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Asymmetric Synthesis of Dihydropyrimidines Using Chiral Schiff Base Copper(II) Complex as a Chiral Catalyst

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Abstract: Asymmetric Biginelli reaction was performed to afford the corresponding chiral 3,4-dihydropyrimidine-2-ones (**DHPO**s), and their sulfur analogs 3,4-dihydropyrimidine-2-thiones (**DHPT**s). These compounds were obtained in high yields with good enantioselectivities (up to 79 ee%, dominant enantiomers: S-configuration and dextrorotatory) in the presence of bis{(S)-(+)-(1-phenylethyl)-[(2-oxo-1H-benzo-1-ylidene)methyl]aminato}copper(II) (**BPACu**) as a chiral catalyst, under the solvent-free conditions. This method has several advantages, for example good enantioselectivities, high to excellent products yields, short times reaction, easy work up and solvent free condition. Also, this catalyst was recyclable for three consecutive runs.
Keywords: Enantioselectivitie synthesis, Asymmetric synthesis, 3,4-dihydropyrimidine-2-one, 3,4-dihydropyrimidine-2-thione, Chiral Schiff Base Copper(II) Complex.

Introduction

The Biginelli reaction, one of the most useful multicomponent reactions, affords 3,4-dihydropyrimidines (**DHP**s)[1, 2]. Academic researches during years from discovery this reaction[3], are shown that **DHPs** have pharmaceutical properties (antiviral, antitumor, antibacterial, and antiinflammatory properties)[4-7]. From structural point of view, due to the stereogenic center (C_4) (Fig. 1), **DHP**s have two enantiomers. Each enantiomer may be show different pharmaceutical activities[8-10]. The methods to obtain of optically pure **DHP** such as chiral auxiliary-assisted [11-15] and the catalytic asymmetric reaction[16-18] (easier methods), have rarely been reported in the literature.

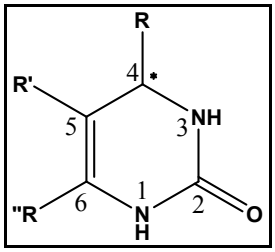


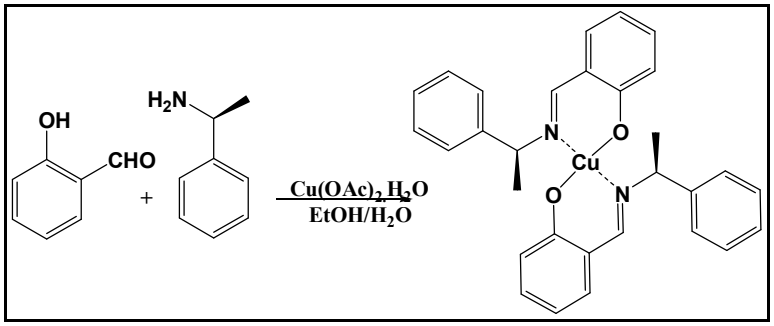
Fig. 1 Structure of DHP

Chiral Schiff Base Copper(II) Complex has shown catalysts effects for asymmetric synthesis (in example cyclopropanations[19, 20], aziridination[21], oxidation[22] and Hetero-Diels-Alder reactions [23, 24]).

In continuation of my investigations on the synthesis of (**DHPO**s & **DHPT**s) via Biginelli protocols [25, 26], here in, I wish to report using efficient synthetic chiral catalysts **BPACu**[24, 27] in the preparation of **DHPO**s & **DHPT**s in high yields with good enantiomer excess.

