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New chiral ferrocenyl P,S-ligands for highly diastereo- and enantioselective Ag(I)-catalyzed asymmetric [3+2] cycloaddition of azomethine ylides

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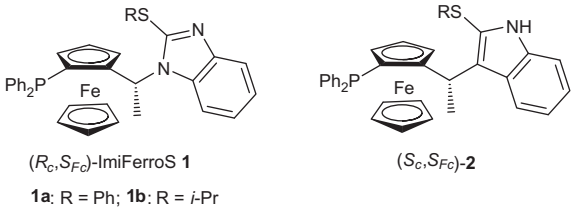
ABSTRACT

A new family of chiral ferrocenyl P,S-ligands incorporating an indole ring at the α-ferrocenylmethyl position has been prepared via a Friedel–Crafts alkylation reaction of (R_c,S_{Fc})-PPFA with a variety of 2-indole thioethers. These newly developed ferrocenyl P,S-ligands proved to be efficient in the AgOAc-catalyzed asymmetric [3+2] cycloaddition of azomethine ylides with various dipolarophiles, giving cycloadducts with high diastereoselectivities and enantioselectivities (up to 99% ee).

1. Introduction

Chiral ferrocenyl derivatives based on *N*,*N*-dimethyl-1-ferrocenylethylamine (Ugi's amine) have found widespread application as chiral ligands or ligand precursors in asymmetric catalysis over the past few decades due to their unique features.[1] Of these features, the most significant is that the functional group (normally a dimethylamino group) at the α-ferrocenylmethyl position on the side chain can be readily replaced with many nucleophiles with full retention of configuration at the stereogenic carbon center.[2] One recent advance for the construction of new chiral ligands is the introduction of a heterocyclic group at the α-ferrocenylmethyl position.[3] The presence of a heterocyclic group on the ferrocene system could significantly improve the structure of the chiral ferrocene scaffold, thus creating new chiral ligands for use in asymmetric reactions in which conventional ligands are not effective. Heterocyclic groups containing an *N*–H fragment were used as nucleophiles, effectively replacing the dimethylamino group of Ugi's amine derivatives and then incorporating a heterocyclic ring through a C–N bond at the α-stereogenic center. With this strategy, some highly effective P,P-, P,N- and P,S-ligands with a heterocyclic motif were developed and employed successfully in a broad range of asymmetric catalysis such as hydrogenations,[3c,e] allylic alkylations,[3b,4] hydroborations,[3a,5] and cycloadditions.[3d,f,g,6] In our recent efforts on the development of new chiral ligands for asymmetric catalysis, we have developed a series of chiral ferrocenyl P,S-ligands with a benzimidazole framework, (R_c,S_{Fc})-ImiFerroS **1** (Fig. 1).

These ligands showed excellent diastereo/enantioselectivities in the Cu-catalyzed [3+2] cycloadditions of azomethine ylides with cyclic enones and the Ag-catalyzed [3+2] cycloadditions of azomethine ylides with acyclic enones. However, in the Ag-catalyzed asymmetric [3+2] cycloaddition of azomethine ylides with α,β-unsaturated esters, such as dimethyl maleate, these ligands displayed only poor to moderate enantioselectivities. We surmised that the presence of the additional N-donor atom in the benzimidazole framework may have some effect on this reaction. In order to investigate this, we therefore set out to construct an indole analogue of (R_c,S_{Fc})-ImiFerroS **1**. By reacting (R_c,S_{Fc})-PPFA **3** with indole, we indeed obtained a new compound that incorporates an indole ring at the α-ferrocenylmethyl position (Scheme 1). Further structural analysis revealed, however, that the substitution had taken place at the C_3-position of the indole ring instead of the N_1-position, giving a Friedel–Crafts-type product **5**. This observation should be interesting with regards to the development of new chiral ligands, since the presence of an *N*–H proton in the ligands may affect their reactivity and enantioselectivity due to any potential secondary effect between the ligand and the substrate. As a result, we developed a series of new ferrocenyl P,S-ligands (S_c,S_{Fc})-**2** bearing an indole ring at the α-ferrocenylmethyl position through a C–C bond, which displayed improved enantioselectivities in the Ag(I)-catalyzed asymmetric [3+2] cycloadditions of azomethine



(R_c,S_{Fc})-ImiFerroS **1**
1a: R = Ph; **1b**: R = *i*-Pr

(S_c,S_{Fc})-**2**

Figure 1. Structures of (R_c,S_{Fc})-ImiFerroS **1** and (S_c,S_{Fc})-**2**.

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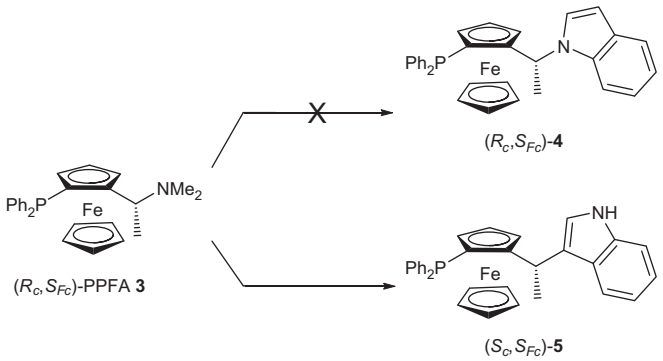


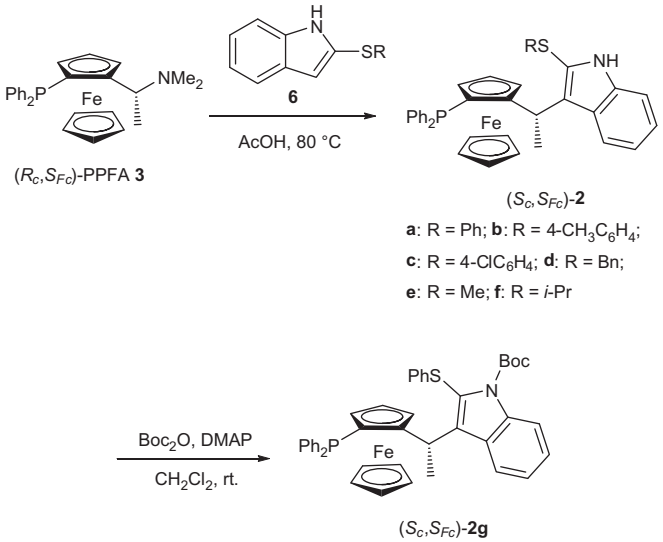
Scheme 1. Construction of the ferrocene/indole skeleton.

ylides with α,β-unsaturated esters in comparison with those obtained with (R_c,S_{Fc})-ImiFerroS **1**.

