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Copper-catalyzed asymmetric conjugate addition of diethylzinc to substituted chalcones using a chiral phosphine ligand

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ABSTRACT

A series of chiral phosphine **PFAM** and phosphine oxide **POFAM** ligands were studied for the copper-catalyzed asymmetric diethylzinc addition to enones. One of these ligands, **PFAM2**, was an efficient catalyst with a variety of enones to give conjugate addition products in up to 96% yield and 92% ee.

1. Introduction

Asymmetric catalysis is a useful technique for enantioselective C–C bond formation reactions.[1] This method can provide large amounts of the desired chiral products by using a small amount of chiral catalyst. The chiral catalysts developed so far have some limitations in terms of reaction dependence, substrate dependence, operational difficulties, and in the synthesis of the chiral ligands. Therefore, the development of new efficient chiral catalysts is one of the active research areas in synthetic organic chemistry. Among the various reactions that can be conducted in a catalytic asymmetric manner, 1,4-conjugate additions (Michael additions) have always attracted considerable attention due to their synthetic utility.[2] Many Cu- and Ni-catalyzed enantioselective additions of Et_2Zn to various enones have been reported. It is evident that in numerous asymmetric conjugate additions, phosphine based chiral ligands have been applied to advantage.[3] In this respect, we have developed **PFAM** (phosphino ferrocenyl aziridinyl methanol) ligands and their phosphine oxide **POFAM** ligands (Fig. 1). These compounds are structurally similar to our previously reported chiral **FAM** ligands.[4] One of these ligands (**POFAM6**) was found to be effective for the catalytic asymmetric synthesis of pyrrolidines by 1,3-dipolar cycloaddition reactions of azomethine ylides.[5] Herein we report another application of **PFAM** ligands, the asymmetric Cu-catalyzed 1,4-conjugate addition of diethylzinc to various enones.

2. Results and discussion

Chiral phosphine **PFAM** and phosphine oxide **POFAM** ligands (Fig. 1) were synthesized as reported previously[5] starting from easily available acryloylferrocene[6] by using the Gabriel–Cromwell reaction.[7]

In order to test the catalytic activity of these ligands in the copper-catalyzed asymmetric conjugate addition of diethylzinc to enones, chalcone **1a** was used as the model substrate. Although the ligand screening experiments revealed that **PFAM1**, **POFAM2**, and **PFAM5** (Table 1, entries 1–3) were the most promising ones for forming the product with (*S*)-configuration, **PFAM2** gave the product in highest yield and ee with the (*R*)-configuration (Table 1, entry 4). Therefore, further optimizations were carried out by using this ligand. As can be seen from Table 1, different copper sources, different solvents, different temperatures, and different concentrations of the catalyst (ligand and metal) were tried. From these experiments the use of 2.5 mol % chiral ligand and 1.5 mol % $Cu(OTf)_2$ with 1,2-dichloroethane (DCE) as the solvent at −20 °C was found to be the optimum conditions.

After determining the optimum conditions, different substrates were used in order to show the applicability of this catalyst. The results of these experiments were summarized in Table 2.

In the first series, we investigated the effect of both electron donating (Table 2, entries 2, 3, and 7) and withdrawing groups (Table 2, entries 4–6) on the R^1 unit of the enone. With the *p*-methyl group, product was formed in about the same ee as the first substrate having no substituent but with a lower yield (entry 2). With a strong electron donor methoxy group, the yield was about the same as the first substrate but this time the ee was lower (entry 3). In the case of electron withdrawing groups, strong electron withdrawing trifluoromethyl group, the product was obtained in the highest yield with a similar ee to the first substrate (entry 4). Although a chlorine on the *para*-position of the substrate showed no significant effect on the yield and ee (entry 5) of the reaction, a bromine substituent formed the product in lower yield but slightly better ee (entry 6) compared to the first substrate.

