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Catalytic asymmetric epoxidation of α,β-unsaturated *N*-acylpyrroles as monodentate and activated ester equivalent acceptors

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Abstract—Catalytic asymmetric epoxidation of α,β-unsaturated *N*-acylpyrroles as monodentate and activated ester equivalent acceptors is described. A Sm(O-i-Pr)$_3$/(R)-H$_8$-BINOL complex promoted the epoxidation reaction to afford products in high yield (up to quant) and high enantiomeric excess (up to >99.5% ee). Reaction proceeded smoothly using cumene hydroperoxide (CMHP) with low explosive hazard, and completed within 0.2–0.5 h with 5 mol % catalyst. Catalyst loading was successfully reduced to as little as 0.02 mol %. The *N*-acylpyrrole properties as well as efficient synthesis of α,β-unsaturated *N*-acylpyrroles are also described.

1. Introduction

Catalytic asymmetric epoxidation of α,β-unsaturated carbonyl compounds is one of the most important transformations in organic synthesis.[1] Although we and others have achieved efficient catalytic asymmetric epoxidation of enones,[1,2] there are few examples of α,β-unsaturated esters as substrates using a salen/Mn complex[3] or chiral ketones[4] as the catalysts. We also recently reported a yttrium/biphenyldiol catalyst for the epoxidation of α,β-unsaturated esters.[5,6] Although excellent enantiomeric excess and yield were achieved with various α,β-unsaturated esters (up to 97% yield, up to 99% ee), there are some practical problems: (a) catalyst loading and reaction rate: 2–10 mol % catalyst loading was essential for good conversion; in many cases it was difficult to complete the conversion with less than 1 mol % catalyst; (b) turnover frequency (TOF) of the catalyst was, in most cases, approximately 1–3 h^{-1}; a higher TOF is desirable. (c) Oxidant: *tert*-butyl hydroperoxide (TBHP) with explosive hazard was essential for good reactivity. From a practical viewpoint, it is desirable to use less explosive (less reactive) cumene hydroperoxide (CMHP). In this manuscript, we report the use of α,β-unsaturated *N*-acylpyrrole (Fig. 1, **1**) as a monodentate and activated α,β-unsaturated ester surrogate to overcome the above-mentioned problems. A Sm(O-i-Pr)$_3$/(R)-H$_8$-BINOL (Fig. 1) complex promoted the epoxidation reaction to afford products in high yield (up to quant) and high enantiomeric excess (up to >99.5% ee). Catalyst loading was also successfully reduced to as little as 0.02 mol % and a high TOF (>3000 h^{-1}) was realized.[7]

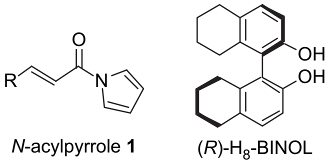

Figure 1. Structures of α,β-unsaturated *N*-acylpyrrole **1** and (R)-H$_8$-BINOL.

2. Design and synthesis of α,β-unsaturated *N*-acylpyrroles

The postulated catalytic cycle of the asymmetric epoxidation reaction is shown in Figure 2. A rare earth metal alkoxide moiety changes to a rare earth metal-peroxide through proton exchange (I). The rare earth metal/BINOL complex also functions as a Lewis acid to activate electron deficient olefins through monodentate coordination (II). Enantioselective 1,4-addition of rare earth metal-peroxide gives intermediate enolate (III), followed by epoxide formation to regenerate the catalyst (IV). In the transition state for the 1,4-addition step, the rare earth metal/BINOL complex,

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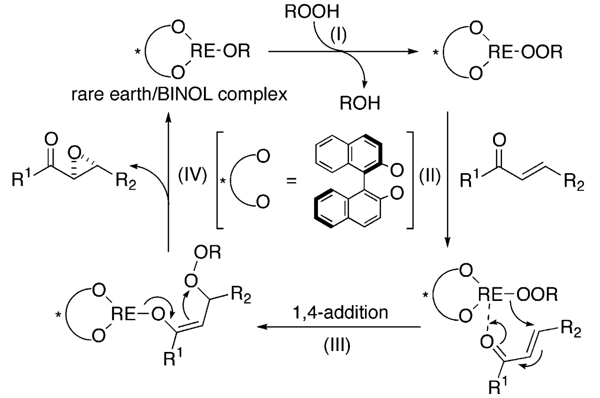
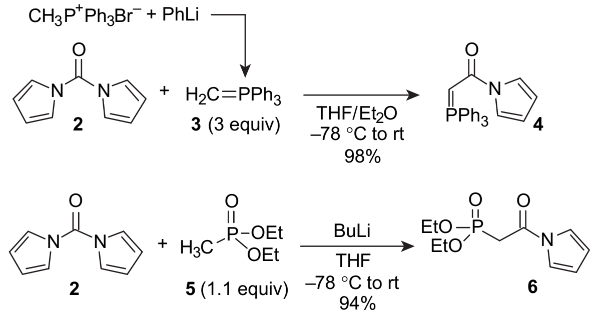


Figure 2. Postulated catalytic cycle of asymmetric epoxidation promoted by rare earth metal alkoxide/BINOL complex.

originally optimized for enones,[2] is postulated to favor the monodentate coordination mode for high enantioselectivity. When a bidentate α,β-unsaturated oxazolidinone amide is used as an activated carboxylic acid derivative, epoxide is obtained in only 73% yield and 87% ee after 24 h, using as much as 20 mol % catalyst loading, probably due to a coordination mode mismatch.[6]

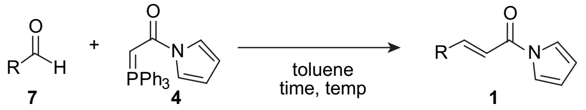
The ideal substrates for epoxidation with rare earth metal/BINOL complexes should (i) favor a monodentate coordination mode similar to enones, (ii) have the same oxidation state as carboxylic acids, and (iii) be activated as an electrophile. To meet these criteria, an α,β-unsaturated *N*-acylpyrrole **1** (Fig. 1) was selected as a template for investigation of the following reasons. The unique properties and reactivity of *N*-acylpyrroles were reported by Evans and co-workers.[8] Because the lone electron pair of the nitrogen in the pyrrole ring is delocalized in an aromatic system, the properties of the carbonyl group are similar to those of a phenyl ketone rather than an amide or an ester. The reactivity of α,β-unsaturated *N*-acylpyrrole is thus much higher than that of simple amide and ester. In contrast to the bidentate α,β-unsaturated oxazolidinone amide, *N*-acylpyrrole is supposed to favor monodentate coordination. Furthermore, the *N*-acylpyrrole moiety is relatively stable compared with the *N*-acylimidazole moiety, as predicted from the difference in the p*K*a values of pyrrole (23.0 in DMSO) and imidazole (18.6 in DMSO). Thus, the *N*-acylpyrrole moiety would be compatible with various catalytic asymmetric reaction conditions. We recently demonstrated the utility of *N*-acylpyrroles as activated monodentate ester equivalents in various other catalytic asymmetric reactions.[9,10] The *N*-acylpyrrole moiety can be transformed to various functional groups.[8,9,10]



Scheme 1. Synthesis of Wittig reagent **4** and HWE reagent **6**.

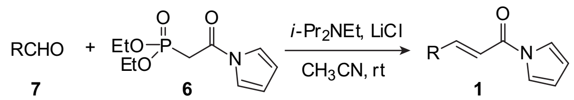
In the literature, the most efficient synthesis of α,β-unsaturated *N*-acylpyrrole was the condensation of cinnamamide and 2,5-dimethoxytetrahydrofuran in acetic acid or with $SOCl_2$ at high temperature,[8a,11] affording **1a** in 60–68% yield. For the synthesis of α,β-unsaturated *N*-acylpyrroles with various functional groups, however, a milder method is necessary. One reason for not using α,β-unsaturated *N*-acylpyrrole widely as an acceptor for 1,4-addition reactions might be the lack of efficient preparation methods under mild conditions. Our synthetic procedure for α,β-unsaturated *N*-acylpyrroles using Wittig reagent **4** and HWE reagent **6** are summarized in Scheme 1, and in Tables 1 and 2. The reaction of carbonyldipyrrole **2**[12] with ylide **3** afforded **4** in 98% yield when 3 equiv of **3** was used (Scheme 1).[13] The HWE reagent **6** was also synthesized by the reaction of **2** with 1.1 equiv of lithiated **5** in 94% yield. The Wittig reaction to afford α,β-unsaturated *N*-acylpyrroles is summarized in Table 1. With aromatic (entries 1–9) and heteroaromatic (entries 10–12) aldehydes, both the chemical yield and *E*/*Z* ratio were good using Wittig reagent **4**. Both the electron donating (entries 3 and 4) and withdrawing (entries 5 and 6) substituents at the *para*-position gave products in high yield and *E*/*Z* ratio (>20/1). With *ortho*-substituents, the *E*/*Z* ratio decreased to 7/1 (entry 8) and 10/1 (entry 9). For enolizable aliphatic aldehydes, HWE reactions with **6** under Masamune–Roush conditions[14] were appropriate (Table 2), and afforded various β-alkyl substituted

