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Valine-derived phosphinothiourea as organocatalyst in enantioselective Morita–Baylis–Hillman reactions of acrylates with aromatic aldehydes

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ABSTRACT

A new type of chiral bifunctional phosphinothiourea derived from L-valine is synthesized and used as an organocatalyst in the enantioselective Morita–Baylis–Hillman reaction of aromatic aldehydes with acrylates. The desired products were obtained in good enantioselectivities (up to 83% ee) and in excellent yields (up to 96%) under mild reaction conditions.

1. Introduction

The Morita–Baylis–Hillman (MBH) reaction is an important carbon–carbon formation process[1] and much research effort has been concentrated on improving its efficiency and selectivity over the last decade.[2] Various chiral organocatalysts including (*S*)-proline,[3] quinidine derivatives,[4] BINOL derivatives,[5] bis(thio)ureas,[6] bifunctional aminothiourea,[7] bifunctional phosphinothiourea,[8] and chiral amino alcohol-derived thiourea[9] have been developed for the asymmetric MBH reaction to achieve high enantioselectivity. Although the MBH reaction of enone with aldehydes and aza-MBH reactions have achieved good results,[2a–d] the asymmetric MBH reaction of aldehydes with acrylates is still a challenge. A few effective chiral organocatalysts have been tested for this process.[2e,4a,c,10] For example, Hatakeyama reported the excellent enantioselective MBH reaction of 1,1,1,3,3,3-hexafluoroisopropyl acrylate (HFIPA) with aldehydes (up to 99% ee),[4a,c] and Shi used a quinidine-derived chiral amine as organocatalyst for the MBH reaction of aldehydes with α-naphthyl acrylate to obtain as high as 92% ee but poor yield (only 17%).[10a] To the best of our knowledge, the best result of the organocatalyzed-MBH reaction of aldehydes with unactivated alkyl acrylates (such as methyl, ethyl, or butyl acrylate) was achieved by using a tertiary amine as a catalyst to give the corresponding adducts with moderate ee.[2e]

The L-valine-derived amino-phosphine **1**[11a] is a useful chiral precursor for constructing N, P-ligands, which are efficient in various metal-catalyzed asymmetric transformations, such as allylic alkylation,[11b–f] transfer hydrogenation,[11g] and diethylzinc addition to enones.[11h] Recently, we developed a new class of phosphinothiourea organocatalysts **2a**–**f** derived from the amino-phosphine **1**, and evaluated them in the enantioselective MBH reaction. Herein we report the MBH reaction of aldehydes and acrylates catalyzed by the bifunctional phosphinothioureas.

2. Results and discussion

The organocatalysts **2a**–**f** are easily prepared by condensation of amino-phosphine **1** with 1.1 equiv of the corresponding iso(thio) cyanate under mild conditions (Scheme 1).

Initially the asymmetric Morita–Baylis–Hillman reaction of 4-nitrobenzaldehyde with methyl acrylate was performed with 10 mol % of catalysts **2a**–**f** at 25 °C in THF under an N_2 atmosphere. The results summarized in Table 1 indicate that the thiourea moiety obviously affected the MBH reaction in terms of both yields and enantioselectivities. The organocatalysts containing aromatic thiourea unit led to higher yields and enantioselectivities than those bearing aliphatic or alicyclic thiourea moiety (entries 1–4 vs entries 5 and 6). There was not an obvious diversity of the enantio selectivities catalyzed by the aromatic thiourea **2a**–**d**, but the yield was lower when **2c** was used as a catalyst. Comparatively, **2a** was the best catalyst for this transformation and furnished the desired product in 93% yield and 81% ee (entry 1). The L-valine-derived phosphinothioureas led to the MBH reaction products with an (*R*)-configuration; the absolute configuration was assigned by comparing the specific rotation value with those reported in the literatures.[4a,10c,12] For comparison, phosphinothiourea **2g** and **2h**[8b] derived from (*R*,*R*)-1-amino-2-(diphenylphosphino)cyclohexane were examined (Scheme 2). As expected, organocatalysts **2g** and **2h** provided (*S*)-configuration MBH products. It is noteworthy that organocatalyst **2g** was more reactive than other screened organocatalysts, and the MBH reaction was completed in 8 h. However, with **2g** and **2h** as catalysts, the enantioselectivity was lower than the corresponding organocatalysts **2a** and **2d**, respectively (entry 7 vs 1, entry 8 vs 4).

