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Copper- and Silver-Catalyzed Diastereo- and Enantioselective Conjugate Addition Reaction of 1-Pyrroline Esters to Nitroalkenes: Diastereoselectivity Switch by Chiral Metal Complexes

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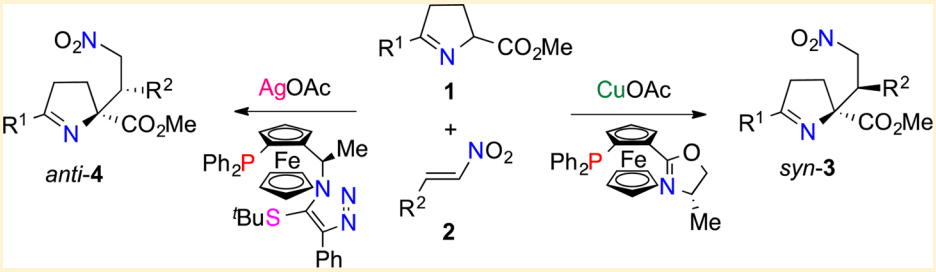
Supporting Information



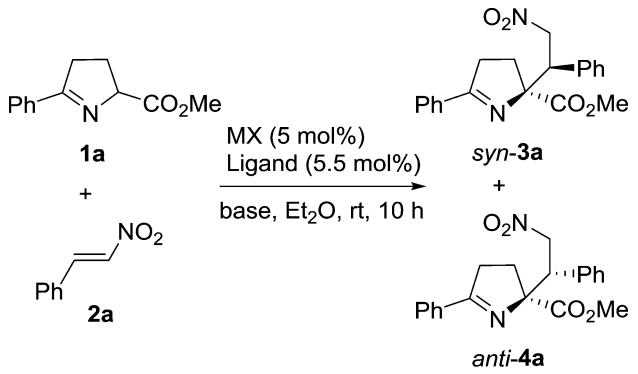
ABSTRACT: *syn*-Diastereoselective conjugate addition of 1-pyrroline esters to nitroalkenes in good yields with an excellent enantioselectivity by using CuOAc/Me-FcPHOX catalyst in the presence of pyridine. In contrast, AgOAc/*t*Bu-ThioClickFerrophos catalyzed the *anti* diastereoselective conjugate addition with a high enantioselectivity without additional base. Thus, the preparation of chiral 1-pyrroline derivatives bearing diverse stereochemistry could be achieved. The diastereoselective reduction of the imine group in the conjugate adduct could afford the 2,5-*cis*-proline ester derivative.

INTRODUCTION

Glycine imino esters are a good azomethine ylides source for the synthesis of α-amino acids derivatives in 1,3-dipolar cycloaddition and conjugate addition with electron-deficient alkenes.[1] Chiral copper and silver phosphine complexes have been proposed as representative catalysts for the reactions, and a good chiral catalyst often gives highly enantio pure α-amino acids.[2] The asymmetric reactions involving azomethine ylides can lead to a discovery of pharmaceutical and biologically active compounds.[3] We have developed ThioClickFerrophos (TCF) as a chiral phosphine ligand for the silver-catalyzed asymmetric reaction with azomethine ylides and shown its silver complex is efficient for the reaction to give α-amino acids in highly diastereo- and enantioselectivity.[4]

Recently, cyclic imino esters (cyclic azomethine ylides) have attracted attention,[5] as they can construct bicyclic amino acids in an one-step reaction with activated alkenes. Waldman and co-workers proposed the 2,3-dihydropyridine esters as a cyclic azomethine ylide, and they undergo the asymmetric 1,3-dipolar cycloaddition with nitroalkenes catalyzed by chiral copper complex to afford a chiral tropane scaffold, 8-azabicyclo[3.2.1]-octane.[6] We[7] and the Wang research group[8] independently have shown that 3,4-dihydro-2*H*-pyrrole esters (1-pyrroline ester) are a good precursor for the cyclic azomethine ylide source for the asymmetric 1,3-dipolar cycloaddition with N-substituted maleimide which affords a 7-azanorbornane (7-azabicyclo[2.2.1]heptane) scaffold in good enantioselectivities. The Wang group more recently reports the asymmetric conjugate addition with alkylidene malonates.[9] Inspired by our and other research groups' efforts, we have studied the silver- and copper-catalyzed reaction of 1-pyrroline ester **1a** with (*E*)-β-nitrostyrene **2a** and found that the exclusive conjugate addition proceeded to afford γ-nitropyrroline esters as a diastereomeric product (*syn*-**3a** or *anti*-**4a**) (Scheme 1). It is interesting that the diastereoselectivity (*syn*/*anti*-selectivity) is dependent on the chiral silver and copper phosphine complex catalyst, so stereodivergent synthesis of pyrroline derivatives should be allowed.[10] Since the γ-amino proline scaffold is found in the natural occurring compounds such as kaitocephalin

Scheme 1. Diastereo- and Enantioselective Conjugate Addition of 2-Pyrroline Ester to Nitroalkene



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(Figure 1), glutamate receptor competitive antagonist, this methodology could provide potential biologically active

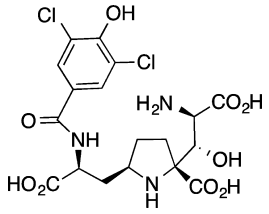

Figure 1. Kaitocephalin.

compounds which may lead to drug discovery.[11] In this paper, we would like report the stereodivergency of the silver- and copper-catalyzed conjugate addition of 1-pyrroline esters to nitroalkenes.

RESULTS AND DISCUSSION

Since such easily accessible chiral phosphine ligands as FcPHOX,[12] FeSulphos,[13] and ThioClickFerrophos[4] often exhibit good ligand ability, bringing good product yield and stereoselectivity (Figure 2), in the 1,3-dipolar cycloaddition of

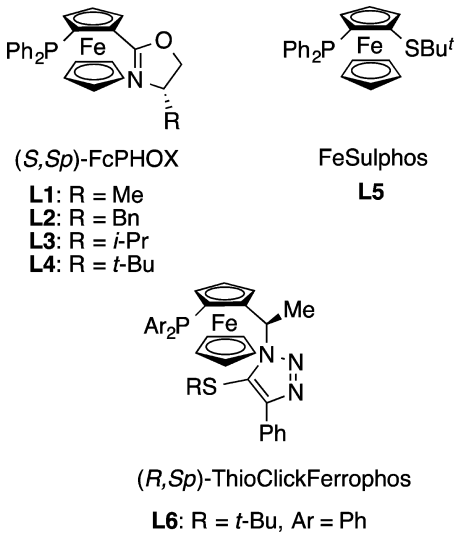

Figure 2. Chiral ferrocenyl phosphine ligands.

azomethine ylides, we first examined the reaction of 2-phenyl-1-pyrroline ester **1a** with (*E*)-*β*-nitrostyrene **2a** using copper and silver salts with the above ligand variations. The model reaction was usually carried out by using 5 mol % of metal salt and ligand in diethyl ether in the presence of 20 mol % of triethylamine at room temperature for 10 h. The results are summarized in Table 1.

The combination of $CuPF_6$ with (*S*,*Sp*)-**L1** gave a mixture of *syn* and *anti* isomer (**3a** and **4a**) of conjugate adduct in 39% in the ratio of *syn*/*anti* = 85/15 (entry 1); diastereomeric ratio was determined by ^{1}H NMR integration of the methyl ester signal. The *syn*/*anti* stereochemistry was defined by the relative configuration of the imino and the phenyl groups in the analogy to the reaction of acyclic glycine imino ester and confirmed by X-ray crystallography (described later). The enantiomeric excess (ee %) of the *syn*-**3a** was determined to be 98% ee by chiral HPLC analysis. **L2** and **L3** also gave the *syn* isomer preferentially in higher yields (47−49%) than that with **L1** but

Table 1. Reaction of 1a with 2a Using Various Copper and Silver Salts with Chiral Ligands[a]

entry	MX	ligand	yield (%)[b]	*syn*/*anti*[c]	ee (%)[d]
1	$Cu(MeCN)_4PF_6$	**L1**	39	85/15	98 (**3a**)
2	$Cu(MeCN)_4PF_6$	**L2**	47	85/15	86 (**3a**)
3	$Cu(MeCN)_4PF_6$	**L3**	49	87/13	80 (**3a**)
4	$Cu(MeCN)_4PF_6$	**L4**	17	84/16	80 (**3a**)
5	$Cu(MeCN)_4PF_6$	**L5**	16	21/79	68 (**4a**)
6	$Cu(MeCN)_4BF_4$	**L1**	60	87/13	98 (**3a**)
7	$Cu(MeCN)_4ClO_4$	**L1**	32	89/11	>99 (**3a**)
8	CuOAc	**L1**	61	89/11	>99 (**3a**)
9	AgOAc	**L1**	95	10/90	57 (**4a**)
10	AgOAc	**L2**	92	9/91	23 (**4a**)
11	AgOAc	**L3**	91	8/92	20 (**4a**)
12	AgOAc	**L4**	63	8/92	4 (**4a**)
13	AgOAc	**L6**	86	2/98	80 (**4a**)
14[e]	AgOAc	**L6**	99	1/99	94 (**4a**)

[a] **1a** (0.25 mmol), **2a** (0.3 mmol), Et_3N (20 mol %), metal salt (5 mol %), ligand (5.5 mol %); Et_2O (2.5 mL), rt, 10 h. [b] Combined isolated yield of **3a** and **4a**. [c] Determined by ^{1}H NMR. [d] Determined by chiral HPLC. [e] Reaction was carried out at −20 °C for 15 h.

in lower ee % (entries 2−3). The more sterically hindered **L4** gave very low yields with lower ee % (entry 4). On the other hand, the combination of **L5** gave the *anti*-**4a** preferentially in low yields with low enantioselectivity. We chose **L1** as the most suitable ligand with respect to enantioselectivity of *syn* isomer and then optimized a copper salt. The combination of **L1** with $Cu(MeCN)_4BF_4$, $Cu(MeCN)_4ClO_4$, and CuOAc was examined, and we found that the combination of CuOAc/**L1** improved the yield, *syn* diastereoselectivity, and enantioselectivity of the *syn* isomer; *syn*-**3a** was obtained more favorably (*syn*/*anti* = 89/11) in 61% total yield with 99% ee (entry 8). The conjugate adduct was the sole product, with no cycloadduct being formed by using every copper catalyst examined here.

