Tetrahedron 72 (2016) 2616–2622

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Chiral ferrocenyl P,S-ligands for highly efficient copper-catalyzed asymmetric [3+2] cycloaddition of azomethine ylides

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ARTICLE INFO

Article history:
Received 6 November 2014
Received in revised form 24 December 2014
Accepted 4 January 2015
Available online 8 January 2015

Keywords:
Asymmetric catalysis
Chiral P,S-ligand
[3+2]-Cycloaddition
Copper
Azomethine ylide

ABSTRACT

A series of chiral ferrocenyl P,S-ligands based on benzimidazole and imidazole backbones have been prepared from Ugi's amine through a three-step transformation. These ligands were successfully employed in the Cu-catalyzed asymmetric [3+2] cycloaddition of azomethine ylides with various electron-deficient olefins, giving the corresponding cycloadducts in high *endo*-selectivities and excellent enantioselectivities (up to 99% ee).

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1. Introduction

The development of ferrocence-based chiral ligands for asymmetric catalysis has made great success over the past decades due to the rigidity, stability and readily structural modification of the ferrocene backbone.[1] Within this context, Ugi's amine (*N*,*N*-dimethyl-1-ferrocenylethylamine) derivatives constitute the largest family of chiral ferrocence ligands, which are synthesized mostly based on two significant features of Ugi's amine: 1) the highly stereoselective *o*-lithiation; and 2) the stereospecific substitution at the α-ferrocenylmethyl position with full retention of the absolute configuration.[2] Recently, a strategy for the development of new ligands by the introduction of a heterocyclic framework into the α-ferrocenylmethyl position has attracted tremendous interest. The presence of a heterocyclic scaffold could significantly change the nature of the chiral ferrocene backbone, therefore resulting in new ligands for the use in those catalytic reactions that are less successful with conventional ligands. Indeed, many chiral ferrocenyl P,P-, P,N-, and P,S-ligands bearing a heterocyclic framework have been developed and found to be highly efficient in a variety of asymmetric catalysis such as hydrogenation, allylic alkylation, hydroboration, cycloaddition, and so on.[3] In 2010, we reported a new class of ferrocene/benzimidazole-based P,S-ligands (we called ImiFerroS), which were readily prepared from Ugi's amine.[4] These ligands proved to be highly effective for the Cu-catalyzed asymmetric [3+2] cycloaddition of azomethine ylides with cyclic α-enones, predominately giving *endo*-cycloadducts in high enantioselectivities of up to >99% ee. As a continuation of this work, herein we report our results in details on the synthesis of ImiFerroS ligands and the investigation of their reactivity in the Cu-catalyzed asymmetric [3+2] cycloaddition of azomethine ylides with various electron-deficient olefins.

2. Results and discussion

2.1. Synthesis of ImiFerroS ligands

ImiferroS ligands **1** can be readily prepared from Ugi's amine by a three-step transformation. A representative synthesis of (R_c,S_{Fc})-ImiFerroS **1a** is shown in Scheme 1 as reported by us previously.[4] Initially, Ugi's amine **2** was subjected to highly diastereoselective *ortho*-lithiation with *n*-BuLi, and then trapping with $ClPPh_2$ to give (*R*)-1-[(*S*)-2-(diphenylphosphino)ferr-ocenyl]ethylamine [(R_c,S_{Fc})-**3**] in 67% yield.[5] Displacement of the amino group by a benzimidazole in HOAc afforded (R_c,S_{Fc})-**4** with the retentive configuration. Subsequent lithiation of the 2-position of benzimidazole ring with *n*-BuLi, followed by trapping with diphenyl disulfide generated the target ferrocenyl P,S-ligand (R_c,S_{Fc})-**1a** in good yields. With the similar procedure, a variety of ImiferroS ligands **1b**–**1e**[4] with

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http://dx.doi.org/10.1016/j.tet.2015.01.003
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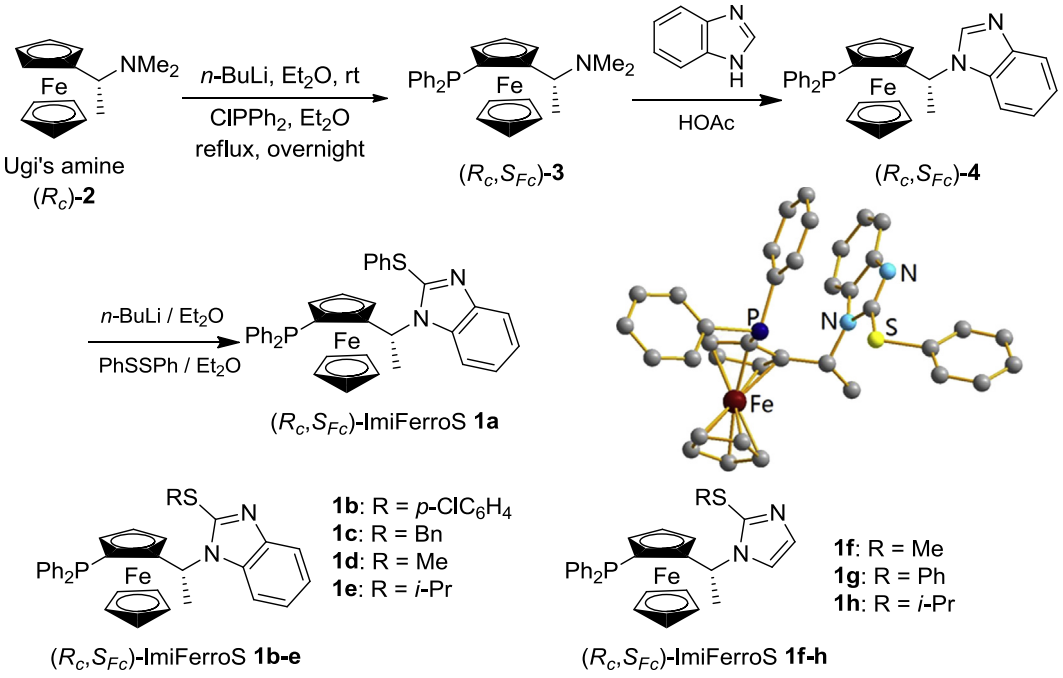