Table 1. Synthesis of α,β-unsaturated *N*-acylpyrrole **1** using Wittig reagent **4**



Entry	Aldehyde R	Product	Temp (°C)	Time (h)	Yield (%)	*E*/*Z*
1	Ph–, **7a**	**1a**	100	48	97	>20/1
2	2-naphthyl, **7b**	**1b**	100	48	Quant	>20/1
3	4-Me–C_6H_4–, **7c**	**1c**	100	48	98	>20/1
4	4-MeO–C_6H_4–, **7d**	**1d**	110	84	97	>20/1
5	4-Br–C_6H_4–, **7e**	**1e**	100	36	98	>20/1
6	4-Cl–C_6H_4–, **7f**	**1f**	100	24	Quant	>20/1
7	3-Cl–C_6H_4–, **7g**	**1g**	100	24	98	>15/1
8	2-Cl–C_6H_4–, **7h**	**1h**	100	24	95	7/1
9	1-naphthyl, **7i**	**1i**	100	48	Quant	10/1
10	2-furyl, **7j**	**1j**	100	48	91	>15/1
11	2-thienyl, **7k**	**1k**	100	36	Quant	>20/1
12	4-pyridyl, **7l**	**1l**	100	48	Quant	>20/1
13	$PhCH_2C(CH_3)_2$–, **7m**	**1m**	110	84	63	>20/1
14	$BnOCH_2C(CH_3)_2$–, **7n**	**1n**	110	84	63	>20/1

Table 2. Synthesis of α,β-unsaturated *N*-acylpyrrole **1** using HWE reagent **6**



Entry	Aldehyde R	Product	Time (h)	Yield (%)	*E*/*Z*
1	$(CH_3)_2CHCH_2$–, **7o**	**1o**	13	96	>20/1
2	*n*-Pr, **7p**	**1p**	12	90	>20/1
3	$PhCH_2CH_2$–, **7q**	**1q**	22	89	>20/1
4	$CH_2{=}CH(CH_2)_8$–, **7r**	**1r**	15	94	>20/1
5	*i*-Pr, **7s**	**1s**	10	90	>20/1
6	*cyclo*-Hex, **7t**	**1t**	24	98	>20/1

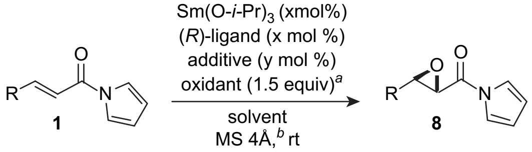
α,β-unsaturated *N*-acylpyrroles in good yield and with high *E*-selectivity.

3. Catalytic asymmetric epoxidation of α,β-unsaturated *N*-acylpyrroles

The catalytic asymmetric epoxidation of **1a** proceeded smoothly, as summarized in Table 3. With 10 mol % of the $Sm(O\text{-}i\text{-}Pr)_3$/(*R*)-BINOL complex,[15] 10 mol % of $Ph_3As(O)$, and 1.5 equiv of TBHP, the reaction was completed within 0.5 h and afforded **8a** in 93% yield and 94% ee (entry 1). The reaction rate was much faster than when using other carboxylic acid derivatives[5,6] and as fast as that using enones.[1,16] The reaction also proceeded smoothly with 5 mol % catalyst (entry 2: 85% yield, 96% ee). To improve the enantioselectivity, various BINOL derivatives were screened to determine that H_8-BINOL functioned best. The H_8-BINOL complex gave better results than the BINOL complex, probably due to the large bite angle.[17] With a $Sm(O\text{-}i\text{-}Pr)_3$/(*R*)-$H_8$-BINOL complex, **8a** was obtained in 99% ee (entry 3). $Ph_3P(O)$ was also effective for *N*-acylpyrrole **1a** (entries 4–6). THF/toluene mixed solvent produced better results than THF alone, and **8a** was obtained in 96–99% ee, depending on the amount of $Ph_3P(O)$ (entries 7–9). Both the reaction rate and selectivity were highest with 100 mol % of $Ph_3P(O)$ (entry 9). Under the best conditions (THF/toluene, $Ph_3P(O)$: 100 mol %), less explosive and less reactive CMHP was also applicable and the reaction reached completion within 0.2 h with 5 mol % catalyst (entry 10, 98% yield, >99.5% ee). The result in entry 10 gave additional practical benefits to the present system compared with our previous reports.[5,6] The substrate scopes for the epoxidation reactions are summarized in entries 10–17.[18] In all the substrates, commercially available CMHP (tech. 80% grade) was used without purification. Various β-aryl substituted α,β-unsaturated *N*-acylpyrroles had high reactivity regardless of the substituents on the aromatic rings, providing epoxides in 91–98% yield and in 99 to >99.5% ee after 0.2 h (entries 10–14). β-Alkyl substituted α,β-unsaturated *N*-acylpyrroles had slightly lower reactivity. The reaction completed within 0.2–0.5 h, giving epoxides in 90–95% yield and 99–>99.5% ee (entries 15–17). Because the reaction proceeded via 1,4-addition of samarium peroxide, chemoselective epoxidation of electron deficient carbon–carbon double bond was realized with α,β-unsaturated *N*-acylpyrrole **1r**.

We then tried to reduce the catalyst loading. As expected from the high reaction rate with 5 mol % catalyst loading (Table 3), catalyst loading was easily reduced. TBHP was utilized instead of CMHP to reduce the catalyst loading and to achieve a higher reaction rate. As summarized in Table 4, the epoxidation reaction of **1a** completed using as little as 1, 0.5, or 0.2 mol % of $Sm(O\text{-}i\text{-}Pr)_3$/$H_8$-BINOL complex with 100 mol % of $Ph_3P(O)$, giving product **8a** in high yield (94% quant) and high ee (96–99% ee) after 0.3–1 h (entries 2–4). The reaction proceeded well with as little as 0.1 mol % catalyst loading (substrate/catalyst=1000), affording product in 90.4% yield (turnover number [TON]=904) and 96% ee (entry 5). With the $Sm(O\text{-}i\text{-}Pr)_3$/$H_8$-BINOL/$Ph_3As(O)$=1/1/1 complex, catalyst loading was further reduced to 0.1, 0.05, and 0.02 mol % (substrate/catalyst=up to 5000) as summarized in entries 6–8. The high catalyst TON (TON=4710) and high TOF (up to $>3000\ h^{-1}$) in entry 8 was far better compared with previous reports from our group.[5,6] Because the commercially available TBHP solution in decane (5–6 M) contains up to 4% water, use of the wet TBHP solution in decane was not suitable for reduced catalyst loading (entries 3–8). Thus, TBHP in toluene (ca. 4.5 M) dried with 4 Å MS (water content ≤0.4%) was alternatively used to avoid decomposition of the $Sm(O\text{-}i\text{-}Pr)_3$/$H_8$-BINOL catalyst by excess H_2O.

