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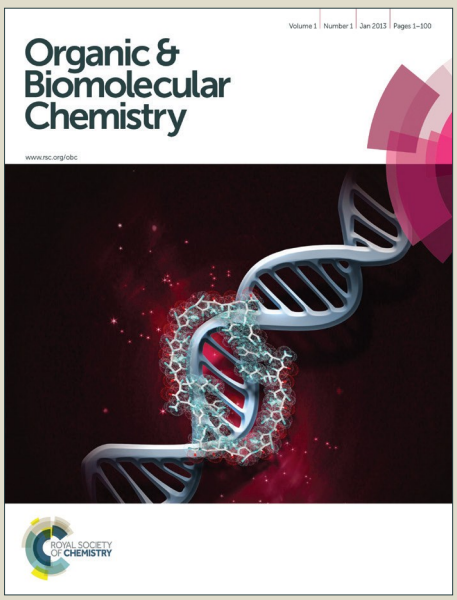

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PAPER

Chiral Bifunctional Ferrocenylphosphines Catalyzed Highly Enantioselective [3+2] Cycloaddition Reaction

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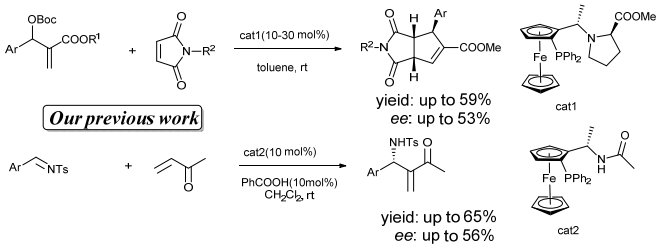
A series of air-stable ferrocenylphosphines **LB1**-**LB8** were designed and prepared with high yields, in which (*R, S*$_{Fc}$)-ferrocenylphosphines **LB5** was found to promote efficiently the asymmetric [3+2] cycloaddition of Morita-Baylis-Hillman carbonates with maleimides to afford the corresponding bicyclic imides with 84-99% *ee* and 67-99% yields. Interestingly, the configuration of these products was contrary to those reported in the literatures.

Introduction

In the past decade, chiral phosphine organocatalysis has been an effective tool for construction of chiral cyclic compounds.[1] So far, these chiral phosphines mainly contain two forms: chiral monodentate phosphines and multi-functional chiral phosphines.[2] As we know, ferrocenylphosphines have often been applied in metal complexes to serve as chiral ligands, however, comparatively few ferrocenylphosphines have been used as asymmetric phosphine catalysis [3+2] annulation reaction.[3] Until 2008, Marinetti *et al*. reported the use of 2-phospha[3]-ferrocenophanes with planar chirality to catalyze asymmetric [3+2] cycloaddition.[4] However, the preparation of 2-phospha[3]-ferrocenophanes involved in low temperature (-70 °C) and using of the dangerous $NaBH_3CN$.[4a,4b] Then, our group has developed a series of ferrocenylphosphines catalysts in simple synthetic ways. Unfortunately, these catalysts are poorly effective in enantioselective organic transformations (Scheme 1).[5] Recently, many research groups highlighted the great potential of multifunctional chiral phosphines as efficient catalysts for asymmetric [3+2] cycloaddition. Notably, major contributions were from Miller,[6] Jacobsen,[7] Shi,[8] and Lu.[9] Very recently, Chen and co-workers reported the use of bifunctional ferrocene-based squaramide-phosphine as efficient catalyst for intramolecular Morita-Baylis-Hillman reaction.[10] However, to the best of our knowledge, no example of a ferrocene-based bifunctional phosphine for highly enantioselective [3+2] cycloaddition has been reported. Herein, we describe the enantioselective [3+2] cycloaddition of MBH carbonates with maleimides[11, 12] catalyzed by novel chiral ferrocene-based bifunctional N-acyl aminophosphines.



Scheme 1 Ferrocenylphosphines in asymmetric organocatalysis

Results and discussion

Our previous work showed that the introduction of Brϕnsted acid or heterocycle group in catalyst were significant.[5] Then, we further designed three types of ferrocenylphosphines (Fig. 1). With the successful use of planar chirality 2-phospha[3]-ferrocenophanes in organocatalysis,[4] so we choose planar chirality as a stereogenic element which contain planar chiral PPh_2-Ferrocene or TMS-Ferrocene and they also could evaluate the influence of the position of diphenylphosphine. In addition, combining with the significance of Brϕnsted acid and heterocycle group, bifunctional or monodentate phosphines were designed to evaluate the influence of Brϕnsted acid and heterocycle group. These ferrocenylphosphines were easily prepared by the condensation reaction of the amide or nucleophilic substitution reaction (Scheme 2). Next, their catalytic activities were evaluated in the cycloaddition reaction of MBH carbonate (**1a**) with maleimide (**2a**) in toluene at room temperature (Table 1). The position of diphenylphosphine was important for enantioselectivities, such as planar chiral **LB8** derived from *o*-diphenylphosphine benzoic acid, which afforded the racemic product **3a** in 55% yield (Table 1, entry 8). So we supposed that the diphenylphosphine and ferrocene should be linked directly to achieve asymmetric organocatalysis. Other planar chiral diphenylphosphines containing amide **LB1-LB3** showed moderate catalytic activities (Table 1, entries 1-3). However, as the configurational isomerism of L-prolinamide-derived

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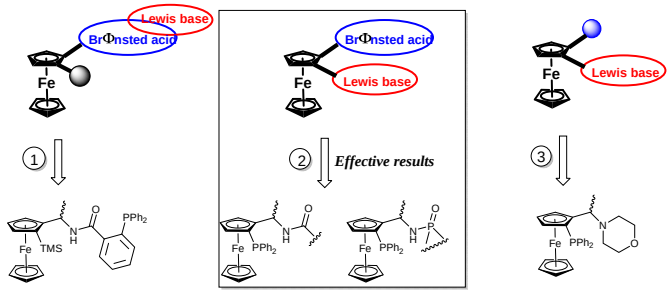
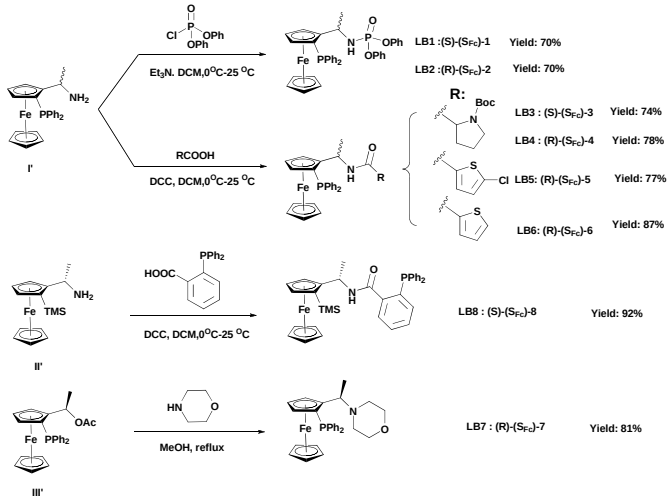