2. Results and discussion

2.1. Synthesis of new chiral ferrocenyl P,S-ligands 2a–g

The synthesis of the target ferrocenyl P,S-ligands is straightforward and is outlined in Scheme 2. Based on our above observations, we reacted (R_c,S_{Fc})-PPFA with a variety of 2-indole thioethers in AcOH at 80 °C to give the corresponding ferrocenyl P,S-compounds **2a–f** in good yields. The structure of (S_c,S_{Fc})-**2a** was confirmed by X-ray analysis (Fig. 2).[7] In order to investigate the effect of the *N*–H proton, a Boc-protected ligand **2g** was also prepared.



Scheme 2. Synthesis of new chiral ferrocenyl P,S-ligands **2a–g** incorporating an indole ring.

2.2. Catalytic asymmetric [3+2] cycloaddition reactions

With these ligands in hand, we next examined their efficiency in the Ag-catalyzed asymmetric [3+2] cycloaddition of azomethine ylides with various electron-deficient olefins.[8] Initially, the cycloaddition of *N*-(4-chlorobenzylidene) glycine methyl ester **7a** with dimethyl maleate was selected as a model reaction. The reaction was performed in Et_2O at 0 °C in the presence of a catalytic amount of Et_3N (10 mol %) and the catalyst (3 mol %) prepared in situ from

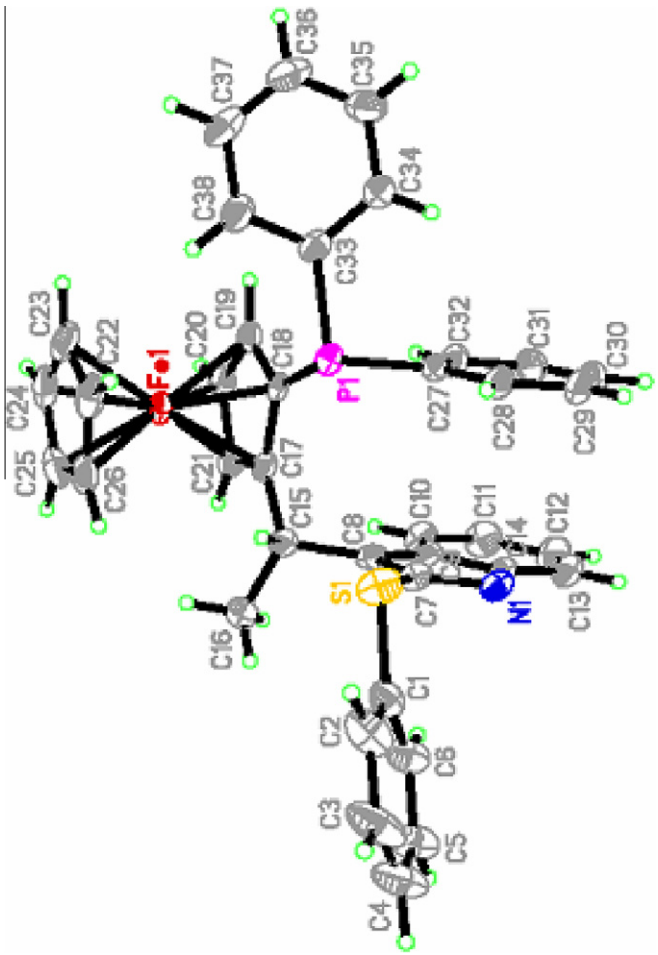
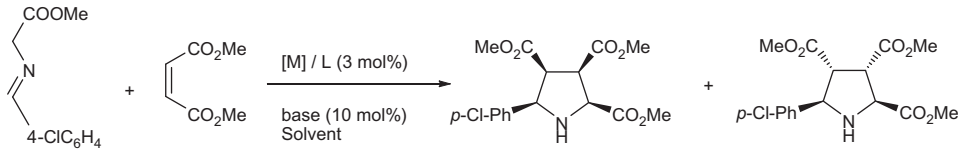


Figure 2. X-Ray structure of (S_c,S_{Fc})-**2a**.

AgOAc and 1.1 equiv of P,S-ligands **2a–f**, and the results are summarized in Table 1. In comparison to (R_c,S_{Fc})-ImiferroS **1a**, these newly developed ferrocenyl P,S-ligands **2a–f** showed significantly improved enantioselectivities in this model reaction, giving the *endo*-cycloadduct **9a** with good diastereoselectivities and enantioselectivities of up to 90% ee (entry 1 vs entries 2–7). The results showed that substituents on the thio group significantly affected the enantioselectivity; ligand **2a** bearing a phenylthio group proved to be the best ligand in terms of the diastereo- and enantioselectivities (*endo*/*exo* = 96/4, and 90% ee for *endo*-adduct) (entry 2). The presence of *N*–H proton in the ligand proved to be highly important. When the Boc-protected ligand **2g** was employed in this model reaction, a dramatically reduced enantioselectivity of 78% ee was observed (entry 8). With ligand **2a**, we next optimized the reaction conditions. The reaction temperature also had a significant impact on the enantioselectivity: when the reaction was performed at lower temperatures, it tended to give better enantioselectivities (entries 9 and 10). When the reaction temperature was carried out at −40 °C, up to 99% ee was achieved (entry 10). The reaction also proved to be highly sensitive to the catalyst precursors. Using $AgBF_4$, $AgPF_6$ or $AgSbF_6$, dramatically decreased the conversions or enantioselectivities (entries 11–13). Solvent screening showed that Et_2O was the best solvent (entries 14–16). Further work on the screening of various bases indicated that Et_3N was the best choice (entries 17–20).

