Organic & Biomolecular Chemistry

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 2614

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Dinuclear zinc catalyzed asymmetric Friedel–Crafts amidoalkylation of indoles with aryl aldimines†

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Received 18th December 2010, Accepted 9th February 2011
DOI: 10.1039/c0ob01200a

The asymmetric Friedel–Crafts amidoalkylation of indoles with aryl aldimines could be efficiently catalyzed by Trost's bis-ProPhenol dinuclear zinc complexes to attain 3-indolyl methanamine derivatives in good to excellent yields (85–98%) with moderate to high enantiomeric ratios (from 70 : 30 up to 95 : 5 er). Remarkably, this approach provides efficient access to enantiomerically enriched 3-indolyl methanamines, which avoids the formation of the undesirable bis- and tris(indolyl)methanes (BIMs and TIMs) byproduct.

The Friedel–Crafts alkylation reaction is a powerful carbon–carbon bond forming process in modern organic synthetic chemistry.[1] In view of the significance of the chirality, enantioselective Friedel–Crafts alkylation reactions, promoted by chiral metal complexes or organocatalysts, have been rapidly developed.[2] Among them, enantioselective Friedel–Crafts alkylation of indoles with aldimines have proven to be an atom-economic method for the preparation of optically active 3-indolyl methanamine derivatives, which show biologically significant activities in pharmaceuticals, agrochemicals, and indole alkaloids.[3] Accordingly, great progress has been made in the last ten years. Johannsen and Zhou's group,[4] respectively, disclosed that copper-BINAP or copper-bisoxazoline complexes could catalyze amidoalkylation of indoles with an imino ester or N-sulfonyl aldimines in high yields and enantioselectivities. Deng *et al*.[5] reported that 9-thiourea cinchona alkaloids, as bifunctional organocatalysts, catalyzed the Friedel–Crafts amidoalkylation with broad substrate generality in high yields with excellent enantioselectivities. Recently, You, Terada and Antilla, respectively, reported that the chiral binaphthyl derived phosphoric acids were applied into the Friedel–Crafts reaction of indoles with imines, affording the optically enriched 3-indolyl methanamine derivatives in good yields and excellent enantioselectivies.[6] Given that the asymmetric Friedel–Crafts amidoalkylation of indoles with imines provides an easy access to enantiomerically enriched 3-indolyl methanamine derivatives, the cultivation of catalytic enantioselective variants of this reaction is still in high demand.

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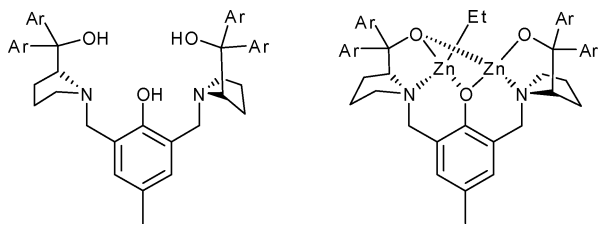
† Electronic supplementary information (ESI) available: Experimental procedures and analysis data. See DOI: 10.1039/c0ob01200a

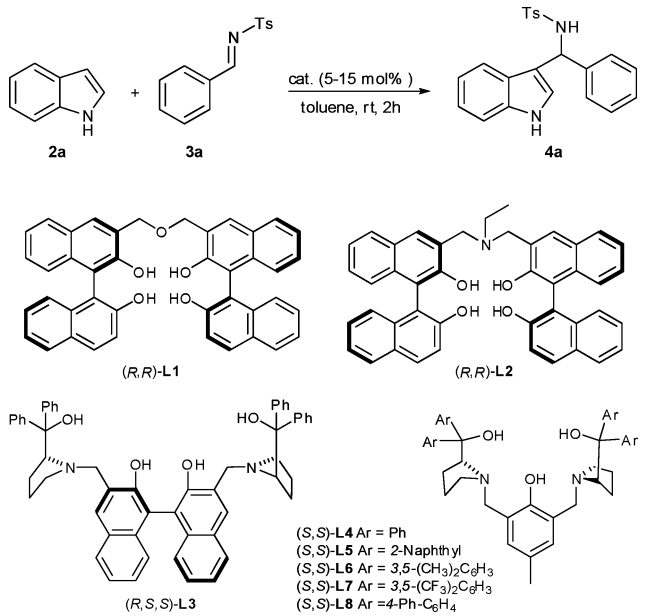
Due to their ability to tightly bind metal ions and to achieve high levels of molecular recognition, the use of enantiopure multidentate crown compounds as ligands has turned out to be effective for designing chiral catalysts.[7] In 2000, Trost and Ito designed and reported the well-organized semi-crown bis-ProPhenol dinuclear zinc catalysts (Scheme 1). So far, Trost's dinuclear zinc catalysts as mimic metalloenzymes have been utilized to catalyze various asymmetric reactions, such as aldol reaction, Mannich reaction, Michael addition, and alkynylation, with excellent enantioselectivities.[8] Recently, Wang's group applied the Trost dinuclear zinc catalyst to conjugate additions of phosphites to α, β-unsaturated N-acylpyrroles and imines, affording aminophosphonates in high yields and excellent enantioselectivities.[9] Moreover, Ding's group found that the bis-ProPhenol dinuclear Zn/Mg complexes could catalyze copolymerization of cyclohexene oxide with CO_2, which displayed completely alternating polycarbonate selectivity and high efficiency.[10] Furthermore, Da's group designed other semicrown chiral BINOL-derived zincate catalysts, which were employed to catalyze direct aldol addition with up to 80% ee.[11] Herein, we report that Trost's dinuclear zinc catalysts can efficiently catalyze the Friedel–Crafts amidoalkylation reaction of indoles with aryl aldimines, affording 3-indolyl methanamines in good to excellent yields (85–98%) with moderate to high enantiomeric ratios (from 70 : 30 to 95 : 5).