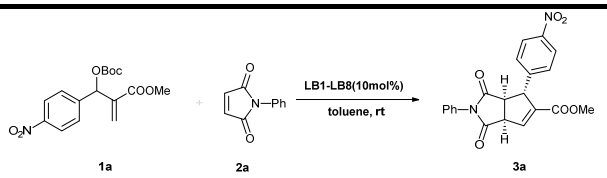
Fig. 1 The design of ferrocenylphosphines



Scheme 2 Synthesis of ferrocenylphosphines **LB1**-**LB8**

ferrocenylphosphines **LB3, LB4** with the configuration of (R)-(S_{Fc}) afforded the product **3a** in 60% *ee*, but still low yield of 27% (Table 1, entry 4). Interestingly, the configuration of product **3a** was reversal and a new enantiomer was obtained. Perhaps a suitable chirality matching of **LB4** can lead to a well stereochemical structure to perform chiral induction. So we considered (*R, S_{Fc}*)-ferrocenylphosphines as efficient stereogenic center to get new enantiomer with good dr and *ee* value. Despite the configuration of **LB7** is (R)-(S_{Fc}), it still afforded low activity with 29% *ee* and 25% yield, and the product of configuration was retention (Table 1, entry 7). Therefore, besides suitable configuration, we found some heterocycle containing amides were also essential. Fortunately, **LB5** and **LB6** containing thiophenecarboxamide presented higher catalytic activity in good yields with good diastereoselctivities and enantioselectivities than others (Table 1, entries 5-6). It may indicate that there exists well steric configuration between diphenylphosphine and thiophene ring, which contributes to good nucleophilicity and chiral induction. Having selected **LB5** as the best catalyst, we immediately examined different solvents and found that the yield of product **3a** decreased with the rise of solvent polarity (Table 1, entries 9-12). Toluene was the best solvent to give the product **3a** in excellent yield, high *dr* and *ee* value (Table 1, entry 5). Lower temperature led to a little reducing of the *ee* value and yield (Table 1, entry 13). When the loading of catalyst **LB5** was reduced to 5 mol%, the reaction enantioselectivity was still good, although the yield had a little decline (Table 1, entry 14).

Table 1 Screening of chiral phosphines for the [3+2] cycloaddition of MBH Carbonate **1a** with maleimide **2a**[a]



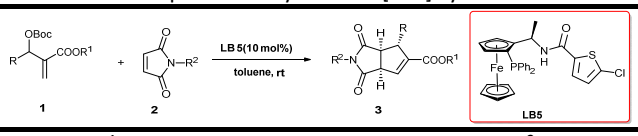
Entry	Cat.	Time(h)	Yield(%)[b]	*ee*(%)[c]
1	**LB 1**	72	36	-31
2	**LB 2**	72	21	33
3	**LB 3**	72	17	-39
4	**LB 4**	72	27	60
5	**LB 5**	48	88	97
6	**LB 6**	48	79	95
7	**LB 7**	72	25	-29
8	**LB 8**	72	55	racemic
9[d]	**LB 5**	48	47	97
10[e]	**LB 5**	48	72	94
11[f]	**LB 5**	48	31	97
12[g]	**LB 5**	48	trace	/
13[h]	**LB 5**	48	45	91
14[i]	**LB 5**	48	60	98

[a]Unless otherwise specified, the reactions were performed with **1a** (0.5 mmol), **2a** (1 mmol) and catalyst (0.05 mmol) in toluene (5.0 mL) at room temperature. [b]Isolated yield of major products with a *dr* value >25:1 if not otherwise specified. [c]The *ee* value was determined by HPLC analysis using a chiral column. [d]Reaction was performed in DCM (5.0 mL). [e]Reaction was performed in Et_2O (5.0 mL). [f]Reaction was performed in $CHCl_3$ (5.0 mL). [g]Reaction was performed in 1,4-dixoane (5.0 mL). [h]Reaction was performed at 0 °C. [i]The catalyst loading was 5 mol%.

With the optimal reaction conditions in hand, we subsequently studied the scope of **LB5** catalyzed asymmetric [3+2] cycloaddition of a variety of MBH carbonates with maleimides (Table 2). In general, excellent diastereoselectivities and enantioselectivities were observed under the optimal conditions. Selecting MBH carbonate **1a** as a constant C_3 synthon and maleimides **2a, 2b-2e** as C_2 synthons (Table 2, entries 1, 4-7), we found they all worked well to give the corresponding products in good yields (68-99%) and good *ee* values (92-97%). Taking N-phenylmaleimide **2a** as a constant C_2 synthon, a variety of MBH carbonates **1** bearing electron-deficient, electron-neutral and electron-rich on the aryl rings or different ester group on the side chain also proceeded smoothly, affording the corresponding products in excellent yields and *ee* values (Table 2, entries 1-3, 10-17). We found that electron-deficient aromatic MBH carbonates performed a little higher reactivity than electron-rich ones.

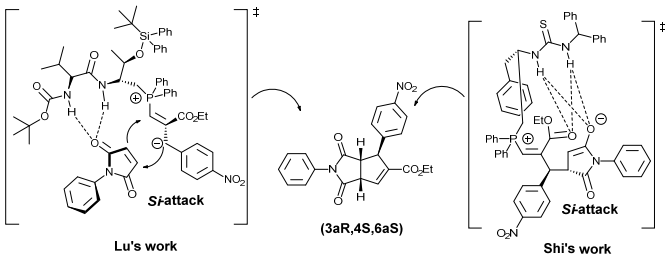
Next, locations of substituents on aryl had also been studied, there were obvious differences between the sterically hindered *ortho* and *meta*- nitro- substituted MBH carbonates **1d-1e**, but little comparability for the chloro-substituted MBH carbonates **1h-1j** in terms of reactivity (Table 2, entries 8-9, 12-14). Due to steric hindrance, *ortho*-nitro-substituted MBH carbonate **1e** could not

Table 2 Scope of the asymmetric [3+2] cycloaddition[a].