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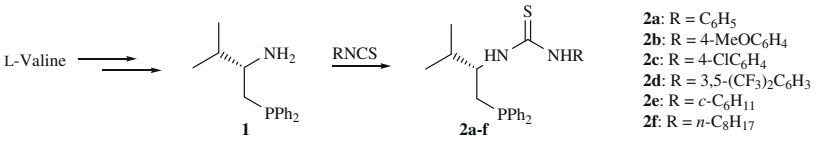
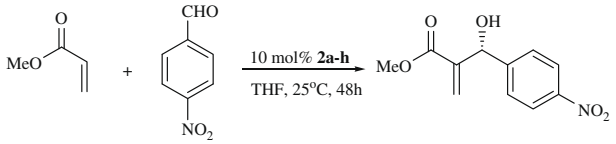


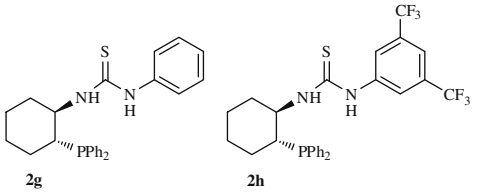
Scheme 1. Synthesis of the phosphinothiourea catalysts.

Table 1
Screening of the catalysts for the reaction of methyl acrylate and 4-nitrobenzaldehyde[a]



Entry	Catalyst	Yield[b] (%)	ee[c] (%)
1	**2a**	93	81[d]
2	**2b**	89	78
3	**2c**	79	80
4	**2d**	94	79
5	**2e**	80	70
6	**2f**	76	76
7[e]	**2g**	96	72[f]
8	**2h**	82	61[f]

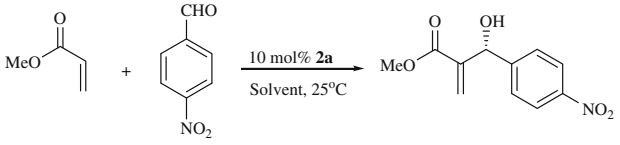
[a] The reactions were conducted with 10 mol % of organocatalyst and 5 equiv of methyl acrylate in THF (0.2 M) under N_2 at 25 °C.
[b] Isolated yields.
[c] Determined by chiral HPLC using Chiralcel OD-H column.
[d] $[\alpha]_D^{20} = -38.8$ (*c* 0.4, MeOH).
[e] The reaction time is 8 h.
[f] The absolute configuration of the MBH reaction product is (*S*).



Scheme 2. Structure of the phosphinothiourea **2g** and **2h**.

Next, we investigated the solvent effects on this process with **2a** as the organocatalyst (Table 2). Among the solvents screened, THF was the optimal one for both yield and ee (entry 1). With ether and 1,4-dioxane as solvents, the product was obtained in moderate ee, and the chemical yields decreased remarkably (entries 2 and 3 vs entry 1). The reaction proceeded quickly in EtOH, but a by-product was formed, and the desired product was provided in 53% yield. In non-protonic polar solvents, such as DMF and DMSO, the MBH product was obtained in moderate yields with low ee (entries 6 and 7). In the case of CH_3CN, the product was provided in very poor ee and in low yield. Furthermore, other reaction conditions including the ratio of acrylate to aldehyde **3/4** and the loading of the catalyst were investigated. The results indicated that when lowering the ratio of **3/4** from **5/1** to **3/1**, the chemical yield was reduced (entry 1 vs entry 11). The catalyst loading affected both the chemical yields and enantioselectivities of the product (entry 1 vs entries 12 and 13). When the catalyst loading was reduced to 5 mol %, the reaction became slower, and only 55% chemical yield was obtained after 72 h, while the enantioselectivity decreased (entry 12). An improvement in the enantioselectivity or yield was not observed when using 20 mol % organocatalyst. Thus 10 mol % of organocatalyst **2a** was selected for further study.