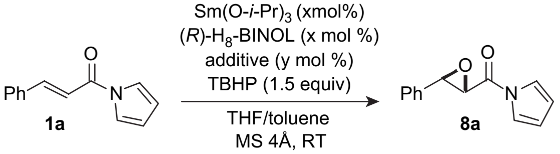
Table 3. Catalytic asymmetric epoxidation reaction of α,β-unsaturated *N*-acylpyrrole



Entry	*N*-Acylpyrrole R	$Sm(O\text{-}i\text{-}Pr)_3$ (x mol %)	Ligand (x mol %)	Additive (y mol %)	Solvent	Oxidant	Time (h)	Yield (%)	ee (%)
1	Ph, **1a**	10	BINOL (10)	$Ph_3As(O)$ (10)	THF	TBHP	0.5	93	94
2	Ph, **1a**	5	BINOL (5)	$Ph_3As(O)$ (5)	THF	TBHP	0.5	85	96
3	Ph, **1a**	5	H_8-BINOL (5)	$Ph_3As(O)$ (5)	THF	TBHP	0.5	94	99
4	Ph, **1a**	5	H_8-BINOL (5)	$Ph_3P(O)$ (15)	THF	TBHP	0.5	84	94
5	Ph, **1a**	5	H_8-BINOL (5)	$Ph_3P(O)$ (50)	THF	TBHP	0.5	88	98
6	Ph, **1a**	5	H_8-BINOL (5)	$Ph_3P(O)$ (100)	THF	TBHP	0.5	85	97
7	Ph, **1a**	5	H_8-BINOL (5)	$Ph_3P(O)$ (15)	THF/toluene	TBHP	0.4	85	96
8	Ph, **1a**	5	H_8-BINOL (5)	$Ph_3P(O)$ (50)	THF/toluene	TBHP	0.5	92	99
9	Ph, **1a**	5	H_8-BINOL (5)	$Ph_3P(O)$ (100)	THF/toluene	TBHP	0.2	97	99
10	Ph, **1a**	5	H_8-BINOL (5)	$Ph_3P(O)$ (100)	THF/toluene	CMHP	0.2	98	>99.5
11	2-naphthyl, **1b**	5	H_8-BINOL (5)	$Ph_3P(O)$ (100)	THF/toluene	CMHP	0.2	93	>99.5
12	4-Me–C_6H_4–, **1c**	5	H_8-BINOL (5)	$Ph_3P(O)$ (100)	THF/toluene	CMHP	0.2	98	>99.5
13	4-MeO–C_6H_4–, **1d**	5	H_8-BINOL (5)	$Ph_3P(O)$ (100)	THF/toluene	CMHP	0.2	91	99
14	4-Cl–C_6H_4–, **1f**	5	H_8-BINOL (5)	$Ph_3P(O)$ (100)	THF/toluene	CMHP	0.2	97	>99.5
15[c]	$PhCH_2CH_2$–, **1q**	5	H_8-BINOL (5)	$Ph_3P(O)$ (100)	THF/toluene	CMHP	0.5	91	99
16	$H_2C{=}CH(CH_2)_8$–, **1r**	5	H_8-BINOL (5)	$Ph_3P(O)$ (100)	THF/toluene	CMHP	0.3	95	99
17	Cyclohex, **1t**	5	H_8-BINOL (5)	$Ph_3P(O)$ (100)	THF/toluene	CMHP	0.2	90	>99.5

[a] TBHP in decane (5–6 M) and CMHP (80% tech. grade) purchased from Aldrich were used as received.
[b] 1000 mg of 4 Å MS $mmol^{-1}$ of compound **1** was used.
[c] CMHP (2.5 equiv) was used.

Table 4. Catalytic asymmetric epoxidation reaction of α,β-unsaturated *N*-acylpyrrole with reduced catalyst loading



Entry	Sm(*O*-*i*-Pr)$_3$ (x mol %)	H$_8$-BINOL (x mol %)	Additive (y mol %)	MS 4 Å (mg mmol^{-1} of **1a**)	Concd Of [**1a**] (M)	Time (h)	Yield (%)	ee (%)
1[a]	5	5	Ph$_3$P(O) (100)	1000	0.1	0.2	97	99
2[a]	1	1	Ph$_3$P(O) (100)	500	1	0.3	94	99
3[b]	0.5	0.5	Ph$_3$P(O) (100)	250	1	0.6	Quant	97
4[b]	0.2	0.2	Ph$_3$P(O) (100)	100	2	1	99	97
5[b]	0.1	0.1	Ph$_3$P(O) (100)	100	2	2	90	96
6[b]	0.1	0.1	Ph$_3$As(O) (0.1)	100	3	0.6	Quant	99
7[b]	0.05	0.05	Ph$_3$As(O) (0.05)	100	3	1	Quant	98
8[b]	0.02	0.02	Ph$_3$As(O) (0.02)	100	3	1.5	94	99

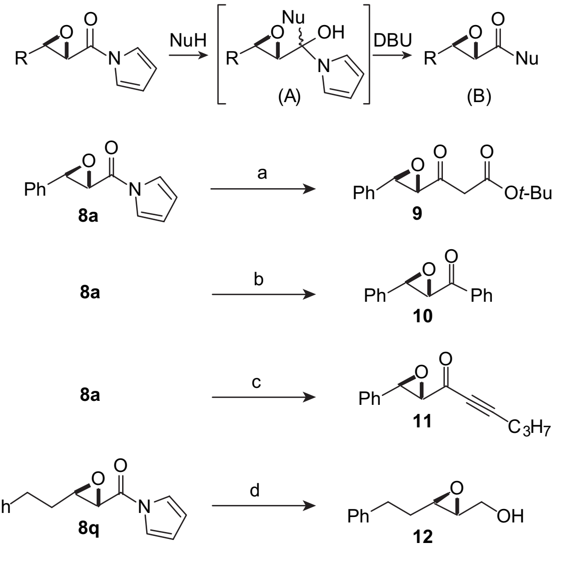
[a] Commercially available TBHP solution in decane (5–6 M) was used.

[b] Dried TBHP solution in toluene was used.

To reduce the catalyst loading, it was important to keep the concentration of the catalyst within 1–5 mM, which was similar to the best conditions with 5 mol % catalyst loading ([Sm(*O*-*i*-Pr)$_3$/H$_8$-BINOL]=5 mM). Thus, the concentration of substrate **1a** increased accordingly when the reaction shown in Table 4 was performed. For example, [**1a**] was 2 M in entry 5 and 3 M in entries 6–8. High volumetric productivity of the present system together with reduced catalyst loading is noteworthy for large scale synthesis. Further experiments to reduce catalyst loading were unsuccessful because it was difficult to maintain the appropriate concentration of Sm catalyst due to solubility problems of product **8a**.

4. Transformation of *N*-acylpyrrole unit

To demonstrate the synthetic utility of the *N*-acylpyrrole unit, several transformations were performed (Scheme 2).[19]



Scheme 2. Transformations of *N*-acylpyrrole units: reagents and conditions: (a) *t*-butyl acetate, BuLi, THF, −78 °C, 10 min; then DBU, CH$_2$Cl$_2$, 25 °C, 20 min, 74% yield (two steps); (b) PhLi, THF, −78 °C, 10 min; then DBU, CH$_2$Cl$_2$, 25 °C, 20 min, 88% yield (two steps); (c) BuLi, 1-pentyne, THF, −78 °C, 10 min; then DBU, CH$_2$Cl$_2$, 0 °C, 10 min, 84% yield (two steps); (d) LiBH$_4$, THF, 0–25 °C, 1 h; then NaBH$_4$, 25 °C, 4 h, 72% yield (two steps).

Reactions with carbon nucleophiles were examined using the procedure reported by Evans and co-workers.[8a] The addition of various nucleophiles afforded relatively stable pyrrole carbinol intermediate (A) in Scheme 2. Treatment of the pyrrole carbinol with DBU promoted the elimination of pyrrole to afford the corresponding product (B). Pyrrolyl epoxide **8a** was converted to β-ketoester **9** in 74% yield by the addition of lithium enolate prepared from *t*-butyl acetate, followed by treatment with DBU. α,β-Epoxy ketone **10** was obtained in 88% yield using PhLi and DBU. The addition of lithiated alkyne gave **11** in 84% yield after treatment with DBU. In two steps, **8q** was reduced to epoxyalcohol **12**; successive treatment with LiBH$_4$ and NaBH$_4$ gave **12** in 72% yield.

5. Conclusion

In summary, the utility of α,β-unsaturated *N*-acylpyrroles as monodentate and activated ester equivalent acceptors was demonstrated in catalytic asymmetric epoxidation reactions. Various α,β-unsaturated *N*-acylpyrroles were synthesized using either Wittig reagent **4** or HWE reagent **6**. A Sm(*O*-*i*-Pr)$_3$/(*S*)-H$_8$-BINOL complex promoted the epoxidation reaction to afford products in high yield (up to quant) and high enantiomeric excess (up to >99.5% ee). The reaction proceeded smoothly using the less explosive CMHP, and completed within 0.2–0.5 h. Catalyst loading was also successfully reduced to as little as 0.02 mol % with TBHP as an oxidant, realizing high TON (up to 4710) and TOF (up to >3000 h^{-1}) of the catalyst.

