

**Sequential Wittig Olefination–Catalytic Asymmetric Epoxidation with Reuse of Waste  $\text{Ph}_3\text{P}(\text{O})$ : Application of  $\alpha,\beta$ -Unsaturated *N*-Acyl Pyrroles as Ester Surrogates\*\***

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The catalytic asymmetric epoxidation of  $\alpha,\beta$ -unsaturated carbonyl compounds is an important transformation in organic synthesis.<sup>[1]</sup> Although we<sup>[2]</sup> and others<sup>[1]</sup> have developed efficient catalytic asymmetric epoxidations of  $\alpha,\beta$ -unsaturated ketones, there are only limited examples of the use of  $\alpha,\beta$ -unsaturated esters as substrates with a salen–Mn complex<sup>[3]</sup> or a chiral ketone<sup>[4]</sup> as the catalyst. In both cases,

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except for the recent report of Shi and co-workers,<sup>[4a]</sup> only  $\beta$ -aryl-substituted  $\alpha,\beta$ -unsaturated esters were used. Although Shi and co-workers reported excellent results for a few  $\beta$ -alkyl-substituted substrates, *trans*- $\beta$ -alkyl-substituted  $\alpha,\beta$ -unsaturated esters could not be used, thus leaving room for improvement in substrate generality. We recently reported the catalytic asymmetric epoxidation of  $\alpha,\beta$ -unsaturated 4-phenylcarboxylic acid imidazolides<sup>[5,6]</sup> and morpholinyl amides<sup>[6]</sup> as ester surrogates. Although moderate to high enantioselectivities were observed for substrates with  $\beta$ -aryl or  $\beta$ -alkyl substituents (imidazolidine: 79–94% *ee*, amide: 99% *ee*), from a practical viewpoint many problems remained: a) a catalyst loading of 10 mol% was essential for good conversion, b) explosive *tert*-BuOOH (TBHP) was essential as the oxidant for good reactivity, and c) the preparation of  $\beta$ -alkyl  $\alpha,\beta$ -unsaturated carboxylic acid imidazolides from aldehydes was lengthy. To address these issues, we report herein the application of  $\alpha,\beta$ -unsaturated *N*-acyl pyrroles, which were found to be highly reactive and versatile substrates, as ester surrogates. Furthermore, these substrates were used in a one-pot sequential Wittig-olefination–catalytic-asymmetric-epoxidation process in which the  $\text{Ph}_3\text{P}(\text{O})$  formed in the Wittig step was reused in the second step. This process provided efficient access to optically active pyrrolyl epoxides from a variety of aldehydes in high yields and with high enantioselectivities. The versatility of the pyrrolyl epoxide products was also demonstrated.

Although the potential of *N*-acyl pyrroles as ester surrogates was reported two decades ago,<sup>[7]</sup> it was only recently that the unique reactivity of *N*-acyl pyrroles was recognized and utilized in organic synthesis, for example, in asymmetric catalysis.<sup>[8]</sup> A recent report by Evans et al.<sup>[9]</sup> on the unique properties of *N*-acyl pyrroles prompted us to investigate the use of  $\alpha,\beta$ -unsaturated *N*-acyl pyrroles as ester surrogates. As summarized in Table 1, the catalytic asymmetric epoxidation of **1a** proceeded smoothly. When the Sm–(*R*)-binol complex (10 mol%)<sup>[10]</sup> and  $\text{Ph}_3\text{As}(\text{O})$  (10 mol%)<sup>[11]</sup>