Table 2
The optimization of the reaction conditions[a]



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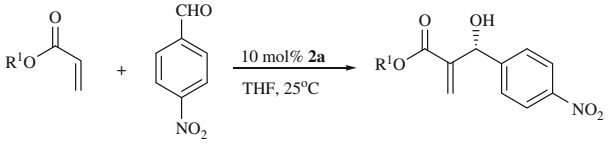
Entry	Solvent	Time (h)	Yield[b] (%)	ee[c] (%)
1	THF	48	93	81
2	Ether	26	77	74
3	1,4-Dioxane	48	54	75
4	Toluene	48	44	63
5	EtOH	20	53	58
6	DMF	48	64	32
7	DMSO	40	77	30
8	CH_2Cl_2	40	67	28
9	$CHCl_3$	48	62	28
10	CH_3CN	48	32	4
11[d]	THF	96	81	80
12[e]	THF	72	55	71
13[f]	THF	48	91	77

[a] Unless stated otherwise, the reactions were conducted with 10 mol % of organocatalyst and 5 equiv of methyl acrylate in solvent (0.2 M) under N_2 at 25 °C.
[b] Isolated yields.
[c] Determined by chiral HPLC using Chiralcel OD-H column.
[d] The reaction was conducted with 3 equiv of methyl acrylate.
[e] The reaction was conducted with 5 mol % of organocatalyst.
[f] The reaction was conducted with 20 mol % of organocatalyst.

Table 3
The MBH reactions of different acrylates with 4-nitrobenzaldehyde catalysed by **2a**[a]



Entry	R^1	Time (h)	Yield[b] (%)	ee[c] (%)
1	Me	48	93	81
2	Et	48	92	80
3	*n*-Bu	48	94	83
4	Bn	42	92	76
5	*t*-Bu	48	72	74
6	Ph	46	24	4
7	1-Naphthyl	46	36	2

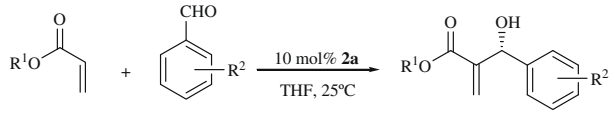
[a] The reactions were conducted with 10 mol % of organocatalyst and 5 equiv of acrylate in THF (0.2 M) under N_2 at 25 °C.
[b] Isolated yields.
[c] Determined by chiral HPLC using Chiralcel OD-H, Chiralpak AS-H, or Chiralpak AD-H column.

Under the established optimal reaction conditions (10 mol % **2a** as a catalyst, 5 equiv of acrylate, THF as the solvent at 25 °C under N_2), the MBH reactions of different acrylates with 4-nitrobenzaldehyde were surveyed using **2a** as a catalyst. The results are summarized in Table 3. There was not obvious change in the enantioselectivities or chemical yields when un-branched alkyl acrylates (R^1 = *n*-Bu, Me and Et) and benzyl acrylate were used as Michael donor, while *t*-butyl acrylate provided lower yield and

enantioselectivity (entries 1–4 vs entry 5). On the other hand, phenyl acrylate and 1-naphthyl acrylate gave the product in very low yields with poor ee and dioxanone was observed as a by-product (entries 6 and 7).[4a] The results indicated that the structure of acrylate is critical for the MBH reaction, and the bulky-hindrance group of the acrylate had a negative effect on the enantioselectivity and chemical yield (entries 1–5 vs entries 6 and 7).

Finally, various aromatic aldehydes were investigated under the optimal reaction conditions (10 mol % **2a** as a catalyst, 5 equiv of acrylate, THF as the solvent at 25 °C under N_2). As indicated in Table 4, the strong electron-deficient benzaldehydes were transformed to the desired products in excellent yields and moderate-to-good enantioselectivities (entries 1–12). The results indicated that the position of the substituent on benzaldehyde was very important for the enantioselectivity, *ortho* substitution such as 2-nitrobenzaldehyde had a deleterious effect on the enantioselectivities (entries 1–3 and 7–9 vs entries 4–6). The 4-trifluoromethylbenzaldehyde reacted with methyl acrylate providing higher ee than other acrylates, but the yield was lower (entries 10–12). The reaction with weakly electron-deficient benzaldehydes and non-substituted benzaldehydes gave relatively poor yields and moderate enantioselectivities (entries 13 and 14).