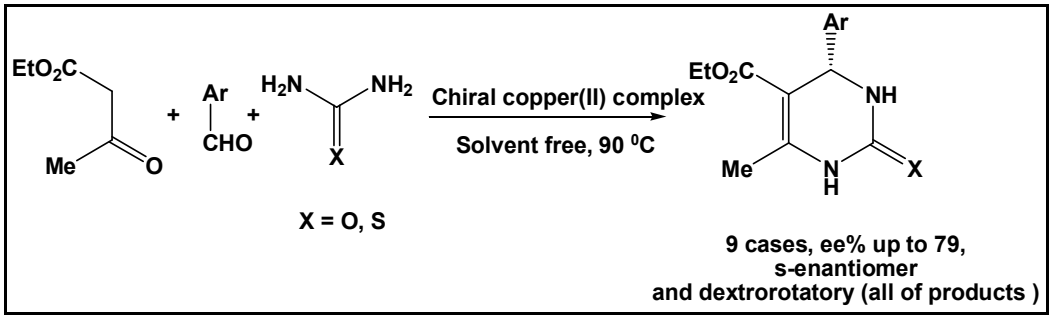
Results and discussion

In this research, initially, the copper chiral complex ((S)-(+)-**BPACu**) was synthesized using of benzaldehyde, (S)-1-phenylethylamine and $Cu(OAc)_2.H_2O$ in manner of reported by Ana L. Iglesias [24] and J. M. Ferna´ndez-G. et al. [27] (Scheme 1).



Scheme 1 Synthesis of chiral copper complex ($C_{30}H_{28}N_2O_2$)

The free-solvent biginelli reaction were performed by the reaction, benzaldehyde and urea with ethyl acetoacetate in the presence of chiral catalyst (20 mol%) to afford the desired **DHPO** (**7a)** in 88% yield (ee% of 73%) as model case study (Scheme 2). Then the reaction conditions were optimized by conducting the reaction at different temperatures, amount of catalyst and times. The results are summarized in Table 1, whereby better yields were obtained when the temperature was at 90 °C with 3 h reaction time and in the presence 5 mol% of catalyst.



Scheme 2 Enantioselective Biginelli reaction

Table 1 Synthesis of 7a under different conditions for optimization of reactions

Temp °C of React.	BPACu as catalyst (mol %)	Time(h)	Product Yield (%)
80	20	4	65
90	20	4	88
100	20	4	82
90	10	4	88
90	5	4	88
90	2.5	4	79
90	***5***	***3***	***88***
90	5	2	67

Several activated and deactivated aromatic aldehydes underwent the reaction to give the corresponding **DHP**s in high yields and good enantioselectivities with (**S**) configuration. The experimental procedure was very simple, convenient, and had the ability to tolerate a variety of other functional groups such as methoxy, nitro, hydroxy, and halides under the reaction conditions (Table 2).

Enantiomeric excess (ee%) (Optical purity) of synthesized **DHP**s, were obtained from the measurement of optical rotation of **DHP**s by polarimeter and comparison with their pure enantiomers (reported by Liu-Zhu Gong et.al. and Chengjian Zhu et.al [16, 17]) (Table 2), using formula as follows:

$$\text{Optical purity} = \%\ \text{enantiomeric excess} = \%\ \text{enantiomer}_1 - \%\ \text{enantiomer}_2 = 100\ [\alpha]_{\text{mixture}} / [\alpha]_{\text{pure sample}}$$

Table 2 Details Biginelli synthesis

Entry	Ar	Urea	Thio Urea	Product Yield %		$[\alpha]_D^{20}$ for pure enantiomer	$[\alpha]_D^{20}$ for reaction mixtue	ee% (calculated)	mp °C found
1	C_6H_5	*		**7a**	88	58 [16]	42.3	73	205-207
2	C_6H_5		*	**7b**	86	68 [16]	51.7	76	206-208
3	2-Cl-C_6H_5	*		**7c**	85	61 [16]	43.3	71	221-223
4	2-Cl-C_6H_5		*	**7d**	83	73 [16]	51.1	70	216-218
5	2-HO-C_6H_5	*		**7e**	**87**	63 [16]	49.8	79	198-201
6	3-MeO-C_6H_5	*		**7f**	82	102.9 [17]	77.2	75	205-207
7	3-(NO_2)-C_6H_4	*		**7g**	86	91 [16]	70.1	77	227-229
8	3-HO-C_6H_4	*		**7h**	88	59 [16]	45.4	77	187-189
9	3-HO-C_6H_4		*	**7i**	86	71 [16]	53.2	75	182-184

For example: the pure enantiomer of **DHP 7a** with **R** configuration has optical specific rotation of -58 ^{o} [16] and therefor the other enantiomer (**(S)-DHP**) has a specific rotation of +58 ^{o}. Specific rotation of the corresponding reaction mixture was obtained +42.3 ^{o} (by polarimeter). The result, optical purity of the mixture was calculated as below.