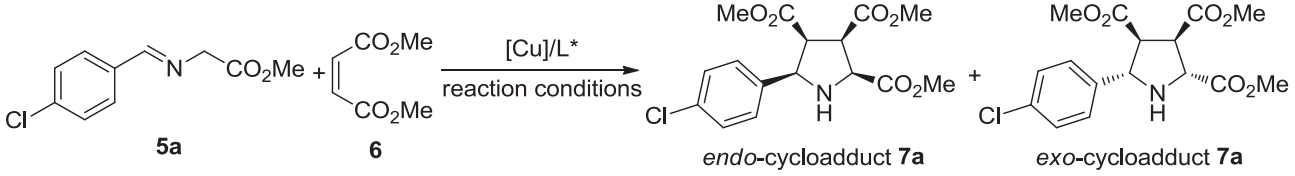
Scheme 1. Synthesis of chiral ferrocenyl P,S-Ligands **1a**–**h** bearing benzimidazole/imidazole ring.

various steric and electronic environments at the thioether moiety, as well as ImiferroS ligands **1f**–**1h** bearing an imidazole ring, were synthesized in moderate to good yields. These ImiferroS ligands are air and moisture-stable, and can be held at ambient temperature for several weeks even in open air. The structure of (R_c,S_{Fc})-ImiFerroS **1a** was unambiguously confirmed by X-ray analysis.[4]

2.2. Cu-catalyzed asymmetric [3+2] cycloaddition of azomethine ylides with dimethyl maleate

In the past decade, catalytic asymmetric [3+2] cycloaddition has achieved significant progress with the development of many outstanding chiral metal catalysts and organocatalysts,[6] which stimulated us to investigate the efficiency of our newly developed ferrocenyl P,S-ligands in this reaction. Our initial efforts focused on the optimization of Cu-catalyzed enantioselective 1,3-dipolar cycloaddition of azomethine ylides with electron-deficient olefins. The cycloaddition of *N*-(4-chlorobenzylidene)glycine methyl ester (**5a**) with dimethyl maleate (**6**) was chosen as a model reaction. The reaction was performed in the presence of a catalyst loading of 1 mol % prepared in situ from copper salts and 1.1 equiv of ferrocenyl P,S-ligands, and some representative results are summarized in Table 1. Copper salts showed a significant effect in the reaction, and $Cu(CH_3CN)_4ClO_4$ displayed the best result in terms of the yield,

Table 1
Reaction condition screening[a]



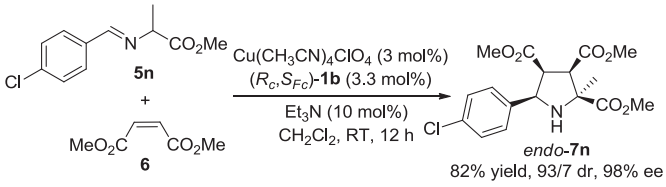
Entry	Ligand	[Cu]	Base	Solvent	*T* (°C)	Yield %[b]	*endo*:*exo*[c]	ee %[d]
1	**1a**	$Cu(OAc)_2$	Et_3N	CH_2Cl_2	25	37	76/24	44
2	**1a**	$Cu(OTf)_2$	Et_3N	CH_2Cl_2	25	72	82/18	56
3	**1a**	$Cu(CH_3CN)_4ClO_4$	Et_3N	CH_2Cl_2	25	80	>95/5	80
4	**1b**	$Cu(CH_3CN)_4ClO_4$	Et_3N	CH_2Cl_2	25	80	>95/5	88
5	**1c**	$Cu(CH_3CN)_4ClO_4$	Et_3N	CH_2Cl_2	25	77	>95/5	60
6	**1d**	$Cu(CH_3CN)_4ClO_4$	Et_3N	CH_2Cl_2	25	78	>95/5	33
7	**1e**	$Cu(CH_3CN)_4ClO_4$	Et_3N	CH_2Cl_2	25	80	>95/5	92
8	**1f**	$Cu(CH_3CN)_4ClO_4$	Et_3N	CH_2Cl_2	25	80	>95/5	60
9	**1g**	$Cu(CH_3CN)_4ClO_4$	Et_3N	CH_2Cl_2	25	87	>95/5	85
10	**1h**	$Cu(CH_3CN)_4ClO_4$	Et_3N	CH_2Cl_2	25	82	>95/5	85
11	**1e**	$Cu(CH_3CN)_4ClO_4$	*i*-Pr_2NEt	CH_2Cl_2	25	88	50/50	90
12	**1e**	$Cu(CH_3CN)_4ClO_4$	K_2CO_3	CH_2Cl_2	25	90	80/20	92
13	**1e**	$Cu(CH_3CN)_4ClO_4$	Et_3N	THF	25	89	95/5	60
14	**1e**	$Cu(CH_3CN)_4ClO_4$	Et_3N	Et_2O	25	45	78/22	<10
15	**1e**	$Cu(CH_3CN)_4ClO_4$	Et_3N	Toluene	25	94	>95/5	96
16	**1e**	$Cu(CH_3CN)_4ClO_4$	Et_3N	Toluene	0	95	>95/5	98

[a] The reaction conditions: [Cu] (1 mol %), L* (1.1 mol %), **5a** (0.5 mmol), **6** (0.6 mmol), solvent (3 mL), base (10 mol %), 12 h.
[b] Isolated yields of a mixture of *endo*- and *exo*-**7a**.
[c] Determined by ^1H NMR analysis.
[d] Determined for *endo*-cycloadduct by chiral HPLC (Chiralpak AS-H column, *i*-PrOH/*n*-hexane 50/50, 205 nm, 0.8 mL/min).

diastereo- and enantioselectivities (entries 1–3). The results indicated that the ligand structure had less influence on the reactivity and diastereoselectivity. In all cases, excellent *endo*-selectivities (*endo*/*exo* >95/5) were observed (entries 3–10). However, the ligand structure dramatically affected the enantioselectivity. Thus, ligand **1d** bearing a methylthio group only gave an ee-value of 33% (entry 6), while the corresponding **1e** bearing an *iso*-propylthio group provided 92% ee (entry 7). The introduction of an imidazole ring instead of the benzimidazole framework improved the reactivity and enantioselectivity in most cases (entries 8–10). For example, ligand **1d** gave the cycloadduct in 78% yield and with 33% ee (entry 6), in contrast, the corresponding **1f** with the imidazole backbone led to the cycloadduct **7a** in 80% yield and with 60% ee (entry 8). However, the best result was obtained with (R_c,S_{Fc})-ImiferroS **1e** bearing a benzimidazole framework and *iso*-propylthio group (entry 7). The reaction proved to be highly sensitive to the base additives. Thus, the use of *i*-Pr_2NEt and K_2CO_3 resulted in dramatically decreased diastereoselectivities, but maintained good yields and high enantioselectivities (entries 11 and 12). The nature of the solvent showed a great impact on the reactivity, diastereoselectivity, and enantioselectivity (entries 13–15). The results suggested that toluene was the best choice, in which *endo*-cycloadduct **7a** was obtained as the only product in 94% yield and with 96% ee (entry 15). The reaction temperature had slight influence on the reactivity and enantioselectivity. Lowering the reaction temperature to 0 °C could further increase the enantioselectivity to 98% ee (entry 16).