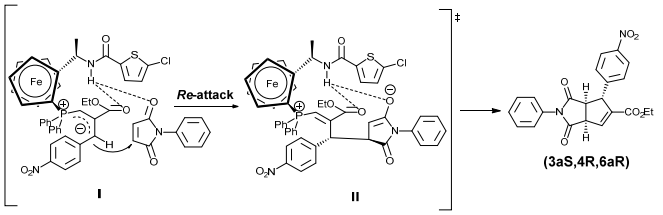


Entry	R/R[1]	R[2]	Yield(%)[b]	ee(%)[c]
1	4-$NO_2C_6H_4$/Me(**1a**)	Ph(**2a**)	88(**3a**)	97
2	4-$NO_2C_6H_4$/Et(**1b**)	Ph(**2a**)	98(**3b**)	97
3	4-$NO_2C_6H_4$/*n*-Bu(**1c**)	Ph(**2a**)	73(**3c**)	96
4	4-$NO_2C_6H_4$/Me(**1a**)	Me(**2b**)	70(**3d**)	-[d]
5	4-$NO_2C_6H_4$/Me(**1a**)	Bn(**2c**)	76(**3e**)	92
6	4-$NO_2C_6H_4$/Me(**1a**)	4-ClC_6H_4(**2d**)	68(**3f**)	95
7	4-$NO_2C_6H_4$/Me(**1a**)	4-$MeOC_6H_4$(**2e**)	99(**3g**)	97
8	3-$NO_2C_6H_4$/Me(**1d**)	Ph(**2a**)	86(**3h**)	84
9	2-$NO_2C_6H_4$/Me(**1e**)	Ph(**2a**)	/	/
10	Ph/Me(**1f**)	Ph(**2a**)	71(**3i**)	99
11	4-FC_6H_4/Me(**1g**)	Ph(**2a**)	68(**3j**)	99
12	2-ClC_6H_4/Me(**1h**)	Ph(**2a**)	69(**3k**)	98
13	3-ClC_6H_4/Me(**1i**)	Ph(**2a**)	77(**3l**)	98
14	4-ClC_6H_4/Me(**1j**)	Ph(**2a**)	70(**3m**)	＞99
15	4-BrC_6H_4/Me(**1k**)	Ph(**2a**)	72(**3n**)	98
16	4-MeC_6H_4/Me(**1l**)	Ph(**2a**)	72(**3o**)	96
17	4-$MeOC_6H_4$/Me(**1m**)	Ph(**2a**)	73(**3p**)	＞99
18	2-furyl/Me(**1n**)	Ph(**2a**)	74(**3q**)	98
19	1-naphthyl/Me(**1o**)	Ph(**2a**)	84(**3r**)	99
20	2-choroquinoline/Me(**1p**)	Ph(**2a**)	67(**3s**)	96
21	2-chorobenzo[h]quinoline/Me(**1q**)	Ph(**2a**)	73(**3t**)	97
22	4-methiazole/Me(**1r**)	Ph(**2a**)	70(**3u**)	96
23	n-Pr/Me(**1s**)	Ph(**2a**)	/	/

[a]Unless otherwise specified, the reactions were performed with **1** (0.5 mmol), **2** (1 mmol) and catalyst (0.05 mmol) in toluene (5.0 mL) at room temperature. [b]Isolated yield of major products with a *dr* value ＞25:1. [c]The *ee* value was determined by HPLC analysis using a chiral column. [d]The ee value was not determined by HPLC.



Scheme 3 Lu's and Shi's transition states



Scheme 4 Possible transition states in this work

give the corresponding product and the *ee* value of *meta*-nitro-substituted product **3h** declined to 84%. In addition, we also synthesized some novel products which contained the heteroaryl or fused heteroaryl with good yields and *ee* values (Table 2, entries 18, 20-22).[13] In the case of alkyl MBH carbonate **1s**, no product was detected even if tested in higher temperature (40°C, 60°C) or more catalyst loading (Table 2, entry 23).

On the basis of predecessors' works[11, 12](Scheme 3) and the results of our experiment,[14] a plausible transition state was proposed to explain the stereochemical consequence of the reaction (Scheme 4), which was contrary to those reported in the literatures[11, 12]. Firstly, **LB5** attacked the MBH carbonate to form the allylic phosphonium **I**, the H-bonding between the **LB5** and maleimide enhanced the reactivity. Secondly, due to spatial induction of thiophene ring on the chain, the allylic phosphorus ylide **I** used its *Re*-face to attack maleimide to form transition state **II**, which was then transformed into (3as,4R,6aR)-**3**.

Conclusions

In conclusion, we have developed a new class of chiral phosphines based on both planar and central chiral ferrocene-based bifunctional N-acyl aminophosphines, and the chiral phosphine **LB5** showed good catalytic activity for the enantioselective [3+2] cycloadditions of MBH carbonates with maleimides. The catalytic reactions provide meaningful products in highly enantioenriched forms. Furthermore, **LB5** was found to be air-stable enough in both solution and solid state.[15] Applying the chiral ferrocenylphosphines to other asymmetric reactions is underway in our laboratory.

Experimental section

Materials and general experimental details

All starting materials were commercially available and were used without further purification. Melting points were determined on a Büchi B-540 capillary melting point apparatus and uncorrected. Optical ratations were determined by using a AUTOPOL V Polarimeter. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian-400 MHz spectrometer at 400 and 100 MHz for solution in $CDCl_3$ with tetramethylsilane (TMS, δ= 0) as an internal standard. The chemical shift (d) were reported in ppm and coupling constants *J* were expressed in Hertz. ^{31}P NMR were measured in $CDCl_3$ with 85% H_3PO_4 as an internal standard on a Varian-400 MHz spectrometer at 161.9 MHz. Less solution mass spectra were obtained with a Trace DSQ mass spectrometer in ESI mode. High resolution mass spectra were acquired with an Agilent 6210 TOF mass spectrometer. The enantiomeric excesses of target molecules were obtained with chiral-phase HPLC analysis, which using Agilent 1200 HPLC (Chromatographic Column: Daicel Chiralcel AD-RH or OD-RH and eluting with acetonitrile /H_2O) with DAD UV detector.

The MBH carbonates **1** were prepared following the literature procedure[16].