Under the optimized reaction conditions, the scope of the present catalytic system in the 1,3-dipolar cycloaddition was tested. As shown in Table 2, various imino esters **7a–j** derived from aromatic

Table 1
Catalytic asymmetric [3+2] cycloaddition reactions of *N*-(4-chlorobenzylidene)glycine methyl ester **7a** with dimethyl maleate **8**[a]

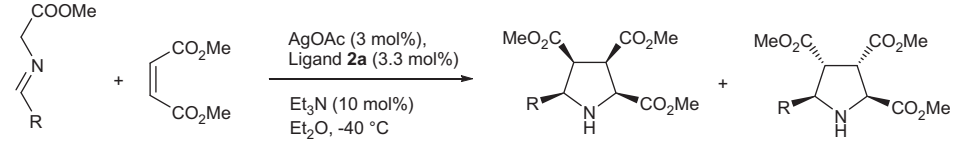


7a **8** *endo*-**9a** *exo*-**9a**

Entry	L	[M]	Temp (°C)	Solvent	Base	*endo*/*exo*[b]	Yield[c] (%)	ee[d] (%)
1	**1a**	AgOAc	0	Et_2O	Et_3N	96/4	93	64
2	**2a**	AgOAc	0	Et_2O	Et_3N	96/4	94	90
3	**2b**	AgOAc	0	Et_2O	Et_3N	95/5	93	75
4	**2c**	AgOAc	0	Et_2O	Et_3N	96/4	94	88
5	**2d**	AgOAc	0	Et_2O	Et_3N	94/6	90	81
6	**2e**	AgOAc	0	Et_2O	Et_3N	94/6	92	69
7	**2f**	AgOAc	0	Et_2O	Et_3N	91/9	90	79
8	**2g**	AgOAc	0	Et_2O	Et_3N	89/11	90	78
9	**2a**	AgOAc	−25	Et_2O	Et_3N	96/4	95	96
10	**2a**	AgOAc	−40	Et_2O	Et_3N	95/5	95	99
11	**2a**	$AgBF_4$	−40	Et_2O	Et_3N	94/6	48	40
12	**2a**	$AgPF_6$	−40	Et_2O	Et_3N	95/5	91	<5
13	**2a**	$AgSbF_6$	−40	Et_2O	Et_3N	83/17	35	56
14	**2a**	AgOAc	−40	CH_2Cl_2	Et_3N	72/28	91	91
15	**2a**	AgOAc	−40	Toluene	Et_3N	94/6	26	90
16	**2a**	AgOAc	−40	THF	Et_3N	91/9	83	8
17	**2a**	AgOAc	−40	Et_2O	*i*-Pr_2NEt	92/8	67	82
18	**2a**	AgOAc	−40	Et_2O	DBU	78/22	92	41
19	**2a**	AgOAc	−40	Et_2O	DABCO	96/4	38	98
20	**2a**	AgOAc	−40	Et_2O	—[e]	97/3	79	83

[a] Reactions were performed in 1.5 mL of solvent with 0.3 mmol of substrate **7a**, 10 mol % of base additives, and 3 mol % of catalyst prepared in situ from AgOAc and 1.1 equiv of ligand at the indicated temperature for 18 h.
[b] Determined by ^1H NMR analysis.
[c] Isolated yields.
[d] Enantiomeric excesses were determined by chiral HPLC (Chiralpak AS-H column, *i*-PrOH/hexane 50/50, 205 nm, 0.8 mL/min).
[e] No base additives.

Table 2
Catalytic asymmetric [3+2] cycloaddition reactions of imino esters **7** with dimethyl maleate **8**[a]



7a-k **8** *endo*-**9a-k** *exo*-**9a-k**

Entry	Substrate (R)	*endo*/*exo* [b]	Yield[c] (%)	ee[d] (%)
1	**7a** (4-ClC_6H_4)	95/5	95	99
2	**7b** (C_6H_5)	96/4	97	91
3	**7c** (4-FC_6H_4)	96/4	95	95
4	**7d** (4-BrC_6H_4)	95/5	92	91
5	**7e** (4-$NO_2C_6H_4$)	91/9	94	91
6	**7f** (4-$CF_3C_6H_4$)	96/4	96	95
7	**7g** (4-MeC_6H_4)	95/5	92	88
8	**7h** (3-$NO_2C_6H_4$)	97/3	93	94
9	**7i** (3-ClC_6H_4)	96/4	95	98
10	**7j** (1-naphthyl)	96/4	92	98
11	**7k** (cyclohexyl)	97/3	28	92[e]

[a] Reactions were performed in 1.5 mL of Et_2O with 0.3 mmol of substrates **7**, 10 mol % of Et_3N, and 3 mol % of catalyst prepared in situ from AgOAc and 1.1 equiv of ligand **2a** at −40 °C for 18 h.
[b] *endo*/*exo*-Ratio was determined by ^1H NMR.
[c] Isolated yields.
[d] Enantiomeric excesses were determined by chiral HPLC.
[e] Enantiomeric excess was determined by chiral GC.

aldehydes were reacted with dimethyl maleate **8** to give the corresponding *endo*-adducts **9a**–**j** in high yields and good to near perfect enantioselectivities (88–99% ee) (entries 1–10). The results show that the electronic properties of the substituent on the aromatic ring had some effect on the enantioselectivities (entries 3–7). The substrates bearing an electron-withdrawing substituent tended