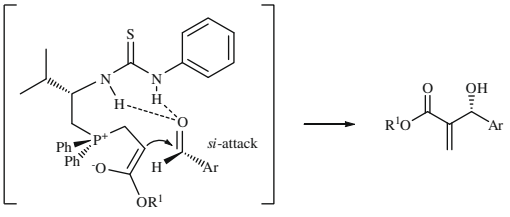
Table 4
The MBH reactions between various aromatic aldehydes with different acrylates catalyzed by **2a**[a]



Entry	R^1	R^2	Time (h)	Yield[b] (%)	ee[c] (%)
1	Me	4-NO_2	48	93	81
2	Et	4-NO_2	48	92	80
3	*n*-Bu	4-NO_2	48	94	83
4	Me	2-NO_2	55	86	55
5	Et	2-NO_2	55	91	50
6	*n*-Bu	2-NO_2	47	94	50
7	Me	3-NO_2	55	86	79
8	Et	3-NO_2	48	87	74
9	*n*-Bu	3-NO_2	47	96	78
10	Me	4-CF_3	55	61	83
11	Et	4-CF_3	55	82	67
12	*n*-Bu	4-CF_3	50	81	66
13	*n*-Bu	4-Br	65	28	59
14	*n*-Bu	H	72	11	56

[a] The reactions were conducted with 10 mol % of organocatalyst and 5 equiv of acrylate in THF (0.2 M) under N_2 at 25 °C.
[b] Isolated yields.
[c] Determined by chiral HPLC using Chiralpak AS-H, Chiralcel OD-H, Chiralcel OJ, or Chiralpak AD-H column.

A possible mechanism of this asymmetric MBH reaction can be explained as a Michael addition and an aldol reaction on the basis of the generally accepted reaction mechanism, and the proposed transition state is illustrated in Scheme 3. The thiourea moiety forms a hydrogen-bond with the aldehyde carbonyl, and the phosphinoyl associated alkoxy enolate attacks the activated carbonyl from the *si*-face to give the product in an (*R*)-configuration.



Scheme 3. Proposed transition state of **2a**-catalyzed MBH reaction.

3. Conclusions

In conclusion, we have developed a new kind of chiral bifunctional phosphinothiourea derived from L-valine. These organocatalysts were efficient for the asymmetric MBH reaction of acrylates with aldehydes. In the presence of 10 mol % **2a**, the MBH product was obtained in up to 83% ee and moderate-to-excellent yields (up to 96%). The advantage of this catalyst is that the chiral starting material is facile and inexpensive. The further refinement of the catalyst structure and extension of the utility to other MBH reactions are under active investigation.

4. Experimental

4.1. General

Melting points are taken without correction. Optical rotations were measured on a WZZ-2A digital polarimeter at the wavelength of the sodium D-line (598 nm). ^{1}H NMR spectra were recorded on Bruker 500 (500 MHz) spectrometer, and chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ, 0.00) with the solvent resonance as an internal standard ($CDCl_3$: 7.24 ppm) and coupling constants (Hz). ^{13}C NMR spectra were recorded on Bruker 500 (125 MHz) or 400 (100 MHz) instrument with complete proton decoupling, and chemical shifts were reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard ($CDCl_3$: 77.0 ppm). High Resolution Mass spectra (HRMS) were recorded on Micromass GCT spectrometer with Electron Ionization (EI) resource. HPLC analysis was performed on Waters 510 with 2487 detector using Daicel Chiralpak AS-H, Chiralcel OD-H, Chiralcel OJ, or Chiralpak AD-H column.

4.2. Synthesis of phosphine-thiourea catalysts 2a–f

To a solution of (*S*)-2-amino-1-diphenylphoshino-3-methylbutane **1**[11a] (271 mg, 1.0 mmol) in 2.0 mL CH_2Cl_2 was added isothiocyanate (1.1 mmol) at room temperature, and the corresponding mixture was stirred at this temperature until the completion of the reaction (monitored by TLC). The solvent was removed under reduced pressure and the residue was purified by column chromatography (petroleum ether/ethyl acetate = 4/1 or 3/1) to afford the chiral phosphine-thiourea compounds **2a**–**f**.