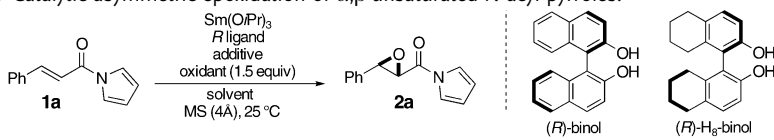
were used, the reaction was complete within 0.5 h and afforded **2a** in 93% yield and with 94% *ee* (Table 1, entry 1). The reaction rate was much faster than for a carboxylic acid imidazolidine or a morpholinyl amide, and as fast as for an enone. The reaction also proceeded smoothly in the presence of 5 mol% of the catalyst (Table 1, entry 2: 85% yield, 96% *ee*). Various binol derivatives were screened in an attempt to improve the enantioselectivity of the reaction, and it was found that  $\text{H}_8$ -binol gave the best results. The superior performance of the  $\text{H}_8$ -binol complex over that of the binol complex is probably a result of the large bite angle in the former complex.<sup>[12]</sup> Compound **2a** was formed with 99% *ee* in the presence of the novel Sm–(*R*)- $\text{H}_8$ -binol complex (Table 1, entry 3).  $\text{Ph}_3\text{P}(\text{O})$  was also an effective additive in the reaction of substrate **1a**<sup>[11]</sup> (Table 1, entries 4–6). A THF/toluene solvent mixture led to better results than THF alone, and **2a** was obtained with 96–99% *ee*, depending on the amount of  $\text{Ph}_3\text{P}(\text{O})$  added (Table 1, entries 7–9). Both the reaction rate and the selectivity were highest when 100 mol% of the  $\text{Ph}_3\text{P}(\text{O})$  additive was used (Table 1, entry 9). Under the best conditions (THF/toluene,  $\text{Ph}_3\text{P}(\text{O})$  (100 mol%)) the reaction proceeded smoothly with a low catalyst loading (1 mol%) to afford **2a** in 94% yield and with 99% *ee* within 0.3 h (Table 1, entry 10). Cumene hydroperoxide (CMHP), which is less explosive and less reactive than TBHP, could also be used. The reaction reached completion in the presence of this oxidant within 0.2 h with 5 mol% of the catalyst (Table 1, entry 11: 91% yield, >99.5% *ee*).<sup>[13]</sup>

One reason that  $\alpha,\beta$ -unsaturated *N*-acyl pyrroles have not been widely used as acceptors in 1,4-addition reactions, despite their high reactivity, might be the lack of an efficient method for their preparation under mild conditions.<sup>[14]</sup> A Wittig reaction of the ylide **3** with aldehydes was examined as a general synthetic approach to a range of functionalized  $\alpha,\beta$ -unsaturated *N*-acyl pyrroles. The ylide **3** was synthesized efficiently in 98% yield in one step from 1,1'-carbonyldipyrrole and methylenetriphenylphosphorane.<sup>[15]</sup> The Wittig reac-

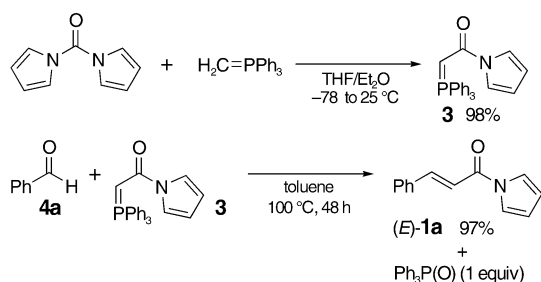
tion of **3** with benzaldehyde (**4a**) proceeded smoothly to afford **1a** in 97% yield, along with a stoichiometric amount of waste  $\text{Ph}_3\text{P}(\text{O})$  (Scheme 1).