Under the optimal reaction conditions, the scope of azomethine ylides for this 1.3-dipolar cycloaddition was investigated, and the results are shown in Table 2. The results demonstrated that the present catalytic system was highly efficient to promote the asymmetric [3+2] cycloaddition of aromatic azomethine ylides with dimethyl maleate. A variety of imino esters derived from substituted benzaldehydes reacted with dimethyl maleate to give the corresponding *endo*-cycloadducts in high yields and with excellent enantioselectivities (95–99% ee) (entries 1–10). The substitution pattern on the phenyl ring had little effect on the reactivity, diastereoselectivity and enantioselectivity. Thus, all 2-, 3-, and 4-Cl substituted substrates (**5a**–**c**) gave nearly same performance (entries 1–3). The electronic property of the substituent slightly affected the enantioselectivity (entries 4–10), and the substrate **5i** bearing a strong electron-withdrawing substituent led to a slightly decreased enantioselectivity to 95% ee (entry 9). 2-Naphthyl-substituted substrate **5k** also worked well, giving *endo*-cycloadduct **7k** as the only product in 90% yield and with 98% ee (entry 11). However, heteroaromatic substrate **5l** turned out to be an inferior reaction partner, providing the cycloadduct **7l** in 83% yield, 91% *endo*-selectivity and with 79% ee for *endo*-cycloadduct (entry 12). Unfortunately, the present catalyst system didn't tolerate non-aromatic substrates. Thus, low conversion was observed when *N*-(cyclohexylmethylene)glycine methyl ester **5m** was subjected to this reaction (entry 13).

The present catalytic system proved to be remarkably tolerant and remain high reactivity for azomethine ylides derived from amino acid esters other than glycinate. Thus, under the optimal reaction conditions, the azomethine ylide **5n** derived from alanine smoothly reacted with dimethyl maleate **6** to predominately give *endo*-cycloadduct **7n** (93/7 dr) in 82% yield and with 98% ee (Scheme 2).



Scheme 2. Cu-catalyzed asymmetric [3+2] cycloaddition of *N*-(4-chlorobenzylidene) alanine methyl ester **5n** with **6**.

High stereoselectivity observed in the cycloaddition can be rationalized by using the proposed transition state as shown in Fig. 1. The in situ-formed azomethine ylide is oriented in a specific way as shown in Fig. 1 after the coordination to Cu-metal center, due to the steric repulsion between the phenyl group in the ylide and the phenyl group on the phosphorus atom of the chiral ligand. The possible coordination of the carbonyl group of dimethyl maleate to the Cu center resulted in the cycloadduct with predominant *endo*-selectivity. Furthermore, the steric congestion imposed by the ferrocene backbone effectively blocks the approach of dimethyl maleate from the *Si* (C=N) face of the ylide. A *Re* face attack leads to the formation of (2*S*,3*R*,4*S*,5*R*)-**7d**, which is compatible with the experimental result.

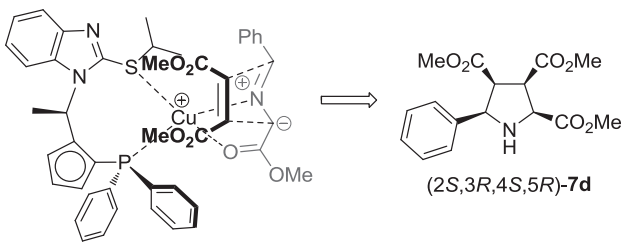
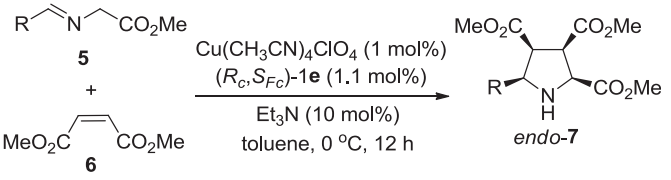


Fig. 1. Proposed model for enantioinduction.

Table 2
Cu-catalyzed asymmetric [3+2] cycloaddition: scope of azomethine ylides[a]



Entry	Substrate (R)	Product	Yield (%)[b]	*endo*/*exo*[c]	ee (%)[d]
1	**5a**: R=4-ClC_6H_4	**7a**	95	>95/5	98
2	**5b**: R=2-ClC_6H_4	**7b**	96	>95/5	98
3	**5c**: R=3-ClC_6H_4	**7c**	95	>95/5	99
4	**5d**: R=C_6H_5	**7d**	89	>95/5	99
5	**5e**: R=4-FC_6H_4	**7e**	87	95/5	98
6	**5f**: R=4-BrC_6H_4	**7f**	92	>95/5	99
7	**5g**: R=4-MeC_6H_4	**7g**	93	>95/5	97
8	**5h**: R=4-MeOC_6H_4	**7h**	91	>95/5	97
9	**5i**: R=4-$NO_2C_6H_4$	**7i**	96	>95/5	95
10	**5j**: R=4-$CF_3C_6H_4$	**7j**	97	>95/5	98
11	**5k**: R=2-naphthyl	**7k**	90	>95/5	98
12	**5l**: R=2-thienyl	**7l**	83	91/9	79
13	**5m**: R=cyclohexanyl	**7m**	—	—	—[e]

[a] Reaction conditions: $Cu(CH_3CN)_4ClO_4$ (1 mol %), (R_c,S_{Fc})-ImiferroS **1e** (1.1 mol %), imino ester **5** (0.5 mmol), 6 (0.6 mmol), Et_3N (10 mol %), toluene (3 mL), 0 °C for 12 h.
[b] Isolated yields of a mixture of *endo*- and *exo*-**7**.
[c] Determined by ^1H NMR.
[d] Determined for *endo*-cycloadduct by chiral HPLC.
[e] Not determined because of low conversion.