In the case of more bulky substituents on the R^1 unit of the enone, ferrocenyl group formed the product in 83% yield with the

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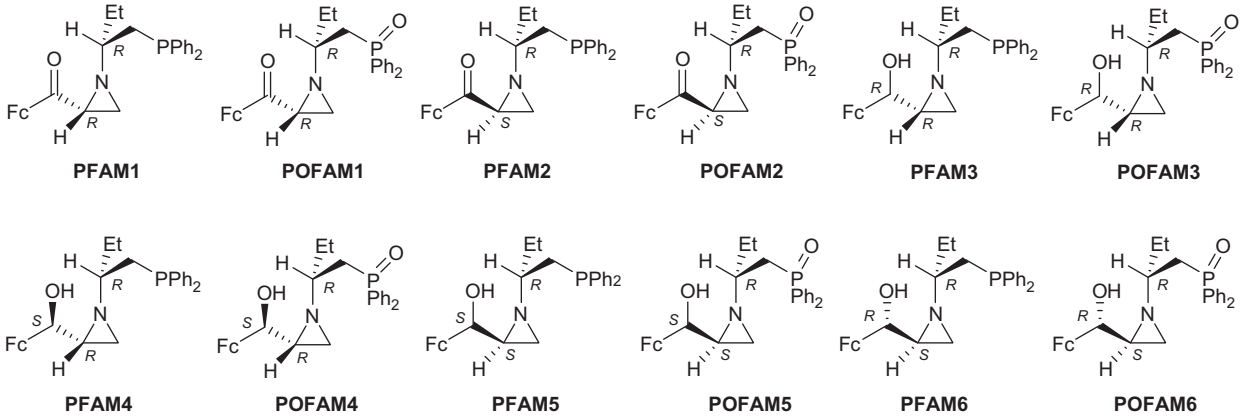
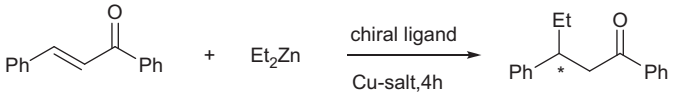


Figure 1. Structures of **PFAM** and **POFAM** ligands.

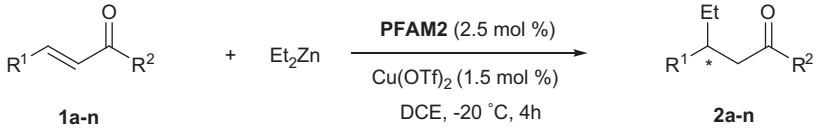
Table 1
Asymmetric ethyl addition to chalcone under different conditions



Entry	Chiral ligand	Ligand (mol %)	Cu salt	Cu salt (mol %)	Temp (°C)	Solvent	Yield[a] (%)	ee[b] (%)	Config.[c]
1	**PFAM1**	12	$Cu(OTf)_2$	10	0	Toluene	66	10	(*S*)
2	**POFAM2**	12	$Cu(OTf)_2$	10	0	Toluene	51	14	(*S*)
3	**PFAM5**	12	$Cu(OTf)_2$	10	0	Toluene	71	14	(*S*)
4	**PFAM2**	12	$Cu(OTf)_2$	10	0	Toluene	75	50	(*R*)
5	**PFAM2**	12	CuCl	10	0	Toluene	70	18	(*R*)
6	**PFAM2**	12	$CuCl_2$	10	0	Toluene	70	12	(*R*)
7	**PFAM2**	12	$Cu(OAc)_2$	10	0	Toluene	70	24	(*R*)
8	**PFAM2**	12	$Cu(OTf)_2$	10	−20	Toluene	85	60	(*R*)
9	**PFAM2**	6	$Cu(OTf)_2$	5	0	Toluene	68	56	(*R*)
10	**PFAM2**	6	$Cu(OTf)_2$	2.5	−20	Toluene/DCE (3:1)	69	72	(*R*)
11	**PFAM2**	2.5	$Cu(OTf)_2$	1.5	−20	DCE	89	88	(*R*)

[a] Isolated yield.
[b] Determined by HPLC using a Chiralcel AD column.
[c] Determined by comparing the literature data.

Table 2
Asymmetric ethyl addition to different enones



1a-n **2a-n**

Entry	R^1	R^2	Substrate	Yield[a] (%)	ee[b] (%)	Optical rotation sign
1	Ph	Ph	**1a**	89	88	–
2	*p*-$CH_3C_6H_4$	Ph	**1b**	79	89	–
3	*p*-$CH_3OC_6H_4$	Ph	**1g**	91	72	–
4	*p*-$CF_3C_6H_4$	Ph	**1c**	96	87	+
5	*p*-ClC_6H_4	Ph	**1d**	88	88	+
6	*p*-BrC_6H_4	Ph	**1i**	81	91	+
7	*m*-$CH_3OC_6H_4$	Ph	**1h**	90	89	+
8	ferrocenyl	Ph	**1e**	83	92	+
9	2-Naphthyl	Ph	**1f**	59	90	+
10	1-Naphthyl	Ph	**1j**	75	76	+
11	Ph	*p*-$CH_3OC_6H_4$	**1k**	91	84	+
12	Ph	*p*-ClC_6H_4	**1l**	88	71	+
13	Ph	*p*-BrC_6H_4	**1m**	84	70	+
14	Ph	*m*-$CH_3OC_6H_4$	**1n**	80	72	–