The starting materials **I'**,**II'**, **III'** were prepared following the literature procedure[17]

General procedure for synthesis of chiral ferrocenylphosphines LB1-LB8

diphenyl (S)-1-[(S)-2-diphenylphosphanyl] ferrocenylethyl phosphoramidate (LB1)

A suspension of (*S*)-1-(*S*)-diphenylphosphisoferrocenyl ethylamine (0.20g, 0.50 mmol) and Et_3N (0.13mg, 1.74mmol) in CH_2Cl_2 (5 mL) was cooled to 0 ^{o}C. Then Diphenyl phosphoryl chloride (0.20 g, 0.75 mmol) in CH_2Cl_2 (5 mL) was added in 10 min and the reaction mixture was stirred at room temperature for 2 h. After the reaction was completed, the solution was then washed with water and extracted with CH_2Cl_2 several times (3 x 10 mL), and the combined organic extracts were dried over Na_2SO_4 , filtered and concentrated. Purified by a flash column chromatography to afford **LB1** (0.23g, 70%) as a yellow solid. m.p.: 116.4-117.6^{o}C; $[a]^{20}_{D}$ = +190.2^{o} (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.49 (m, 2H), 7.39 (d, *J* = 5.6 Hz, 3H), 7.35-7.28 (m, 5H), 7.25 – 7.10 (m, 10H), 4.54 (dd, *J* = 15.4, 8.4 Hz, 1H), 4.40 (s, 2H), 4.28 (t, *J* = 2.4 Hz, 1H), 3.99 (s, 5H), 3.80 – 3.76 (m, 1H), 1.38 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 150.9, 139.0, 138.9, 136.8, 135.1, 134.9, 132.5, 132.4, 129.6(2C), 129.5(2C), 129.3, 128.1(4C), 124.8(2C), 120.6, 120.5, 120.3, 120.2, 97.7, 73.0, 71.9, 70.8, 69.9(5C), 69.4, 48.6, 26.1; ^{31}P NMR (162 MHz, $CDCl_3$, 85 % H_3PO_4): δ -2.42 (d, *J* =13.6 Hz), -23.47; MS (ESI) m/z (%): 646.0 (100) $[M+H]^+$. HRMS (ESI) Calcd. for $C_{36}H_{33}FeNNaO_3P_2$ 668.1178 $[M+Na]^+$, found 668.1175.

The **LB2** was prepared following the same procedure as a yellow solid, $[a]^{20}_{D}$ = -287.5 (c 1.0, $CHCl_3$)

tert-butyl 2-[(S)-1-(S)-2-(diphenylphosphanyl) ferrocenylethyl carbamoyl] pyrrolidine-1-carboxylate (LB3)

A suspension of N-Boc-L-proline (0.27g, 1.25 mmol) and DCC (0.26g, 1.25mmol) in CH_2Cl_2 (5 mL) was cooled to 0 ^{o}C. Then (*S*)-1-(*S*)-diphenylphosphisoferrocenyl ethylamine (0.20g, 0.50 mmol) in CH_2Cl_2 (5 mL) was added in 10 min and the reaction mixture was stirred at room temperature for 2 h. After the reaction was completed, water was added to quench the reaction , then filtered and extracted with CH_2Cl_2 several times (3 x 10 mL), and the combined organic extracts were dried over Na_2SO_4 , filtered and concentrated. The residue was purified by a flash column chromatography to afford **LB3** (0.23g, 74%) as a yellow solid. m.p.: 161.7-162.4 ^{o}C; $[a]^{20}_{D}$ = +167.2^{o} (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.50 (m, 2H), 7.37 (d, *J* = 4.8 Hz, 3H), 7.25 – 7.18 (m, 3H), 7.15-7.10 (m, 2H), 6.74 (s, 1H), 5.21 (s, 1H), 4.44 (q, *J*= 2.0 Hz, 1H), 4.35 (s, 1H), 4.09 (s, 1H), 3.94 (s, 5H), 3.48 (s, 1H), 3.10 (s, 1H), 2.14 – 1.87 (m, 2H), 1.75 – 1.51 (m, 2H), 1.47 – 1.33 (m, 12H), 1.20 – 1.10 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 154.9, 140.0, 137.5, 135.2, 132.4, 129.3, 128.2(2C), 128.1(2C), 127.8, 80.5, 74.1, 72.2, 70.6, 69.9(5C), 61.8, 49.6 47.5, 45.1, 34.0, 28.7(3C), 25.9, 25.1, 25.0, 24.2, 23.0; ^{31}P-NMR (162 MHz, $CDCl_3$, 85 % H_3PO_4):δ -25.36; MS (ESI) m/z (%): 611.4 (100) $[M+H]^+$; HRMS (ESI) Calcd. for $C_{34}H_{39}FeN_2NaO_3P$ 633.1940 $[M+Na]^+$, found: 633.1932.

The **LB4** was prepared following the same procedure as a yellow solid, $[a]^{20}_{D}$ = -311.0 (c 1.0, $CHCl_3$)

(R)-5-chloro-N-[1'-(S)-2'-(diphenylphosphanyl)ferrocenyl)ethyl]thiophene-2-carboxamide (LB5)

Following a similar procedure as **LB3, LB5** (0.25g, 77%), a yellow solid, m.p.:120.9-122.3 ^{o}C; $[\alpha]^{20}$D= -284.0^{o} (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, CDCl3) δ 7.56 – 7.49 (m, 2H), 7.39 (d, J = 4.8 Hz, 3H), 7.19 (d, *J* = 3.6 Hz, 5H), 7.10 (brs, 1H), 6.98 (d, *J* = 4.0 Hz, 1H), 6.81 (d, *J* = 4.0 Hz, 1H), 5.26 (q, *J* = 7.2 Hz, 1H), 4.52 (s, 1H), 4.35 (t, *J* = 2.4 Hz, 1H), 4.01 (s, 5H), 3.84 (t, *J* = 1.2 Hz, 1H), 1.40 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 154.8, 138.5, 137.9, 136.2, 134.9, 134.8, 134.7, 132.6, 132.4, 129.5(2C), 128.3(3C), 126.7(2C), 95.5, 73.7, 72.3, 71.3, 70.1(5C), 69.7, 46.0, 23.0; ^{31}P NMR (162 MHz, $CDCl_3$, 85 % H_3PO_4): δ -23.47; MS (ESI) m/z (%): 558.4 (100) $[M+H]^+$. HRMS (ESI) Calcd. for $C_{29}H_{25}ClFeNNaOPS$ 580.0325 $[M+Na]^+$, found: 580.0345.

(R)-N-[1'-(S)-2'-(diphenylphosphanyl)ferrocenyl)ethyl]thiophene-2-carboxamide (LB6)

Following a similar procedure as **LB3, LB6** (0.23g, 87%), a yellow solid, m.p. 70.1-71.4^{o}C; $[\alpha]^{20}_{D}$= -344.1^{o} (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 2H), 7.44 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.40-7.39 (m, 4H), 7.33 (dd, *J* = 0.8, 3.6 Hz, 1H), 7.21 – 7.16 (m, 5H),

7.02 (dd, *J* = 5.2, 3.6 Hz, 1H), 5.27 (m, 1H), 4.53 (d, *J* = 0.8Hz, 1H), 4.34 (t, *J* = 2.4 Hz, 1H), 4.01 (s, 5H), 3.85 (t, *J* = 1.2 Hz, 1H), 1.39 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 139.5, 138.4, 136.2, 135.0, 134.8, 132.6, 132.4, 129.5(2C), 128.3(3C), 128.2(2C), 127.8, 127.5, 96.2, 73.2, 72.1, 71.6, 70.0(5C), 69.6, 46.0, 23.3. ^{31}P NMR (162 MHz, $CDCl_3$, 85 % H_3PO_4): δ -23.17. MS (ESI) m/z (%): 546.1 (100) $[M+Na]^+$; HRMS (ESI) Calcd. for $C_{29}H_{25}FeNNaOPS$ 546.0714 $[M+Na]^+$, found: 546.0714.

