5 mL), DCM (2 mL). [b] Isolated yield based on benzaldehyde. [c] Detected by TLC plate. [d] Isolated yield based on consumed benzaldehydes and unconsumed benzaldehyde was recovered. [e] 12% of **8d** was recovered.

which was more stable than **9a**.[8] **8b** with Cl and **8c** with H at *para* position were transferred to *Z*-olefin in 65% and 50% yields after 48 h under 20 ℃, respectively (Entries 4 and 5). **8d** with electron-donating group gave normal B-H product and elimination produce in 38% and 33% yields, respectively (Entry 6). To our surprise, **9d** which was hard to be obtained in 1,4-diazabicyclo[2.2.2]octane (DABCO) system, was easy to be obtained in current thiepin-$TiCl_4$ system. In present reaction system only B-H product **9a** would be obtained in high yield within short reaction time probably due to the high reaction activity of *p*-nitrobenzaldehyde. So *p*-nitrobenzaldehyde was chosen as carbonyl electrophilic reagent in further exploration.

For normal Baylis-Hillman products have an array of multifunctional groups which could be subjected to numerous transformations and proved to be valuable building blocks for bioactive compounds and natural products, and there was one chiral center, it would be valuable to investigate enatioselective Chalcogeno-Baylis-Hillman reactions of *p*-nitrobenzaldehyde with a series of active alkenes including acrylonitrile, methyl acrylate, ethyl acrylate and *α*-naphthyl acrylate catalyzed by (*S*)-thiepin-$TiCl_4$ complex. The results are shown in Table 3. Under –20 ℃, **8a** was transferred to **9a** in 11% *ee* and 89% yield after 1.5 h (Entry 1). Although lowing reaction temperature would benefit the enantiomeric excess, the yields of *p*-nitrobenzaldehyde and activated alkenes except MVK were very low under –20 ℃ even with 48 h reaction time, so we kept the stereochemistry investigation at 20 ℃ (Entries 2—6). The enatiomeric excess values were below 10% while acrylonitrile (**11a**), methyl acrylate (**11b**), and ethyl acrylate (**11c**) were submitted to the treatment (Entries 2—4). To our surprise, in the treatment of *α*-naphthyl acrylate (**11d**), 50% *ee* and 86% yield based on consumed *p*-nitrobenzaldehyde were obtained (Entry 5). Then 64% enatioselectivity was obtained while increasing the catalyst loading to 20 mol% (Entry 6). The absolute configuration of **11d** was determined as *S*-configuration by comparison of the HPLC retention time with the reported ones.[9]

Table 3 Enatioselective Chalcogeno-Baylis-Hillman reactions catalyzed by (*S*)-thiepin-$TiCl_4$ complex[a]



Entry	EWG	Temp./℃	Time/h	Yield[b]/%	*ee*[c]/%
1	$COCH_3$ (MVK)	–20	1.5	89	11
2	CN (**11a**)	20	48	81	4
3	$COOCH_3$ (**11b**)	20	48	19 (88)[d]	5
4	$COOC_2H_5$ (**11c**)	20	48	14 (89)[d]	2
5	 (**11d**)	20	48	17 (86)[d]	50 (*S*)[e]
6[f]		20	48	23 (88)[d]	64 (*S*)[e]

[a] Conditions: *p*-nitrobenzaldehyde (0.2 mmol), acrylates (0.24 mmol), (*S*)-thiepin (0.02 mmol), $TiCl_4$ (0.2 mmol), DCM (2 mL), then Et_3N (0.5 mL), DCM (2 mL). [b] Isolated yield based on *p*-nitrobenzaldehyde. [c] Determined by chiral HPLC. [d] Isolated yield based on consumed *p*-nitrobenzaldehyde. [e] The absolute configuration was determined by comparison of the HPLC retention time with the reported ones. HPLC condition: 2-propanol/hexane (V : V=20 : 80, 0.6 mL/min), t_R=30.62 min (*S*) and 32.08 min (*R*). [f] The loading of catalyst (*S*)-thiepin was 20 mol%.