2.3. Cu-catalyzed asymmetric [3+2] cycloaddition of *N*-(4-chlorobenzylidene)glycine methyl ester with various electron-deficient olefins

To further extend the scope of the present catalytic system, the 1,3-dipolar cycloaddition of *N*-(4-chlorobenzylidene)glycine methyl ester **5a** with other electron-deficient olefins was then performed,

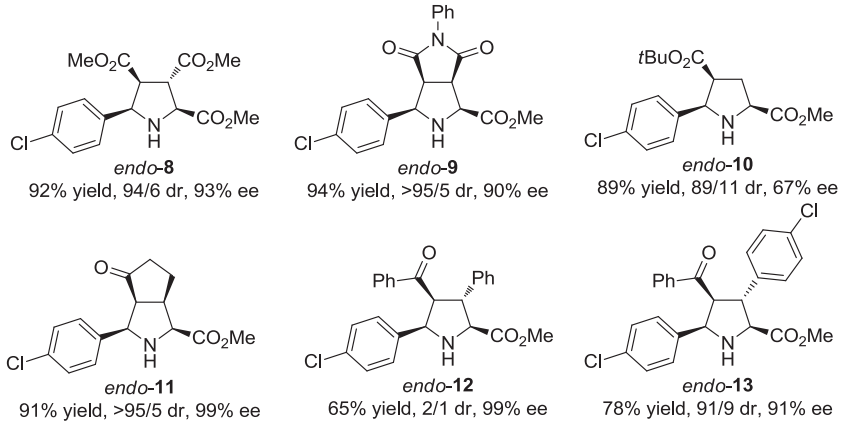


Fig. 2. Cycloadducts of the reaction of *N*-(4-chlorobenzylidene)glycine methyl ester **5a** with various electron-deficient olefins.

and the results are listed in Fig. 2. With dimethyl fumarate and *N*-phenylmaleimide, high *endo*-selectivities and good enantioselectivities were achieved. However, for *tert*-butyl acrylate, the present catalytic system proved to be less efficient, displaying only moderate enantioselectivity (67% ee). As we have demonstrated previously, the present catalytic system was highly effective for cyclic α-enones, such as 2-cyclopentenone, giving the sole *endo*-cycloadduct **11** in excellent enantioselectivity (99% ee). However, for acyclic α-enones, high enantioselectivities but moderate diastereoselectivities were observed.

3. Conclusion

In conclusion, we have developed a series of ferrocenyl P,S-ligands with a benzimidazole or an imidazole framework. These ligands can be easily prepared from Ugi's amine through a three-step transformation, and showed high air- and moisture-stability. These ligands proved to be highly efficient in the Cu-catalyzed asymmetric [3+2] cycloaddition of azomethine ylides with various electron-deficient olefins, giving the cycloadducts in high *endo*-selectivities (up to >95/5 dr) and good to excellent enantioselectivities (up to 99% ee). Further applications of these ferrocenyl P,S-ligands in other type of asymmetric reactions are currently in progress.

4. Experimental section

4.1. General remarks

All reactions were carried out under a nitrogen atmosphere. All solvents were purified by standard procedure, and commercially obtained reagents were used without further purification. ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer in chloroform-d.[3] Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. ^{13}C NMR spectra were recorded on a Bruker 100 MHz spectrometer in chloroform-d[3]. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. ^{31}P NMR spectra were recorded on a Bruker 162 MHz spectrometer in chloroform-d[3], chemical shifts are reported in ppm with the external 85% H_3PO_4 signal at 0.0 ppm as a standard. All reactions were monitored by TLC with silica gel-coated plates. Enantiomeric ratios were determined by chiral HPLC using a chiralpak AS-H column or a chiralcel OD-H with *n*-hexane and *i*-PrOH as solvents. Optical rotations were recorded on a Jasco P-1020 polarimeter. The absolute configuration of the known products were determined by comparing optical rotation with the reported data.

4.2. Synthesis of 1-{(*R*)-1-[(*S*)-2-diphenylphosphinoferrocenyl]ethyl}benzimidazole (4)

A solution of 4.41 g (10 mmol) of (R_c,S_{Fc})-**3** together with 5.8 g (50 mmol) of benzimidazole in 50 mL of degassed acetic acid was warmed to 80 °C and stirred at this temperature for 8 h. The reaction mixture was then concentrated in vacuum and neutralized with 50 mL of saturated $NaHCO_3$. The mixture was extracted three times with CH_2Cl_2, washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by recrystallization with ethanol to afford the pure product as a brown solid (7.78 g, 93% yield). Mp: 198–199 °C; $[\alpha]_D^{25}$=−300.7 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (s, 1H), 7.37–7.45 (m, 4H), 7.32–7.34 (m, 3H), 7.01–7.04 (m, 2H), 7.08–7.14 (m, 2H), 6.84 (m, 1H), 6.64–6.68 (m, 2H), 6.47–6.51 (m, 2H), 5.96 (m, 1H), 4.82 (s, 1H), 4.36 (s, 1H), 4.17 (s, 5H), 3.85 (s, 1H), 1.93 (d, *J*=6.8 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$): δ −25.3; ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 141.0, 136.4, 136.4, 136.2, 136.1, 134.9, 134.7, 131.9, 131.6, 131.4, 129.2, 128.2, 128.1, 127.8, 127.4, 127.3, 122.1, 121.4, 119.9, 110.4, 91.9, 91.7, 72.7 (d, *J*=4 Hz), 70.8, 70.2.

4.3. General procedure for the synthesis of (R_c,S_{Fc})-ImiFerroS 1a–h

To a suspension of (R_c,S_{Fc})-**4** (514 mg, 1 mmol) in 10 mL of dried diethyl ether was added a solution of *n*-BuLi (0.6 mL, 2.5 M) in hexane at −30 °C. After the addition was completed, the reaction mixture was warmed to room temperature and stirred for 4 h. A solution of disulfide (1.1 mmol) in 10 mL of dried diethyl ether was added at 0 °C, and the solution was stirred at room temperature overnight. The reaction mixture was quenched with 10 mL of saturated $NaHCO_3$, and then was extracted three times with 10 mL of CH_2Cl_2. The combined organic phase was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (ethyl acetate/petroleum ether=1/20) to afford a pure product.