Although the functional-group tolerance of the Wittig reaction is good because of the mild conditions, this olefination is generally considered to be somewhat inefficient as a result of the production of  $\text{Ph}_3\text{P}(\text{O})$  as a by-product. We hypothesized that the reuse of waste  $\text{Ph}_3\text{P}(\text{O})$  in the epoxidation reaction as a modulator for the Sm– $\text{H}_8$ -binol complex would partially compensate this disadvantage of the Wittig reaction. Thus, a sequential Wittig olefination–catalytic asymmetric epoxidation was designed in which the  $\text{Ph}_3\text{P}(\text{O})$  produced in the first (Wittig) reac-

**Table 1:** Catalytic asymmetric epoxidation of  $\alpha,\beta$ -unsaturated *N*-acyl pyrroles.

							
Entry	Ligand (mol%) <sup>[a]</sup>	Additive (mol%)	Solvent	Oxidant	<i>t</i> [h]	Yield [%] <sup>[b]</sup>	<i>ee</i> [%] <sup>[c]</sup>
1	binol (10)	$\text{Ph}_3\text{As}(\text{O})$ (10)	THF	TBHP	0.5	93	94
2	binol (5)	$\text{Ph}_3\text{As}(\text{O})$ (5)	THF	TBHP	0.5	85	96
3	$\text{H}_8$ -binol (5)	$\text{Ph}_3\text{As}(\text{O})$ (5)	THF	TBHP	0.5	94	99
4	$\text{H}_8$ -binol (5)	$\text{Ph}_3\text{P}(\text{O})$ (15)	THF	TBHP	0.5	84	94
5	$\text{H}_8$ -binol (5)	$\text{Ph}_3\text{P}(\text{O})$ (50)	THF	TBHP	0.5	88	98
6	$\text{H}_8$ -binol (5)	$\text{Ph}_3\text{P}(\text{O})$ (100)	THF	TBHP	0.5	85	97
7	$\text{H}_8$ -binol (5)	$\text{Ph}_3\text{P}(\text{O})$ (15)	THF/toluene	TBHP	0.4	85	96
8	$\text{H}_8$ -binol (5)	$\text{Ph}_3\text{P}(\text{O})$ (50)	THF/toluene	TBHP	0.5	92	99
9	$\text{H}_8$ -binol (5)	$\text{Ph}_3\text{P}(\text{O})$ (100)	THF/toluene	TBHP	0.2	97	99
10	$\text{H}_8$ -binol (1)	$\text{Ph}_3\text{P}(\text{O})$ (100)	THF/toluene	TBHP	0.3	94	99
11	$\text{H}_8$ -binol (5)	$\text{Ph}_3\text{P}(\text{O})$ (100)	THF/toluene	CMHP	0.2	91	>99.5

[a] Sm(OiPr)<sub>3</sub>/ligand 1:1. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral phase.



**Scheme 1.** Synthesis of the ylide **3** and Wittig reaction.

tion was reused as an additive in the second (epoxidation) reaction. When **4a** was subjected to this olefination–epoxidation sequence, **2a** was produced in 96% yield (two steps) and with 99.8% *ee* (Scheme 2a). As expected, the selectivity and reactivity were much lower when the reaction was performed in two separate steps and no  $\text{Ph}_3\text{P}(\text{O})$  was added in the second step (75.2% *ee*, Scheme 2b). When  $\text{Ph}_3\text{P}(\text{O})$  (15 mol % or 50 mol %) was added in the second step after isolation of intermediate **1a** and removal of the  $\text{Ph}_3\text{P}(\text{O})$  by-product (1 equiv) as waste, **2a** was obtained with 96.8% *ee* or 98.8% *ee*, respectively (Scheme 2b). These results suggested that  $\text{Ph}_3\text{P}(\text{O})$  did indeed function as an effective additive to improve the yield and enantioselectivity of the epoxidation reaction, but that only 0.5–1 equivalent of  $\text{Ph}_3\text{P}(\text{O})$  was required to promote high enantioselectivity. The fact that only one purification step was required in the one-pot process (Scheme 2a), in contrast to the two required in the reaction sequence in Scheme 2b, clearly shows the higher total efficiency of the one-pot sequential process for the synthesis of the epoxide **2a** from the aldehyde **4a**. The total efficiency of