Conclusions

We have designed unique C_2-symmetric chiral thiepin which can be readily synthesized starting from industrial thiophene. Thorough investigation of this asymmetric Baylis-Hillman reaction we found that our catalyst could asymmetrically induce Baylis-Hillman reaction. We believe that appropriately modified thiepin would achieve better asymmetric induced effect in Baylis-Hillman reaction and the synthesis is currently in progress in our laboratory.

Acknowledgement

The work was partially supported by the Science and Technology Commission of Shanghai Municipality (No. 12ZR1431100). Support from Prof. Gang Zhao was also greatly appreciated.

References

[1] (a) Zeng, X. P.; Liu, Y. L.; Ji, C. B.; Zhou, J. *Chin. J. Chem.* **2012**, *30*, 2631; (b) Yang, W. H.; Sha, F.; Zhang, X.; Yuan, K.; Wu, X. Y. *Chin. J. Chem.* **2012**, *30*, 2652.

[2] Kataoka, T.; Iwama, T.; Tsujiyama, S. I. *Chem. Commun.* **1998**, 197.

[3] (a) Kataoka, T.; Iwama, T.; Tsujiyama, S. I.; Kanematsu, K.; Iwamura, K.; Watanabe, S. I. *Chem. Lett.* **1999**, *28*, 257; (b) Iwama, T.; Tsujiyama, S. I.; Kinoshita, H.; Kanematsu, K.; Tsurukami, Y.; Iwamura, T.; Watanabe, S. I.; Kataoka, T. *Chem. Pharm. Bull.* **1999**, *47*, 956; (c) Walsh, L. M.; Winn, C. L.; Goodman, J. M. *Tetrahedron Lett.* **2002**, *43*, 8219; (d) Kataoka, T.; Kinoshita, H. *Eur. J. Org. Chem.* **2005**, 45.

[4] (a) Reddy, J. S.; Kale, T.; Balaji, G.; Chandrasekaran, A.; Thayumanavan, S. *J. Phys. Chem. Lett.* **2011**, *2*, 648; (b) Mazzeo, M.; Vitale, V.; Sala, F. D.; Anni, M.; Barbarella, G.; Favaretto, L.; Sotgiu, G.; Cingolani, R.; Gigli, G. *Adv. Mater.* **2005**, *17*, 34; (c) Zeng, W. D.; Cao, Y. M.; Bai, Y.; Wang, Y. H.; Shi, Y. S.; Zhang, M.; Wang, F. F.; Pan, C. Y.; Wang, P. *Chem. Mater.* **2010**, *22*, 1915; (d) Evans, N. R.; White, A. J. P. *Org. Biomol. Chem.* **2013**, *11*, 3871; (e) Han, H.; Zhao, H. L.; Song, J. S.; Li, C. L.; Wang, H. *J. Org. Chem.* **2013**, *78*, 2726.

[5] (a) Benincori, T.; Cesarotti, E.; Piccolo, O.; Sannicolò, F. *J. Org. Chem.* **2000**, *65*, 2043; (b) Benaglia, M.; Benincori, T.; Mussini, P.; Pilati, T.; Rizzo, S.; Sannicolò, F. *J. Org. Chem.* **2005**, *70*, 7488; (c) Bashilov, V. V.; Dolgushin, F. M.; Petrovskii, P. V.; Sokolov, V. I.; Sada, M.; Benincori, T.; Zotti, G. *J. Organometallic Chem.* **2005**,

690, 4330.
[6] (a) Wiklund, E.; Håkansson, R. *Chemica Scripta* **1974**, *6*, 76; (b) Wiklund, E.; Håkansson, R. *Chemica Scripta* **1974**, *6*, 174; (c) Almqvist, A.; Håkansson, R. *Chemica Scripta* **1976**, *10*, 120.
[7] Shi, M.; Jiang, J. K. *Tetrahedron* **2000**, *56*, 4793.
[8] Shi, M.; Jiang, J. K.; Cui, S. C. *Tetrahedron* **2001**, *57*, 7343.
[9] Yang, K. S.; Lee, W. D.; Pan, J. F.; Chen, K. *J. Org. Chem.* **2003**, *68*, 915.

(Zhao, C.)