[a] Isolated yield.
[b] Determined by HPLC using a Chiracel AD column.

highest ee (entry 8). The 2-naphthyl substituted enone formed the product in lowest yield but with a good ee (entry 9). The 1-naphthyl substituted enone, on the other hand, formed the product in moderate yield and ee (entry 10).

In the second series, we investigated the effect of substituents on the R^2 unit of enone (Table 2, entries 11–14). *p*-Methoxyphenyl substituted enone (entry 11) gave the product in the same yield as the *p*-methoxyphenyl on R^1 group (entry 3) but with a better ee. For the *p*-bromo, *p*-chloro, and *m*-methoxy cases, the enantioselectivity was around 70% and the yield varied between 80% and 88%. Cyclohexenone was also tried as the substrate which gave the product in 90% yield but with low ee (26%).

3. Conclusion

The application of chiral **PFAM** and **POFAM** ligands in Cu-catalyzed diethylzinc additions to enones was investigated. Using 2.5 mol % of **PFAM2** ligand with 1.5 mol % $Cu(OTf)_2$), products were obtained in up to 96% yield and 91% ee. The substituents on the β-aryl group of the enone, in general, gave the products in good yields and ee's except for *p*-methoxy-substituted system, which formed the product in moderate ee. Substituents on the α-aryl group of the enone gave the products in good yields but moderate ee's except for the *p*-methoxy case, which formed the product in good ee. The chiral ligand **PFAM2** can be synthesized on a gram scale and is stable for months with careful handling and storage; otherwise it is air sensitive and labile to oxidation, slowly converting to **POFAM2**. The catalytic effect of these ligands for other asymmetric reactions is currently under investigation in our laboratory and will be reported in due course.

4. Experimental

^1H and ^{13}C NMR samples were prepared in 1:1 $CDCl_3$–CCl_4 and recorded at 400 MHz and 100 MHz, respectively. ^1H NMR data are reported as chemical shifts (δ, ppm) relative to tetramethylsilane (δ 0.00). Optical rotations were measured in a 1 dm cell using a Rudolph Research Analytical Autopol III. The products were purified by flash column chromatography on Silica Gel 60 (Merck, 230–400 mesh ASTM). TLC analyses were performed on 250 μm Silica Gel 60 F254 plates. Enantiomeric excess (ee) was determined by chiral HPLC. 1,2-Dichloroethane (DCE) was distilled over CaH_2 prior to use.

4.1. Representative procedure for enantioselective addition of diethylzinc to enones

Under N_2 atmosphere, chiral ligand **PFAM2** (5 mg, 2.5 mol %) and $Cu(OTf)_2$ (2.17 mg, 1.50 mol %) were charged into DCE (900 μL). After stirring the reaction mixture for 15 minutes, enone **1a** (83.4 mg, 0.40 mmol) in DCE (350 μL) was added dropwise. The reaction mixture was then cooled to −20 °C followed by the addition of Et_2Zn (500 μL, from 1 M solution in toluene). The stirring was continued for 4 h at −20 °C. The reaction mixture was quenched with sat. NH_4Cl (20 mL) and the mixture was extracted with diethylether (3 × 20 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. Upon purification by flash column chromatography using silica gel (20:1, hexane/EtOAc), product **2a** was obtained in 89% yield (85 mg, 0.36 mmol).