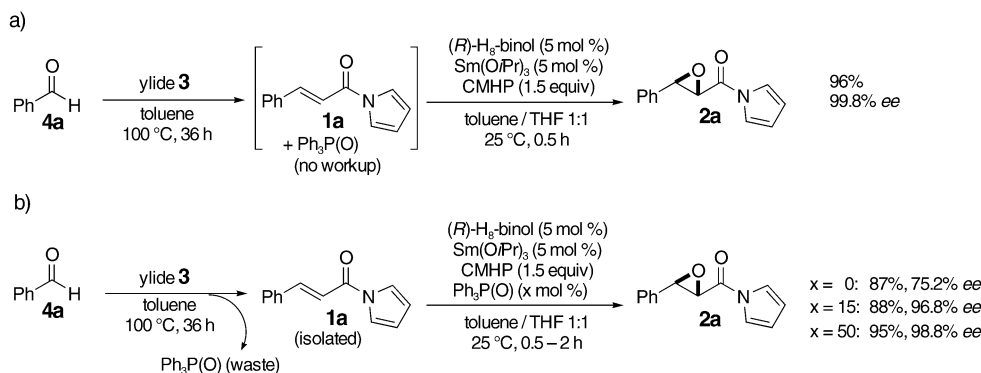
this system is also superior to previous results with carboxylic acid imidazolides<sup>[5,6]</sup> and morpholinyl amides,<sup>[6]</sup> which were synthesized and purified prior to use.

As summarized in Table 2, the sequential reaction described herein has broad substrate generality and affords the desired epoxides with excellent enantioselectivities (96 to > 99.5% *ee*) and in good yields (Table 2, entries 1–13: 72–96% yield from the corresponding aldehydes). Aromatic aldehydes with various substituents (Table 2, entries 1–7), functionalized aliphatic linear and branched aldehydes (Table 2, entries 8–12), and  $\alpha,\beta$ -unsaturated aldehydes (Table 2, entry 13) were all suitable substrates. The reaction proceeded chemoselectively with the aldehyde **4l**, which contains a methyl ketone (Table 2, entry 12). In many examples, less explosive CMHP was used as the oxidant instead of TBHP, which demonstrates an additional practical benefit of this methodology. When the chiral aldehyde **4n** was used, the sequential reaction proceeded in an almost com-

**Table 2:** Sequential Wittig olefination–catalytic asymmetric epoxidation with achiral aldehydes.

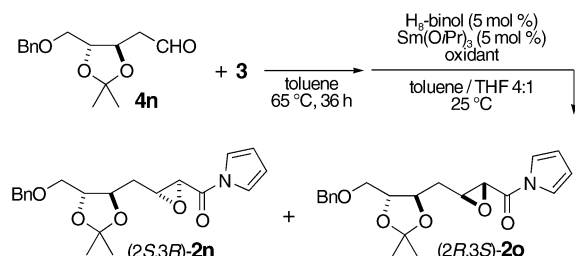
Entry	R	Wittig reaction T [°C]	Wittig reaction t [h]	Epoxidation t [h]	Yield [%] <sup>[a]</sup>	<i>ee</i> [%] <sup>[b]</sup>
1	$\text{C}_6\text{H}_5$ -	<b>4a</b> 100	48	0.5	96	> 99.5
2	<i>p</i> -Me- $\text{C}_6\text{H}_4$ -	<b>4b</b> 100	48	2.5	92	99
3	<i>p</i> -Cl- $\text{C}_6\text{H}_4$ -	<b>4c</b> 100	24	0.5	100	99
4 <sup>[c]</sup>	<i>p</i> -MeO- $\text{C}_6\text{H}_4$ -	<b>4d</b> 110	84	0.5	87	98
5 <sup>[c]</sup>	<i>o</i> -Cl $\text{C}_6\text{H}_4$ -	<b>4e</b> 100	24	0.5	83	97
6	2-naphthyl	<b>4f</b> 100	48	2	100	99
7	1-naphthyl	<b>4g</b> 100	48	0.5	85	99
8	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2$ -	<b>4h</b> 80	24	0.5	84	97
9	$\text{PMBOCH}_2\text{CH}_2$ -	<b>4i</b> 80	24	0.5	91	97
10	$\text{CH}_2=\text{CH}(\text{CH}_2)_8$ -	<b>4j</b> 100	25	0.5	82	96
11	<i>c</i> - $\text{C}_6\text{H}_{11}$	<b>4k</b> 100	72	2	75	98
12	$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2$ -	<b>4l</b> 80	36	0.5	93	96
13 <sup>[c,d]</sup>	<i>trans</i> - $\text{CH}_3(\text{CH}_2)_2\text{CH}=\text{CH}$ -	<b>4m</b> 100	72	2	72	96