***N*-[(*R*)-1-(*S*)-2-diphenylphosphinoferrocenyl]ethylpyrrolidine (LB7)**

A solution of (*S*)-1-(*R*) diphenylphosphisoferrocenyl ethyl acetate (0.23g, 0.5 mmol) and morpholine (0.17g, 2.0 mmol) in methanol (5 mL) was refluxed for 5h. The solvent was removed under induced pressure and the residue was purified by column chromatography to afford **LB7** (0.19g, 81%) as a yellow solid 180.9-182.0 °C; $[\alpha]^{20}_D$= -341.6° (c 1.0, $CHCl_3$), (Lit.[2a] no data); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.54 (m, 2H), 7.36-7.35 (m, 3H), 7.22 (s, 5H), 4.39 (s, 1H), 4.28–4.16 (m, 3H), 3.95 (s, 5H), 3.00-2.81(m, 4H), 2.34-2.28 (m, 4H), 1.33 (d, *J* = 6.4 Hz, 3H); HRMS (ESI) Calcd. for $C_{28}H_{30}FeNOP$ 483.1409 $[M]^+$. found 483.1415.

(S)-2-(diphenylphosphanyl)-N-[1'-(S)-2'-trimethylsilyferrocenyl]-ethylbenzamide (LB8)

Following a similar procedure as **LB3, LB8** (0.52g, 92%), a yellow solid, m.p. 65.9-67.3°C; $[\alpha]^{20}_D$=+29.6° (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 1H), 7.40 – 7.33 (m, 2H), 7.31 (m, 8H), 7.22 (m, 3H), 6.89 (dd, *J* = 6.8, 4.0 Hz, 1H), 5.73 (d, *J* = 7.2 Hz, 1H), 5.01 (t, *J* = 6.8 Hz, 1H), 4.26 (t, *J* = 2.4 Hz, 1H), 4.22 (s, 1H), 4.11 (s, 5H), 4.05 (q, *J* =1.2 Hz, 1H), 1.44 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 137.2, 135.5, 134.7, 134.1, 134.0, 133.9, 133.8, 133.7, 133.5, 129.9, 129.5, 129.4, 128.9, 128.8, 128.7, 128.6, 128.5, 127.6, 74.8, 69.9, 69.1(5C), 58.5, 49.8, 46.1, 32.7, 30.9, 26.5, 25.0, 20.0; ^{31}P NMR (162 MHz, $CDCl_3$, 85 % H_3PO_4): δ -10.19; MS (ESI) m/z (%): 590.4 (100) $[M+H]^+$. HRMS (ESI) Calcd. for $C_{34}H_{36}FeNNaOPSi$ 612.1546 $[M+Na]^+$. found: 612.1517.

Representative procedure for the enantioselective [3+2] cycloaddition

21 chiral products were synthesized which contain 5 novel compounds (3h and 3s-3v).

A solution of methyl 2-(((*tert*-butoxycarbonyl)oxy)-(4-nitrophenyl)methyl)- acrylate **1a** (0.17g, 0.5 mmol) and *N*-Phenyl maleimide **2a** (0.17g, 1 mmol) and chiral ferrocenylphosphine **LB5** (27.9mg, 0.05 mmol) in toluene (5.0 mL) was stirred at room temperature for 48h. The solvent was removed under reduced pressure and the residue was purified by column chromatography to give **3a** (0.17 g, 88%) as a white solid.

(3a*S*, 4*R*, 6a*R*)-methyl 4-(4-nitrophenyl)-1,3-dioxo- 2-phenyl-1,2,3, 3a,4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (3a). White solid; m.p. :80.0-82.1°C; $[\alpha]^{20}_D$= -386.2° (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.8 Hz, 2H), 7.52 – 7.46 (m, 2H), 7.45 – 7.40 (m, 3H), 7.30 – 7.27 (m, 2H), 7.07 (dd, *J* = 2.4, 1.6 Hz, 1H),4.79-4.78 (m, 1H), 4.38-4.35 (m, 1H), 3.70 (s, 3H), 3.53 (dd, *J* = 7.6, 2.4 Hz, 1H); MS (ESI) m/z (%): 391.1 (100) $[M-H]^-$; Enantiomeric excess was determined by HPLC with a Chiral OD-RH column [λ=214 nm; eluent: acetonitrile/water = 60/40; flow rate: 0.5 mL/min; t_{major}=15.499 min, t_{minor}= 13.264 min; *ee*=97 %].

(3a*S*, 4*R*, 6a*R*)-ethyl 4-(4-nitrophenyl)-1,3-dioxo- 2-phenyl-1,2,3,3a, 4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (3b). White solid; m.p. :71.5-73.2°C; $[\alpha]^{20}_D$= -467.4° (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.4 Hz, 2H), 7.52 – 7.46 (m, 2H), 7.45 – 7.40 (m, 3H), 7.31 – 7.27 (m, 2H), 7.06 (dd, *J* = 2.8, 2.0 Hz, 1H), 4.78-4.77 (m, 1H), 4.38-4.35 (m, 1H), 4.20 – 4.04 (m, 2H), 3.53 (dd, *J* = 7.6, 2.0 Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 3H); MS (ESI) m/z (%): 405.1 (100) $[M-H]^-$; Enantiomeric excess was determined by HPLC with a Chiral OD-RH column [λ=214 nm; eluent: acetonitrile/water = 60/40; flow rate: 0.5 mL/min; t_{major}=17.556 min, t_{minor}= 14.869 min; *ee*=97 %

The (**3a*R*, 4*S*, 6a*S***)-**3b** was reported in literature [11,12] {lit[12] 96% *ee*, $[\alpha]^{20}_D$= +383.9° (c 1.0, $CHCl_3$), lit[11] 98% *ee*, $[\alpha]^{25}_D$= +210.3° (c 1.0, $CHCl_3$)}; The above obtained product **3b** had $[\alpha]^{20}_D$= -467.4° (c 1.0, $CHCl_3$), which was contrary to the reported ones. So the absolution configuration of compound **3b** was (**3a*S*, 4*R*, 6a*R***)

(3a*S*, 4*R*, 6a*R*)-butyl 4-(4-nitrophenyl)-1,3-dioxo- 2-phenyl-1,2,3,3a, 4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (3c). White solid; m.p. :47.4-49.0°C; $[\alpha]^{20}_D$= -220.8°(c 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.4 Hz, 2H), 7.52-7.48 (m, 2H), 7.46 – 7.39 (m, 3H), 7.32 – 7.26 (m, 2H), 7.07 (s, 1H), 4.77 (s, 1H), 4.38-4.36 (m, 1H), 4.16 – 3.99 (m, 2H), 3.53 (d, *J* = 7.6 Hz, 1H), 1.58 – 1.49 (m, 2H), 1.27-1.19 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H); MS (ESI) m/z (%): 433.1 (100) $[M-H]^-$; Enantiomeric excess was determined by HPLC with a Chiral OD-RH column [λ=214 nm; eluent: acetonitrile/water = 60/40; flow rate: 0.5 mL/min; t_{major}=26.321 min, t_{minor}=22.514 min; *ee*=96 %].