6. Experimental

6.1. General

Infrared (IR) spectra were recorded on a JASCO FTIR 410 Fourier transform infrared spectrophotometer. NMR spectra were recorded on a JEOL JNM-LA500 spectrometer, operating at 500 MHz for ^{1}H NMR and 125.65 MHz for ^{13}C NMR. Chemical shifts in CDCl$_3$ were reported downfield from TMS (=0) or in the scale relative to CHCl$_3$ (7.24 ppm) for ^{1}H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to $CHCl_3$ (77.0 ppm) as an internal reference. Optical rotations were measured on a JASCO P-1010 polarimeter. ESI mass spectra were measured on Waters-ZQ4000. FAB mass spectra were measured on JMS-MS 700V. Column chromatography was performed with silica gel Merck 60 (230–400 mesh ASTM). The enantiomeric excess (ee) was determined by HPLC analysis. HPLC was performed on JASCO HPLC systems consisting of the following: pump, PU-2080; detector, UV-2075, measured at 254 nm; column, DAICEL CHIRALCEL OJ, CHIRALPAK AD, AS, AD-H; mobile phase, hexane/2-propanol; flow rate, 1.0 mL min^{-1}. Reactions were carried out in dry solvent under argon atmosphere, unless otherwise stated. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Sm(*O*-*i*-Pr)$_3$ was purchased from Kojundo Chemical Laboratory Co., Ltd (fax: +81 492 84 1351; e-mail: sales@kojundo.co.jp). Cumene hydroperoxide (CMHP: 80% tech. grade) and *tert*-butyl hydroperoxide (TBHP: 5–6 M in decane) were purchased from Aldrich and used as received. Other reagents were purified by the usual methods.

6.2. Synthesis of pyrrolylmethylenetriphenylphosphorane (ylide: 4)

To a suspension of methyltriphenylphosphonium bromide (12.9 g, 36 mmol) in THF (14 mL) at 0 °C was added PhLi (Et_2O solution, 28.1 mL, 36 mmol). The mixture was stirred at 25 °C for 60 min to afford methylenetriphenylphosphorane **3**. Then, the mixture was cooled down to −78 °C, and then the solution of 1,1′-carbonyldipyrrole **2** (1.92 g, 12 mmol) in THF (18 mL) was added. The cooling bath was removed and the reaction mixture was stirred overnight at room temperature. H_2O was added and the mixture was extracted with ethyl acetate/CH_2Cl_2=5/1 (×3). The organic layers were washed with brine and dried over $MgSO_4$. After evaporation, the residue was purified by silica gel flash column chromatography to afford ylide **4** (4.33 g, 11.7 mmol, 98% yield); IR (KBr) ν 3434, 3048, 1601, 1438 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.68 (m, 6H), 7.56 (m, 3H), 7.47 (m, 6H), 7.33–7.35 (m, 2H), 6.15–6.18 (m, 2H), 3.71 (d, J=9.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 38.0 (d, $J_{(C–P)}$=125 Hz), 109.3, 118.3, 126.4 (d, $J_{(C–P)}$=91.5 Hz), 128.8 (d, $J_{(C–P)}$=12.4 Hz), 132.1 (d, $J_{(C–P)}$=2.1 Hz), 132.9 (d, $J_{(C–P)}$=10.3 Hz); ESIMS *m/z* 370 $[M+H]^+$; HRMS (FAB) *m/z* calcd for $C_{24}H_{21}ONP$ $[M+H]^+$: 370.1361; found: 370.1369.

6.3. General procedure of Wittig reaction for the synthesis of α,β-unsaturated *N*-acylpyrroles 1

To the suspension of ylide **4** (240 mg, 0.65 mmol) in toluene (1.25 mL) was added benzaldehyde **7a** (50.8 μL, 0.5 mmol). The suspension was stirred for 48 h at 100 °C, and cooled down to room temperature. The reaction mixture was evaporated under reduced pressure, and the residue was purified by silica gel flash column chromatography (hexane/ethyl acetate=20/1) to give **1a** in 97% yield.

6.4. Preparation of HWE reagent 6

To a stirred solution of diethyl methylphosphonate (**5**, 12.4 mL, 84.9 mmol) in THF (300 mL) at −78 °C was added BuLi (85.2 mmol, 53.9 mL, 1.58 M in hexane) slowly over 30 min. The mixture was stirred at −65 °C for 90 min, and then carbonyldipyrrole (**2**, 12.5 g, 77.6 mmol) in THF (35 mL) was added slowly over 20 min. The mixture was stirred at the same temperature for 1 h, and then the mixture was gradually warmed to room temperature over 2 h. The reaction mixture was quenched with satd aq NH_4Cl and the mixture was vigorously stirred for 2 h at room temperature. The mixture was extracted with ethyl acetate. The organic layer was washed with brine, and dried over Na_2SO_4. After removing the solvent, the residue was purified by silica gel flash column chromatography (hexane/ethyl acetate=2/1 to 0/1) to give **6** (18.0 g, 94% yield); IR (neat) ν 587, 746, 922, 973, 1025, 1164, 1255, 1336, 1472, 1713, 2985, 3288 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26–1.29 (m, 6H), 3.43 (d, J=22.5 Hz, 2H), 4.11–4.16 (m, 4H), 6.27–6.28 (m, 2H), 7.30 (br s, 2H); ^{13}C NMR ($CDCl_3$) δ 162.6, 119.6, 113.5, 62.8, 34.9 (d, $J_{(C–P)}$=133 Hz), 16.0; ESIMS *m/z* 268 $[M+Na]^+$; HRMS (FAB) *m/z* calcd for $C_{10}H_{16}O_4NCsP$ $[M+Cs]^+$: 377.9871; found: 377.9868.

6.5. Representative HWE procedure for the synthesis of α,β-unsaturated *N*-acylpyrrole 1

LiCl (2.54 g, 60 mmol) in a 500 mL flask was flame dried prior to use. Then, CH_3CN (200 mL) was added, and the mixture was cooled at 0 °C. To the mixture were added phosphonate **6** (8.06 g, 33 mmol) and Hünig's base (10.2 mL, 60 mmol). The mixture was stirred at 0 °C for 20 min, and then was added aldehyde **7o** (3.22 mL, 30 mmol). The mixture was stirred at room temperature for 13 h, and H_2O was added. The mixture was extracted with ethyl acetate. The organic layer was washed with brine, and was dried over Na_2SO_4. After removing the solvent, the residue was purified by silica gel flash column chromatography (hexane/ethyl acetate=30/1) to give **1o** (5.16 g, 96% yield).

6.5.1. (2*E*)-3-Phenyl-1-pyrrol-1-yl-2-propen-1-one (1a). Colorless solid; IR (KBr) ν 1688, 1624, 1467, 1351 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.98 (d, J=15.6 Hz, 1H), 7.61 (dd, J=3.7, 3.4 Hz, 2H), 7.40–7.49 (m, 4H), 7.13 (d, J=15.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 162.9, 147.5, 134.2, 130.9, 129.0, 128.4, 119.2, 115.7, 113.3; ESIMS: *m/z* 220 $[M+Na]^+$; HRMS (FAB) *m/z* calcd for $C_{13}H_{12}ON$ $[M+H]^+$: 198.0920; found: 198.0919.

6.5.2. (2*E*)-3-(2-Naphthyl)-1-pyrrol-1-yl-2-propen-1-one (1b). Colorless solid; IR (KBr) ν 1680, 1617, 1466, 1300 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.15 (d, J=15.3 Hz, 1H), 8.03 (s, 1H), 7.84–7.91 (m, 3H), 7.75 (m, 1H), 7.51–7.57 (m, 4H), 7.26 (d, J=15.3 Hz, 1H), 6.30–6.35 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 163.0, 147.6, 134.5, 133.3, 131.7, 130.8, 128.8, 128.7, 127.6, 126.9, 123.4, 119.3, 115.8, 113.3; ESIMS: *m/z* 270 $[M+Na]^+$; HRMS (FAB) *m/z* calcd for $C_{17}H_{14}ON$ $[M+H]^+$: 248.1075; found: 248.1075.

6.5.3. (2*E*)-3-(4-Methylphenyl)-1-pyrrol-1-yl-2-propen-1-one (1c). Colorless solid; IR (KBr) ν 1686, 1621, 1467, 1352 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.96 (d, J=15.6 Hz, 1H), 7.51 (d, J=8.0 Hz, 2H), 7.45 (br s, 2H), 7.22 (d, J=8.0 Hz, 2H), 7.09 (d, J=15.6 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 163.1, 147.6, 141.6, 131.5, 129.7, 128.5, 119.2, 114.5, 113.2, 21.5; ESIMS: *m/z* 234 $[M+Na]^+$; HRMS (FAB) *m/z* calcd for $C_{14}H_{14}NO$ $[M+H]^+$: 212.1075; found: 212.1076.