(R_c,S_{Fc})-ImiFerroS **1a** was obtained as a yellow solid in 86% yield. Mp: 165–167 °C; $[\alpha]_D^{25}$: −239.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.47 (m, 4H), 7.26–7.32 (m, 9H), 7.00–7.02 (m, 2H), 6.85 (m, 1H), 6.58 (m, 2H), 6.47–6.50 (m, 3H), 4.89 (s, 1H), 4.42 (d, *J*=2.0 Hz, 1H), 4.16 (s, 5H), 3.77 (s, 1H), 1.67 (s, 3H); ^{31}P NMR (162 MHz, $CDCl_3$): δ −25.2; ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1, 135.9, 135.0, 134.8, 131.5, 131.3, 130.9, 129.3, 129.2, 129.0, 128.1, 128.0, 127.7, 127.5, 127.3, 122.1, 121.5, 119.8, 111.6; HRMS calcd for $C_{37}H_{31}FeN_2PS$ [M+H]: 623.1317, found 623.1389.

(R_c,S_{Fc})-ImiFerroS **1b** was obtained as a yellow solid in 67% yield. Mp: 151–152 °C; $[\alpha]_D^{25}$=−220.8 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.44 (m, 2H), 7.31–7.36 (m, 5H), 7.24–7.29 (m, 4H),

7.01 (m, 2H), 6.81–6.85 (m, 1H), 6.55–6.57 (m, 2H), 6.44–6.48 (m, 3H), 4.91 (s, 1H), 4.42 (s, 1H), 4.15 (s, 5H), 3.78 (s, 1H), 1.73 (d, J=10.4 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$): δ −24.9; ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8, 143.5, 136.8, 136.2, 136.1, 135.1, 134.9, 133.6, 132.1, 131.4, 131.2, 129.4, 129.1, 128.2, 128.1, 127.1, 127.3, 127.3, 122.2, 121.5, 119.8, 111.7, 90.8 (d, J=24.0 Hz), 77.7 (d, J=10.4 Hz), 73.1, 70.9, 70.3, 69.1, 51.8, 18.8; HRMS calcd for $C_{37}H_{30}ClFeN_2PS$ [M+H]: 657.0984, found 657.0975.

(R_c,S_{Fc})-ImiFerroS **1c** was obtained as a yellow solid in 62% yield. Mp: 146–148 °C; $[\alpha]_D^{25}$=−311.9 (c 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.44 (m, 4H), 7.28–7.34 (m, 6H), 7.26–7.27 (m, 3H), 6.97–6.99 (m, 2H), 6.86 (m, 1H), 6.53–6.60 (m, 2H), 6.49–6.51 (m, 2H), 5.98–6.00 (m, 1H), 4.88 (s, 1H), 4.39 (s, 1H), 4.13 (s, 5H), 3.75 (s, 1H), 1.70 (d, J=6.6 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$): δ −24.9; ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8, 137.1, 136.2, 136.1, 135.0, 134.8, 131.6, 131.4, 129.3, 129.0, 128.7, 128.1, 128.0, 127.7, 127.6, 127.2, 127.2, 121.0, 120.9, 118.2, 111.0, 90.8 (d, J=24.0 Hz), 77.8 (d, J=10.8 Hz), 72.9 (d, J=3.2 Hz), 71.0, 70.3, 68.8, 51.2, 38.1, 18.3; HRMS calcd for $C_{38}H_{33}FeN_2PS$ [M+H]: 637.1530, found 637.1516.

(R_c,S_{Fc})-ImiFerroS **1d** was obtained as a yellow solid in 75% yield. Mp: 99–100 °C; $[\alpha]_D^{25}$=−352.3 (c 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (m, 2H), 7.31 (m, 3H), 7.23–7.25 (m, 2H), 6.86–6.99 (m, 3H), 6.49–6.59 (m, 4H), 5.95–5.97 (m, 1H), 4.92 (s, 1H), 4.40 (s, 1H), 4.17 (s, 5H), 3.74 (s, 1H), 2.65 (s, 3H), 1.84 (d, J=6.6 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$): δ −24.5; ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9, 136.7, 136.6, 135.9, 135.9, 134.9, 134.8, 131.3, 129.0, 128.1, 128.0, 127.7, 127.2, 127.1, 120.9, 120.7, 117.9, 110.7, 90.5 (d, J=24.0 Hz), 77.8 (d, J=9.2 Hz), 73.1, 71.2, 70.3, 68.7, 51.0, 18.4, 15.3; HRMS calcd for $C_{32}H_{29}FeN_2PS$ [M+H]: 561.1217, found 561.1198.

(R_c,S_{Fc})-ImiFerroS **1e** was obtained as a yellow solid in 63% yield. Mp: 137–138 °C; $[\alpha]_D^{23}$=−343.5 (c 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.44 (m, 2H), 7.30 (m, 3H), 7.23–7.25 (m, 1H), 7.21 (m, 1H), 6.90–6.91 (m, 2H), 6.81 (m, 1H), 6.48–6.54 (m, 4H), 6.01–6.03 (m, 1H), 4.90 (s, 1H), 4.40 (s, 1H), 4.16 (s, 5H), 3.95–3.99 (m, 1H), 3.75 (s, 1H), 1.82 (d, J=6.6 Hz, 3H), 1.47 (d, J=6.0 Hz, 3H), 1.40 (d, J=6.6 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$): δ −24.9; ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 137.0, 136.9, 136.0, 135.9, 135.0, 134.8, 131.6, 131.4, 128.9, 128.1, 128.0, 127.5, 127.1, 127.0, 120.8, 120.6, 118.1, 111.0, 90.9 (d, J=26.4 Hz), 77.8 (d, J=10.4 Hz), 73.0, 71.0, 70.2, 68.8, 51.0, 38.9, 23.9, 23.6, 18.4; HRMS calcd for $C_{34}H_{33}FeN_2PS$ [M+H]: 589.1530, found 589.1545.

(R_c,S_{Fc})-ImiFerroS **1f** was obtained as an orange needle in 71% yield. Mp: 151–152 °C; $[\alpha]_D^{23}$=−240.3 (c 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49–7.53 (m, 2H), 7.35–7.36 (m, 3H), 7.08–7.12 (m, 1H), 6.99–7.05 (m, 2H), 6.73–6.76 (m, 2H), 6.63 (s, 1H), 6.57 (s, 1H), 5.71–5.77 (m, 1H), 4.67 (s, 1H), 4.40 (s, 1H), 4.12 (s, 5H), 3.81 (s, 1H), 2.33 (s, 3H), 1.76 (d, J=6.8 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$): δ −24.1; ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.3, 21.9, 50.5 (d, J=9 Hz), 69.2, 69.5, 70.1, 71.6, 72.4, 76.3 (d, J=10 Hz), 92.9 (d, J=25 Hz), 117.4, 127.7, 127.9, 128.1, 128.9, 129.2, 131.7, 135.2 (d, J=21 Hz), 136.8 (d, J=9 Hz), 137.8, 140.5; HRMS calcd for $C_{28}H_{27}FeN_2PS$ [M+H]: 511.1060, found 511.1061.