4.2.1. Phosphine-thiourea catalyst 2a

White solid, 60% yield, mp: 54.6–55.7 °C; $[\alpha]_D^{25} = +32.1$ (*c* 0.7, $CHCl_3$); IR (KBr, cm^{-1}): ν 3229, 3056, 2957, 1598, 1540, 1494, 1043, 565; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.8 (s, 1H), 7.49–7.42 (m, 4H), 7.40–7.35 (t, 2H, J = 7.7 Hz), 7.34–7.23 (m, 7H), 7.07 (d, 2H, J = 7.7 Hz), 5.97 (d, 1H), 4.59 (br, 1H), 2.44–2.38 (m, 1H), 2.32–2.24 (m, 1H), 2.17–2.09 (m, 1H), 0.87 (d, 3H, J = 6.8 Hz), 0.83 (d, 3H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.08, 137.99, 136.19, 132.96 (d, J = 5.2 Hz), 132.77 (d, J = 5.2 Hz), 129.99, 128.86, 128.60, 128.57, 128.53, 128.49, 126.94, 125.09, 58.36 (d, J = 14.2 Hz), 31.77 (d, J = 8.6 Hz), 31.23 (d, J = 13.5 Hz), 18.88, 18.03; HRMS (EI) calcd for $C_{24}H_{27}N_2PS$ ($[M]^+$) 406.1633, obsd 406.1635.

4.2.2. Phosphine-thiourea catalyst 2b

Colorless oil, 73% yield, $[\alpha]_D^{25} = +51.0$ (*c* 0.5, $CHCl_3$); IR (KBr, cm^{-1}): ν 3378, 2943, 1535, 1509, 1240, 1159, 1031, 693; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.59 (s, 1H), 7.53–7.40 (m, 4H), 7.38–7.30

(m, 6H), 7.00 (d, 2H, J = 8.4 Hz), 6.88 (d, 2H, J = 8.80 Hz), 5.77 (d, 1H, J = 8.4 Hz), 4.57 (br, 1H), 3.83 (s, 3H), 2.46–2.38 (m, 1H), 2.31–2.22 (m, 1H), 2.19–2.06 (m, 1H), 0.90–0.84 (d, 3H, J = 6.8 Hz), 0.84–0.78 (d, 3H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.84, 158.59, 132.99 (d, J = 5.2 Hz), 132.81 (d, J = 5.2 Hz), 130.65, 128.72, 128.70, 128.65, 128.63, 127.52, 114.99, 57.92 (d, J = 10.6 Hz), 55.48, 31.87 (d, J = 8.6 Hz), 30.84, 18.83, 18.05; HRMS (EI) calcd for $C_{25}H_{29}N_2OPS$ ($[M]^+$) 436.1738, obsd 436.1740.

4.2.3. Phosphine-thiourea catalyst 2c

White solid, 70% yield, mp: 121.2–122.2 °C; $[\alpha]_D^{25} = +59.0$ (c 0.5, $CHCl_3$); IR (KBr, cm^{-1}): ν 3225, 3037, 2960, 1528, 1494, 1341, 1299, 1085, 685; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.52–7.40 (m, 5H), 7.38–7.29 (m, 7H), 7.00 (d, 2H, J = 5.79 Hz), 5.89 (br, 1H), 4.59 (br, 1H), 2.50–2.42 (m, 1H), 2.32–2.22 (m, 1H), 2.18–2.09 (m, 1H), 0.92–0.82 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.08, 137.88, 134.86, 132.92 (d, J = 10.0 Hz), 132.73 (d, J = 10.0 Hz), 132.30, 130.01, 128.97, 128.91, 128.65, 128.61, 128.58, 128.54, 126.25, 58.45 (d, J = 14.0 Hz), 31.91 (d, J = 8.5 Hz), 31.48 (d, J = 13.1 Hz), 18.74, 18.27; HRMS (EI) calcd for $C_{24}H_{26}ClN_2PS$ ($[M]^+$) 440.1243, obsd 440.1276.