4.1.1. 1,3-Diphenyl-1-pentanone 2a

Using the general procedure, **2a** was obtained as a white solid (87 mg, 92% yield); $[\alpha]_D^{25} = -1.7$ (*c* 3.2, EtOH) for 90% ee; HPLC: Chiralcel AD column, UV detection at 240 nm, eluent: hexane/2-propanol = 95:5, flow 1.0 mL min^{-1},20 °C, t_R (+)-**2a**: 7.0 min; for (*S*), t_R (−)-**2a**: 8.5 min for (*R*). All spectroscopic data are consistent with those reported in the literature.[8a–c]

4.1.2. 1-Phenyl-3-*p*-tolylpentan-1-one 2b

Using the general procedure, **2b** was obtained as a pale yellow oil (99 mg, 98% yield), $[\alpha]_D^{25} = -3.8$ (*c* 2.2, EtOH) for 85% ee; HPLC: Chiralcel AD column, UV detection at 240 nm, eluent: hexane/2-propanol = 95:5, flow 1.0 mL min^{-1}, 20 °C, t_R (+)-**2b**: 6.6 min for minor enantiomer, t_R (−)-**2b**: 8.9 min for major enantiomer. All spectroscopic data are consistent with those reported in the literature.[8b]

4.1.3. 3-(4-Methoxyphenyl)-1-phenylpentan-1-one 2c

Using the general procedure, **2c** was obtained as a yellow solid (98 mg, 91% yield), mp: 49–50 °C; $[\alpha]_D^{25} = -6.4$ (*c* 3.4, EtOH) for 72% ee; HPLC: Chiralcel AD column, UV detection at 240 nm, eluent: hexane/2-propanol = 95:5, flow 1.0 mL min^{-1}, 20 °C, t_R (+)-**2c**: 9.1 min for (*S*), t_R (−)-**2c**: 13.2 min. for (*R*). All spectroscopic data are consistent with those reported in the literature.[8b,8c]

4.1.4. 3-(4-(Trifluoromethyl)phenyl)-1-phenylpentan 1-one 2d

Using the general procedure, **2d** was obtained as a yellow oil (118 mg, 96% yield), $[\alpha]_D^{25} = +7.7$ (*c* 3.6, EtOH) for 87% ee; HPLC: Chiralcel AD column, UV detection at 240 nm, eluent: hexane/2-propanol = 95:5, flow 1.0 mL min^{-1}, 20 °C, t_R (−)-**2d**: 6.3 min for the minor enantiomer, t_R (+)-**2d**: 8.2 min for the major enantiomer. All spectroscopic data are consistent with those reported in the literature.[8a]

4.1.5. 3-(4-Chlorophenyl)-1-phenylpentan-1-one 2e

Using the general procedure, **2e** was obtained as a colorless oil (96 mg, 88% yield), $[\alpha]_D^{25} = +0.6$ (*c* 3.6, EtOH) for 88% ee; HPLC: Chiralcel AD column, UV detection at 240 nm, eluent: hexane/2-propanol = 98:2, flow 0.5 mL min^{-1}, 20 °C, t_R (+)-**2e**: 26.9 min for (*S*), t_R (−)-**2e**: 28.4 min for (*R*). All spectroscopic data are consistent with those reported in the literature.[8a]

4.1.6. 3-(4-Bromophenyl)-1-phenylpentan-1-one 2f

Using the general procedure, **2f** was obtained as oil (103 mg, 81% yield), $[\alpha]_D^{25} = +3.3$ (*c* 1.9, EtOH) for 91% ee; HPLC: Chiralcel AD column, UV detection at 240 nm, eluent: hexane/2-propanol = 95:5, flow 1.0 mL min^{-1}, 20 °C, t_R (−)-**2f**: 23.0 min for the minor enantiomer, t_R (+)-**2f**: 29.0 min for the major enantiomer. All spectroscopic data are consistent with those reported in the literature.[8d]

4.1.7. 3-(3-Methoxyphenyl)-1-phenylpentan-1-one 2g

Using the general procedure, **2g** was obtained as a pale yellow waxy oil (96 mg, 90% yield), $[\alpha]_D^{25} = +0.8$ (*c* 2.3, EtOH) for 89% ee; HPLC: Chiralcel AD column, UV detection at 240 nm, eluent: hexane/2-propanol = 95:5, flow 1.0 mL min^{-1}, 20 °C, t_R (+)-**2g**: 17.0 min, t_R (−)-**2g**: 20.1 min. All spectroscopic data are consistent with those reported in the literature.[4e]