(R_c,S_{Fc})-ImiFerroS **1g** was obtained as an orange needle in 51% yield. Mp: 120–122 °C; $[\alpha]_D^{23}$=−116.8 (c 0.8, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.49 (m, 2H), 7.34–7.35 (m, 3H), 7.12–7.20 (m, 6H), 7.01–7.05 (m, 2H), 6.75–6.79 (m, 2H), 6.69–6.71 (m, 2H), 6.03–6.06 (m, 1H), 4.63 (s, 1H), 4.39 (s, 1H), 4.09 (s, 5H), 3.81 (s, 1H), 1.54 (d, J=6.8 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$): δ −24.9; ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.1, 51.3 (d, J=9 Hz), 69.1, 69.6, 70.1, 72.5 (d, J=4 Hz), 93.0 (d, J=25 Hz), 119.0, 126.4, 127.8, 127.9, 128.2 (d, J=8 Hz), 128.7, 128.9, 129.2, 129.9, 131.8 (d, J=19 Hz), 135.1 (d, J=21 Hz), 135.4, 135.7, 136.8 (d, J=9 Hz), 137.5; HRMS calcd for $C_{33}H_{29}FeN_2PS$ [M+H]: 573.1217, found 573.1207.

(R_c,S_{Fc})-ImiFerroS **1h** was obtained as an orange needle in 57% yield. Mp: 149–150 °C; $[\alpha]_D^{23}$=−273.5 (c 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.53 (m, 2H), 7.35–7.36 (m, 3H), 7.06–7.08 (m, 1H), 6.99–7.02 (m, 2H), 6.72–6.76 (m, 2H), 6.66 (s, 1H), 6.59 (s, 1H), 5.81–5.83 (m, 1H), 4.66 (s, 1H), 4.41 (s, 1H), 4.09 (s, 5H), 3.84 (s, 1H), 3.45–3.50 (m, 1H), 1.76 (d, J=6.8 Hz, 3H), 1.22–1.25 (m, 6H); ^{31}P NMR (162 MHz, $CDCl_3$): δ −24.5; ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.2, 23.3, 23.9, 50.6 (d, J=9 Hz), 69.3, 69.6, 69.9, 70.1, 70.7, 72.4 (d, J=4 Hz), 76.4 (d, J=10 Hz), 93.3 (d, J=25 Hz), 117.5, 127.7 (d, J=6 Hz), 127.8, 128.1 (d, J=7 Hz), 128.7, 129.2, 131.7 (d, J=18 Hz), 135.2 (d, J=21 Hz), 137.1 (d, J=8 Hz), 137.9 (d, J=8 Hz), 139.2; HRMS calcd for $C_{30}H_{31}FeN_2PS$ [M+H]: 539.1373, found 539.1391.

4.4. General procedure for catalytic asymmetric 1,3-dipolar cycloaddition of azomethine ylides

Under nitrogen atmosphere, a solution of $[Cu(CH_3CN)_4]ClO_4$ (0.005 mmol) and (R_c,S_{Fc})-ImiFerroS **1e** (0.0055 mmol) in 1 mL of toluene was stirred at room temperature for 1 h. The reaction mixture was cooled to 0 °C, and then a solution of imino esters **5** (0.5 mmol) in 2 mL of toluene, Et_3N (0.05 mmol) and dimethyl dimelate **6** (0.6 mmol) were added successively. Once the material consumed (monitored by TLC), the mixture was filtered through Celite. The filtrate was concentrated in vacuum to give an *endo*/*exo* ratio of the crude product (determined by ^{1}H NMR). The residue was purified by flash chromatography (petroleum/EtOAc, 2/1) to afford the cycloadduct, which was then analyzed by chiral HPLC to determine the enantiomeric excess.

*4.4.1. Trimethyl (2S,3R,4S,5R)-5-(4-chlorophenyl)pyrroli-dine-2,3,4-tricarboxylate (endo-**7a**).*[30] White solid, 95% yield, *endo*/*exo* >95/5, 98% ee. Chiralpak AS-H column, 40 °C, 205 nm, *n*-hexane/*i*-propanol=50/50, flow rate=0.8 mL/min, t_r=7.67 and 10.1 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (s, 4H), 4.46 (d, J=8.0 Hz, 1H), 4.16 (d, J=12.0 Hz, 1H), 3.81 (s, 3H), 3.69–3.74 (m, 1H), 3.69 (s, 3H), 3.55–3.59 (m, 1H), 3.28 (s, 3H), 3.23 (br, 1H).

*4.4.2. Trimethyl (2S,3R,4S,5R)-5-(2-chlorophenyl)pyrroli-dine-2,3,4-tricarboxylate (endo-**7b**).*[30] White solid, 96% yield, *endo*/*exo* >95/5, 98% ee. Chiralpak AS-H column, 40 °C, 205 nm, *n*-hexane/*i*-propanol=50/50, flow rate=0.8 mL/min, t_r=7.38 and 20.1 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.50 (d, J=8.0 Hz, 1H), 7.35–7.37 (d, J=8.0 Hz, 1H), 7.20–7.29 (m, 2H), 4.78 (d, J=8.0 Hz, 1H), 4.19 (d, J=12.0 Hz, 1H), 3.84 (s, 3H), 3.79–3.88 (m, 2H), 3.67 (s, 3H), 3.25 (br, 1H), 3.19 (s, 3H).

*4.4.3. Trimethyl (2S,3R,4S,5R)-5-(3-chlorophenyl)pyrroli-dine-2,3,4-tricarboxylate (endo-**7c**).*[30] White solid, 95% yield, *endo*/*exo* >95/5, 99% ee. Chiralpak AS-H column, 40 °C, 205 nm, *n*-hexane/*i*-propanol=50/50, flow rate=0.8 mL/min, t_r=7.26 and 11.8 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (s, 1H), 7.18 (s, 3H), 4.39 (d, J=4.0 Hz, 1H), 4.11 (d, J=8.0 Hz, 1H), 3.74 (s, 3H), 3.64–3.69 (m, 1H), 3.62 (s, 3H), 3.50–3.54 (m, 1H), 3.37 (s, 1H), 3.23 (s, 3H).