It is interesting that when AgOAc was used instead of CuOAc with **L1**, diastereoselectivity was inverse, *anti*-**4a** being produced as a major product (*syn*/*anti* = 10/90) with moderate ee % (entry 9). No cycloadduct was again observed in the silver-catalyzed reaction similar to the copper-catalyzed reaction. The combination with **L2**−**L4** also afforded the *anti* isomer selectively but with low ee % (entries 10−12), although the yield of product was high. The use of **L6** afforded good yield of product, exclusive *anti* diastereoselectivity, and high enantioselectivity; the *anti*-**4a** was obtained in 96% de in 80% ee. The reaction at −20 °C improved *anti* diastereoselectivity and enantioselectivity up to 98% de and 94% ee, respectively (entry 14). Here, we can conclude that the CuOAc/**L1** complex gave the *syn*-**3a** selectively and that the AgOAc/**L6** gave *anti*-**4a** selectively. The divergence of the conjugate adduct of the 1-pyrroline ester with nitroalkene can be achieved by choosing a metal complex.

We next optimized the reaction conditions in copper and silver complex catalyzed reactions by varying solvents and bases, and the results are summarized in Table 2 (for copper) and Table 3 (for silver). In entries 1−7 of Table 2, the reaction was conducted in various solvents (THF; tetrahydrofuran, DOX; 1,4-dioxane, DME; dimethoxyenthane, toluene, dichloromethane) in the presence or absence of triethylamine, and diethyl ether was recognized as the most suitable solvent. The entries 8−14 show the results of the reaction in diethyl

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Table 2. Optimization of Solvents and Bases in Copper/L1-Catalyzed Reaction[a]

entry	solvent	base	yield (%)[b]	*syn*/*anti*[c]	ee (%) (**3a**)[d]
1	Et_2O	–	76	89/11	>99
2	Et_2O	Et_3N	61	89/11	>99
3	THF	Et_3N	59	89/11	>99
4	DOX	Et_3N	58	75/25	>99
5	DME	Et_3N	53	82/18	>99
6	toluene	Et_3N	57	90/10	>99
7	CH_2Cl_2	Et_3N	51	84/16	97
8	Et_2O	pyridine	78	92/8	99
9	Et_2O	DABCO	74	89/11	>99
10	Et_2O	DIPEA	63	89/11	>99
11	Et_2O	DBU	54	76/24	>99
12	Et_2O	NaOAc	70	91/9	>99
13	Et_2O	K_2CO_3	63	89/11	>99
14	Et_2O	Cs_2CO_3	57	90/10	>99

[a]**1a** (0.25 mmol), **2a** (0.3 mmol), base (20 mol %), CuOAc (5 mol %), **L1** (5.5 mol %); solvent (2.5 mL), rt, 10 h. [b]Combined isolated yield of *syn*-**3a** and *anti*-**4a**. [c]Determined by ^{1}H NMR. [d]Determined by chiral HPLC.

Table 3. Optimization of Solvents and Bases in Silver-/L6-Catalyzed Reaction[a]

entry	solvent	base	yield (%)[b]	*syn*/*anti*[c]	ee (%) (**4a**)[d]
1	Et_2O	–	92	1/99	94
2	Et_2O	Et_3N	99	1/99	95
3	Et_2O	DIPEA	92	2/98	95
4	THF	Et_3N	96	3/97	90
5	DME	Et_3N	99	2/98	89
6	toluene	Et_3N	78	3/97	79
7	CH_2Cl_2	Et_3N	80	7/93	81

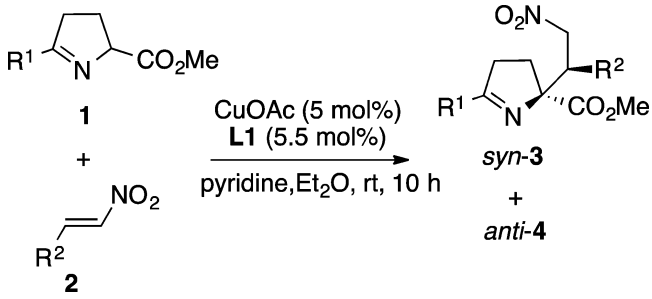
[a]**1a** (0.25 mmol), **2a** (0.3 mmol), base (20 mol %), AgOAc (5 mol %), **L6** (5.5 mol %); solvent (2.5 mL), −20 °C, 15 h. [b]Combined isolated yield of *syn*-**3a** and *anti*-**4a**. [c]Determined by ^{1}H NMR. [d]Determined by chiral HPLC.

ether using various organic and inorganic bases; the addition of pyridine gave the best yield, *syn*/*anti* ratio, and ee % of the *anti* isomer.

In entries 1−7 of Table 3, the reaction was performed in various solvents in the presence or absence of triethylamine at −20 °C for 15 h, and diethyl ether was recognized as the most suitable solvent with respect to diastereo- and enantioselectivity (*anti*/*syn* = 1/99, 92% ee). Diisopropylethyl amine (DIPEA) slightly improved the ee %. It should be worth noting that the reaction can be carried out without additional base and that high *anti*-selectivity and enantioselectivity of *anti*-**4a** were observed. So we determined that base was not always necessary for the optimal reaction conditions and that base could be added occasionally if yield and selectivity should be improved.

We then examined the scope of substrate in both CuOAc/**L1**- and AgOAc/**L6**-catalyzed reactions under the corresponding optimal reaction conditions: We usually carried out the reaction in diethyl ether at room temperature for 10 h in the presence of pyridine (although *anti*-**4a** was obtained in a good yield with high ee % without additional base). Table 4, entries 1−5, shows the results of the copper-catalyzed reaction with some aryl-substituted pyrroline esters **1**. The reaction proceeded smoothly to afford the *syn* conjugate adduct **3a**−**3d** in good yields with good diastereo- and enantioselectivities. The electron-donating and -withdrawing substituents had

Table 4. Scope of Substrate in the *syn* Selective Copper-Catalyzed Reaction[a]



entry	R^1	R^2	yield (%)[b]	*syn*/*anti*[c]	ee %(**3**)[d]
1	Ph	Ph	78, **3a**	92/8	99
2	*p*-MeC_6H_4	Ph	83, **3b**	74/26	>99
3	*p*-$MeOC_6H_4$	Ph	69, **3c**	86/14	>99
4	*p*-ClC_6H_4	Ph	73, **3d**	72/28	99
5	*p*-BrC_6H_4	Ph	75, **3e**	79/21	98
6	Ph	*o*-MeC_6H_4	84, **3f**	81/19	>99
7	Ph	*m*-MeC_6H_4	79, **3g**	85/15	>99
8	Ph	*p*-MeC_6H_4	85, **3h**	89/11	>99
9	Ph	*p*-$MeOC_6H_4$	86, **3i**	81/19	>99
10	Ph	*p*-ClC_6H_4	73, **3j**	88/12	99
11	Ph	*p*-BrC_6H_4	76, **3k**	86/14	94
12	Ph	*p*-$NO_2C_6H_4$	69, **3l**	76/24	ND
13	Ph	2-thienyl	80, **3m**	91/9	>99
14	Ph	Fc	70, **3n**	83/17	>99

[a]**1** (0.25 mmol), **2a** (0.3 mmol), pyridiene (20 mol %), CuOAc (5 mol %), **L1** (5.5 mol %); Et_2O (2.5 mL), rt, 10 h. [b]Combined isolated yield of *syn*-**3a** and *anti*-**4a**. [c]Determined by ^{1}H NMR. [d]Determined by chiral HPLC.

limited impact on the reaction, *syn* isomers being produced as a major isomer in excellent enantioselectivities. In entries 6−14, the results of the reaction with various aryl-substituted nitroalkenes are shown. Reactions of pyrroline ester **1a** with various (*E*)-2-aryl-1-nitroalkenes, with *o*-, *m*- or *p*-substituents on the phenyl ring, proceeded with *syn*-selectivities of 72/28−89/11 and excellent enantioselectivites (94−99% ee) regardless of the electronic property and positions of substituents. The ee % of *p*-nitro-substituted **3l** was determined because an appropriate chiral column could not be found (entry 14). The heteroaryl substituent such as 2-thienyl can be used as a substrate giving good yield of the *syn* isomer with high ee %. Here, we were successful in obtaining a single crystal suitable for X-ray analysis in the ferrocenyl-substituted substrate *syn*-**3n** (see the Supporting Information (SI)) and clearly determined the relative and absolute configurations as (2*S*, 1′*S*) [if the substituent was phenyl, the absolute configuration should be (2*S*, 1′*R*)].