Optical purity, % = 100 $[a]_{\text{mixture}} / [a]_{\text{pure sample}}$ = 100 (+42.3) / +58 = 73%

Interestingly, the catalyst can be recycled for three consecutive runs without significant loss of activity (Table 3). For this purpose, after completion of the reaction, the reaction mixture was cooled to room temperature and then diethyl ether was added. The precipitated solid was recovered by filtration, and reused for the similar reaction.

Table 3 Recycled of BPACu in the synthesis of Biginelli reactions

Catalyst	Runs			
	1	2	3	4
Product yield (%)	88	87	80	61

Experimental

All reactions were carried out in an efficient hood. The starting materials were purchased from Merck and Fluka chemical companies. Melting points were determined with a Branstead Electrothermal model 9200 apparatus and are uncorrected. Optical rotations were determined at 25 °C with a Bellingham & Stanley P20 Polarimeter. IR spectra were recorded on a Perkin Elmer RX 1 Fourier transform infrared spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 and Acetone-d_6 on Bruker Avance 300 MHz spectrometers. Elemental analyses were carried out by a Perkin Elmer 2400 series II CHN/O analyzer.

Synthesis of bis{(S)-(+)-(1-phenylethyl)-[(2-oxo-1H-benzo-1-ylidene)methyl]aminato}co-pper(II) (BPACu) [23, 27]:

To a solution of the salicylaldehyde (0.002 mol) in EtOH (200 cm^3) was added a solution of (S)-(-)-1-phenylethylamine (0.002 mol) in EtOH (200 cm^3) followed by $Cu(OAc)_2.H_2O$ (0.0011mol) in H_2O (10 cm^3). The mixture was refluxed under nitrogen atmosphere for 18 h, then concentrated until a black mass was observed. It was then cooled in an ice bath until precipitation was completed, the black solid was collected by filtration, washed with a mixture cold H_2O-EtOH 9:1 and dried. Recrystallization from CH_2Cl_2-EtOH gave the complex as black crystals in 55% Yield; mp 148-149 °C (Found C, 70.29; H, 5.44; N, 5.58. Calc. for $C_{30}H_{28}N_2O_2Cu$: C, 70.36; H, 5.51; N, 5.47 %).

General procedure synthesis of DHPs:

A mixture of an aldehyde (2 mmol), ethyl acetoacetate (2 mmol), urea or thiourea (3 mmol) and catalyst **BPACu** (5 mol %) was heated on oil-bath with stirring at 90 °C for three hours (Tables 1 and 2). After cooling, diethylether was added and then precipitated solid was isolated by filtration. The solvent removed by evaporation, the crude product was recrystallized from ethanol to give the corresponding pure product. In all of products, the dominant enantiomer was the dextrorotatory and **S-**enantiomer.

(+)-5-Ethoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (7a): ee% = 73; $[\alpha]_D^{20}$ = +42.3 ° (c=0.5, MeOH); mp 204-206 ºC; IR (KBr): 3243, 1732, 1653, 1593, 600-800 cm^{-1}; ^{1}H NMR (300 MHz, Acetone- d_6) δ:1.11-1.16 (t, 3H, *J* = 7.1 Hz), 2.37 (s, 3H), 3.99-4.07 (q, 2H, *J* = 7.1 Hz), 5.35 (s, 1H), 6.8 (s, 1H), 7.36-7.22 (m, 5H), 8.29 (s, 1H); ^{13}C NMR (75 MHz, Acetone- d_6) δ: 14.4, 18.3, 55.9, 60.2, 100.9, 125.4, 127.6, 129.2, 133.3, 144.1, 148.9, 166.1; Anal. Calcd for $C_{14}H_{16}N_2O_3$: C, 64.60; H, 6.20; N, 10.76. Found: C, 64.25; H, 5.99; N, 10.98.