6.5.4. (2*E*)-3-(4-Methoxyphenyl)-1-pyrrol-1-yl-2-propen-1-one (1d). Colorless solid; IR (KBr) ν 1687, 1625, 1603, 1512, 1466, 1248 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.94 (d, *J*=15.3 Hz, 1H), 7.57 (d, *J*=8.5 Hz, 2H), 7.45 (br s, 2H), 6.99 (d, *J*=15.3 Hz, 1H), 6.93 (d, *J*=8.5 Hz, 2H), 6.33 (br s, 2H), 3.85 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 163.2, 161.9, 147.3, 130.2, 127.0, 119.2, 114.4, 113.0, 55.4; ESIMS: *m/z* 250 [M+Na]$^+$; HRMS (FAB) *m/z* calcd for $C_{14}H_{14}O_2N$ [M+H]$^+$: 228.1024; found: 228.1020.

6.5.5. (2*E*)-3-(4-Bromophenyl)-1-pyrrol-1-yl-2-propen-1-one (1e). Colorless solid; IR (KBr) ν 2922, 1685, 1622, 1471 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.92 (d, *J*=15.6 Hz, 1H), 7.45–7.59 (m, 6H), 7.13 (d, *J*=15.6 Hz, 1H), 6.36–6.38 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 162.7, 146.1, 133.1, 132.3, 129.8, 125.3, 119.2, 116.3, 113.5; ESIMS: *m/z* 298, 300 [M+Na]$^+$; HRMS (FAB) *m/z* calcd for $C_{13}H_{11}ONBr$ [M+H]$^+$: 276.0014; found: 276.0019.

6.5.6. (2*E*)-3-(4-Chlorophenyl)-1-pyrrol-1-yl-2-propen-1-one (1f). Colorless solid; IR (KBr) ν 1674, 1620, 1469, 1352, 1255 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.87 (d, *J*=15.6 Hz, 1H), 7.49 (d, *J*=8.6 Hz, 2H), 7.39 (dd, *J*=2.5, 2.2 Hz, 2H), 7.34 (d, *J*=8.6 Hz, 2H), 7.04 (d, *J*=15.6 Hz, 1H), 6.30 (dd, *J*=2.5, 2.2 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 162.6, 146.0, 136.9, 132.7, 129.6, 129.3, 119.2, 116.2, 113.5; ESIMS: *m/z* 254 [M+Na]$^+$; HRMS (FAB) *m/z* calcd for $C_{13}H_{11}ONCl$ [M+H]$^+$: 232.0529; found: 232.0529.

6.5.7. (2*E*)-3-(3-Chlorophenyl)-1-pyrrol-1-yl-2-propen-1-one (1g). Colorless solid; IR (KBr) ν 1685, 1623, 1466 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.90 (d, *J*=15.6 Hz, 1H), 7.60 (s, 1H), 7.35–7.49 (m, 5H), 7.14 (d, *J*=15.6 Hz, 1H), 6.36–6.39 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 162.5, 145.8, 136.0, 135.0, 130.7, 130.3, 127.9, 126.8, 119.2, 117.1, 113.6; ESIMS: *m/z* 254, 256 [M+Na]$^+$; HRMS (FAB) *m/z* calcd for $C_{13}H_{11}ONCl$ [M+H]$^+$: 232.0529; found: 232.0534.

6.5.8. (2*E*)-3-(2-Chlorophenyl)-1-pyrrol-1-yl-2-propen-1-one (1h). Colorless solid; IR (KBr) ν 1685, 1621, 1469, 1349, 1285 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.30 (d, *J*=15.6 Hz, 1H), 7.64 (d, *J*=5.8 Hz, 1H), 7.39 (br s, 3H), 7.28 (m, 2H), 7.09 (d, *J*=15.6 Hz, 1H), 6.30 (br s, 2H); ^{13}C NMR (CDCl$_3$) δ 162.5, 143.3, 135.4, 132.6, 131.5, 130.4, 127.9, 127.1, 119.3, 118.6, 113.5; ESIMS: *m/z* 254 [M+Na]$^+$; HRMS (FAB) *m/z* calcd for $C_{13}H_{11}ONCl$ [M+H]$^+$: 232.0529; found: 232.0526.

6.5.9. (2*E*)-3-(1-Naphthyl)-1-pyrrol-1-yl-2-propen-1-one (1i). Colorless solid; IR (KBr) ν 1682, 1616, 1471, 1357 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.76 (d, *J*=15.0 Hz, 1H), 8.18 (d, *J*=8.3 Hz, 1H), 7.88 (d, *J*=8.3 Hz, 1H), 7.79 (d, *J*=7.0 Hz, 1H), 7.42–7.57 (m, 5H), 6.31 (br s, 2H); ^{13}C NMR (CDCl$_3$) δ 162.8, 144.6, 133.7, 131.7, 131.5, 131.2, 128.8, 127.1, 126.4, 125.4, 125.2, 123.3, 119.3, 118.4, 113.4, 113.2; ESIMS: *m/z* 270 [M+Na]$^+$; HRMS (FAB) *m/z* calcd for $C_{17}H_{14}ON$ [M+H]$^+$: 248.1075; found: 248.1077.

6.5.10. (2*E*)-3-(2-Furyl)-1-pyrrol-1-yl-2-propen-1-one (1j). Colorless solid; IR (KBr) ν 1688, 1618, 1468 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.73 (d, *J*=15.3 Hz, 1H), 7.55 (br s, 1H), 7.45–7.48 (m, 2H), 7.04 (d, *J*=15.3 Hz, 1H), 6.74 (d, *J*=3.1 Hz, 1H), 6.53 (dd, *J*=1.9, 3.1 Hz, 1H), 6.34–6.37 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 162.8, 150.9, 145.2, 133.1, 119.1, 116.6, 113.2, 113.0, 112.7; ESIMS: *m/z* 210 [M+Na]$^+$; HRMS (FAB) *m/z* calcd for $C_{11}H_{10}O_2N$ [M+H]$^+$: 188.0711; found: 188.0716.

6.5.11. (2*E*)-1-Pyrrol-1-yl-3-(2-thienyl)-2-propen-1-one (1k). Colorless solid; IR (KBr) ν 1686, 1609, 1466 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.10 (d, *J*=15.0 Hz, 1H), 7.43–7.47 (m, 3H), 7.37 (d, *J*=3.4 Hz, 1H), 7.10 (dd, *J*=3.4, 4.5 Hz, 1H), 6.92 (d, *J*=15.0 Hz, 1H), 6.34–6.38 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 162.7, 139.8, 139.5, 132.4, 129.3, 128.4, 119.1, 114.2, 113.3; ESIMS: *m/z* 226 [M+Na]$^+$; HRMS (FAB) *m/z* calcd for $C_{11}H_{10}ONS$ [M+H]$^+$: 204.0483; found: 204.0489.

6.5.12. (2*E*)-3-(4-Pyridyl)-1-pyrrol-1-yl-2-propen-1-one (1l). Colorless solid; IR (KBr) ν 1687, 1466 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.70 (d, *J*=4.9 Hz, 1H), 7.87 (d, *J*=15.5 Hz, 1H), 7.43–7.46 (m, 4H), 7.29 (d, *J*=15.5 Hz, 1H), 6.36–6.38 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 162.0, 150.7, 144.4, 141.2, 121.9, 120.3, 119.2, 113.9; ESIMS: *m/z* 199 [M+H]$^+$; HRMS (FAB) *m/z* calcd for $C_{12}H_{11}ON_2$ [M+H]$^+$: 199.0871; found: 199.0871.

6.5.13. (2*E*)-4,4-Dimethyl-5-phenyl-1-pyrrol-1-yl-2-penten-1-one (1m). IR (KBr) ν 2956, 1682, 1629, 1469, 1349, 1297 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.05–7.38 (m, 8H), 6.25–6.29 (m, 3H), 2.71 (s, 2H), 1.12 (s, 6H); ^{13}C NMR (CDCl$_3$) δ 163.0, 160.7, 137.4, 130.4, 130.2, 128.1, 127.9, 126.4, 119.2, 116.3, 113.1, 48.5, 38.5, 26.1; ESIMS: *m/z* 276 [M+Na]$^+$; HRMS (FAB) *m/z* calcd for $C_{17}H_{20}ON$ [M+H]$^+$: 254.1545; found: 254.1542.