In Table 5 entries 1−5 and 6−14, the scope of substrates in the AgOAc/**L6**-catalyzed reaction with respect to 1-pyrroline esters and nitroalkenes is summarized, respectively. It is worth noting that the reaction can be carried out −20 °C in diethyl ether without additional base and that high *anti*-selectivity and enantioselectivity of *anti*-**4a** were observed. The reaction could be carried out without additional base, but triethylamine was added in the reaction with *p*-bromo-substituted 1-pyrroline ester in order to improve the yield and selectivity. As shown in the table, a wide range of 1-pyrroline esters and nitroalkenes can be employed as substrates, such as either electron-withdrawing or -donating substituents, even heteroaryl

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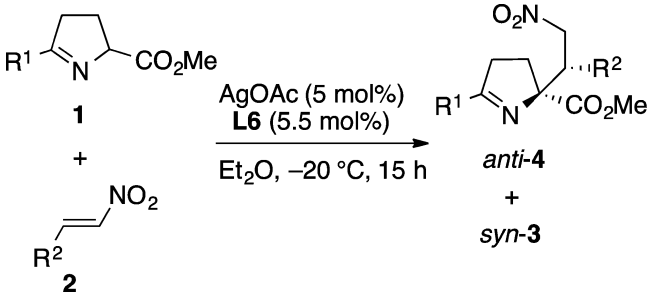
Table 5. Scope of Substrate in the *anti* Selective Silver-Catalyzed Reaction[a]



entry	R^1	R^2	yield (%)[b]	*syn*/*anti*[c]	ee % (**4**)[d]
1	Ph	Ph	92, **4a**	1/99	94
2	*p*-MeC_6H_4	Ph	94, **4b**	3/97	94
3[e]	*p*-$MeOC_6H_4$	Ph	86, **4c**	5/95	86
4	*p*-ClC_6H_4	Ph	90, **4d**	3/97	90
5[f]	*p*-BrC_6H_4	Ph	98, **4e**	1/99	92
6	Ph	*o*-MeC_6H_4	84, **4f**	3/97	94
7	Ph	*m*-Me C_6H_4	92, **4g**	1/99	92
8	Ph	*p*-MeC_6H_4	86, **4h**	1/99	91
9	Ph	*p*-$MeOC_6H_4$	88, **4i**	1/99	93
10	Ph	*p*-ClC_6H_4	90, **4j**	1/99	91
11[e]	Ph	*p*-BrC_6H_4	84, **4k**	1/99	93
12[e]	Ph	*p*-$NO_2C_6H_4$	54, **4l**	1/99	98
13	Ph	2-thienyl	95, **4m**	1/99	95
14[e]	Ph	Fc	82, **4n**	11/89	83

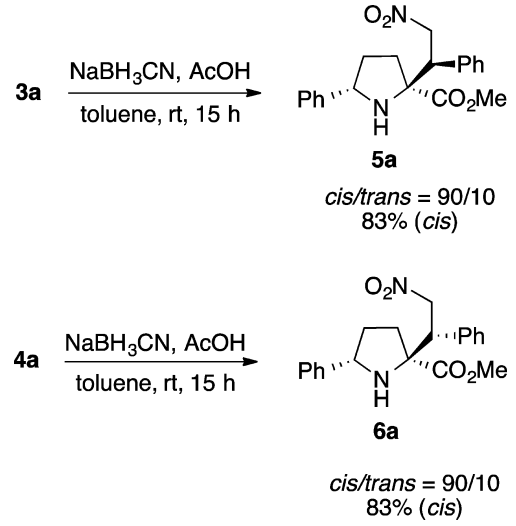
[a]**1** (0.25 mmol), **2a** (0.3 mmol), AgOAc (5 mol %), **L6** (5.5 mol %); Et_2O (2.5 mL), − 20 °C, 15 h. [b]Combined isolated yield of *syn*-**3a** and *anti*-**4a**. [c]Determined by ^1H NMR. [d]Determined by chiral HPLC. [e]THF was used as a solvent. [f]Triethylamine (20 mol %) was added.

substrate, as well as the copper-catalyzed reaction; the reaction proceeded at −20 °C to produce the *anti* conjugate adduct **4a**−**4n** predominantly with high enantioselectivities. The *p*-NO_2 substituent may be an exception giving a low yield of *anti* conjugate adduct but with high ee %. We were able to clearly determine the relative and absolute configurations of the ferrocenyl-substituted conjugate adduct **4n** as (2*S*, 1′*R*) [if the substituent was phenyl, then the absolute configuration should be (2*S*, 1′*S*)]. It must be noted that no cycloadducts were observed for every substrate examined here in either silver or copper-catalyzed reactions.

Reductions of the imine group of **3a** and **4a** were investigated. Treatment of **3a** and **4a** with $NaBH_3CN$ in toluene in the presence of acetic acid at room temperature afforded the corresponding proline ester quantitatively; the *cis* isomer (2*S*,5*S*,1′*R*)-**5a** and (2*S*,5*S*,1′*S*)-**6a**, were produced, respectively, as a major product in 83% yield (*cis*/*trans* = 90/10) was the nitro group (Scheme 2).[14] The relative configuration of **5a** and **6a** could be assigned by NOESY spectroscopic analysis (see SI).

To shed light on the reaction mechanism, the Gibbs free energy (298 K, 1 atm) of two possible intermediates for the Cu-catalyzed reaction (Figure 3a, **A** and **B**) was calculated by DFT at B97-D3(bj)/def2-TZVPP//B97-D3(bj)/def2-SVP level.[15] The optimized structures showed distorted tetrahedral geometries about the copper center. The structure of **A** was 3.8 kcal/mol more stable than that of **B**. The result was consistent with the calculation by Hou and co-workers for the copper complex with the corresponding acyclic imino ester.[10i] According to Hou's conclusion, the negatively charged C3

Scheme 2. Reduction of the Imine Group in 3a and 4a by $NaBH_3CN$



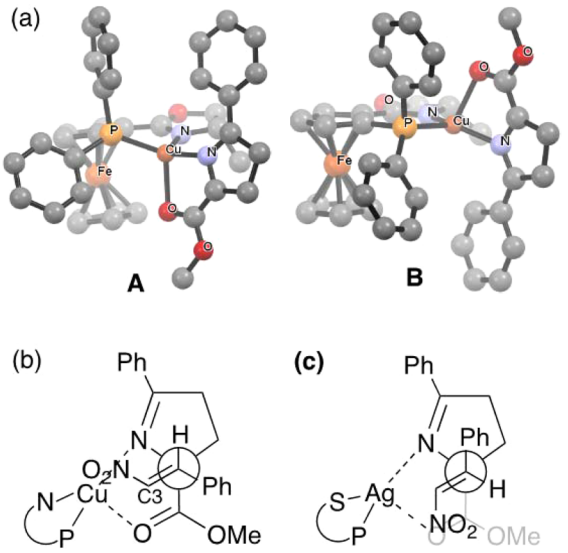


Figure 3. (a) Possible intermediate Cu complexes optimized by DFT calculation at B97-D3(bj)/def2-SVP level. All hydrogen atoms are omitted for clarity. (b) Transition structure model of CuOAc/**L1**-catalyzed conjugate addition. (c) Transition structure model of AgOAc/**L6**-catalyzed conjugate addition.

atom should direct toward the copper in the transition structure. Thus, nitroalkene should approach the *si* face of the pyrroline ester from its *re* face, avoiding the sterically hindered oxazolyl moiety in **L1**. These requirements and *syn*-selectivity suggest the transition structure for the CuOAc/**L1**-catalyzed conjugate addition of 1-pyrroline esters, as shown in Figure 3b depicted by Newman projection. On the other hand, our attempt to optimize the intermediate in the silver-catalyzed reaction was unsuccessful. The *anti*-selective conjugate addition catalyzed by AgOAc/**L6** may proceed through the transition structure in Figure 3c.

■ CONCLUSIONS

We have succeeded in a stereodivergent asymmetric conjugate addition of 1-pyrroline esters to nitroalkenes, where *syn* and *anti* adducts can be prepared selectively by using copper and

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silver catalysts, respectively. CuOAc/**L1** catalyzed a *syn*-selective conjugate addition with an excellent enantioselectivity in the presence of pyridine, while AgOAc/**L6** afforded the *anti* adduct exclusively with a high enantioselectivity without additional base. The conversion of the β-nitropyrrlines to β-aminopyrrolidines is now in progress, and new aspects will be reported in due course.

EXPERIMENTAL SECTION

General Procedure for the Copper-Catalyzed Asymmetric Conjugate Addition of 1 to 2. All reactions were carried out under nitrogen atmosphere with oven-dried glassware. In a 20 mL Schlenk tube containing a stirring bar, CuOAc (1.5 mg, 0.013 mmol) and **L1** (6.2 mg, 0.014 mmol) were dissolved in dry Et_2O (2.5 mL) and stirred at room temperature for 30 min. Then, **1a** (50.8 mg, 0.25 mmol) and **2a** (44.7 mg, 0.30 mmol) were added. The resulting mixture was stirred at the same temperature for 10 h and then filtered through Celite and concentrated in vacuo. The residue was isolated by PTLC (*n*-hexane/EtOAc = 2:1).