(3a*S*,4*R*,6a*R*)-methyl 4-(4-nitrophenyl)-2-methyl-1,3-dioxo-1,2,3, 3a,4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (3d). White solid; m.p. :165.7-167.1°C; $[\alpha]^{20}_D$= -313.6°(c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 6.98 (s, 1H), 4.65 (s, 1H), 4.24 – 4.18 (m, 1H), 3.66 (s, 3H), 3.35(dd, *J* = 7.6, 2.0 Hz, 1H), 3.03 (s, 3H); MS (ESI) m/z (%): 329.0 (100) $[M-H]^-$;

(3a*S*,4*R*,6a*R*)-methyl 2-benzyl-4-(4-nitrophenyl)-1,3-dioxo-1,2,3, 3a,4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (3e). white solid; m.p.: 58.9-60.0 °C; $[\alpha]^{20}_D$ =-239.6° (c 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.34 (m, 4H), 7.31 – 7.28 (m, 3H), 7.00 – 6.93 (m, 1H), 4.66 (d, 3.2 Hz, 3H), 4.22 – 4.19 (m, 1H), 3.66 (s, 3H), 3.34 (dd, *J* = 7.6, 2.4 Hz, 1H); MS (ESI) m/z (%): 405.1 (100) $[M-H]^-$; Enantiomeric excess was determined by HPLC with a Chiral OD-RH column [λ=214 nm; eluent: acetonitrile/water = 60/40; flow rate: 0.5 mL/min; t_{major} = 20.327 min, t_{minor} = 16.997 min; *ee* = 92%].

(3a*S*,4*R*,6a*R*)-methyl 2-(4-chlorophenyl)-4-(4-nitrophenyl)-1,3-dioxo-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (3f). white solid; m.p.: 98.6-100.2 °C; $[\alpha]^{20}_D$= -355.2° (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.4 Hz, 2H), 7.48 – 7.42(m, 5H), 7.28-7.27 (m, 1H), 7.07-7.06 (m, 1H), 4.78 (s, 1H), 4.40 – 4.36 (m, 1H), 3.70 (s, 3H), 3.54 (dd, *J* = 7.6, 2.0 Hz, 1H); MS (ESI) m/z (%): 425.0 (100) $[M-H]^-$; Enantiomeric excess was determined by HPLC with a Chiral OD-RH column [λ=214 nm; eluent: acetonitrile/water = 60/40; flow rate: 0.5 mL/min; t_{major} = 17.405 min, t_{minor} = 15.684 min; *ee* = 95%].

(3a*S*,4*R*,6a*R*)-methyl 2-(4-methoxyphenyl)-4-(4-nitrophenyl)-1,3-dioxo-1,2,3,3a,4,6a- hexahydrocyclopenta[c]pyrrole -5-carboxylate (3g). white solid; m.p.: 100.6-102.1 °C; $[\alpha]^{20}_{D}$= -355.2° (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.4 Hz, 2H), 7.42(d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 8.8 Hz, 2H), 7.06 (s, 1H), 6.99(d, *J* = 9.2 Hz, 2H), 4.77 (s, 1H), 4.35 (s, 1H), 3.84 (s, 3H), 3.69 (s, 3H), 3.51(dd, *J* = 5.6, 1.2 Hz, 1H); MS (ESI) m/z (%): 421.0 (100) $[M-H]^-$; Enantiomeric excess was determined by HPLC with a Chiral AD-RH column [λ=274 nm; eluent: acetonitrile/0.05mol/L KH_2PO_4 = 70/30(0-5min)-90/10(5-20min); flow rate: 0.6 mL/min; t_{major} = 13.868 min, t_{minor} = 5.740 min; *ee* = 97%].

(3a*S*, 4*R*, 6a*R*)-methyl 4-(3-nitrophenyl)-1,3-dioxo-2-phenyl-1,2,3, 3a,4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (3h). White solid; m.p. :125.1-126.5 °C; $[\alpha]^{20}_{D}$= -618.8° (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.04 (s, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.58 – 7.40 (m, 4H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.06 (s, 1H), 4.78 (s, 1H), 4.42-4.40 (m, 1H), 3.70 (s, 3H), 3.55 (d, *J* = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 173.5, 162.9, 148.7, 143.7, 140.5, 138.9, 133.7, 131.4, 130.1, 129.3, 129.0（2C）, 126.3（2C）, 122.7, 121.7, 53.3, 53.3, 52.6, 52.4. MS (ESI) m/z (%)：391.5 (100) $[M-H]^-$; HRMS (ESI) Calcd. for $C_{21}H_{16}N_2NaO_6$ 415.0901 $[M+Na]^+$, found: 415.0914; Enantiomeric excess was determined by HPLC with a Chiral OD-RH column [λ=214 nm; eluent: acetonitrile/water = 60/40; flow rate: 0.5 mL/min; t_{major}=11.948 min, t_{minor}= 9.879 min; *ee*=84 %].

(3a*S*,4*R*,6a*R*)-methyl 1,3-dioxo-2,4-diphenyl-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (3i). White solid; m.p.:144.0-145.7 °C; $[\alpha]^{20}_{D}$= -364.4° (c 0.9, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.43 – 7.34 (m, 3H), 7.29-7.27 (m, 3H), 7.25 – 7.23 (m, 2H), 6.99 (dd, *J* = 2.4, 1.2 Hz, 1H), 4.69 (brs, 1H), 4.33 – 4.30 (m, 1H), 3.68 (s, 3H), 3.55 (dd, *J* = 7.6, 2.0 Hz, 1H); MS (ESI) m/z (%)：348.0 (100) $[M+H]^+$; Enantiomeric excess was determined by HPLC with a Chiral OD-RH column [λ=214 nm; eluent: acetonitrile/water=65/35; flow rate: 0.5 mL/min; t_{major}= 10.449 min, t_{minor}= 7.962 min; *ee*= 99%]

(3a*S*,4*R*,6a*R*)-methyl 4-(4-fluorophenyl)-1,3-dioxo-2-phenyl-1,2,3, 3a,4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (3j). White solid; m.p.: 134.9-135.3 °C; $[\alpha]^{20}_{D}$= -787° (c 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 2H), 7.40 – 7.37 (m, 1H), 7.26 – 7.24 (m, 2H), 7.20-7.17 (m, 2H), 7.05-7.00 (m, 2H), 6.96 (q, *J* = 1.6 Hz, 1H), 4.65 (s, 1H), 4.31 – 4.28 (m, 1H), 3.67 (s, 3H), 3.49 (dd, *J* = 7.2, 2.0 Hz, 1H); MS (ESI) m/z (%): 366.0 (100) $[M+H]^+$; Enantiomeric excess was determined by HPLC with a Chiral OD-RH column [λ=214 nm; eluent: acetonitrile/water = 65/35; flow rate: 0.4 mL/min; t_{major}= 11.225 min, t_{minor}= 9.768 min; *ee*= 99 %].