6.5.14. (2*E*)-5-Benzyloxy-4,4-dimethyl-1-pyrrol-1-yl-2-penten-1-one (1n). Pale yellow oil; IR (neat) ν 2963, 2868, 1697, 1637, 1467, 1344, 1305, 1267 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.22–7.36 (m, 8H), 6.50 (d, *J*=15.6 Hz, 1H), 6.29 (dd, *J*=2.5, 2.2 Hz, 2H), 4.51 (s, 2H), 3.31 (s, 2H), 1.15 (s, 6H); ^{13}C NMR (CDCl$_3$) δ 163.1, 158.8, 138.2, 128.3, 127.5, 127.4, 119.2, 117.0, 113.0, 77.9, 73.3, 38.8, 23.9; ESIMS: *m/z* 306 [M+Na]$^+$; HRMS *m/z* calcd for $C_{18}H_{21}O_2N$ [M+H]$^+$: 284.1650; found: 284.1647.

6.5.15. (2*E*)-5-Methyl-1-pyrrol-1-yl-2-hexen-1-one (1o). Colorless liquid; IR (neat) 3150, 2958, 1697, 1641,1468, 1408, 1356, 1281, 1122, 742 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.41 (t, *J*=2.1 Hz, 2H), 7.29 (dt, *J*=7.6, 15.3 Hz, 1H), 6.58 (d, *J*=15.3 Hz, 1H), 6.35 (t, *J*=2.1 Hz, 2H), 2.29–2.22 (m, 2H), 1.87 (sept, *J*=6.7 Hz, 1H), 1.00 (d, *J*=6.7 Hz, 6H); ^{13}C NMR (CDCl$_3$) δ 162.7, 151.8, 120.4, 119.2, 113.1, 42.0, 27.9, 22.4; EIMS: *m/z* 177 [M+]; HRMS (EI) *m/z* calcd for $C_{11}H_{15}NO$ [M$^+$]: 177.1154; found: 177.1163.

6.5.16. (2*E*)-1-Pyrrol-1-yl-2-hexen-1-one (1p). Light yellow liquid; IR (neat) 3149, 2961, 1698, 1641, 1468, 1355, 1277, 1121, 1072, 940 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.38 (t, *J*=2.3 Hz, 2H), 7.27 (dt, *J*=7.2, 15.2 Hz, 1H), 6.56 (d, *J*=15.2 Hz, 1H), 6.32 (t, *J*=2.3 Hz, 2H), 2.34–2.29 (m, 2H), 1.62–1.51 (m, 2H), 0.98 (t, *J*=7.5 Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 162.8, 152.7, 119.5, 119.2, 113.1, 34.8, 21.3, 13.7; MS: *m/z* 163 [M$^+$]; HRMS (EI) *m/z* calcd for C_{10}H13NO [M$^+$]: 163.0997; found: 163.0997.

6.5.17. (2*E*)-5-Phenyl-1-pyrrol-1-yl-2-penten-1-one (1q). Colorless oil; IR (neat) ν 1694, 1643, 1467, 1363, 1280 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.38–7.16 (m, 8H), 6.53 (d, *J*=15.0 Hz, 1H), 6.31 (dd, *J*=2.5, 2.2 Hz, 2H), 2.85 (t, *J*=7.6 Hz, 2H), 2.71–2.62 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 162.6, 151.2, 140.4, 128.5, 128.3, 126.2, 120.1, 119.1, 113.1, 34.3, 34.2; ESIMS: *m/z* 308 [M+Na]$^+$; HRMS (FAB) *m/z* calcd for $C_{15}H_{16}ON$ [M+H]$^+$: 226.1232; found: 226.1234.

6.5.18. (2*E*)-1-Pyrrol-1-yl-tridec-2,12-dien-1-one (1r). Colorless oil; IR (neat) ν 2926, 2854, 1702, 1642, 1467, 1351, 1291 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.38 (t, *J*=2.4 Hz, 2H), 7.27 (m, 1H), 6.55 (d, *J*=15.0 Hz, 1H), 6.32 (dd, *J*=2.5, 2.2 Hz, 2H), 5.81 (m, 1H), 4.99 (d, *J*=16.9 Hz, 1H), 4.93 (d, *J*=10.1 Hz, 1H), 2.33 (m, 2H), 2.03 (m, 2H), 1.25–1.59 (m, 12H); ^{13}C NMR (CDCl$_3$) δ 167.8, 152.9, 139.1, 119.3, 119.2, 114.1, 113.1, 33.7, 32.8, 29.3, 29.3, 29.1, 29.0, 28.8, 28.0; ESIMS: *m/z* 282 [M+Na]$^+$; HRMS (FAB) *m/z* calcd for $C_{17}H_{26}ON$ [M+H]$^+$: 260.2014; found: 260.2014.

6.5.19. (2*E*)-3-Cyclohexyl-1-pyrrol-1-yl-2-propen-1-one (1t). Colorless oil; IR (neat) ν 2926, 2852, 1696, 1634, 1468, 1346, 1286 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.38 (dd, *J*=2.5, 2.2 Hz, 2H), 7.22 (dd, *J*=15.3, 7.1 Hz, 1H), 6.50 (dd, *J*=15.3, 1.3 Hz, 1H), 6.32 (dd, *J*=2.5, 2.2 Hz, 2H), 2.26 (m, 1H), 1.65–1.90 (m, 5H), 1.15–1.40 (m, 5H); ^{13}C NMR (CDCl$_3$) δ 163.1, 157.6, 119.1, 116.9, 113.0, 41.0, 31.6, 25.8, 25.6; ESIMS: *m/z* 226 [M+Na]$^+$; HRMS (FAB) *m/z* calcd for $C_{15}H_{23}O_4$ [M+H]$^+$: 204.1388; found: 204.1382.

6.6. General procedure for catalytic asymmetric epoxidation reaction with 5 mol % catalyst loading

MS (4 Å, 500 mg, powdered) in a flask was dried prior to use at 160 °C under vacuum (0.7 KPa) for 3 h. To a stirred suspension of $Ph_3P(O)$ (139 mg, 0.5 mmol), (*R*)-H$_8$-BINOL (7.36 mg, 0.025 mmol), and 4 Å MS in THF (1.0 mL) and toluene (1.2 mL) at 25 °C was added Sm(*O*-*i*-Pr)$_3$ (0.125 mL, 0.025 mmol, 0.2 M in THF). The mixture was stirred for 10 min at 25 °C and cumene hydroperoxide (CMHP) (0.14 mL, 0.75 mmol, 80% tech. grade) was added. After 5 min, the color of the mixture became pale orange, and then **1a** (98.6 mg, 0.5 mmol) was added. The reaction was quenched with 2.5% aq citric acid. The mixture was extracted with ethyl acetate (×3). Then combined organic layers were washed successively with satd aq NaHCO$_3$ and brine, and then dried over MgSO$_4$. The solvent was evaporated and the resulting crude residue was purified by flash silica gel column chromatography (ethyl acetate/hexane=1/20) to afford **8a** (98% yield, >99.5% ee).

6.7. Procedure for catalytic asymmetric epoxidation reaction with reduced catalyst loading (0.02 mol %)

MS (4 Å, 1000 mg, powdered) in a flask was dried prior to use at 160 °C under vacuum (0.7 KPa) for 3 h. To a stirred suspension of **1a** (1.97 g, 10 mmol), $Ph_3As(O)$ (0.644 mg, 0.002 mmol), and (*R*)-H$_8$-BINOL (0.589 mg, 0.002 mmol) in THF (2.0 mL) at 25 °C was added Sm(*O*-*i*-Pr)$_3$ (10 μL, 0.002 mmol, 0.2 M in THF). The mixture was stirred for 15 min at 25 °C and then the mixture was cooled to 0 °C. *tert*-Butyl hydroperoxide (TBHP) (15 mmol, 4.5 M in toluene, dried with 4 Å MS) was added slowly over 60 min (45 min at 0 °C, then 15 min at 25 °C). The stirring was continued for additional 30 min at 25 °C and quenched with 2.5% aq citric acid. The mixture was filtered through Celite and the filtrate was extracted with ethyl acetate. Then combined organic layers were washed successively with satd aq NaHCO$_3$ and brine, and then dried over MgSO$_4$. The solvent was evaporated and the resulting crude residue was purified by flash silica gel column chromatography (ethyl acetate/hexane=1/15) to afford **8a** (2.01 g, 94.2% yield, 99% ee).

6.7.1. (2*S*,3*R*)-*trans*-2,3-Epoxy-3-phenyl-1-pyrrol-1-yl-propan-1-one (8a). IR (KBr) ν 3149, 1714, 1287, 904 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.32–7.42 (m, 7H), 6.33–6.36 (m, 2H), 4.20 (d, *J*=1.9 Hz, 1H), 4.01 (d, *J*=1.9 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 57.3, 58.8, 114.1, 119.0, 125.7, 128.8, 129.2, 134.4, 164.3; ESIMS *m/z* 236 [M+Na]$^+$; $[\alpha]_D^{24}$ +150 (*c* 1.07, CHCl$_3$) (>99.5% ee); HRMS calcd for $C_{13}H_{12}NO_2$ [M+H]$^+$: 214.0868; found: 214.0870; HPLC (DAICEL CHIRALPAK AD, 2-propanol/hexane=2/98, flow 1.0 mL min^{-1}, detection at 254 nm) t_R 28.0 min (minor) and 36.0 min (major).