(S)-Methyl 2-((R)-2-Nitro-1-phenylethyl)-5-phenyl-3,4-dihydro-2H-pyrrole-2-carboxylate ***3a***. White solid; 68.7 mg, 78% yield; mp 91−92 °C; IR (KBr, cm^{-1}) ν 3030, 2955, 1730, 1604, 1575, 1543, 1496, 1449, 1432, 1378, 1241, 1167, 1091; ^1H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, J = 6.5 Hz, 2H), 7.50−7.18 (m, 8H), 5.23 (dd, J = 4.2, 13.2 Hz, 1H), 5.08 (dd, J = 10.3, 13.2 Hz, 1H), 3.90 (dd, J = 4.2, 10.3 Hz, 1H), 3.63 (s, 3H), 2.95−3.12 (m, 2H), 2.48−2.55 (m, 1H), 2.14−2.06 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.6, 172.5, 136.3, 133.5, 131.5, 129.8, 128.7, 128.6, 128.5, 128.3, 128.2, 85.7, 77.5, 52.5, 52.4, 35.5, 31.4; HPLC: Daicel Chiralpak ID-3 column (hexane/2-propanol = 98/2, 1.0 mL/min, 250 nm); t_R = 28.4 (major), t_R = 33.5 min (minor); $[\alpha]_D^{27}$ = −49.0 (c = 0.11, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{20}H_{21}N_2O_4$ $[M + H]^+$ 353.1501, found: 353.1504.

(S)-Methyl 5-(4-Methylphenyl)-2-((R)-2-nitro-1-phenylethyl)-3,4-dihydro-2H-pyrrole-2-carboxylate ***3b***. Yellow oil; 76.4 mg, 83% yield; IR (KBr, cm^{-1}) ν 3032, 2952, 2918, 1737, 1614, 1557, 1548, 1495, 1455, 1431, 1378, 1247, 1165, 1044; ^1H NMR (300 MHz, $CDCl_3$) δ 7.73−7.70 (d, J = 8.2 Hz, 2H), 7.25−7.22 (d, J = 3.5 Hz, 2H), 7.19−7.16 (m, 5H), 5.22 (dd, J = 4.1, 13.5, 1H), 5.07 (dd, J = 10.5, 13.5 Hz, 1H), 3.88 (dd, J = 4.1, 10.5 Hz, 1H), 3.66 (s, 3H), 3.05−2.97 (m, 2H), 2.54−2.47 (m, 1H), 2.45 (s, 3H), 2.13−2.05 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.5, 174.2, 141.8, 135.3, 130.8, 129.8, 129.3, 128.4, 128.2, 128.0, 85.7, 77.5, 52.4, 52.5, 35.4, 31.5, 21.7; HPLC: Daicel Chiralpak ID-3 column (hexane/2-propanol = 98/2, 1.0 mL/min, 250 nm); t_R = 31.8 (major), t_R = 37.7 min (minor); $[\alpha]_D^{28.2}$ = −34.2 (c = 0.16, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{21}H_{22}NaN_2O_4$ $[M + Na]^+$ 389.1477, found: 389.1473.

(S)-Methyl 5-(4-Methoxylphenyl)-2-((R)-2-nitro-1-phenylethyl)-3,4-dihydro 2H-pyrrole-2-carboxylate ***3c***. Yellow oil; 66.0 mg, 69% yield; IR (KBr, cm^{-1}) ν 2952, 2838, 1736, 1605, 1551, 1514, 1459, 1378, 1253, 1173, 1112, 1031; ^1H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, J = 9.1 Hz, 2H), 7.38−7.25 (m, 5H), 6.92 (d, J = 8.5 Hz, 2H), 5.23 (dd, J = 4.1, 13.5 Hz, 1H), 5.07 (dd, J = 10.3, 13.5 Hz, 1H), 3.87 (dd, J = 4.1, 10.6 Hz, 1H), 3.84 (s, 3H), 3.62 (s, 3H), 3.10−2.90 (m, 1H), 2.54−2.45 (m, 1H), 2.13−2.02 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.2, 172.7, 162.2, 136.4, 130.0, 129.1, 128.7, 128.2, 126.3, 113.9, 85.6, 77.6, 55.5, 52.5, 52.4, 35.4, 31.4. HPLC: Daicel Chiralpak ID-3 (hexane/2-propanol = 95/5, 1.0 mL/min, 250 nm); t_R = 38.9 (major), t_R = 41.8 min (minor); $[\alpha]_D^{28}$ = −64.1 (c = 0.10, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{21}H_{22}N_2NaO_5$ $[M + Na]^+$ 405.1426, found: 405.1440.

(S)-Methyl 5-(4-Chlorophenyl)-2-((R)-2-nitro-1-phenylethyl)-3,4-dihydro-2H-pyrrole2-carboxylate ***3d***. Yellow oil; 70.6 mg, 73% yield; IR (KBr, cm^{-1}) ν 2951, 2858, 1735, 1617, 1598, 1552, 1492, 1378, 1227, 1173, 1091, 1011; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, J = 8.5 Hz, 2H), 7.41−7.26 (m, 7H), 5.25 (dd, J = 4.3, 13.4 Hz, 1H), 5.05 (dd, J = 10.2, 13.4 Hz, 1H), 3.89 (dd, J = 4.3, 10.2 Hz, 1H), 3.64 (s, 3H), 3.10−2.89 (m, 2H), 2.57−2.48 (m, 1H), 2.15−2.04 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.0, 172.3, 137.7, 136.2, 132.0, 129.6, 129.1, 128.9, 128.8, 128.3, 85.9, 77.4, 52.6, 52.3, 35.5, 31.4; HPLC: Daicel Chiralpak ID-3 column (hexane/2-propanol = 95/5, 1.0 mL/min, 250 nm); t_R = 21.3 (minor), t_R = 22.3 min (major); $[\alpha]_D^{28}$ = −57.90 (c = 0.27, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{20}H_{20}ClN_2O_4$ $[M + H]^+$ 387.1112, found: 387.1107.

(S)-Methyl 5-(4-Bromophenyl)-2-((R)-2-nitro-1-phenylethyl)-3,4-dihydro-2H-pyrrole-2-carboxylate ***3e***. Yellow oil; 80.9 mg, 75% yield; IR (KBr, cm^{-1}) ν 2952, 2859, 1735, 1616, 1591, 1552, 1488, 1457, 1378, 1222, 1070, 1008; ^1H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.23−7.14 (m, 5H), 5.23 (dd, J = 4.1, 13.2 Hz, 1H), 5.05 (dd, J = 10.2, 13.2 Hz, 1H), 3.89 (dd, J = 4.1, 10.2 Hz, 1H), 3.64 (s, 3H), 3.08−2.90 (m, 1H), 2.57−2.48 (m, 1H), 2.16−2.07 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 172.1, 136.0, 132.2, 131.8, 129.7, 129.0, 128.6, 128.2, 126.1, 85.7, 77.3, 52.5, 52.2, 35.3, 31.2; HPLC: Daicel Chiralpak ID-3 column (hexane/2-propanol = 95/5, 1.0 mL/min, 250 nm); t_R = 23.3 (minor), t_R = 24.7 min (major); $[\alpha]_D^{24}$ = −34.2 (c = 0.16, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{20}H_{19}BrN_2NaO_4$ $[M + Na]^+$ 453.0426, found: 453.0426.

(S)-Methyl 2-((R)-1-(2-Methylphenyl)-2-nitroethyl)-5-phenyl-3,4-dihydro-2H-pyrrole-2-carboxylate ***3f***. Yellow oil; 76.9 mg, 84% yield; IR (KBr, cm^{-1}) ν 3070, 3025, 2953, 2918, 1732, 1617, 1552, 1493, 1448, 1378, 1242, 1164, 1121, 1073; ^1H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, J = 7.6 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.50−7.41 (m, 3H), 7.22−7.13 (m, 3H), 5.03 (dd, J = 4.1 Hz, J = 13.1 Hz, 1H), 4.92 (dd, J = 10.1, 13.1 Hz, 1H), 4.34 (dd, J = 4.1, 10.1 Hz, 1H), 3.58 (s, 3H), 3.10−2.93 (m, 2H), 2.59−2.52 (m, 1H), 2.43 (s, 3H), 2.13−2.06 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.9, 172.9, 137.8, 135.4, 133.5, 131.5, 130.9, 128.6, 128.3, 127.8, 127.1, 126.6, 86.1, 77.9, 52.5, 46.2, 35.2, 31.2, 20.1. HPLC: Daicel Chiralpak ID-3 (hexane/2-propanol = 95/5, 1.0 mL/min, 250 nm); t_R = 14.8 (major), t_R = 17.4 min (minor); $[\alpha]_D^{29}$ = −4.9 (c = 0.13, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{21}H_{22}N_2NaO_4$ $[M + Na]^+$ 389.1477, found: 389.1489.