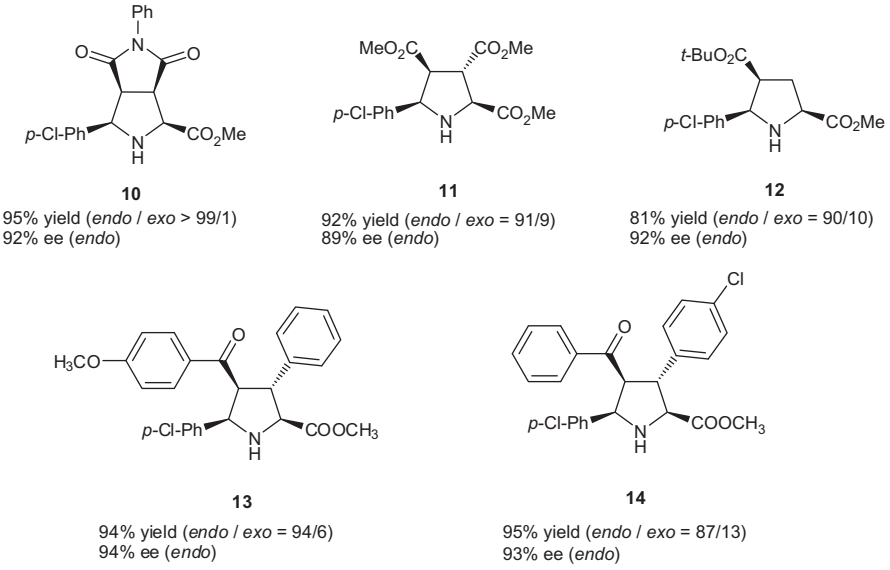


Figure 3. Cycloaddition of **7a** with other dipolarophiles.

to give higher enantioselectivities than those with an electron-donating group. An azomethine ylide from 1-naphthylaldehyde also proved to be a suitable substrate in this transformation, producing *endo*-cycloadduct in 98% ee (entry 10). However, for alkyl substituted substrate **7k**, the present catalytic system showed low reactivity (entry 11).

In order to further extend the scope of this catalytic system, the reaction of methyl *N*-(4-chlorobenzylidene)glycinate **7a** with other dipolarophiles was then carried out, and the results are summarized in Figure 3. With *N*-phenylmaleimide, high *endo*-selectivity (*endo*/*exo* >99/1) and good enantioselectivity (92% ee) were achieved. For dimethyl fumarate, the major *endo*-cycloadduct **11** was obtained in 92% yield and 89% ee. The reaction with *tert*-butyl acrylate gave a sightly lower yield (81%) but good enantioselectivity (92% ee). The reaction of **7a** with chalcones was also performed, producing cycloadducts **13** and **14** with good *endo*-selectivities and enantioselectivities.

3. Conclusion

In conclusion, we have developed a new family of chiral ferrocenyl P,S-ligands with an indole fragment through a highly efficient and simple synthesis route. These ligands were evaluated in the Ag(I)-catalyzed asymmetric [3+2] cycloaddition of azomethine ylides with various electronic-deficient alkenes, in which the corresponding cycloadducts were obtained with high *endo*-selectivities and good to excellent enantioselectivities (up to 99% ee). Further applications of these new ligands in other type of asymmetric reactions are currently in progress.

4. Experimental

4.1. General

All reactions were carried out under a nitrogen atmosphere. All solvents were purified by standard procedures, and commercially obtained reagents were used without further purification. ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer in deuterated chloroform. 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 deuterated chloroform. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. HPLC analyses were performed on an Agilent 1100 series instrument with a chiral column (Chiralcel AS-H) with hexane and *i*-PrOH as solvents. GC analyses were performed on a HP4890D instrument with a chiral column (Chiral Select-1000 column) using hydrogen as carrier gas. Optical rotations were recorded on a Jasco P-1020 polarimeter. The absolute configurations of the known products were determined by comparing specific rotations with the reported data.

4.2. General procedure for the synthesis of ligands 2a–f

A solution of 5.29 g (12 mmol) of (R_c,S_{Fc})-**3** together with 4 mmol of indole thioether in 10 mL of degassed acetic acid was warmed to 80 °C and stirred at this temperature for 2 h. The reaction mixture was then concentrated in vacuo 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 flash chromatography (ethyl acetate/petroleum ether = 1/50) and recrystallization with hexane and CH_2Cl_2 to afford the corresponding ligand.

4.2.1. 3-{(*S*)-1-[(*S*)-2-(Diphenylphosphino)ferrocenyl]ethyl}-2-(phenylthio)indole (S_c,S_{Fc})-2a

Yellow solid, 85% yield. Mp = 200–202 °C; $[\alpha]_D^{20} = -100.7$ (*c* 0.12, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74 (d, *J* = 8.0 Hz, 3H), 3.62 (s, 1H), 4.11 (s, 5H), 4.29–4.30 (m, 1H), 4.85–4.87 (m, 2H), 6.46–6.50 (m, 2H), 6.54–6.58 (m, 2H), 6.81–6.88 (m, 2H), 6.93–6.95 (m, 1H), 7.02–7.05 (m, 3H), 7.09–7.11 (m, 2H), 7.16–7.19 (m, 2H), 7.31 (s, 3H), 7.44 (s, 2H), 7.56 (d, *J* = 8.0 Hz, 1H); ^{31}P NMR (162 MHz, $CDCl_3$): δ −23.3; ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1 (d, *J* = 2.0 Hz), 137.8 (d, *J* = 9.0 Hz), 137.2, 135.3 (d, *J* = 21.0 Hz), 131.4 (d, *J* = 19.0 Hz), 129.0, 128.8, 127.9 (d, *J* = 8.0 Hz), 127.5, 126.8, 126.7, 126.6, 125.8, 125.5, 122.6, 120.5, 120.4, 119.0, 110.8, 98.3 (d, *J* = 24.0 Hz), 75.3 (d, *J* = 8.0 Hz), 71.8 (d, *J* = 4.0 Hz), 70.1 (d, *J* = 4.0 Hz), 69.9, 68.1, 31.1 (d, *J* = 7.0 Hz), 20.7; HRMS (*m*/*z*) calcd for $C_{38}H_{32}FeNPS$: 621.1343, found: 621.1357.