*4.4.4. Trimethyl (2S,3R,4S,5R)-5-phenylpyrrolidine-2,3,4-tricarboxylate (endo-**7d**).*[30] White solid, 89% yield, *endo*/*exo* >95/5, 99% ee. Chiralpak AS-H column, 40 °C, 205 nm, *n*-hexane/*i*-propanol=50/50, flow rate=0.8 mL/min, t_r=6.72 and 11.7 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19–7.29 (m, 5H), 4.42 (d, J=8.0 Hz, 1H), 4.10 (d, J=8.0 Hz, 1H), 3.74 (s, 3H), 3.64–3.68 (m, 1H), 3.62 (s, 3H), 3.50–3.53 (m, 1H), 3.16 (s, 3H).

*4.4.5. Trimethyl (2S,3R,4S,5R)-5-(4-fluorophenyl)pyrroli-dine-2,3,4-tricarboxylate (endo-**7e**).*[30] White solid, 87% yield, *endo*/*exo*=95/5, 98% ee. Chiralpak AS-H column, 40 °C, 205 nm, *n*-hexane/*i*-propanol=50/50, flow rate=0.8 mL/min, t_r=7.19 and 9.99 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22–7.26 (m, 2H), 6.89–6.93 (m, 2H), 4.38 (d, J=4.0 Hz, 1H), 4.05 (d, J=8.0 Hz, 1H), 3.70 (s, 3H), 3.61–3.65 (m, 1H), 3.59 (s, 3H), 3.46–3.50 (m, 1H), 3.16 (s, 3H), 2.83 (s, 1H).

*4.4.6. Trimethyl (2S,3R,4S,5R)-5-(4-bromophenyl)pyrroli-dine-2,3,4-tricarboxylate (endo-**7f**).*[30] White solid, 92% yield, *endo*/*exo* >95/5,

99% ee. Chiralpak AS-H column, 40 °C, 205 nm, *n*-hexane/*i*-propanol=50/50, flow rate=0.8 mL/min, t_r=7.99 and 10.8 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.39 (m, 2H), 7.16–7.18 (m, 2H), 4.38 (d, *J*=8.0 Hz, 1H), 4.09 (d, *J*=8.0 Hz, 1H), 3.73 (s, 3H), 3.64–3.68 (m, 1H), 3.62 (s, 3H), 3.49–3.54 (m, 1H), 3.26 (s, 1H), 3.21 (s, 3H).

*4.4.7. Trimethyl (2S,3R,4S,5R)-5-(4-methylphenyl)pyrroli-dine-2,3,4-tricarboxylate (endo-**7g**).*[3o] White solid, 93% yield, *endo*/*exo* >95/5, 97% ee. Chiralpak AS-H column, 40 °C, 205 nm, *n*-hexane/*i*-propanol=50/50, flow rate=0.8 mL/min, t_r=6.91 and 13.4 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15–7.17 (m, 2H), 7.06–7.08 (m, 2H), 4.40 (d, *J*=8.0 Hz, 1H), 4.12 (d, *J*=12.0 Hz, 1H), 3.75 (s, 3H), 3.66–3.69 (m, 1H), 3.63 (s, 3H), 3.48–3.51 (m, 1H), 3.27 (s, 1H), 3.21 (s, 3H), 2.26 (s, 3H).

*4.4.8. Trimethyl (2S,3R,4S,5R)-5-(4-methoxyphenyl)pyrroli-dine-2,3,4-tricarboxylate (endo-**7h**).*[3o] White solid, 91% yield, *endo*/*exo* >95/5, 97% ee. Chiralpak AS-H column, 40 °C, 205 nm, *n*-hexane/*i*-propanol=50/50, flow rate=0.8 mL/min, t_r=9.79 and 16.2 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.28 (m, 2H), 6.85–6.87 (m, 2H), 4.48 (d, *J*=4.0 Hz, 1H), 4.18 (d, *J*=8.0 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.69–3.73 (m, 1H), 3.70 (s, 3H), 3.52–3.55 (m, 1H), 3.28 (s, 3H).

*4.4.9. Trimethyl (2S,3R,4S,5R)-5-(4-nitrophenyl)pyrrolidine-2,3,4-tricarboxylate (endo-**7i**).*[3o] White solid, 96% yield, *endo*/*exo* >95/5, 95% ee. Chiralpak AS-H column, 40 °C, 205 nm, *n*-hexane/*i*-propanol=50/50, flow rate=0.8 mL/min, t_r=37.1 and 43.7 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11–8.14 (m, 2H), 7.51–7.53 (m, 2H), 4.52 (d, *J*=8.0 Hz, 1H), 4.14 (d, *J*=8.0 Hz, 1H), 3.77 (s, 3H), 3.66–3.74 (m, 1H), 3.63 (s, 3H), 3.59–3.61 (m, 1H), 3.21 (s, 3H), 2.95 (br, 1H).

*4.4.10. Trimethyl (2S,3R,4S,5R)-5-(4-trifluoromethylphenyl)-pyrrolidine-2,3,4-tricarboxylate (endo-**7j**).*[3o] White solid, 97% yield, *endo*/*exo* >95/5, 98% ee. Chiralpak AS-H column, 40 °C, 205 nm, *n*-hexane/*i*-propanol=50/50, flow rate=0.8 mL/min, t_r=5.87 and 7.15 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.60 (m, 2H), 7.49–7.51 (m, 2H), 4.55 (d, *J*=8.0 Hz, 1H), 4.20 (d, *J*=8.0 Hz, 1H), 3.82 (s, 3H), 3.73–3.78 (m, 1H), 3.70 (s, 3H), 3.61–3.65 (m, 1H), 3.26 (s, 3H), 3.07 (br, 1H).

*4.4.11. Trimethyl (2S,3R,4S,5R)-5-(naphthalen-2-yl)pyrroli-dine-2,3,4-tricarboxylate (endo-**7k**).*[3o] White solid, 90% yield, *endo*/*exo* >95/5, 98% ee. Chiralpak AS-H column, 40 °C, 205 nm, *n*-hexane/*i*-propanol=50/50, flow rate=0.8 mL/min, t_r=9.19 and 17.1 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75–7.79 (m, 4H), 7.38–7.44 (m, 3H), 4.60 (d, *J*=8.0 Hz, 1H), 4.20 (d, *J*=8.0 Hz, 1H), 3.80 (s, 3H), 3.73–3.77 (m, 1H), 3.63–3.66 (m, 5H), 3.12 (s, 3H).