(S)-Methyl 2-((R)-1-(3-Methylphenyl)-2-nitroethyl)-5-phenyl-3,4-dihydro-2H-pyrrole-2-carboxylate ***3g***. Yellow oil; 72.4 mg, 79% yield; IR (KBr, cm^{-1}) ν 3034, 2952, 2920, 1733, 1655, 1609, 1551, 1492, 1449, 1433, 1378, 1218, 1162, 1077, 1011; ^1H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, J = 7.0 Hz, 2H), 7.49−7.39 (m, 3H), 7.22−7.06 (m, 4H), 7.22−7.13 (m, 3H), 5.27 (dd, J = 4.1 Hz, 13.5 Hz, 1H), 5.09 (dd, J = 10.3, 13.5 Hz, 1H), 3.85 (dd, J = 4.1, 10.3 Hz, 1H), 3.65 (s, 3H), 3.13−2.90 (m, 2H), 2.55−2.46 (m, 1H), 2.30 (s, 3H), 2.13−2.03 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.0, 172.4, 138.2, 136.0, 133.5, 131.5, 130.1, 129.0, 128.7, 128.6, 128.3, 125.8, 85.7, 77.4, 52.5, 52.3, 35.5, 31.1, 21.5. HPLC: Daicel Chiralpak ID-3 (hexane/2-propanol = 95/5, 1.0 mL/min, 250 nm); t_R = 16.8 (major), t_R = 21.2 min (minor); $[\alpha]_D^{28}$ = −66.2 (c = 0.16, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{21}H_{23}N_2O_4$ $[M + H]^+$ 367.1658, found: 367.1643.

(S)-Methyl 2-((R)-1-(4-Methylphenyl)-2-nitroethyl)-5-phenyl-3,4-dihydro-2H-pyrrole2-carboxylate ***3h***. Yellow oil; 77.9 mg, 85% yield; IR (KBr, cm^{-1}) ν 3030, 2952, 2922, 1735, 1617, 1551, 1514, 1498, 1449, 1378, 1234, 1164, 1079; ^1H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, J = 7.9 Hz, 2H), 7.51−7.40 (m, 3H), 7.25−7.10(m, 4H), 5.24 (dd, J = 3.8, 13.5 Hz, 1H), 5.07 (dd, J = 10.6, 13.5 Hz, 1H), 3.83 (dd, J = 3.8, 10.5 Hz, 1H), 3.65 (s, 3H), 3.12−3.95 (m, 1H), 2.56−2.47 (m, 1H), 2.31 (s, 3H), 2.14−2.04 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.0, 172.5, 138.0, 133.6, 133.1, 131.5, 129.5, 129.0, 128.7, 128.3, 85.9, 77.7, 52.6, 52.2, 35.6, 31.3, 21.2. HPLC: Daicel Chiralpak ID-3 (hexane/2-propanol = 95/5, 1.0 mL/min, 250 nm); t_R = 19.4 (major), t_R = 24.6 min (minor); $[\alpha]_D^{28}$ = +64.7 (c = 0.06, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{21}H_{22}N_2NaO_4$ $[M + Na]^+$ 389.1477, found: 389.1479.

(S)-Methyl 2-((R)-1-(4-Methoxyphenyl)-2-nitroethyl)-5-phenyl-3,4-dihydro2H-pyrrole-2-carboxylate ***3i***. Yellow oil; 82.2 mg, 86% yield; IR (KBr, cm^{-1}) ν 2922, 2834, 1737, 1619, 1549, 1511, 1446, 1379, 1345, 1249, 1179, 1118; ^1H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, J = 6.5 Hz, 2H), 7.50−7.40 (m, 3H), 7.29 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 9.1 Hz, 2H), 5.17 (dd, J = 4.4, 13.2 Hz, 1H), 5.02 (dd, J = 10.5, 13.2 Hz, 1H), 3.85 (dd, J = 4.1, 10.5 Hz, 1H), 3.76 (s, 3H), 3.63 (s, 3H), 3.14−2.95 (m, 2H), 2.56−2.47 (m, 1H), 2.14−2.03 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.0, 172.6, 159.4, 133.5, 131.5, 130.3, 128.6, 128.3, 128.1, 114.1, 85.9, 77.7, 55.3, 52.5, 51.8, 35.5, 31.3. HPLC: Daicel Chiralpak ID-3 (hexane/2-propanol = 95/5, 1.0 mL/

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min, 250 nm); t_R = 32.9 (major), t_R = 41.0 min (minor); $[\alpha]_D^{28}$ = +30.09 (c = 0.10, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{21}H_{22}NaN_2O_5$ $[M + Na]^+$ 405.1426, found: 405.1426.

(S)-Methyl 2-((R)-1-(4-Chlorophenyl)-2-nitroethyl)-5-phenyl-3,4-dihydro-2H-pyrrole2-carboxylate ***3j***. Yellow oil; 70.6 mg, 73% yield; IR (KBr, cm^{-1}) ν 3031, 2952, 1740, 1618, 1576, 1547, 1493, 1428, 1376, 1236, 1162, 1114, 1092, 1044, 1017; ^1H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, J = 6.7 Hz, 2H), 7.50−7z.28 (m, 7H), 7.38−7.27 (dd, J = 6.7 Hz, 4H), 5.12 (dd, J = 4.1, 13.5 Hz, 1H), 4.98 (dd, J = 10.5, 13.5 Hz, 1H), 3.92 (dd, J = 4.1, 10.5 Hz, 1H), 3.61 (s, 3H), 3.13−3.03 (m, 2H), 2.57−2.47 (m, 1H), 2.12−2.02 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.4, 172.4, 135.0, 134.2, 133.4, 131.7, 130.6, 128.9, 128.7, 128.3, 85.5, 77.3, 52.6, 51.6, 35.5, 31.6. HPLC: Daicel Chiralpak ID-3 (hexane/2-propanol =98/2, 1.0 mL/min, 250 nm); t_R = 28.2 (major), t_R = 30.5 min (minor); $[\alpha]_D^{28}$ = −23.6 (c = 0.14, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{20}H_{19}ClNaN_2O_4$ $[M + Na]^+$ 409.0931, found: 409.0939.

(S)-Methyl 2-((R)-1-(4-Bromophenyl)-2-nitroethyl)-5-phenyl-3,4-dihydro-2H-pyrrole2-carboxylate ***3k***. Yellow oil; 81.9 mg, 76% yield; IR (KBr, cm^{-1}) ν 3030, 2952, 1734, 1656, 1615, 1551, 1490, 1448, 1433, 1378, 1240, 1164, 1112, 1074, 1011; ^1H NMR (300 MHz, $CDCl_3$) δ 7.90−7.87 (m, 2H), 7.53−7.41 (m, 5H), 7.33−7.29 (m, 2H), 5.12 (dd, J = 4.1, 13.4 Hz, 1H), 4.98 (dd, J = 10.5, 13.4 Hz, 1H), 3.90 (dd, J = 4.1, 10.5 Hz, 1H), 3.61 (s, 3H), 3.14−3.03 (m, 2H), 2.57−2.47 (m, 1H), 2.13−2.02 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.4, 172.4, 135.6, 133.4, 131.9, 131.7, 131.0, 128.7, 128.4, 122.5, 85.5, 77.3, 52.7, 51.8, 35.6, 31.7. HPLC: Daicel Chiralpak ID-3 (hexane/2-propanol = 98/2, 1.0 mL/min, 250 nm); t_R = 30.1 (major), t_R = 32.9 min (minor); $[\alpha]_D^{28}$ = −42.69 (c = 0.18, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{20}H_{20}BrN_2O_4$ $[M + H]^+$ 431.0606, found: 431.0589.

(S)-Methyl 2-((R)-1-(4-Nitrophenyl)-2-nitroethyl)-5-phenyl-3,4-dihydro-2H-pyrrole2-carboxylate ***3l***. Yellow oil; 68.5 mg, 69% yield; IR (KBr, cm^{-1}) ν 2953, 2924, 1735, 1656, 1607, 1553, 1522, 1496, 1449, 1432, 1378, 1348, 1243, 1165, 1111, 1013; ^1H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, J = 8.8 Hz, 2H), 7.91 (d, J = 6.7 Hz, 2H), 7.70 (d, J = 9.1 Hz, 2H), 7.55−7.43 (m, 3H), 5.07 (dd, J = 3.8, 13.5 Hz, 1H), 4.96 (dd, J = 10.5, 13.5 Hz, 1H), 4.12 (dd, J = 3.8, 10.5 Hz, 1H), 3.59 (s, 3H), 3.14−3.09 (m, 1H), 2.59−2.50 (m, 2H), 2.17−2.07 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.9, 172.2, 147.8, 144.4, 133.1, 131.9, 130.5, 128.8, 128.4, 123.8, 85.2, 77.0, 52.8, 51.6, 35.6, 32.0. $[\alpha]_D^{29}$ = +2.19 (c = 0.07, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{20}H_{20}N_3O_6$ $[M + H]^+$ 398.1352, found: 398.1348.