(+)-5-Ethoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-thione (7b): ee% = 76; $[\alpha]_D^{20}$ = +51.7 ° (c=0.5, MeOH); mp 206-208 ºC; IR (KBr): 3328, 2979, 1668, 1573, 1465, 600-800 cm $^{-1}$; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 1.08-1.1 (t, 3H, *J* = 7.1 Hz), 2.27 (s, 3H), 3.96-4.03 (q, 2H, *J* = 7.1 Hz), 5.16 (s, 1H), 7.19-7.36 (m, 5H), 8.29 (s, 1H), 9.65 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 14.0, 17.1, 54.3, 59.5, 101.3, 126.8, 128.1, 128.9, 143.0, 145.3, 165.1, 174.2; Anal. Calcd for $C_{14}H_{16}N_2O_2S$: C, 60.85; H, 5.84; N, 10.14. Found: C, 60.80; H, 5.73; N, 10.21.

(+)-5-Ethoxycarbonyl-6-methyl-4-(2-chlorophenyl)-3,4-dihydropyrimidin-2(1H)-one (7c): ee% = 71; $[\alpha]_D^{20}$ = +43.3 ° (c=0.5, MeOH); mp 221-223 ºC; IR (KBr): 1706, 1648, 1462, 784, 750, 600-800 cm $^{-1}$; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 1.00-1.1 (t, 3H, *J* = 7.1 Hz), 2.23 (s, 3H), 3.9-4.0 (q, 2H, *J* = 7.1 Hz), 5.12 (s, 1H), 7.21-7.39 (m, 4H), 7.74 (s, 1H), 9.22 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 14.0, 17.7, 51.2, 59.3, 98.9, 127.4, 129.8, 131.8, 134.2, 141.8, 143.0, 148.6, 151.2, 165.1; Anal. Calcd for $C_{14}H_{15}ClN_2O_3$: C, 57.05; H, 5.13; N, 9.50. Found: C, 56.96; H, 5.02; N, 9.59.

(+)-5-Ethoxycarbonyl-6-methyl-4-(2-chlorophenyl)-3,4-dihydropyrimidin-2(1H)-Thione (7d): ee% = 70; $[\alpha]_D^{20}$ = +51.1 ° (c=0.5, MeOH); mp 216-218 ºC; IR (KBR): 3187, 2980, 1687, 1520, 1346, 856, 600-800 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 0.97-1.01 (t, 3H, *J* = 7.1 Hz), 2.3 (s, 3H), 3.8-3.9 (q, 2H, *J* = 7.1 Hz), 5.6 (s, 1H), 7.2-7.4 (m, 4H), 9.6 (s, 1H), 10.4 (s, 1H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ: 13.8, 17.0, 51.3, 59.7, 99.4, 126.5, 127.6, 128.4, 131.7, 140.8, 145.3, 153.1, 164.7, 173.9; Anal. Calcd for $C_{14}H_{15}ClN_2O_2S$: C, 54.10; H, 4.86; N, 9.01. Found: C, 54.02; H, 4.78; N, 9.13.

(+)-5-Ethoxycarbonyl-6-methyl-4-(2-hydroxyphenyl)-3,4-dihydropyrimidin-2(1H)-One (7e): ee% = 79; $[\alpha]_D^{20}$ = +49.8 ° (c=0.5, MeOH); mp 188-201 ºC; IR (KBr): 3260, 3119, 2980, 1692, 1644, 1457, 855,600-800

cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ: 1-1.17 (t, 3H, *J* = 7.1 Hz), 3.3 (s, 3H), 3.8-3.9 (q, 2H, *J* = 7.1 Hz), 4.13 (s, 1H), 5.4 (s, 1H), 6.9-7.14 (m, 4H), 9.03 (s, 1H), 9.5 (s, 1H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ: 14.1, 17.6, 49.3, 58.1, 98.8, 123.7, 126.4, 127.9, 130.4, 146.5, 148.9, 152.0, 154.3, 165.4; Anal. Calcd for $C_{14}H_{16}N_2O_4$: C, 60.86; H, 5.84; N, 10.14. Found: C, 60.79; H, 5.75; N, 10.19.