6.7.2. (2*S*,3*R*)-*trans*-2,3-Epoxy-3-(2-naphthyl)-1-pyrrol-1-yl-propan-1-one (8b). IR (KBr) ν 1716, 1288, 910, 818 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.82–7.89 (m, 4H), 7.50–7.53 (m, 2H), 7.41 (br, 1H), 7.37 (dd, *J*=8.3, 1.2 Hz, 1H), 6.33–6.36 (m, 2H), 4.37 (br, 1H), 4.11 (d, *J*=1.8 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 57.5, 59.1, 114.2, 119.1, 122.2, 125.9, 126.8, 126.8, 127.9, 127.9, 128.9, 131.8, 133.0, 133.7, 164.3; ESIMS *m/z* 286 [M+Na]$^+$; $[\alpha]_D^{24}$ +169 (*c* 1.01, CHCl$_3$); HRMS calcd for $C_{17}H_{14}NO_2$ [M+H]$^+$: 264.1024; found: 264.1023; HPLC (DAICEL CHIRALPAK AD, 2-propanol/hexane=2/98, flow 1.0 mL min^{-1}, detection at 254 nm) t_R 31.4 min (minor) and 40.0 min (major).

6.7.3. (2*S*,3*R*)-*trans*-2,3-Epoxy-3-(4-methylphenyl)-1-pyrrol-1-yl-propan-1-one (8c). IR (KBr) ν 3152, 1713, 1284, 800 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.20–7.26 (m, 2H), 6.35–6.37 (m, 2H), 4.18 (d, *J*=1.7 Hz, 1H), 4.02 (d, *J*=1.7 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 21.2, 57.3, 58.9, 114.1, 119.0, 125.7, 129.5, 131.4, 139.3, 164.5; ESIMS *m/z* 250 [M+Na]$^+$; $[\alpha]_D^{25}$ +153 (*c* 1.22, CHCl$_3$); HRMS calcd for $C_{14}H_{14}NO_2$ [M+H]$^+$: 228.1024; found: 228.1026; HPLC (DAICEL CHIRALCEL OJ, 2-propanol/hexane=2/98, flow 1.0 mL min^{-1}, detection at 254 nm) t_R 33.1 min (major) and 50.2 min (minor).

6.7.4. (2*S*,3*R*)-*trans*-2,3-Epoxy-3-(4-methoxyphenyl)-1-pyrrol-1-yl-propan-1-one (8d). IR (KBr) ν 1715, 1288, 910, 818 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.39 (br, 2H), 7.26 (d, *J*=8.7 Hz, 2H), 6.91 (d, *J*=8.7 Hz, 2H), 6.33–6.35 (m, 2H), 4.14 (d, *J*=1.9 Hz, 1H), 4.00 (d, *J*=1.9 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 55.4, 57.3, 58.8, 114.1, 114.3, 119.0, 126.3, 127.2, 160.5, 164.5; ESIMS *m/z* 266 [M+Na]$^+$; $[\alpha]_D^{25}$ +163 (*c* 0.93, CHCl$_3$); HRMS calcd for $C_{14}H_{14}NO_3$ [M+H]$^+$: 244.0973; found: 244.0968; HPLC (DAICEL CHIRALPAK AS-H, 2-propanol/hexane=20/80, flow 1.0 mL min^{-1}, detection at 254 nm) t_R 20.2 min (minor) and 37.1 min (major).

6.7.5. (2*S*,3*R*)-3-(4-Chlorophenyl)-*trans*-2,3-epoxy-1-pyrrol-1-yl-propan-1-one (8f). IR (KBr) ν 1740, 1288, 798 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35–7.39 (m, 4H), 7.26–7.28 (m, 2H), 6.34–6.36 (m, 2H), 4.18 (d, J=1.7 Hz, 1H), 3.96 (d, J=1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 56.5, 57.4, 113.5, 118.2, 126.3, 128.3, 132.2, 134.5, 163.2; ESIMS *m/z* 270 (for ^{35}Cl), 272 (for ^{37}Cl) $[M+Na]^+$; $[\alpha]_D^{25}$ +153 (*c* 1.11, $CHCl_3$); HRMS calcd for $C_{13}H_{11}ClNO_2$ $[M+H]^+$: 248.0478; found: 248.0474; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane=5/95, flow 1.0 mL min^{-1}, detection at 254 nm) t_R 15.9 min (major) and 18.3 min (minor).

6.7.6. (2*S*,3*R*)-*trans*-2,3-Epoxy-5-phenyl-1-pyrrol-1-yl-pentan-1-one (8q). IR (neat) ν 1723, 1288 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25–7.30 (m, 2H), 7.16–7.23 (m, 5H), 6.28–6.31 (m, 2H), 3.69 (d, J=1.9 Hz, 1H), 3.30 (dt, J=5.8, 1.9 Hz, 1H), 2.85–2.91 (m, 1H), 2.75–2.82 (m, 1H), 2.00–2.11 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 31.7, 33.0, 53.7, 58.8, 113.9, 118.9, 126.4, 128.3, 128.7, 140.2, 165.4; ESIMS *m/z* 264 $[M+Na]^+$; $[\alpha]_D^{24}$ +3.74 (*c* 0.98, $CHCl_3$); HRMS calcd for $C_{15}H_{16}NO_2$ $[M+H]^+$: 242.1181; found: 242.1178; HPLC (DAICEL CHIRALPAK AD, 2-propanol/hexane=2/98, flow 1.0 mL min^{-1}, detection at 254 nm) t_R 22.3 min (minor) and 29.6 min (major).

6.7.7. (2*S*,3*R*)-*trans*-2,3-Epoxy-1-pyrrol-1-yl-tridec-12-en-1-one (8r). IR (KBr) ν 2918, 1719, 1296, 922 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.39–7.41 (m, 2H), 6.33–6.35 (m, 2H), 5.74–5.83 (m, 1H), 4.94–5.00 (m, 1H), 4.89–4.93 (m, 1H), 3.75 (d, J=1.8 Hz, 1H), 3.25 (ddd, J=4.9, 3.1, 1.8 Hz, 1H), 1.99–2.04 (m, 2H), 1.63–1.78 (m, 2H), 1.42–1.53 (m, 2H), 1.22–1.39 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 25.7, 28.9, 29.0, 29.2, 29.3, 29.3, 31.6, 33.8, 53.8, 59.5, 113.9, 114.2, 119.0, 139.1, 165.7; ESIMS *m/z* 298 $[M+Na]^+$; $[\alpha]_D^{25}$ +0.87 (*c* 1.05, $CHCl_3$); HRMS calcd for $C_{17}H_{26}NO_2$ $[M+H]^+$: 276.1963; found: 276.1960; HPLC (DAICEL CHIRALPAK AD, 2-propanol/hexane=2/98, flow 1.0 mL min^{-1}, detection at 254 nm) t_R 15.8 min (minor) and 18.6 min (major).

6.7.8. (2*S*,3*R*)-3-Cyclohexyl-*trans*-2,3-epoxy-1-pyrrol-1-yl-propan-1-one (8t). IR (KBr) ν 3147, 2926, 1718, 1290, 901 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38–7.41 (m, 2H), 6.32–6.35 (m, 2H), 3.82 (d, J=2.2 Hz, 1H), 3.07 (dd, J=2.2, 6.7 Hz, 1H), 1.86–1.91 (m, 1H), 1.73–1.80 (m, 3H), 1.65–1.70 (m, 1H), 1.38–1.47 (m, 1H), 1.11–1.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 25.3, 25.4, 25.9, 28.7, 29.3, 39.6, 52.7, 63.5, 113.8, 118.9, 165.8; ESIMS *m/z* 242 $[M+Na]^+$; $[\alpha]_D^{24}$ −26.1 (*c* 1.02, $CHCl_3$); HRMS calcd for $C_{13}H_{18}NO_2$ $[M+H]^+$: 220.1337; found: 220.1336; HPLC (DAICEL CHIRALPAK AD, 2-propanol/hexane=2/98, flow 1.0 mL min^{-1}, detection at 254 nm) t_R 11.9 min (minor) and 15.9 min (major).