(S)-Methyl 2-((R)-2-Nitro-1-(thiophen-2-yl)-ethyl)-5-phenyl-3,4-dihydro-2H-pyrrole2-carboxylate ***3m***. Yellow solid; 71.7 mg, 80% yield; mp 82−83 °C; IR (KBr, cm^{-1}) ν 3079, 2952, 1737, 1618, 1576, 1556, 1448, 1380, 1258, 1077, 1028; ^1H NMR (300 MHz, $CDCl_3$) δ 7.87 (m, 2H), 7.51−7.39 (m, 3H), 7.23 (m, 1H), 7.01 (m, 1H), 6.94 (dd, J = 3.7, 10.2 Hz, 1H), 5.34 (dd, J = 4.1, 13.5 Hz, 1H), 5.10 (dd, J = 10.2, 13.5 Hz, 1H), 4.20 (dd, J = 3.8, 10.2 Hz, 1H), 3.72 (s, 3H), 3.24−3.02 (m, 1H), 2.62−2.52 (m, 1H), 2.14−2.03 (m, 1H), 2.14−2.03 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.6, 172.2, 138.3, 133.4, 131.6, 128.7, 128.4, 127.9, 126.8, 126.0, 85.8, 78.6, 52.8, 48.3, 36.1, 31.5. HPLC: Daicel Chiralpak ID-3 (hexane/2-propanol = 98/2, 1.0 mL/min, 250 nm); t_R = 23.0 (minor), t_R = 25.3 min (major); $[\alpha]_D^{28}$ = −99.8 (c = 0.10, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{18}H_{18}N_2NaO_4S$ $[M + Na]^+$ 381.0885, found: 381.0885.

(S)-Methyl 2-((R)-2-Nitro-1-ferrocenyl-ethyl)-5-phenyl-3,4-dihydro-2H-pyrrole2-carboxylate ***3n***. Yellow solid; 80.6 mg, 70% yield; mp 119−120 °C; IR (KBr, cm^{-1}) ν 2952, 2920, 1737, 1607, 1573, 1550, 1437, 1386, 1342, 1246, 1220, 1166; ^1H NMR (300 MHz, $CDCl_3$) δ 7.74 (dd, J = 1.8, 8.2 Hz, 2H), 7.47−7.36 (m, 3H), 5.36 (d, J = 7.0, 14.1 Hz, 1H), 5.12 (dd, J = 3.8, 14.1 Hz, 1H), 4.23 (m, 1H), 4.15 (m, 7H including Cp), 4.05 (dd, J = 3.8, 7.0 Hz, 1H), 4.02 (dd, J = 4.1, 10.8 Hz, 1H), 3.94 (m, 1H), 3.64 (s, 3H), 3.05−2.74 (m, 1H), 2.74−2.53 (m, 2H), 1.97−1.87 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.8, 172.4, 133.7, 131.2, 128.6, 128.2, 86.6, 85.0, 77.6, 70.2, 69.0, 68.3, 68.1, 66.5, 52.5, 45.9, 36.0, 29.9. HPLC: Daicel Chiralpak ID-3 (hexane/2-propanol = 95/5, 1.0 mL/min, 250 nm); t_R = 26.1 (minor), t_R = 27.2 min (major); $[\alpha]_D^{30}$ = −9.5 (c = 0.10, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{24}H_{24}FeN_2NaO_4$ $[M + Na]^+$ 483.0983, found: 483.0977.

General Procedure for the Silver-Catalyzed Asymmetric Conjugate Addition of 1 to 2. All reactions were carried out under nitrogen atmosphere with oven-dried glassware. In a 20 mL Schlenk tube containing a stirring bar, AgOAc (2.1 mg, 0.013 mmol) and **L6** (8.6 mg, 0.014 mmol) were dissolved in dry Et_2O (2.5 mL) and stirred at −20 °C for 30 min. Then, **1a** (50.8 mg, 0.25 mmol) and **2a** (44.7 mg, 0.30 mmol) were added. The resulting mixture was stirred at the same temperature for 15 h and then filtered through Celite and concentrated in vacuo. The residue was isolated by PTLC (n-hexane/EtOAc = 2:1).

(S)-Methyl 2-((S)-2-Nitro-1-phenylethyl)-5-phenyl-3,4-dihydro-2H-pyrrole2-carboxylate ***4a***. White solid; 81.1 mg, 92% yield; mp =127−128 °C; IR (KBr, cm^{-1}) ν 3034, 2957, 1733, 1607, 1572, 1556, 1536, 1496, 1447, 1434, 1382, 1246, 1075; ^1H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, J = 6.5 Hz, 2H), 7.51−7.40 (m, 3H), 7.18 (m, 5H), 5.14 (dd, J = 11.2, 13.2 Hz, 1H), 4.99 (dd, J = 4.1, 13.2 Hz, 1H), 4.39 (dd, J = 4.1, 11.2 Hz, 1H), 3.79 (s, 3H), 2.86−2.75 (m, 1H), 2.24−2.17 (m, 1H), 2.13−1.93 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.7, 174.1, 135.2, 133.5, 131.4, 129.8, 128.7, 128.5, 128.2, 128.1, 84.8, 77.6, 53.0, 50.2, 35.4, 31.5; HPLC: Daicel Chiralpak ID-3 (hexane/2-propanol = 95/5, 1.0 mL/min, 250 nm); t_R = 19.0 (minor), t_R = 22.5 min (major); $[\alpha]_D^{23}$ = −207.5 (c = 0.13, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{20}H_{21}N_2O_4$ $[M + H]^+$ 353.1501, found: 353.1494.

(S)-Methyl 5-(4-Methylphenyl)-2-((S)-2-nitro-1-phenylethyl)-3,4-dihydro-2H-pyrrole2-carboxylate ***4b***. Yellow oil; 86.0 mg, 94% yield; IR (KBr, cm^{-1}) ν 3034, 2958, 2933, 1732, 1606, 1553, 1541, 1497, 1457, 1433, 1380, 1243, 1166, 1049; ^1H NMR (300 MHz, $CDCl_3$) δ 7.73−7.70 (d, J = 8.2 Hz, 2H), 7.25−7.22 (d, J = 3.5 Hz, 2H), 7.19−7.16 (m, 5H), 5.13 (dd, J = 10.8, 13.4, 1H), 4.99 (dd, J = 4.1, 13.4 Hz, 1H), (dd, J = 3.5, 7.7 Hz, 1H), 4.38 (dd, J = 4.1, 10.8 Hz, 1H), 3.80 (s, 3H), 2.84−2.73 (m, 1H), 2.41 (s, 3H), 2.22−2.11 (m, 1H), 2.05−1.60 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.5, 174.2, 141.8, 135.3, 130.8, 129.8, 129.3, 128.4, 128.2, 128.0, 84.7, 77.7, 53.0, 50.2, 35.3, 31.5, 21.6; HPLC: Daicel Chiralpak ID-3 (hexane/2-propanol = 98/2, 1.0 mL/min, 250 nm); t_R = 28.7 (minor), t_R = 40.9 min (major); $[\alpha]_D^{24}$ = −217.1 (c = 0.11, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{21}H_{22}NaN_2O_4$ $[M + Na]^+$ 389.1477, found: 389.1496.

(S)-Methyl 5-(4-Methoxylphenyl)-2-((S)-2-nitro-1-phenylethyl)-3,4-dihydro-2Hpyrrole-2-carboxylate ***4c***. Yellow oil; 82.2 mg, 86% yield; IR (KBr, cm^{-1}) ν 2954, 2840, 1729, 1605, 1552, 1515, 1456, 1379, 1253, 1173, 1112, 1029; ^1H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, J = 9.1 Hz, 2H), 7.18 (m, 5H), 6.94 (d, J = 8.5 Hz, 2H), 5.13 (dd, J = 10.8, 13.2 Hz, 1H), 4.98 (dd, J = 4.1, 13.2 Hz, 1H), 4.37 (dd, J = 4.1, 10.8 Hz, 1H), 3.86 (s, 3H), 3.80 (s, 3H), 2.83−2.71 (m, 1H), 2.22−2.11 (m, 1H), 2.04−1.89 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.9, 174.4, 162.2, 135.4, 130.0, 129.9, 128.5, 128.1, 126.3, 114.0, 84.7, 77.7, 55.5, 53.0, 50.3, 35.3, 31.6. HPLC: Daicel Chiralpak ID-3 (hexane/2-propanol = 95/5, 1.0 mL/min, 250 nm); t_R = 35.2 (minor), t_R = 45.5 min (minor); $[\alpha]_D^{24}$ = −235.1 (c = 0.13, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{21}H_{22}N_2NaO_5$ $[M + Na]^+$ 405.1426, found: 405.1423.

(S)-Methyl 5-(4-Chlorophenyl)-2-((S)-2-nitro-1-phenylethyl)-3,4-dihydro-2H-pyrrole2-carboxylate ***4d***. White solid; 86.9 mg, 90% yield; mp =97−99 °C; IR (KBr, cm^{-1}) ν 2954, 2860, 1729, 1605, 1596, 1552, 1491, 1379, 1253, 1173, 1112, 1029; ^1H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 8.8 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 7.23−7.14 (m, 5H), 5.11 (dd, J = 10.8, 13,5 Hz, 1H), 4.97 (dd, J = 4.1, 13.5 Hz, 1H), 4.37 (dd, J = 4.1, 10.8 Hz, 1H), 3.80 (s, 3H), 2.80−2.69 (m, 1H), 2.25−2.15 (m, 1H), 2.08−1.87 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.5, 173.9, 137.6, 135.1, 131.8, 129.8, 129.5, 128.9, 128.5, 128.2, 84.8, 77.5, 53.1, 50.2, 35.3, 31.6; HPLC: Daicel Chiralpak ID-3 column (hexane/2-propanol = 95/5, 1.0 mL/min, 250 nm); t_R = 17.1 (minor), t_R = 25.5 min (major); $[\alpha]_D^{23}$ = −244.9 (c = 0.11, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{20}H_{20}ClN_2O_4$ $[M + H]^+$ 387.1112, found: 387.1116.