(3a*S*,4*R*,6a*R*)-methyl 4-(4-chlorophenyl)-1,3-dioxo-2-phenyl-1,2,3, 3a,4,6a -hexahydrocyclopenta[c]pyrrole -5 carboxylate (3k). White solid; m.p.:171.6-173.2 °C; $[\alpha]^{20}_{D}$ = -608.9° (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.44 (m, 2H), 7.41 – 7.37 (m, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.97 (dd, *J* =2.4, 1.6 Hz, 1H), 4.64 (s, 1H), 4.31 – 4.28 (m, 1H), 3.67 (s, 3H), 3.48 (dd, *J* = 7.2, 2.0 Hz, 1H); MS (ESI) m/z (%): 380.1 (100) $[M-H]^-$; Enantiomeric excess was determined by HPLC with a Chiral OD-RH column [λ=214 nm; eluent: acetonitrile/water = 60/40; flow rate: 0.5 mL/min; t_{major}=16.723 min, t_{minor}= 13.630 min; *ee*＞ 99 %].

(**3a*S*,4*R*,6a*R*)-methyl 4-(2-chlorophenyl)-1,3-dioxo-2-phenyl-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (3l)**. White solid; m.p.: 167.9-169.2 °C; $[\alpha]^{20}_{D}$= -427.7° (c 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.36 (m, 4H), 7.28 (d, *J*=1.2 Hz, 2H), 7.24 – 7.19 (m, 3H), 7.05 – 7.04 (m, 1H), 5.13 (s, 1H), 4.29 – 4.26 (m, 1H), 3.66 (s, 3H), 3.56 – 3.53 (dd, *J*=7.2, 1.2 Hz, 1H); MS (ESI) m/z (%): 382.0 (100) $[M+H]^+$; Enantiomeric excess was determined by HPLC with a Chiral OD-RH column [λ=214 nm; eluent: acetonitrile/water = 60/40; flow rate: 0.5 mL/min; t_{major}= 14.237 min , t_{minor}= 11.274 min; *ee*= 98 %].

(3a*S*,*4R*,6a*R*)-methyl 4-(3-chlorophenyl)-1,3-dioxo-2-phenyl-1,2,3, 3a,4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (3m). White solid; m.p.: 49.9-51.1 °C; $[\alpha]^{20}_{D}$= -297.4° (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.43 – 7.39 (m, 1H), 7.32 – 7.25 (m, 4H), 7.20 (s, 1H), 7.16-7.14 (m, 1H), 7.02-7.01 (m, 1H), 4.66 (s, 1H), 4.34 – 4.31 (m, 1H), 3.70 (s, 3H), 3.51 (dd, *J* = 7.6, 2.0 Hz, 1H); MS (ESI) m/z (%): 380.0 (100) $[M-H]^-$; Enantiomeric excess was determined by HPLC with a Chiral OD-RH column [λ=214 nm; eluent: acetonitrile/water = 60/40; flow rate: 0.5 mL/min; t_{major}= 18.294 min, t_{minor}= 12.307 min; *ee*= 98 %].

(3a*S*,*4R*,6a*R*)-methyl 4-(4-bromophenyl)-1,3-dioxo-2-phenyl-1,2,3, 3a,4,6a-hexahydrocyclopenta[c]pyrrole-5carboxylate (3n). White solid; m.p.: 174.5-176.5 °C; $[\alpha]^{20}_{D}$= -336.9° (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.44 (t, *J* = 7.2 Hz, 4H), 7.24 (s, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.97 (s, 1H), 4.62 (s, 1H), 4.30 – 4.28 (m, 1H), 3.67 (s, 3H), 3.48 (d, *J* = 6.0 Hz, 1H); MS (ESI) m/z (%): 424.1(100) $[M-H]^-$; Enantiomeric excess was determined by HPLC with a Chiral OD-RH column [λ=214 nm; eluent: acetonitrile/water = 60/40; flow rate: 0.5 mL/min; t_{major}=19.117 min, t_{minor}=15.285 min; *ee*= 98 %].

(3a*S*,*4R*,6a*R*)-methyl 4-(*p*-tolyl) 1,3-dioxo-2-phenyl-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (3o). White solid; m.p.: 143.4-145.4 °C $[\alpha]^{20}_{D}$ = -372.7° (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.24 (d, *J* = 4.4 Hz, 2H), 7.11 (q, *J* = 8.0 Hz, 4H), 6.93 (m, 1H), 4.63 (s, 1H), 4.29 – 4.26 (m, 1H), 3.65 (s, 3H), 3.49 (dd, *J* = 7.2, 1.6 Hz, 1H), 2.33 (s, 3H); MS (ESI) m/z (%): 360.2 (100) $[M-H]^-$; Enantiomeric excess was determined by HPLC with a Chiral OD-RH column [λ=214 nm; eluent: acetonitrile/water = 60/40; flow rate: 0.5 mL/min; t_{major}= 13.535 min, t_{minor}= 12.233 min; *ee*= 96 %].

(3a*S*,*4R*,6a*R*)-methyl 4-(4-methoxyphenyl)-1,3-dioxo-2-phenyl-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (3p). White solid; m.p. :99.8-102.2 °C; $[\alpha]^{20}_{D}$= -405.8° (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.26 – 7.23 (m, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 6.92 – 6.91 (m, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.62 (s, 1H), 4.29 – 4.26 (m, 1H), 3.78 (s, 3H), 3.65 (s, 3H), 3.49 (dd, *J* = 7.6, 2.0 Hz, 1H); MS (ESI) m/z (%): 378.0 (100) $[M+H]^+$; Enantiomeric excess was determined by HPLC with a Chiral OD-RH column [λ=214 nm; eluent: acetonitrile/water = 60/40; flow rate: 0.5 mL/min; t_{major}= 12.056 min, *ee*＞ 99 %].