4.2.4. Phosphine-thiourea catalyst 2d

White solid, 72% yield, mp: 168.8–170.2 °C; $[\alpha]_D^{25} = +7.0$ (c 0.5, CH_2Cl_2); IR (KBr, cm^{-1}): ν 3250, 3080, 2960, 1554, 1460, 1383, 1273, 1187, 1145, 1026, 581; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.01 (br, 1H), 7.65 (s, 3H), 7.45–7.38 (m, 4H), 7.34–7.26 (m, 6H), 6.09 (br, 1H), 4.62 (br, 1H), 2.53–2.51 (m, 1H), 2.32–2.27 (m, 1H), 2.20–2.05 (m, 1H), 0.98–0.89 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 180.54, 139.41(m), 138.54, 138.46, 133.64, 133.49, 133.32, 133.18, 129.78, 129.62, 129.36, 129.31,126.71, 124.55, 123.97, 122.38, 120.25, 119.63, 59.33 (d, J = 12.9 Hz), 32.78, 31.39, 19.20, 18.99; HRMS (EI) calcd for $C_{26}H_{25}N_2F_6PS$ ($[M]^+$) 542.1380, obsd 542.1392.

4.2.5. Phosphine-thiourea catalyst 2e

Colorless oil, 65% yield, $[\alpha]_D^{25} = -81.7$ (c 0.3, $CHCl_3$); IR (KBr, cm^{-1}): ν 3279, 3049–2925, 2852–1547, 1538, 1532, 1023, 557; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.52–7.41 (m, 4H), 7.41–7.31 (m, 6H), 5.44 (br, 1H), 2.52–2.41 (m, 1H), 2.39–2.26 (m, 1H), 2.22–2.16 (m, 1H), 1.95–1.81 (m, 2H), 1.76–1.64 (m, 2H), 1.40–1.20 (m, 4H), 1.20–1.00 (m, 3H), 0.98–0.93 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.08, 138.01, 133.01, 132.90, 132.82, 132.71, 128.94, 128.64, 128.91, 128.68, 128.65, 128.62, 128.58, 57.72, 52.47, 32.74, 32.20 (d, J = 8.3 Hz), 31.42, 25.38, 24.62, 24.58, 18.97, 18.06; HRMS (EI) calcd for $C_{24}H_{33}N_2PS$ ($[M]^+$) 412.2102, obsd 412.2105.

4.2.6. Phosphine-thiourea catalyst 2f

Colorless oil, 65% yield, $[\alpha]_D^{25} = -11.0$ (c 0.5, $CHCl_3$); IR (KBr, cm^{-1}): ν 3270, 3064, 2921, 2853, 2127, 1543, 1351, 741, 690; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.53–7.42 (m, 4H), 7.47–7.29 (m, 6H), 5.46 (br, 1H), 3.20–2.70 (br, 1H), 2.51–2.42 (m, 1H), 2.45–2.36 (m, 1H), 2.19–2.06 (m, 1H), 1.47–1.39 (m, 2H), 1.37–1.20 (m, 12H), 0.98–0.91 (m, 6H), 0.91–0.88 (t, 3H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 181.18, 137.32, 132.98 (d, J = 6.6 Hz), 132.79 (d, J = 6.8 Hz), 129.08, 128.71, 128.68, 128.65, 128.62, 57.70, 43.53, 32.19 (d, J = 8.2 Hz), 31.75, 31.18, 29.21, 29.14, 28.83, 26.88, 22.61, 18.84, 18.14, 14.07; HRMS (EI) calcd for $C_{26}H_{39}N_2PS$ ($[M]^+$) 442.2572, obsd 442.2573.

4.3. General procedure for the organocatalytic Morita–Baylis–Hillman reaction

To a solution of the phosphine-thiourea (0.02 mmol) in THF (1.0 mL) was added the acrylate (1.0 mmol) at 25 °C under N_2. After stirring at this temperature for 10 min, the aromatic aldehyde (0.2 mmol) was added. And the reaction mixture was stirred at 25 °C until the completion of the reaction (monitored by TLC). The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography to afford the Baylis–Hillman adduct and the ee value was determined by HPLC analysis on a chiral stationary phase.

Acknowledgments

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