(S)-Methyl 5-(4-Bromophenyl)-2-((S)-2-nitro-1-phenylethyl)-3,4-dihydro-2H-pyrrole2-carboxylate ***4e***. White solid; 105.4 mg, 98%

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yield; mp =111−112 °C; IR (KBr, cm^{-1}) ν 2951, 2860, 1736, 1618, 1590, 1543, 1487, 1381, 1228, 1067, 1051, 1009; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.23−7.14 (m, 5H), 5.11 (dd, J = 10.8, 13.5 Hz, 1H), 4.97 (dd,, J = 4.1, 13.5 Hz, 1H), 4.37 (dd, J = 4.1, 10.8 Hz, 1H), 3.82 (s, 3H), 2.80−2.70 (m, 1H), 2.25−2.15 (m, 1H), 2.09−1.87 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.7, 174.0, 135.1, 132.3, 132.0, 129.8, 129.7, 128.6, 128.2, 126.2, 84.9, 77.5, 53.1, 50.3, 35.3, 31.7; HPLC: Daicel Chiralpak ID-3 column (hexane/2-propanol = 95/5, 1.0 mL/min, 250 nm); t_R = 20.2 (minor), t_R = 31.3 min (major); $[\alpha]_D^{24}$ = −235.1 (c = 0.13, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{20}H_{19}BrN_2NaO_4$ $[M + Na]^+$ 453.0426, found: 453.0420.

(S)-Methyl 2-((S)-1-(2-Methylphenyl)-2-nitroethyl)-5-phenyl-3,4-dihydro-2H-pyrrole2-carboxylate ***4f.*** Yellow oil; 76.9 mg, 84% yield; IR (KBr, cm^{-1}) ν 3061, 3027, 2953, 2922, 1721, 1618, 1547, 1493, 1450, 1379, 1259, 1159, 1123, 1081; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, J = 6.5 Hz, 2H), 7.51−7.40 (m, 3H), 7.15−7.03 (m, 3H), 6.91 (t, J = 7.6 Hz, 1H), 5.18 (dd, J = 10.8, 13.8 Hz, 1H), 5.04 (dd, J = 3.8, 13.8 Hz, 1H), 4.82 (dd, J = 3.8, 10.8 Hz, 1H), 3.79 (s, 3H), 2.88−2.77 (m, 1H), 2.47 (s, 1H), 2.24−2.11 (m, 2H), 1.81−1.71 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.7, 174.4, 138.3, 134.1, 133.5, 131.4, 130.8, 128.7, 128.2, 127.7, 127.6, 126.1, 84.8, 78.2, 53.1, 43.8, 35.5, 31.2, 20.5. HPLC: Daicel Chiralpak ID-3 (hexane/2-propanol = 98/2, 1.0 mL/min, 250 nm); t_R = 22.3 (minor), t_R = 24.4 min (major); $[\alpha]_D^{25}$ = −244.3 (c = 0.14, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{21}H_{22}N_2NaO_4$ $[M + Na]^+$ 389.1477, found: 389.1464.

(S)-Methyl 2-((S)-1-(3-Methylphenyl)-2-nitroethyl)-5-phenyl-3,4-dihydro-2H-pyrrole2-carboxylate ***4g.*** Yellow oil; 84.2 mg, 92% yield; IR (KBr, cm^{-1}) ν 3031, 2952, 2922, 1731, 1617, 1553, 1492, 1449, 1434, 1379, 1238, 1160, 1078, 1057, 1006; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, J = 6.6 Hz, 2H), 7.52−7.40 (m, 3H), 7.09−6.96 (m, 4H), 5.12 (dd, J = 10.8, 13.5 Hz, 1H), 4.97 (dd, J = 4.1, 13.5 Hz, 1H), 4.33 (dd, J = 4.1, 10.8 Hz, 1H), 3.81 (s, 3H), 2.83−2.73 (m, 1H), 2.22−2.13 (m, 1H), 2.11 (s, 3H) 2.09−1.87 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.7, 174.2, 137.9, 134.9, 133.4, 131.4, 130.7, 128.8, 128.6, 128.3, 128.1, 126.8, 84.7, 77.5, 53.0, 50.2, 35.4, 31.5, 21.2. HPLC: Daicel Chiralpak ID-3 (hexane/2-propanol = 95/5, 1.0 mL/min, 250 nm); t_R = 17.0 (minor), t_R = 19.3 min (major); $[\alpha]_D^{30}$ = −199.1 (c = 0.05, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{21}H_{22}N_2NaO_4$ $[M + Na]^+$ 389.1477, found: 389.1491.

(S)-Methyl 2-((S)-1-(4-Methylphenyl)-2-nitroethyl)-5-phenyl-3,4-dihydro-2H-pyrrole2-carboxylate ***4h.*** Yellow oil; 78.7 mg, 86% yield; IR (KBr, cm^{-1}) ν 3029, 2952, 2922, 1731, 1618, 1552, 1515, 1496, 1449, 1379, 1239, 1167, 1085; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, J = 6.7 Hz, 2H), 7.51−7.40 (m, 3H), 7.07 (d, J = 8.2 Hz, 2H), 6.98 (d, J = 7.9 Hz, 2H), 5.11 (dd, J = 10.8, 13.2 Hz, 1H), 4.97 (dd, J = 4.1, 13.2 Hz, 1H), 4.35 (dd, J = 4.1, 10.8 Hz, 1H), 3.79 (s, 3H), 2.86−2.74 (m, 1H), 2.24 (s, 3H), 2.22−2.15 (m, 1H), 2.11−2.00 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.6, 174.2, 137.8, 133.5, 132.1, 131.4, 129.6, 129.2, 128.7, 128.2, 84.9, 77.8, 53.0, 49.9, 35.4, 31.5, 21.1. HPLC: Daicel Chiralpak ID-3 (hexane/2-propanol = 95/5, 1.0 mL/min, 250 nm); t_R = 18.7 (minor), t_R = 22.2 min (major); $[\alpha]_D^{26}$ = −223.4 (c = 0.19, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{21}H_{22}N_2NaO_4$ $[M + Na]^+$ 389.1477, found: 389.1494.

(S)-Methyl 2-((S)-1-(4-Methoxyphenyl)-2-nitroethyl)-5-phenyl-3,4-dihydro-2Hpyrrole-2-carboxylate ***4i.*** White oil; 84.1 mg, 88% yield; IR (KBr, cm^{-1}) ν 2953, 2838, 1729, 1612, 1551, 1514, 1449, 1434, 1379, 1251, 1180, 1120; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, J = 6.7 Hz, 2H), 7.51−7.28 (m, 3H), 7.10 (d, J = 8.8 Hz, 2H), 6.71 (d, J = 8.5 Hz, 2H), 5.09 (dd, J = 11.1, 13.2 Hz, 1H), 4.96 (dd, J = 4.1, 13.2 Hz, 1H), 4.33 (dd, J = 4.1, 11.1 Hz, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 2.86−2.74 (m, 1H), 2.21−2.14 (m, 1H), 2.10−1.97 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.6, 174.3, 159.3, 133.5, 131.4, 130.8, 128.7, 128.2, 126.9, 113.9, 84.9, 77.8, 55.2, 53.0, 49.6 35.4, 31.5. HPLC: Daicel Chiralpak ID-3 (hexane/2-propanol = 95/5, 1.0 mL/min, 250 nm); t_R = 27.8 (minor), t_R = 36.8 min (major); $[\alpha]_D^{25}$ = −194.0 (c = 0.12, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{21}H_{22}NaN_2O_5$ $[M + Na]^+$ 405.1426, found: 405.1440.

(S)-Methyl 2-((S-1-(4-Chlorophenyl)-2-nitroethyl)-5-phenyl-3,4-dihydro-2H-pyrrole2-carboxylate ***4j.*** Yellow oil; 86.9 mg, 90% yield; IR (KBr, cm^{-1}) ν 3030, 2953, 1732, 1618, 1552, 1494, 1449, 1434, 1378, 1240, 1163, 1114, 1092, 1056, 1014; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, J = 6.7 Hz, 2H), 7.52−7.41 (m, 3H), 7.19−7.12 (m, 4H), 5.11 (dd, J = 11.1, 13.5 Hz, 1H), 4.99 (dd, J = 4.1, 13.5 Hz, 1H), 4.37 (dd, J = 4.1, 11.1 Hz, 1H), 3.79 (s, 3H), 2.92−2.80 (m, 1H), 2.26−2.10 (m, 2H), 1.99−1.88 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.9, 173.9, 134.2, 133.9, 133.2, 131.6, 131.1, 128.7, 128.2, 84.6, 77.6, 53.1, 49.6, 35.4, 31.5. HPLC: Daicel Chiralpak ID-3 (hexane/2-propanol = 95/5, 1.0 mL/min, 250 nm); t_R = 14.7 (minor), t_R = 19.7 min (major); $[\alpha]_D^{26}$ = −219.7 (c = 0.10, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{20}H_{19}ClKN_2O_4$ $[M+K]^+$ 425.0670, found: 425.0669.