Scheme 1 Trost's dinuclear zinc catalysts.

Initially, several semi-crown dinuclear zinc catalysts were examined for the Friedel–Crafts alkylation of indole **2a** with N-Ts aldimine **3a** in toluene at rt under a catalyst loading of 10 mol%. As shown in Table 1, the ligands of (*R*,*R*)-**L1**,[12a] (*R*,*R*)-**L2**[12b] and (*R*,*S*,*S*)-**L3**[11] were found to be ineffective for the reaction, affording essentially only trace amounts of the desired products (entries 1–3). Subsequently, we tested Trost's dinuclear zinc catalysts for this transformation. The bis-ProPhenol ligands (*S*,*S*)-**L4–8**, varied with different substituents on (*S*)-prolinol, were

Table 1 Examination of the catalysts



Entry[a]	Ligand	Cat. (mol%)	M[b]	Yield (%)[c]	er[d]
1	**L1**	10	$ZnEt_2$	Trace	—
2	**L2**	10	$ZnEt_2$	Trace	—
3	**L3**	10	$ZnEt_2$	Trace	—
4	**L4**	10	$ZnEt_2$	95	92 : 8
5[e]	**L4**	10	$ZnEt_2$	90	75 : 25
6[f]	**L4**	10	$ZnEt_2$	96	90 : 10
7	**L5**	10	$ZnEt_2$	90	76 : 24
8	**L6**	10	$ZnEt_2$	95	48 : 52
9	**L7**	10	$ZnEt_2$	92	77 : 23
10	**L8**	10	$ZnEt_2$	90	88 : 12
11	**L4**	5	$Cu(OTf)_2$	0 (90[g])	—
12	**L4**	5	$ZnEt_2$	82	69 : 31
13	**L4**	15	$ZnEt_2$	92	80 : 20

[a] The reactions were performed under N_2 at rt for two hours. [b] $ZnEt_2$, 1.0 M in toluene. [c] Isolated yields. [d] Determined on a chiralcel OD-H column. [e] Indole : **3a** = 2 : 1. [f] Indole : **3a** = 6 : 1. [g] Yield of bisindolylmethanes (BIMs).

smoothly synthesized according to the literature reports.[8,10] Then the dinuclear zinc catalyst derived from $ZnEt_2$ and (*S*,*S*)-**L4** was prepared *in situ* by the addition of a solution of diethylzinc into a solution of (*S*,*S*)-**L4** in toluene according to the molar ratio of 2 : 1 at 0 °C.[8b] After adding aldimine **3a** and five equivalents of indole **2a** into the above catalyst solution, the mixture was stirred at room temperature for two hours. To our delight, the desired product **4a** could be isolated in 95% yield and 92 : 8 er (Table 1, entry 4). Then decreasing the amount of indole **2a** to two equivalents was found to considerably affect the yield and the enantiomeric ratio (90% and 75 : 25 er) (entry 5). When increasing the amount of indole **2a** to six equivalents, the desired product **4a** was obtained in 96% yield and 90 : 10 er (entry 6). After screening the ligands (*S*,*S*)-**L4–8**, the results indicated that ligand (*S*,*S*)-**L4** was the best choice in terms of enantioselectivity and yield (entry 4 *vs.* entries 7–10). It should be noted that, for the dinuclear zinc complex catalyzed Friedel–Crafts amidoalkylation, the undesirable bis- and/or tris(indolyl)methanes (BIMs and TIMs)[13] byproducts were not observed during the reaction course. However, when the