4.2.2. 3-{(*S*)-1-[(*S*)-2-(Diphenylphosphino)ferrocenyl]ethyl}-2-[(4-methylphenyl)- thio]indole (S_c,S_{Fc})-2b

Yellow solid, 82% yield. Mp = 230–232 °C; $[\alpha]_D^{20} = -86.8$ (*c* 0.11, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74 (d, *J* = 8.0 Hz, 3H), 2.26 (s,

3H), 3.60 (s, 1H), 4.09 (s, 5H), 4.29 (m, 1H), 4.83–4.87 (m, 2H), 6.44–6.48 (m, 2H), 6.52–6.56 (m, 2H), 6.79–6.85 (m, 2H), 6.90–7.06 (m, 7H), 7.29 (s, 3H), 7.39–7.43 (m, 2H), 7.53 (d, J = 8.0 Hz, 1H); ^{31}P NMR (162 MHz, $CDCl_3$): δ −23.3; ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2 (d, J = 9.0 Hz), 138.0 (d, J = 10.0 Hz), 137.1, 135.5, 135.3 (d, J = 21.0 Hz), 134.1 (d, J = 2.0 Hz), 131.3 (d, J = 19.0 Hz), 129.8, 128.7, 127.8 (d, J = 8.0 Hz), 127.4, 127.0, 126.7 (d, J = 6.0 Hz), 126.5, 125.9, 122.4, 121.2, 120.3, 118.9, 110.7, 98.3 (d, J = 24.0 Hz), 75.5 (d, J = 9.0 Hz), 71.8 (d, J = 5.0 Hz), 70.1 (d, J = 4.0 Hz), 69.8, 68.0, 31.0 (d, J = 8.0 Hz), 21.0, 20.6; HRMS (m/z) calcd for $C_{39}H_{34}FeNPS$: 635.1499, found: 635.1488.

4.2.3. 3-{(*S*)-1-[(*S*)-2-(Diphenylphosphino)ferrocenyl]ethyl}-2-[(4-chlorophenyl)- thio]indole (S_c,S_{Fc})-2c

Yellow solid, 77% yield. Mp = 207–209 °C; $[\alpha]_D^{20} = -67.4$ (c 0.15, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.72 (d, J = 4.0 Hz, 3H), 3.61 (s, 1H), 4.09 (s, 5H), 4.28 (s, 1H), 4.82 (s, 2H), 6.45–6.46 (m, 2H), 6.53–6.54 (m, 2H), 6.79–6.93 (m, 5H), 7.02–7.13 (m, 4H), 7.29 (s, 3H), 7.41 (s, 2H), 7.54 (d, J = 8.0 Hz, 1H); ^{31}P NMR (162 MHz, $CDCl_3$): δ −23.4; ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1 (d, J = 7.0 Hz), 137.7 (d, J = 10.0 Hz), 137.3, 136.7, 135.2 (d, J = 21.0 Hz), 131.4 (d, J = 19.0 Hz), 129.0, 128.8, 128.0, 127.9, 127.8, 126.8 (d, J = 7.0 Hz), 126.6, 125.7, 122.8, 120.6, 119.8, 119.2, 110.9, 98.1 (d, J = 24.0 Hz), 75.2 (d, J = 5.0 Hz), 71.8 (d, J = 4.0 Hz), 70.1 (d, J = 4.0 Hz), 69.9, 68.2, 31.1 (d, J = 7.0 Hz), 20.7; HRMS calcd for $C_{38}H_{31}ClFeNPS$: 655.0953, found: 655.0974.

4.2.4. 3-{(*S*)-1-[(*S*)-2-(Diphenylphosphino)ferrocenyl]ethyl}-2-(benzylthio)indole (S_c,S_{Fc})-2d

Yellow solid, 80% yield. Mp = 69–71 °C; $[\alpha]_D^{20} = -239.6$ (c 0.12, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.59 (d, J = 8.0 Hz, 3H), 3.63 (s, 1H), 3.85–3.94 (m, 2H), s1 (s, 5H), 4.29 (d, J = 4.0 Hz, 1H), 4.77–4.83 (m, 2H), 6.38–6.42 (m, 2H), 6.49–6.53 (m, 2H), 6.78–7.08 (m, 7H), 7.21–7.23 (m, 3H), 7.29–7.30 (m, 3H), 7.42–7.50 (m, 3H); ^{31}P NMR (162 MHz, $CDCl_3$): δ −22.8; ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0, 138.7 (d, J = 9.0 Hz), 138.3 (d, J = 9.0 Hz), 136.8, 135.4 (d, J = 21.0 Hz), 131.2 (d, J = 18.0 Hz), 129.0, 128.8, 128.5, 127.8 (d, J = 8.0 Hz), 127.1, 126.8 (d, J = 6.0 Hz), 126.4, 126.1, 125.8, 123.4, 122.0, 120.3, 118.8, 110.5, 98.9 (d, J = 25.0 Hz), 75.3 (d, J = 9.0 Hz), 71.7 (d, J = 4.0 Hz), 70.2 (d, J = 5.0 Hz), 69.8, 68.1, 41.2 (d, J = 4.0 Hz), 31.0 (d, J = 8.0 Hz), 20.7; HRMS calcd for $C_{39}H_{34}FeNPS$: 635.1499, found: 635.1494.