*4.4.12. Trimethyl (2S,3R,4S,5R)-5-(2-thienyl)pyrrolidine-2,3,4-tricarboxylate (endo-**7l**).*[3o] White solid, 83% yield, *endo*/*exo*=91/9, 79% ee. Chiralpak AS-H column, 40 °C, 205 nm, *n*-hexane/*i*-propanol=50/50, flow rate=0.8 mL/min, t_r=7.04 and 14.4 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22–7.23 (m, 1H), 7.03–7.04 (m, 1H), 6.95–6.97 (m, 1H), 4.65 (d, *J*=4.0 Hz, 1H), 4.18 (d, *J*=12.0 Hz, 1H), 3.80 (s, 3H), 3.72 (s, 3H), 3.68–3.71 (m, 1H), 3.52–3.55 (m, 1H), 3.43 (s, 3H), 3.02 (br, 1H).

*4.4.13. Trimethyl (2S,3R,4S,5R)-2-methyl-5-(4-chlorophenyl)-pyrrolidine-2,3,4-tricarboxylate (endo-**7n**).*[3o] White solid, 82% yield, *endo*/*exo*=93/7, 98% ee. Chiralpak AS-H column, 40 °C, 230 nm, *n*-hexane/*i*-propanol=90/10, flow rate=0.8 mL/min, t_r=8.66 and 9.53 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.35 (m, 4H), 4.61 (d, *J*=8.0 Hz, 1H), 3.80 (s, 3H), 3.75 (s, 3H), 3.45–3.48 (m, 1H), 3.26–3.30 (m, 1H), 3.26 (s, 3H), 1.69 (s, 3H).

*4.4.14. Trimethyl (2S,3S,4S,5R)-5-(4-chlorophenyl)pyrroli-dine-2,3,4-tricarboxylate (endo-**8**).*[3o] White solid, 92% yield, *endo*/*exo*=94/6, 93% ee. Chiralpak AS-H column, 40 °C, 205 nm, *n*-hexane/*i*-propanol=90/10, flow rate=0.8 mL/min, t_r=9.90 and 10.5 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (s, 4H), 4.57 (d, *J*=8.0 Hz, 1H), 4.13 (d, *J*=8.0 Hz, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 3.59–3.60 (m, 1H), 3.50–3.52 (m, 1H), 3.19 (s, 3H), 2.69 (s, 1H).

*4.4.15. Methyl (1S,3R,3aS,6aR)-4,6-dioxo-3-phenyl-5-(4-chlorophenyl) octahydrocyclopenta[c]pyrrole-1-carboxylate (endo-**9**).*[3o] White solid, 94% yield, *endo*/*exo* >95/5, 90% ee. Chiralpak AS-H column, 40 °C, 215 nm, *n*-hexane/*i*-propanol=80/20, flow rate=0.8 mL/min, t_r=21.6 and 53.8 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.38 (m, 4H), 7.31–7.32 (m, 3H), 7.11–7.12 (m, 2H), 4.54 (d, *J*=4.0 Hz, 1H), 4.10 (d, *J*=4.0 Hz, 1H), 3.84 (s, 3H), 3.67–3.68 (m, 1H), 3.51–3.53 (m, 1H), 2.29 (br, 1H).

*4.4.16. 4-t-Butyl 2-methyl (2S,4S,5R)-5-(4-chlorophenyl)pyr-rolidine-2,4-dicarboxylate (endo-**10**).*[3o] White solid, 89% yield, *endo*/*exo*=89/11, 67% ee. Chiralpak AS-H column, 40 °C, 230 nm, *n*-hexane/*i*-propanol=90/10, flow rate=0.8 mL/min, t_r=7.58 and 10.5 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19–7.25 (m, 4H), 4.35–4.37 (m, 1H), 3.83–3.88 (m, 1H), 3.72 (s, 3H), 3.15–3.16 (m, 1H), 2.70 (s, 1H), 2.30–2.38 (m, 1H), 2.20–2.27 (m, 1H), 0.99 (s, 9H).

*4.4.17. Methyl (1S,3R,3aS,6aR)-3-(4-chlorophenyl)octahydro-4-oxocyclopenta[c]pyrrole-1-carboxylate (endo-**11**).*[4] White solid, 91% yield, *endo*/*exo* >95/5, 99% ee. Chiralpak AS-H column, 40 °C, 215 nm, *n*-hexane/*i*-propanol=80/20, flow rate=1.0 mL/min, t_r=22.7 and 30.6 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 4H), 4.48 (d, *J*=9.6 Hz, 1H), 4.14 (d, *J*=7.2 Hz, 1H), 3.83 (s, 3H), 3.24 (m, 1H), 2.91 (t, 1H), 2.58 (br s, 1H), 2.20–2.01 (m, 3H), 1.86–1.84 (m, 1H).

*4.4.18. Methyl (2S,3R,4S,5R)-4-benzoyl-3-phenyl-5-(4-chlorophenyl) pyrrolidine-2-carboxylate (endo-**12**).*[4] White solid, 65% yield, *endo*/*exo*=2/1, 99% ee. Chiralpak AS-H column, 40 °C, 215 nm, *n*-hexane/*i*-propanol=80/20, flow rate=1.0 mL/min, t_r=8.49 and 12.3 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 2H), 7.26–7.44 (m, 8H), 7.06 (s, 4H), 5.01 (d, *J*=8.8 Hz, 1H), 4.53 (t, 1H), 4.23 (d, *J*=8.8 Hz, 1H), 4.11 (t, 1H), 3.75 (s, 3H), 2.81 (br, 1H).

*4.4.19. Methyl (2S,3R,4S,5R)-4-benzoyl-3,5-di(4-chlorophenyl) pyrrolidine-2-carboxylate (endo-**13**).*[4] White solid, yield 78%, *endo*/*exo*=91/9, 91% ee. Chiralpak AS-H, 40 °C, 215 nm, *n*-hexane/*i*-propanol=80/20, flow rate=1.0 mL/min, t_r=9.0 and 11.2 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J*=8.0 Hz, 2H), 7.46 (t, 1H), 7.29–7.33 (m, 5H), 7.02–7.08 (m, 4H), 4.99 (d, *J*=8.0 Hz, 1H), 4.49 (t, 1H), 4.17 (d, *J*=8.0 Hz, 1H), 4.10 (t, 1H), 3.74 (s, 3H), 2.78 (br, 1H).

Acknowledgements

We are grateful for the financial support from the Dalian Institute of Chemical Physics (CAS). F.-Z. Han also thanks the National Natural Science Foundation of China (21402102) for the financial support.

Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2015.01.003.

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