6.8. Transformation of *N*-acylpyrrole unit (Scheme 2)

6.8.1. *tert*-Butyl (4*R*,5*S*)-*trans*-4,5-epoxy-3-oxo-5-phenylpentanoate (9). To a solution of 0.75 M LDA in THF/hexane (1.0 mL, 0.75 mmol) at −78 °C was added *t*-butyl acetate (0.10 mL, 0.742 mmol) slowly over 4 min. The mixture was stirred for 20 min at −78 °C. To this mixture a solution of **8a** (56 mg, 0.262 mmol) in THF (0.8 mL) was added at −78 °C. After stirring for 10 min at −78 °C, satd aq NH_4Cl (1 mL) was added. The mixture was extracted with ethyl acetate. Organic layer was washed with 1 M HCl, pH 7 phosphate buffer, brine, and then dried over Na_2SO_4. After evaporation, the residual oil was dissolved in CH_2Cl_2 (5 mL), DBU (90 mg, in 1 mL CH_2Cl_2) was then added and stirred for 20 min at 25 °C. To the reaction mixture was added $CHCl_3$, and then 1 M HCl was added. The organic layer was washed with pH 7 phosphate buffer, brine, and then dried over Na_2SO_4, filtered, and concentrated. After evaporation, the residue was purified by silica gel column chromatography (hexane/diethyl ether=15/1 to 10/1) to give **9** (51.5 mg, 0.196 mmol, 74% yield) as pale yellow oil: IR (neat) 3437, 2979, 2932, 1733, 1713, 1652, 1457, 1369, 1325, 1253, 1154 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.24–7.43 (m, 5H), 4.06 (d, J=1.7 Hz, 1H), 3.60 (d, J=1.7 Hz, 1H), 3.43 (d, J=3.1 Hz, 2H), 1.47 (s, 9H); ^{13}C NMR ($CDCl_3$) major peaks δ 198.8, 165.6, 134.7, 129.1, 128.7, 128.6, 125.6, 91.7, 82.5, 63.0, 58.0, 45.3, 28.2, 28.1, 27.9; minor peaks δ 172.0, 170.2, 135.7, 81.6, 59.3, 59.1, 31.1; ESIMS *m/z* 285 $[M+Na]^+$; $[\alpha]_D^{24}$ +40.5 (*c* 0.7, $CHCl_3$); HRMS (FAB) *m/z* calcd for $C_{15}H_{19}O_4$ $[M+H]^+$: 263.1283; found: 263.1283.

6.8.2. (2*S*,3*R*)-*trans*-2,3-Epoxy-1,3-diphenylpentan-1-one (10). To a solution of bromobenzene (116 mg, 0.738 mmol) in THF (1.2 mL) at −78 °C was added BuLi (1.58 M in hexane, 0.47 mL, 0.695 mmol). The mixture was stirred for 10 min at the same temperature. A solution of **8a** (96 mg, 0.45 mmol) in THF (1.2 mL) was added at −78 °C. After stirring for 10 min at −78 °C, satd aq NH_4Cl (1.5 mL) was added. The mixture was extracted with ethyl acetate. The organic layer was washed with aq NaH_2PO_4, satd aq $NaHCO_3$, brine, and then dried over Na_2SO_4. After evaporation, the residue was dissolved in CH_2Cl_2, DBU (50 μL) was then added, and the mixture was stirred for 20 min at 25 °C. The mixture was diluted with $CHCl_3$, washed with 1 M HCl, satd aq $NaHCO_3$, brine, and then dried over Na_2SO_4. After evaporation, the residue was purified by silica gel column chromatography (hexane/diethyl ether=10/1) to give **10** (89 mg, 0.3968 mmol, 88% yield) as colorless oil. Analytical data were identical to the reported data.

6.8.3. (1*S*,2*R*)-*trans*-1,2-Epoxy-3-oxo-1-phenyl-4-octyne (11). To a solution of 1-pentyne (0.167 mL, 1.7 mmol) in THF (1.4 mL) at −78 °C was added BuLi (1.56 M in hexane, 0.96 mL, 1.5 mmol). The mixture was stirred for 30 min at the same temperature. To this mixture a solution of **8a** (105 mg, 0.492 mmol) in THF (1.4 mL) was added at −78 °C. After stirring for 10 min at −78 °C, satd aq NH_4Cl (2 mL) was added. The mixture was extracted with ethyl acetate. The organic layer was washed with 1 M HCl, satd aq $NaHCO_3$, brine, and then dried over Na_2SO_4. After evaporation, the obtained residue was dissolved in CH_2Cl_2 (15 mL), DBU (0.184 M in CH_2Cl_2, 0.1 mL, 0.0184 mmol) was then added, and stirred for 10 min at 0 °C. The mixture was diluted with $CHCl_3$, washed with 1 M HCl, satd aq $NaHCO_3$, brine, and then dried over Na_2SO_4. After evaporation, the residue was purified by silica gel column chromatography (hexane/diethyl ether=15/1 to 10/1) to give **11** (88.7 mg, 0.414 mmol, 84% yield) as yellow oil: IR (neat) 2965, 2935, 2875, 2210, 1667, 1457, 1405, 1257, 1179 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.27–7.50 (m, 5H), 4.17 (d, J=1.5 Hz, 1H), 3.61 (d, J=1.8 Hz, 1H), 2.41 (t, J=7.3 Hz, 2H), 1.65 (dq, J=7.3, 7.3 Hz, 2H), 1.04

(t, J=7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 182.6, 134.8, 129.0, 128.7, 125.7, 98.8, 78.3, 63.6, 58.6, 21.1, 13.4; ESIMS *m/z* 237 [M+Na]$^+$; $[\alpha]_D^{24}$ +166 (*c* 0.95, $CHCl_3$); HRMS (FAB) *m/z* calcd for $C_{14}H_{15}O_2$ [M+H]$^+$: 215.1072; found: 215.1074.

6.8.4. (2*R*,3*R*)-*trans*-2,3-Epoxy-5-phenyl-1-pentanol (12). To a suspension of $LiBH_4$ (15.6 mg, 0.72 mmol) in THF (0.8 mL) at 0 °C, was added a solution of **8q** (50.5 mg, 0.209 mmol) in THF (0.8 mL). The mixture was stirred for 20 min at 0 °C, and then at 25 °C for 40 min. The reaction mixture was poured to ethyl acetate/satd aq NH_4Cl mixture at 0 °C. The organic layer was separated, washed with pH 7 phosphate buffer, brine, and then dried over Na_2SO_4. After evaporation, the residual oil was dissolved in THF (1 mL), and the solution was added to the suspension of $NaBH_4$ (27 mg, 0.71 mmol) in THF (1.5 mL) at 25 °C. After stirring for 4 h, the reaction mixture was poured to ethyl acetate/satd aq NH_4Cl mixture at 0 °C. Organic layer was separated, washed with pH 7 phosphate buffer, brine, and then dried over Na_2SO_4. After evaporation, the residue was purified by silica gel column chromatography (hexane/ethyl acetate=3/1) to give **12** (0.151 mmol, 72% yield) as colorless oil: IR (neat) 3409, 2926, 1603, 1496, 1454, 1231, 1087, 878 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.18–7.32(m, 5H), 3.81–3.88 (m, 1H), 3.54–3.60 (m, 1H), 2.98–3.02 (m, 1H), 2.80–2.88 (m, 2H), 2.70–2.78 (m, 1H), 1.84–1.97 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 141.0, 128.4, 128.3, 126.0, 61.6, 58.7, 55.3, 33.2, 32.1; ESIMS *m/z* 201 [M+Na]$^+$; $[\alpha]_D^{25}$ +42.6 (*c* 2.41, $CHCl_3$); HRMS (FAB) *m/z* calcd for $C_{11}H_{15}O_2$ [M+H]$^+$: 179.1072; found: 179.1073.

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Laboratory Co., Ltd (fax: +81 492 84 1351; e-mail: sales@kojundo.co.jp).

16. Reaction rate tendency: chalcone>*N*-acylpyrrole **1a**> benzalacetone. *N*-Acylpyrrole **1a** had slightly lower reactivity than chalcone, and showed slightly higher reactivity than benzalacetone.
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18. The present catalysis is applicable to various α,β-unsaturated *N*-acylpyrroles shown in Tables 1 and 2 to give epoxides in good yield and ee, except for **1m** and **1n**. Epoxidation of α,β-unsaturated *N*-acylpyrroles **1m** and **1n** did not proceed due to steric hindrance.
19. *N*-Acylpyrrole unit can also be transformed into ethyl ester in good yield by treatment with either EtSLi in EtOH or NaOEt in EtOH. See, Refs. 7, 9, and 10.