4.2.5. 3-{(*S*)-1-[(*S*)-2-(Diphenylphosphino)ferrocenyl]ethyl}-2-(methylthio)indole (S_c,S_{Fc})-2e

Yellow solid, 81% yield. Mp = 150–152 °C; $[\alpha]_D^{20} = -215.0$ (c 0.13, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.77 (d, J = 8.0 Hz, 3H), 2.29 (s, 3H), 3.59 (s, 1H), 4.11 (s, 5H), 4.27–4.28 (m,1H), 4.81–4.84 (m, 2H), 6.37–6.41 (m, 2H), 6.49–6.52 (m, 2H), 6.77–6.80 (m, 1H), 6.86–6.90 (m, 2H), 6.97–7.01 (m, 1H), 7.10 (s, 1H), 7.26–7.28 (m, 3H), 7.39–7.42 (m, 2H), 7.49 (d, J = 8.0 Hz, 1H); ^{31}P NMR (162 MHz, $CDCl_3$): δ −23.0; ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3 (d, J = 9.0 Hz), 138.0 (d, J = 10.0 Hz), 136.7, 135.3 (d, J = 21.0 Hz), 131.3 (d, J = 18.0 Hz), 128.7, 127.8 (d, J = 8.0 Hz), 126.6 (d, J = 6.0 Hz), 126.3, 126.0, 125.1, 124.8, 121.9, 120.1, 118.8, 110.4, 98.5 (d, J = 24.0 Hz), 75.3 (d, J = 8.0 Hz), 71.7 (d, J = 4.0 Hz), 70.1 (d, J = 3.0 Hz), 69.8, 68.0, 30.8 (d, J = 8.0 Hz), 20.9, 19.8; HRMS calcd for $C_{33}H_{30}FeNPS$: 559.1186, found: 559.1179.

4.2.6. 3-{(*S*)-1-[(*S*)-2-(Diphenylphosphino)ferrocenyl]ethyl}-2-(*i*-propylthio)indole (S_c,S_{Fc})-2f

Yellow solid, 84% yield. Mp = 120–122 °C; $[\alpha]_D^{20} = -248.4$ (c 0.12, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21–1.26 (m, 6H), 1.77 (s, 3H), 3.13–3.18 (m, 1H), 3.55 (s, 1H), 4.12 (s, 5H), 4.26 (s, 1H), 4.77–4.83 (m, 2H), 6.38–6.41 (m, 2H), 6.50–6.54 (m, 2H), 6.78–7.02 (m, 5H), 7.23–7.40 (m, 5H), 7.50 (d, J = 8.0 Hz, 1H); ^{31}P NMR (162 MHz, $CDCl_3$): δ −23.3; ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1 (d, J = 10.0 Hz), 136.7, 135.2 (d, J = 21.0 Hz), 131.3 (d, J = 19.0 Hz), 128.6, 127.8 (d, J = 8.0 Hz), 126.7 (d, J = 7.0 Hz), 126.4, 126.3, 126.0, 123.5, 121.9, 120.2, 118.6, 110.4, 98.6 (d, J = 24.0 Hz), 75.4 (d, J = 9.0 Hz), 71.8 (d, J = 5.0 Hz), 70.2 (d, J = 4.0 Hz), 69.8, 67.9, 40.1 (d, J = 3.0 Hz), 30.8 (d, J = 7.0 Hz), 24.2, 23.5, 20.7; HRMS calcd for $C_{35}H_{34}FeNPS$: 587.1499, found: 587.1482.

4.3. Synthesis of *N*-*tert*-butyloxycarbonyl-3-{(*S*)-1-[(*S*)-2-(diphenylphosphino)- ferrocenyl]ethyl}-2-(phenylthio)-indole (S_c,S_{Fc})-2g

To a solution of (S_c,S_{Fc})-**2a** (621.5 mg, 1 mmol) and DMAP (2.44 mg, 0.02 mmol) in CH_2Cl_2 (4 mL) was added $(Boc)_2O$ (240.2 mg, 1.1 mmol) and the solution was stirred at room temperature for 2 h. The resulting mixture was evaporated under reduced pressure and purified by flash column chromatography to afford the *N*-Boc-protected ligand (S_c,S_{Fc})-**2g**. Yellow solid, 80% yield. Mp = 89–92 °C; $[\alpha]_D^{20} = -96.9$ (c 0.12, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.35 (s, 9H), 1.63 (d, J = 8.0 Hz, 3H), 3.61 (s, 1H), 4.14 (s, 5H), 4.29 (s, 1H), 4.82 (s, 1H), 5.05–5.10 (m, 1H), 6.56–6.58 (m, 4H), 6.85 (s, 1H), 6.95–6.97 (m, 2H), 7.02–7.07 (m, 2H),7.15–7.19 (m, 3H), 7.30 (s, 3H), 7.43 (s, 2H), 7.51 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H); ^{31}P NMR (162 MHz, $CDCl_3$): δ −23.8; ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 139.8 (d, J = 2.0 Hz), 138.0, 137.6 (d, J = 11.0 Hz), 137.2 (d, J = 9.0 Hz), 135.0 (d, J = 21.0 Hz), 134.8, 131.5 (d, J = 20.0 Hz), 128.8, 128.6, 127.9 (d, J = 7.0 Hz), 127.0, 126.8 (d, J = 6.0 Hz), 125.4, 124.7 (d, J = 6.0 Hz), 121.8, 121.7, 120.3, 115.6, 97.0 (d, J = 23.0 Hz), 83.2, 76.2 (d, J = 9.0 Hz), 72.1 (d, J = 5.0 Hz), 70.3, 69.9, 67.9, 31.7 (d, J = 6.0 Hz), 27.9, 27.8, 19.6; HRMS (m/z) calcd for $C_{43}H_{40}FeNO_2PS$: 721.1867, Found: 721.1881.

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

Under a nitrogen atmosphere, a solution of AgOAc (0.009 mmol) and ligand **2** (0.0099 mmol) in 1.5 mL of Et_2O was stirred at room temperature for 1 h. Imino esters (0.3 mmol), Et_3N (4.2 μL, 0.03 mmol), and dimethyl maleate (0.36 mmol) were added successively. Once the starting materials were consumed (monitored by TLC), the mixture was passed through a short column of silica gel and the diastereometric ratio (*endo*/*exo*) was determined by NMR spectroscopic analysis after removal of the solvent. The residue was purified by column chromatography on silica gel, and then submitted to ee analysis by HPLC with a chiral column.