(+)-5-Ethoxycarbonyl-6-methyl-4-(3-methoxyphenyl)-3,4-dihydropyrimidin-2(1H)-One (7f): ee% = 75; $[\alpha]_D^{20}$ = +77.2 ° (c=0.31, EtOAc); mp 205-207 ºC; IR (KBr): 3242, 2937, 1700, 1649, 1226, 774, 600-800 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ: 1.07-1.12 (t, 3H, *J* = 7.1 Hz), 2.2 (s, 3H), 3.7 (s, 3H), 3.9-4 (q, 2H, *J* = 7.1 Hz), 5.01 (s, 1H), 6.7-7.2 (m, 4H), 7.7 (s, 1H), 9.1 (s, 1H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ: 14.1, 17.7, 53.4, 54.4, 59.2, 102.6, 112.6, 113.3, 118.9, 129.8, 143.0, 148.6, 152.5, 157.7, 165.3; Anal. Calcd for $C_{14}H_{16}N_2O_2S$: C, 60.85; H, 5.84; N, 10.14. Found: C, 60.80; H, 5.73; N, 10.21. Anal. Calcd for $C_{14}H_{16}N_2O_4$: C, 60.86; H, 5.84; N, 10.14. Found: C, 60.77; H, 5.75; N, 10.23.

(+)-5-Ethoxycarbonyl-6-methyl-4-(3-nitrophenyl)-3,4-dihydropyrimidin-2(1H)-One (7g): ee% = 77; $[\alpha]_D^{20}$ = +70.1 ° (c=0.5, MeOH); mp 227-229 ºC; IR (KBr); (3333, 2932, 1707, 1528, 1349, 738, 600-800) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ: 1.01-1.10 (t, 3H, *J* = 6.2 Hz),2.2 (s, 3H), 3.9-3.99 (q, 2H, *J* = 6.2 Hz), 5.28 (s, 1H), 7.6-8.1 (m, 4H), 7.89 (s, 1H), 9.3 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 14.1,17.7, 53.7, 59.6, 99.9, 121.4, 122.1, 129.2, 132.6, 145.1, 145.6, 147.6, 149.2, 151.9, 151.9, 165.0; Anal. Calcd for $C_{14}H_{15}N_3O_5$: C, 55.08; H, 4.95; N, 13.76. Found: C, 55.01; H, 4.87; N, 13.82.

(+)-5-Ethoxycarbonyl-6-methyl-4-(3-hydroxyphenyl)-3,4-dihydropyrimidin-2(1H)-one (7h): ee% = 77; $[\alpha]_D^{20}$ = +45.4 ° (c=0.5, MeOH); mp 189-189 ºC; IR (KBr: 3260, 3119, 2980, 1692, 1644, 855, 600-800 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ: 1.10-1.13 (t, 3H, *J* = 7.1 Hz), 2.2 (s, 3H), 3.9-4 (q, 2H, *J* = 7.1 Hz), 5.04 (s, 1H), 7.4-8.2 (m, 4H), 7.41 (s, 1H), 9.15 (s, 1H), 9.4 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 14.2, 17.8, 53.8, 59.4, 99.5, 113.4, 114.3, 116.2, 129.3, 146.4, 148.9, 152.6, 157.4, 165.6; Anal. Calcd for $C_{14}H_{16}N_2O_4$: C, 60.86; H, 5.84; N, 10.14. Found: C, 60.74; H, 5.77; N, 10.25.

(+)-5-Ethoxycarbonyl-6-methyl-4-(3-hydroxyphenyl)-3,4-dihydropyrimidin-2(1H)-thione (7i): ee% = 75; $[\alpha]_D^{20}$ = +53.2 ° (c=0.5, MeOH); mp 182-184 ºC; IR (KBr): 3260,3119, 2980, 1692, 1644, 855, 600-800 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ: 1.09-1.13 (t, 3H, *J* = 7.1 Hz), 2.4 (s, 3H), 3.9-4 (q, 2H, *J* = 7.1 Hz), 5.06 (s, 1H), 7.07-7.26 (m, 4H), 9.5 (s,1H), 9.6 (s, 1H), 10.4 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 14.0, 17.1, 54.3, 59.7, 99.4, 113.6, 114.6, 117.8, 129.4, 130.2, 144.3, 157.8, 165.6, 174.3; Anal. Calcd for $C_{14}H_{16}N_2O_4$: C, 60.86; H, 5.84; N, 10.14. Found: C, 60.78; H, 5.77; N, 10.19.

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