[a] Yield of the isolated product **2** (from **4**). [b] Determined by HPLC analysis on a chiral phase. [c] *t*BuOOH was used as the oxidant. [d] Catalyst: 10 mol %.



**Scheme 2.** Wittig olefination–catalytic asymmetric epoxidation as a) a one-pot sequential process and b) a stepwise process with isolation of the Wittig product and addition of external  $\text{Ph}_3\text{P}(\text{O})$ .

pletely catalyst-controlled manner (Scheme 3 and Table 3). The epoxide was obtained in a **2n/2o** ratio of >99:1 with the *R*-configured catalyst (matched pair, Table 3, entry 1) and in a **2n/2o** ratio of 1:36 with the *S*-configured catalyst (mismatched pair, Table 3, entry 3). When achiral epoxidation systems were used, much lower selectivity was observed (d.r. 54:46).<sup>[16]</sup>



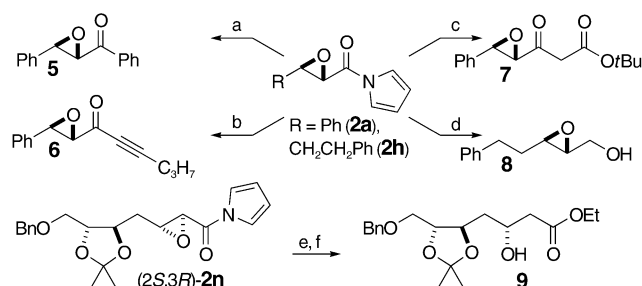
**Scheme 3.** Sequential Wittig olefination-catalytic asymmetric epoxidation with the chiral aldehyde **4n**.

**Table 3:** Sequential Wittig olefination-catalytic asymmetric epoxidation with the chiral aldehyde **4n**.

Entry	Ligand	<i>t</i> [h]	Oxidant	Yield [%] <sup>[a]</sup>	d.r. <sup>[b]</sup> ( <b>2n/2o</b> )
1	( <i>R</i> )-H <sub>8</sub> -binol	0.7	CMHP	80	>99:1
2	( <i>S</i> )-H <sub>8</sub> -binol	0.9	CMHP	60	1:56
3	( <i>S</i> )-H <sub>8</sub> -binol	0.7	TBHP	78	1:36

[a] Yield of the isolated product **2n** (from **4n**). [b] Determined by HPLC analysis.

The versatility of the pyrrolyl epoxide products was demonstrated by transformations of **2** into compounds **5–9** (Scheme 4). The addition of various carbon nucleophiles followed by treatment with DBU afforded **5–7** in good yields.<sup>[17]</sup> The epoxy alcohol **8** was obtained by the stepwise reduction of **2h** with LiBH<sub>4</sub> and NaBH<sub>4</sub>. After the epoxide opening of **2n**, EtSLi in EtOH was determined to be a suitable reagent for the conversion of the *N*-acyl pyrrole into the corresponding ethyl ester **9** in high yield at room temperature.