4.4.1. Trimethyl (2*S*,3*R*,4*S*,5*R*)-5-(4-chlorophenyl)pyrrolidine-2,3,4-tricarboxyl- ate *endo*-9a

White solid, 95% yield (*endo*/*exo* = 95/5), 99% ee. $[\alpha]_D^{20} = +14.2$ (c 0.17, $CHCl_3$). Chiral AS-H column, 40 °C, 205 nm, *n*-hexane/*i*-propanol = 50/50, flow rate = 0.8 mL/min, t_R = 7.7 and 10.5 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (s, 4H), 4.40 (d, J = 4.0 Hz, 1H), 4.10 (d, J = 12.0 Hz, 1H), 3.74 (s, 3H), 3.64–3.69 (m, 1H), 3.63 (s, 3H), 3.52–3.54 (m, 1H), 3.22 (s, 3H), 3.03 (br, 1H).

4.4.2. Trimethyl (2*S*,3*R*,4*S*,5*R*)-5-phenylpyrrolidine-2,3,4-tricarboxylate *endo*-9b

White solid, 97% yield (*endo*/*exo* = 96/4), 91% ee. $[\alpha]_D^{20} = +62.1$ (c 0.13, $CHCl_3$). Chiral AS-H column, 205 nm, *n*-hexane/*i*-propanol = 50/50, flow rate = 0.8 mL/min, t_R = 6.5 and 11.4 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17–7.29 (m, 5H), 4.42 (d, J = 8.0 Hz, 1H), 4.10 (d, J = 8.0 Hz, 1H), 3.74 (s, 3H), 3.64–3.66 (m, 1H), 3.62 (s, 3H), 3.51–3.53 (m, 1H), 3.16 (s, 4H).

4.4.3. Trimethyl (2*S*,3*R*,4*S*,5*R*)-5-(4-fluorophenyl)pyrrolidine-2,3,4-tricarboxyl- ate *endo*-9c

White solid, 95% yield (*endo*/*exo* = 96/4), 95% ee. $[\alpha]_D^{20} = +68.1$ (*c* 0.12, $CHCl_3$). Chiral AS-H column, 40 °C, 205 nm, *n*-hexane/*i*-propanol = 50/50, flow rate = 0.8 mL/min, t_R = 7.0 and 9.9 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), 3.61–3.63 (m, 1H), 3.59 (s, 3H), 3.48–3.50 (m, 1H), 3.16 (s, 3H), 2.83 (br, 1H).

4.4.4. Trimethyl (2*S*,3*R*,4*S*,5*R*)-5-(4-bromophenyl)pyrrolidine-2,3,4-tricarboxyl- ate *endo*-9d

White solid, 92% yield (*endo*/*exo* = 95/5), 91% ee. $[\alpha]_D^{20} = +52.6$ (*c* 0.12, $CHCl_3$). Chiral AS-H column, 40 °C, 205 nm, *n*-hexane/*i*-propanol = 50/50, flow rate = 0.8 mL/min, t_R = 8.0 and 11.3 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 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), 3.49–3.53 (m, 1H), 3.26 (s, 1H), 3.21 (s, 3H).

4.4.5. Trimethyl (2*S*,3*R*,4*S*,5*R*)-5-(4-nitrophenyl)pyrrolidine-2,3,4-tricarboxylate *endo*-9e

White solid, 94% yield (*endo*/*exo* = 91/9), 91% ee. $[\alpha]_D^{20} = +16.7$ (*c* 0.12, $CHCl_3$). Chiral AS-H column, 40 °C, 205 nm, *n*-hexane/*i*-propanol = 50/50, flow rate = 0.8 mL/min, t_R = 12.7 and 14.2 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 12.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 4.52 (d, *J* = 8.0 Hz, 1H), 4.14 (d, *J* = 8.0 Hz, 1H), 3.74 (s, 3H), 3.69–3.72 (m, 1H), 3.63 (s, 3H), 3.59–3.61 (m, 1H), 3.21 (s, 3H).

4.4.6. Trimethyl (2*S*,3*R*,4*S*,5*R*)-5-(4-(trifluoromethyl)phenyl)-pyrrolidine-2,3,4- tricarboxylate *endo*-9f

White solid, 96% yield (*endo*/*exo* = 96/4), 95% ee. $[\alpha]_D^{20} = +43.2$ (*c* 0.13, $CHCl_3$). Chiral AS-H column, 40 °C, 205 nm, *n*-hexane/*i*-propanol = 50/50, flow rate = 0.8 mL/min, t_R = 6.0 and 7.3 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 12.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 4.48 (d, *J* = 4.0 Hz, 1H), 4.12 (d, *J* = 8.0 Hz, 1H), 3.75 (s, 3H), 3.67–3.69 (m, 1H), 3.63 (s, 3H), 3.57–3.59 (m, 1H), 3.23 (s, 1H), 3.19 (s, 3H).

4.4.7. Trimethyl (2*S*,3*R*,4*S*,5*R*)-5-*p*-tolylpyrrolidine-2,3,4-tricarboxylate *endo*-9g

White solid, 92% yield (*endo*/*exo* = 95/5), 88% ee. $[\alpha]_D^{20} = +18.9$ (*c* 0.11, $CHCl_3$). Chiral AS-H column, 40 °C, 205 nm, *n*-hexane/*i*-propanol = 50/50, flow rate = 0.8 mL/min, t_R = 6.4 and 12.7 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 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 (2*S*,3*R*,4*S*,5*R*)-5-(3-nitrophenyl)pyrrolidine-2,3,4-tricarboxylate *endo*-9h

White solid, 93% yield (*endo*/*exo* = 97/3), 94% ee. $[\alpha]_D^{20} = +48.4$ (*c* 0.07, $CHCl_3$). Chiral AS-H column, 40 °C, 205 nm, *n*-hexane/*i*-propanol = 50/50, flow rate = 0.8 mL/min, t_R = 11.3 and 15.9 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 1H), 8.05–8.07 (m, 1H), 7.70–7.71 (m, 1H), 7.43–7.47 (m, 1H), 4.54 (d, *J* = 8.0 Hz, 1H), 4.16 (d, *J* = 8.0 Hz, 1H), 3.74 (s, 3H), 3.71–3.74 (m, 1H), 3.62–3.63 (m, 4H), 3.25 (s, 1H), 3.21 (s, 3H).