4.1.8. 3-Ferrocenyl-1-phenylpentan-1-one 2h

Using the general procedure, **2h** was obtained as a yellow oil (115 mg, 83% yield), $[\alpha]_D^{25} = +67.0$ (*c* 4.5, EtOH) for 92% ee; HPLC: Chiralcel OD-H column, UV detection at 240 nm, eluent: hexane/2-propanol = 98:2, flow 1.0 mL min^{-1}, 20 °C, t_R (+)-**2h**: 13.8 min for the major enantiomer, t_R (−)-**2h**: 14.7 min for the minor enantiomer. All spectroscopic data are consistent with those reported in the literature.[8c]

4.1.9. 3-(Naphthalen-2-yl)-1-phenylpentan-1-one 2i

Using the general procedure, **2i** was obtained as a pale yellow solid (68 mg, 59% yield), $[\alpha]_D^{25} = +9.1$ (*c* 2.1, EtOH) for 90% ee;

HPLC: Chiralcel AD column, UV detection at 240 nm, eluent: hexane/2-propanol = 95:5, flow 1.0 mL min^{-1}, 20 °C, t_R (−)-**2i**: 22.9 min for the minor enantiomer, t_R (+)-**2i**: 29.1 min for the major enantiomer. All spectroscopic data are consistent with those reported in the literature.[4e]

4.1.10. 3-(Naphthalen-1-yl)-1-phenylpentan-1-one 2j

Using the general procedure, **2j** was obtained as a solid (86 mg, 75% yield), $[\alpha]_D^{25} = +47.0$ (*c* 2.8, EtOH) for 76% ee; HPLC: Chiralcel AD column, UV detection at 240 nm, eluent: hexane/2-propanol = 95:5, flow 1.0 mL min^{-1}, 20 °C, t_R (−)-**2j**: 18.5 min for the minor enantiomer, t_R (+)-**2j**: 20.4 min for the major enantiomer. All spectroscopic data are consistent with those reported in the literature.[8e]

4.1.11. 1-(4-Methoxyphenyl)-1-phenylpentan-1-one 2k

Using the general procedure, **2k** was obtained as a solid (97 mg, 91% yield), $[\alpha]_D^{25} = +5.3$ (*c* 3.1, EtOH) for 84% ee; HPLC: Chiralcel AD column, UV detection at 240 nm, eluent: hexane/2-propanol = 95:5, flow 1.0 mL min^{-1}, 20 °C, t_R (−)-**2k**: 10.6 min for the minor enantiomer, t_R (+)-**2k**: 11.9 min for the major enantiomer. All spectroscopic data are consistent with those reported in the literature.[8d]

4.1.12. 1-(4-Chlorophenyl)-1-phenylpentan-1-one 2l

Using the general procedure, **2l** was obtained as a solid (96 mg, 88% yield), $[\alpha]_D^{25} = +5.3$ (*c* 3.7, EtOH) for 71% ee; HPLC: Chiralcel AD column, UV detection at 240 nm, eluent: hexane/2-propanol = 95:5, flow 1.0 mL min^{-1}, 20 °C, t_R (−)-**2l**: 30.6 min for the minor enantiomer, t_R (+)-**2l**: 39.0 min for the major enantiomer. All spectroscopic data are consistent with those reported in the literature.[3h]

4.1.13. 1-(4-Bromophenyl)-1-phenylpentan-1-one 2m

Using the general procedure, **2m** was obtained as solid (107 mg, 84% yield), $[\alpha]_D^{25} = +4.6$ (*c* 3.9, EtOH) for 70% ee; HPLC: Chiralcel AD column, UV detection at 240 nm, eluent: hexane/2-propanol = 95:5, flow 1.0 mL min^{-1}, 20 °C, t_R (−)-**2m**: 33.4 min for the minor enantiomer, t_R (+)-**2m**: 42.6 min for the major enantiomer. All spectroscopic data are consistent with those reported in the literature.[8d]

4.1.14. 1-(3-Methoxyphenyl)-1-phenylpentan-1-one 2n

Using the general procedure, **2n** was obtained as solid (86 mg, 80% yield), $[\alpha]_D^{25} = -4.8$ (*c* 2.2, EtOH) for 72% ee; HPLC: Chiralcel AD column, UV detection at 240 nm, eluent: hexane/2-propanol = 95:5, flow 1.0 mL min^{-1}, 20 °C, t_R (−)-**2n**: 29.3 min for the minor enantiomer, t_R (+)-**2n**: 32.7 min for the major enantiomer All spectroscopic data are consistent with those reported in the literature.[8e]

Acknowledgments

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