(S)-Methyl 2-((S)-1-(4-Bromophenyl)-2-nitroethyl)-5-phenyl-3,4-dihydro-2H-pyrrole2-carboxylate ***4k.*** Yellow oil; 90.4 mg, 84% yield; IR (KBr, cm^{-1}) ν 3031, 2952, 1731, 1656, 1617, 1552, 1490, 1449, 1434, 1378, 1241, 1168, 1114, 1056, 1011;^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, J = 6.5 Hz, 2H), 7.53−7.41 (m, 3H), 7.33 (d, J = 8.5 Hz, 3H), 7.08 (d, J = 8.5 Hz, 2H), 5.10 (dd, J = 10.8, 13.5 Hz, 1H), 4.98 (dd, J = 4.1, 13.5 Hz, 1H), 4.36 (dd, J = 4.1, 10.8 Hz, 1H), 3.79 (s, 3H), 2.92−2.81 (m, 1H), 2.26−2.12 (m, 2H), 1.98−1.88 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.9, 173.8, 134.5, 133.2, 131.7, 131.6, 131.5, 128.8, 128.2, 122.4, 84.5, 77.6, 53.1, 49.6, 35.4, 31.5. HPLC: Daicel Chiralpak ID-3 (hexane/2-propanol = 95/5, 1.0 mL/min, 250 nm); t_R = 14.8 (minor), t_R = 20.4 min (major); $[\alpha]_D^{26}$ = −201.0 (c = 0.08, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{20}H_{19}BrN_2NaO_4$ $[M + Na]^+$ 453.0426, found: 453.0452.

(S)-Methyl 2-((S)-1-(4-Nitrophenyl)-2-nitroethyl)-5-phenyl-3,4-dihydro-2H-pyrrole2-carboxylate ***4l.*** Yellow oil; 53.8 mg, 54% yield; IR (KBr, cm^{-1}) ν 2956, 2925, 1721, 1638, 1612, 1553, 1521, 1497, 1448, 1437, 1378, 1347, 1239, 1170, 1112, 1028; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, J = 8.8 Hz, 2H), 7.84 (d, J = 7.0 Hz, 2H), 7.56−7.40 (m, 5H), 5.19 (dd, J = 10.8, 13.8 Hz, 1H), 5.06 (dd, J = 4.1, 13.8 Hz, 1H), 4.52 (dd, J = 4.1, 10.8 Hz, 1H), 3.81 (s, 3H), 2.97−2.86 (m, 1H), 2.32−2.20 (m, 2H), 1.92−1.82 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.2, 173.5, 147.8, 143.4, 133.0, 131.9, 130.9, 128.9, 128.2, 123.6, 84.3, 77.4, 53.3, 49.8, 35.5, 31.7. HPLC: Daicel Chiralpak ID-3 (hexane/2-propanol = 95/5, 1.0 mL/min, 250 nm); t_R = 37.8 (minor), t_R = 57.3 min (major); $[\alpha]_D^{24}$ = −212.4 (c = 0.11, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{20}H_{20}N_3O_6$ $[M + H]^+$ 398.1352, found: 398.1364.

(S)-Methyl 2-((S)-2-Nitro-1-(thiophen-2-yl)-ethyl)-5-phenyl-3,4-dihydro-2H-pyrrole2-carboxylate ***4m.*** White solid; 85.4 mg, 95% yield; mp 94−96 °C; IR (KBr, cm^{-1}) ν 3082, 2956, 1734, 1607, 1572, 1557, 1446, 1384, 1257, 1075, 1011; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, J = 6.5 Hz, 2H), 7.53−7.42 (m, 3H), 7.15 (d, J = 4.7 Hz, 1H), 6.91 (d, J = 2.3 Hz, 1H), 6.86 (dd, J = 3.5, 5.3 Hz, 1H), 4.99 (m, 1H), 4.77 (dd, J = 5.0, 9.4 Hz, 1H), 3.79 (s, 3H), 3.03−2.92 (m, 1H), 2.49−2.38 (m, 1H), 2.31−2.21 (m, 1H), 2.14−2.04 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.6, 173.7, 137.5, 133.5, 131.6, 128.8, 128.7, 128.4, 126.6, 126.6, 84.8, 79.2, 53.1, 46.2, 35.9, 31.5. HPLC: Daicel Chiralpak ID-3 (hexane/2-propanol = 95/5, 1.0 mL/min, 250 nm); t_R = 17.6 (minor), t_R = 20.2 min (major); $[\alpha]_D^{25}$ = −242.1 (c = 0.10, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{18}H_{18}N_2NaO_4S$ $[M + Na]^+$ 381.0885, found: 381.0904.

(S)-Methyl 2-((S)-2-Nitro-1-ferrocenyl-ethyl)-5-phenyl-3,4-dihydro-2H-pyrrole2-carboxylate ***4n.*** Yellow solid; 94.5 mg, 82% yield; mp 147−151 °C; IR (KBr, cm^{-1}) ν 2950, 2915, 1725, 1601, 1571, 1560, 1450, 1380, 1344, 1253, 1204, 1104; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 6.5 Hz, 2H), 7.47−7.36 (m, 3H), 5.06 (d, J = 5.3 Hz, 2H), 4.35 (t, J = 5.3 Hz, 1H), 4.26 (m, 1H), 4.15 (m, 6H, including Cp), 4.05 (m, 1H), 3.74 (s, 3H), 3.70 (m, 1H), 2.89−2.79 (m, 1H), 2.31−2.10 (m, 2H), 2.04−1.94 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 173.7, 133.6, 131.3, 128.6, 128.5, 128.2, 86.0, 85.9, 77.8, 70.3, 69.1, 68.6, 67.7, 67.1, 52.7, 44.4, 35.8, 29.9. HPLC: Daicel Chiralpak ID-3 (hexane/2-propanol = 95/5, 1.0 mL/min, 250 nm); t_R = 30.3 (minor), t_R = 53.4 min (major); $[\alpha]_D^{25}$ = +64.382 (c = 0.13, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{24}H_{24}FeN_2NaO_4$ $[M + Na]^+$ 483.0983, found: 483.0982.

Reduction of 4a. To a screw capped vial, **4a** (70.4 mg, 0.20 mmol), sodium cyanoborohydride (150.8 mg, 2.4 mmol), and acetic acid (137 mL, 2.4 mmol) were dissolved in dry toluene (2.0 mL) and

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stirred for 15 h at room temperature. Water was added, and the mixture was extracted with ethyl acetate (10 mL). The organic layers were washed with water and brine. The organic extracts were dried over Na_2SO_4, concentrated, and purified by PTLC (silicagel, chloroform).

(2S,5S)-Methyl 2-((R)-2-Nitro-1-phenylethyl)-5-phenylpyrrolidine-2-carboxylate ***5a***. White solid; 59 mg, yield 83%; mp 99−101 °C; IR (KBr, cm^{-1}) ν 3340, 3064, 3026, 2952, 1737, 1602, 1552, 1493, 1455, 1377, 1251, 1122, 1028; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44−7.23 (m, 10H), 5.19 (dd, J = 10.6, 13.1 Hz, 1H), 4.91 (dd, J = 3.7, 13.1 Hz, 1H), 4.15 (dd, J = 3.7, 10.6 Hz, 1H), 4.02 (dd, J = 3.9, 10.6 Hz, 1H), 3.54 (s, 3H), 2.85 (br, 1H), 2.41−2.33 (m, 1H), 2.29−2.22 (m, 2H), 2.16−2.10 (m, 1H), 1.69−1.58 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.6, 143.4, 136.8, 128.8, 128.5, 128.4, 128.3, 127.5, 126.5, 77.2, 71.3, 62.2, 52.3, 51.0, 35.1, 34.6; $[\alpha]_D^{26}$ = −201.0 (c = 0.08, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{20}H_{23}N_2O_4$ $[M + H]^+$ 355.1658, found: 355.1670.

(2S,5S)-Methyl 2-((S)-2-Nitro-1-phenylethyl)-5-phenylpyrrolidine-2-carboxylate ***6a***. Yellow oil; 59 mg, 83% yield; IR (KBr, cm^{-1}) ν 3341, 3063, 3032, 2952, 1726, 1603, 1551, 1494, 1452, 1379, 1245, 1118, 1031; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39−7.21 (m, 10H), 4.91 (dd, J = 10.6, 13.0 Hz, 1H), 4.84 (dd, J = 5.4, 13.0 Hz, 1H), 4.15 (dd, J = 6.7, 9.1 Hz, 1H), 4.01 (dd, J = 4.8, 9.7 Hz, 1H), 3.75 (s, 3H), 2.77 (br, 1H), 2.24−2.14 (m, 1H), 2.07−1.87 (m, 2H), 1.26−1.13 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.6, 143.7, 135.7, 129.6, 128.4, 128.3, 127.2, 126.7, 77.2, 71.0, 61.5, 52.9, 51.0, 33.7, 32.8; $[\alpha]_D^{26}$ = +8.70 (c = 0.15, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{20}H_{22}KN_2O_4$ $[M+K]^+$ 393.1217, found: 393.1203.

■ ASSOCIATED CONTENT

Supporting Information

, cif for . The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02024.

^{1}H and ^{13}C NMR spectra (PDF) and HPLC analytical data for **3a**−**3n**, **4a**−**4n**, **5a**, and **6a** and computationally optimized coordinates (PDF)

Crystallographic data for **3n** (CIF)

Crystallographic data for **4n** (CIF)

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Notes

The authors declare no competing financial interest.

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