(3a*S*,*4R*,6a*R*)-methyl 4-(furan-2-yl)-1,3-dioxo-2-phenyl-1,2,3, 3a,4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (3q). White solid; 115.6-117.3 °C; $[\alpha]^{20}_{D}$= -387.5° (c 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H), 7.41 – 7.37 (m, 1H), 7.32 (d, *J* = 2.0 Hz, 1H), 7.26 – 7.24 (m, 2H), 6.91 (dd, *J* = 2.0, 1.6 Hz, 1H), 6.31 (dd, *J* = 3.2, 2.0 Hz, 1H), 6.21 (d, *J* = 3.2 Hz, 1H), 4.78 – 4.77 (m, 1H), 4.34 – 4.31 (m, 1H), 3.72 (s, 3H), 3.71 (d, *J* = 2.0 Hz, 1H); MS (ESI) m/z (%): 336.2 (100) $[M-H]^-$; Enantiomeric excess was determined by HPLC with a Chiral AD-RH column [λ=274 nm; eluent: acetonitrile

/ 0.05mol.L^{-1} KH_2PO_4= 70/30; flow rate: 0.6 mL/min; t_{major}= 5.855 min, t_{minor}= 4.143 min; *ee*= 98%].

(3a*S*,4*R*,6a*R*)-methyl 4-(naphthalen-1-yl)1,3-dixo-2-phenyl-1,2,3, 3a,4,6a–hexahydrocyclopenta[c]pyrrole-5-carboxylate (3r). White solid; m.p.: 168.9-170.2°C; $[\alpha]^{20}_D$= -327.0° (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.53 – 7.47 (m, 2H), 7.45 – 7.37 (m, 2H), 7.34 – 7.30 (m, 2H), 7.18 (dd, *J* = 2.0, 1.6 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 1H), 5.52 (s, 1H), 4.21 (d, *J* = 7.2 Hz, 1H), 3.69 (s, 3H), 3.54 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 174.0, 163.6, 139.3, 137.0, 134.3, 131.6, 131.0, 129.2(2C), 128.8(3C), 128.4, 126.9, 126.4(2C), 126.2, 125.2, 123.8, 122.4, 53.0, 52.7, 52.3, 49.1; MS (ESI) m/z (%)：398.3 (100) $[M+H]^+$; HRMS (ESI) Calcd. for $C_{25}H_{19}NNaO_4$ 420.1206 $[M+Na]^+$, found: 420.1217; Enantiomeric excess was determined by HPLC with a Chiral OD-RH column [λ=224 nm; eluent: acetonitrile/water=80/20; flow rate: 0.5 mL/min; t_{major}= 17.390 min, t_{minor}= 8.729 min; *ee*= 99%].

(3a*S*,4*R*,6a*R*)-methyl 4-(2-chloroquinolin-3-yl) 1,3-dioxo-2-phenyl-1,2,3,3a,4,6a–hexahydrocyclopenta[c]pyrrole-5-carboxylate (3s). White solid; m.p.: 96.1-98.0°C; $[\alpha]^{20}_D$= -531.8° (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.87 (s, 1H), 7.81 – 7.73 (m, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.19 (s, 1H), 5.20 (s, 1H), 4.35 (d, *J* = 4.0 Hz, 1H), 3.69 (s, 3H), 3.66 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 173.5, 162.9, 150.0, 147.0, 140.1, 139.5, 132.7, 131.5, 130.7, 129.2(2C), 128.9(2C), 128.3, 127.5(2C), 127.1, 126.3(2C), 53.3, 52.5, 51.9, 51.0; MS (ESI) m/z (%)：433.7 (100) $[M+H]^+$; HRMS (ESI) Calcd. for $C_{24}H_{18}ClN_2O_4$ 433.0950 $[M+H]^+$, found: 433.0942; Enantiomeric excess was determined by HPLC with a Chiral OD-RH column [λ=236 nm; eluent: acetonitrile/water=60/40; flow rate: 0.5 mL/min; t_{major}= 14.734 min, t_{minor}= 10.592 min; *ee*= 96%].

(3a*S*,4*R*,6a*R*)-methyl 4-(2-chlorobenzo[h]quinolin-3-yl)1,3-dioxo-2-phenyl-1,2,3,3a,4,6a–hexahydrocyclopenta[c]pyrrole-5-carboxylate (3t). White solid; m.p.: 183.4-185.0 °C; $[\alpha]^{20}_D$= -271.8° (c 1.0, $CHCl_3$); δ 9.20 (d, *J* = 7.6 Hz, 1H), 7.91 (d, *J* = 7.2 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.78 – 7.69 (m, 2H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.52-7.41 (m, 4H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.20 (s, 1H), 5.24 (s, 1H), 4.38 (s, 1H), 3.74 (s, 1H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 173.6, 163.0, 148.9, 145.7, 140.0, 139.6, 133.8, 133.1, 131.5, 130.2, 129.2(2C), 128.9(2C), 128.7, 127.8, 127.5, 126.4(2C), 126.2, 125.4, 124.7, 124.3, 53.4, 52.4, 51.9, 51.1; MS (ESI) m/z (%)：483.4 (100) $[M+H]^+$; HRMS (ESI) Calcd. for $C_{28}H_{19}ClN_2NaO_4$ 505.0926 $[M+Na]^+$, found: 505.0912; Enantiomeric excess was determined by HPLC with a Chiral OD-RH column [λ=236 nm; eluent: acetonitrile/water=65/35; flow rate: 0.5 mL/min; t_{major}= 29.965 min, t_{minor}= 18.806 min; *ee*= 97%].

(3a*S*,4*R*,6a*R*)-methyl 4-(4-methylthiazol-5-yl)1,3-dioxo-2-phenyl-1,2,3,3a,4,6a–hexahydrocyclopenta[c]pyrrole-5-carboxylate (3u). white solid; m.p.: 55.1-56.7°C; $[\alpha]^{20}_D$= -711.7° (c 0.35, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.39(t, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.92 (s, 1H), 4.98 (s, 1H), 4.33 (s, 1H), 3.70 (s, 3H), 3.52 (s, 1H); 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 173.5, 162.7, 149.9, 141.2, 137.9, 137.8, 132.5, 131.4, 129.2(2C), 128.9(2C), 126.3(2C), 53.1, 52.7, 52.4, 45.9, 15.4; MS (ESI) m/z (%)：369.7 (100) $[M+H]^+$; HRMS (ESI) Calcd. for $C_{19}H_{17}N_2O_4S$ 369.0904 $[M+H]^+$, found: 369.0913; Enantiomeric excess was determined by HPLC with a Chiral OD-RH column [λ=214 nm; eluent: acetonitrile/water=55/45; flow rate: 0.5 mL/min; t_{major}= 9.435 min, t_{minor}= 7.361 min; *ee*= 96%].

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