**Scheme 4.** Various transformations of the pyrrolyl epoxides **2**. a) PhLi, THF; then DBU, CH<sub>2</sub>Cl<sub>2</sub>, 88%; b) BuLi, 1-pentyne, THF; then DBU, CH<sub>2</sub>Cl<sub>2</sub>, 84%; c) *tert*-butyl acetate, LDA, THF; then DBU, CH<sub>2</sub>Cl<sub>2</sub>, 74%; d) LiBH<sub>4</sub>, THF; then NaBH<sub>4</sub>, 72%; e) (PhSe)<sub>2</sub>, NaBH<sub>4</sub>, EtOH/AcOH, 94%; f) EtSLi, EtOH, 92%. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, LDA = lithium diisopropylamide.

In summary, we have developed a sequential Wittig-olefination-catalytic-asymmetric-epoxidation process, which utilizes *N*-acyl pyrroles as ester surrogates and provides efficient one-pot access to optically active epoxides. Good yields and excellent enantioselectivities were observed for a broad range of aldehyde substrates. The Ph<sub>3</sub>P(O) produced in the first step is used to modulate the second step, and CMHP, which is less explosive and thus more practical than TBHP, can be used as the oxidant. The reaction of the ylide **3** with aldehydes proved to be an efficient method for the synthesis of a variety of functionalized α,β-unsaturated *N*-acyl pyrroles, which should also be suitable substrates for asymmetric 1,4-addition reactions.

## Experimental Section

Benzaldehyde (**4a**; 50.8 μL, 0.5 mmol) was added to a stirred suspension of the ylide **3** (139.1 mg, 0.65 mmol) in toluene (1.25 mL) at 25 °C. The mixture was stirred for a further 36 h at 100 °C, then cooled to 25 °C. Toluene (1.25 mL) and a suspension of the catalyst prepared from Sm(OiPr)<sub>3</sub> (125 μL, 0.025 mmol, 0.2 M in THF), (*R*)-H<sub>8</sub>-binol (7.4 mg, 0.025 mmol), CMHP (231 μL, 0.75 mmol, 3.25 M in toluene), and molecular sieves (4 Å) were added to the reaction mixture at 25 °C. The mixture was stirred for a further 0.5 h at 25 °C, then the reaction was quenched with aqueous citric acid (2.5 %), and the mixture was filtered through celite. The filtrate was extracted three times with ethyl acetate, and the combined organic layers were washed with saturated, aqueous NaHCO<sub>3</sub>, then brine, and dried over MgSO<sub>4</sub>. The solvent was evaporated, and the resulting crude residue was purified by flash column chromatography (silica gel, ethyl acetate/hexane 1:20) to afford **2a** (102.4 mg, 96 % yield, >99.5 % ee).

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- [11] Standard conditions for asymmetric epoxidations with lanthanide complexes: Ln(OiPr)<sub>3</sub>/binol/Ph<sub>3</sub>As(O) 1:1:1 and Ln(OiPr)<sub>3</sub>/binol/Ph<sub>3</sub>P(O) 1:1:3; see references [2], [5], and [6]. When an imidazolidine or an amide was the substrate, a catalyst loading of 10 mol % was essential for the reaction to reach completion.
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- [14] The preparation of  $\alpha,\beta$ -unsaturated *N*-acyl pyrroles from the corresponding  $\alpha,\beta$ -unsaturated amides was reported by Evans et al.; see reference [9] and references therein. The reaction of lithiated pyrrole with an acyl halide did not proceed cleanly, although the equivalent reaction of 2-substituted pyrroles has been described; see reference [8c].
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- [16] Use of the system Et<sub>2</sub>Zn/*o*-methoxyphenol/*t*BuOOH led to the epoxide in 76% yield in 18 h at 25°C with low selectivity (d.r. 54:46). Other conditions, such as H<sub>2</sub>O<sub>2</sub>-urea with a base, *m*CPBA, or aqueous NaClO with a phase-transfer catalyst either resulted in the decomposition of the enone or afforded the product in low yield (<20%).
- [17] For reactions of the *N*-acyl pyrrole unit, see reference [9] and references therein.