4.4.9. Trimethyl (2*S*,3*R*,4*S*,5*R*)-5-(3-chlorophenyl)pyrrolidine-2,3,4-tricarboxyl- ate *endo*-9i

White solid, 95% yield (*endo*/*exo* = 96/4), 98% ee. $[\alpha]_D^{20} = +50.7$ (*c* 0.17, $CHCl_3$). Chiral AS-H column, 40 °C, 205 nm, *n*-hexane/*i*-propanol = 50/50, flow rate = 0.8 mL/min, t_R = 7.0 and 11.6 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), 4.10 (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).

4.4.10. Trimethyl (2*S*,3*R*,4*S*,5*R*)-5-(naphthalen-1-yl)pyrrolidine-2,3,4-tricarboxylate *endo*-9j

White solid, 92% yield (*endo*/*exo* = 96/4), 98% ee. $[\alpha]_D^{20} = +40.7$ (*c* 0.09, $CHCl_3$). Chiral AS-H column, 205 nm, 40 °C, *n*-hexane/*i*-propanol = 50/50, flow rate = 0.8 mL/min, t_R = 7.9 and 14.2 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).

4.4.11. Trimethyl (2*S*,3*R*,4*S*,5*S*)-5-cyclohexylpyrrolidine-2,3,4-tricarboxylate *endo*-9k

White solid, 28% yield (*endo*/*exo* = 97/3), 92% ee. $[\alpha]_D^{20} = +26.4$ (*c* 0.17, $CHCl_3$). Capillary GC, Chiral Select 1000 column, 30 m × 0.25 mm, 160 °C, 15 psi, Carrier gas: H_2, t_R = 35.6 and 40.7 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.99 (d, *J* = 8.0 Hz, 1H), 3.67 (s, 3H), 3.60 (s, 3H), 3.58 (s, 3H), 3.45–3.49 (m, 1H), 3.08–3.11 (m, 1H), 2.78 (s, 1H), 2.71–2.75 (m, 1H), 1.96–2.00 (m, 1H), 1.72–1.75 (m, 1H), 1.55–1.66 (m, 3H), 1.24–1.32 (m, 1H), 0.83–1.20 (m, 5H).

4.4.12. Methyl (1*S*,3*R*,3*aS*,6*aR*)-4,6-dioxo-3,5-diphenylocta-hydrocyclopenta[c] pyrrole-1-carboxylate *endo*-10

White solid, 95% yield (*endo*/*exo* >99/1), 92% ee. $[\alpha]_D^{20} = +139.5$ (*c* 0.12, $CHCl_3$). Chiral AS-H column, 40 °C, 215 nm, *n*-hexane/*i*-propanol = 80/20, flow rate = 1.0 mL/min, t_R = 6.5 and 14.0 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).

4.4.13. Trimethyl (2*S*,3*S*,4*S*,5*R*)-5-phenylpyrrolidine-2,3,4-tricarboxylate *endo*-11

White solid, 92% yield (*endo*/*exo* = 91/9), 89% ee. $[\alpha]_D^{20} = +16.9$ (*c* 0.59, $CHCl_3$). Chiral AS-H column, 40 °C, 205 nm, *n*-hexane/*i*-propanol = 90/10, flow rate = 0.8 mL/min, t_R = 20.5 and 22.5 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (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 (br, 1H).

4.4.14. 4-*t*-Butyl 2-methyl (2*S*,4*S*,5*R*)-5-phenylpyrrolidine-2,4-dicarboxylate *endo*-12

White solid, 81% yield (*endo*/*exo* = 90/10), 92% ee. $[\alpha]_D^{20} = +27.1$ (*c* 0.23, $CHCl_3$). Chiral AS-H column, 40 °C, 230 nm, *n*-hexane/*i*-propanol = 90/10, flow rate = 0.8 mL/min, t_R = 5.8 and 7.8 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15–7.25 (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), 2.30–2.34 (m, 1H), 2.22–2.25 (m, 1H), 0.99 (s, 9H).

4.4.15. Methyl (2*S*,3*S*,4*S*,5*R*)-5-(4-chlorophenyl)-4-(4-methoxybenzoyl)-3-phenyl- pyrrolidine-2-carboxylate *endo*-13

White solid, 94% yield (*endo*/*exo* = 94/6), 94% ee. $[\alpha]_D^{20} = -154.0$ (*c* 0.12, $CHCl_3$). Chiral AS-H column, 40 °C, 215 nm, *n*-hexane/*i*-propanol = 80/20, flow rate = 1.0 mL/min, t_R = 6.3 and 7.5 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.56 (m, 2H), 7.29–7.35 (m, 4H), 7.22–7.24 (m, 1H), 7.06 (s, 4H), 6.73–6.75 (m, 2H), 4.93 (d, *J* = 8.0 Hz, 1H), 4.42–4.46 (m, 1H), 4.15–4.17 (m, 1H), 4.06–4.08 (m, 1H), 3.78 (s, 3H), 3.72 (s, 3H), 2.79 (br, 1H).

4.4.16. Methyl (2*S*,3*S*,4*S*,5*R*)-4-benzoyl-3,5-bis(4-chlorophenyl)-pyrrolidine-2- carboxylate *endo*-14

White solid, 95% yield (*endo*/*exo* = 87/13), 93% ee. $[\alpha]_D^{20} = -65.7$ (*c* 0.11, $CHCl_3$). Chiral AS-H column, 40 °C, 215 nm, *n*-hexane/*i*-propanol = 80/20, flow rate = 1.0 mL/min, t_R = 11.0 and 14.6 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.55 (m, 2H), 7.40–7.44 (m, 1H),

7.25–7.30 (m, 6H), 7.02 (s, 4H), 4.95 (d, J = 8.0 Hz, 1H), 4.44–4.48 (m, 1H), 4.06–4.14 (m, 2H), 3.70 (s, 3H), 2.84 (br, 1H).

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