Table 2 Optimization of reaction conditions

Entry	Solvent	Time	Yield (%)[a]	er[b]
1	Toluene	2 h	95	92 : 8
2	Xylene	2 h	90	82 : 18
3	Benzene	2 h	82	71 : 29
4	$CHCl_3$	2 h	91	77 : 23
5	DCM	2 h	92	90 : 10
6	$ClCH_2CH_2Cl$	2 h	90	87 : 13
7	THF	2 h	65	83 : 17
8[c]	Toluene	6 h	91	64 : 36
9[d]	Toluene	40 min	95	83 : 17

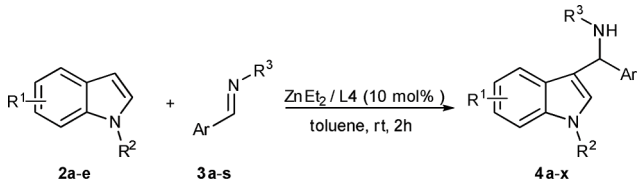
[a] Isolated yields. [b] Determined on a chiralcel OD-H column. [c] The reaction was performed at 0 °C. [d] The reaction was performed at 50 °C.

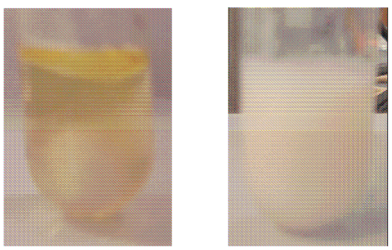
$Cu(OTf)_2$ was used as the metal source, the reaction gave the bis(indolyl)methanes (BIMs)[13c] as the sole product in 90% yield (Table 1, entry 11). In addition, when the catalyst loading was decreased to 5 mol%, the reaction gave a reduced yield and an enantiomeric ratio (entry 12). When increasing the catalyst loading to 15 mol%, the yield was not influenced too much but the er also dropped (entry 13). Therefore, 10 mol% of $ZnEt_2$/(*S*,*S*)-**L4** as the catalyst and five equivalents of indole **2a** were chosen for the Friedel–Crafts amidoalkylation of **3a** with **2a**.

Further results on the optimization of the other parameters for the reaction of **3a** and **2a** catalyzed by dinuclear zinc $ZnEt_2$/(*S*,*S*)-**L4**, including reaction solvent and temperature, are summarized in Table 2. The reaction in toluene and dichloromethane, compared with the other solvents examined, gave the highest yields and enantiomeric ratios (entries 1–6). The reaction in THF proceeded in an obviously sluggish manner affording the desired product in 65% yield and 83 : 17 er (entry 7). Furthermore, when the reaction temperature was decreased to 0 °C, the reaction became obviously slow, and the enantiomeric ratio was dramatically reduced to 64 : 36 (entry 8). However, when increasing the reaction temperature to 50 °C, the reaction could be complete in 40 min. The desired product **4a** was obtained in 95% yield, albeit with moderate enantiomeric ratio (83 : 17) (entry 9). Thus, toluene as the reaction media and room temperature were optimal conditions for the Friedel–Crafts amidoalkylation.

Having established the optimized reaction conditions, we then explored the substrate scope and limitation of the present protocol. The results are summarized in Table 3. It should be noted that most of the reactions proceeded very quickly. The reaction mixture generally becomes cloudy and thick within 10 min (photographs i and ii for entry 1). Substrates **3b–g** bearing either electron-withdrawing substituents (-F, -Cl, -Br, $-CF_3$) or electron-donating substituents (-Me, -OMe) at the *para*-position on the phenyl group were well tolerated and led to their desired products **4b–g** in good to excellent yields (90–98%), albeit accompanied with varying levels of enantiomeric ratios (entries 2–7). Among them, the substrate **3g** bearing a *para*-CF_3 group gave the desired product **4g** in 98% yield with 94 : 6 er (entry 7). For substrates **3h–m** bearing *ortho*- and *meta*-substituents on the phenyl group, the desired products **4h–m** could be obtained in 92–98% yields but also with the varying levels of enantiomeric ratios from 76 : 24 to 92 : 8 (entries 8–13). To our delight, substrate **3n** bearing 2,4-dichloro groups furnished the desired product **4n** in 98% yield with 95 : 5 er (entry 14). Substrates **3o–q** bearing naphthyl and

Table 3 Substrate scope in the reaction





i[a] ii[a]

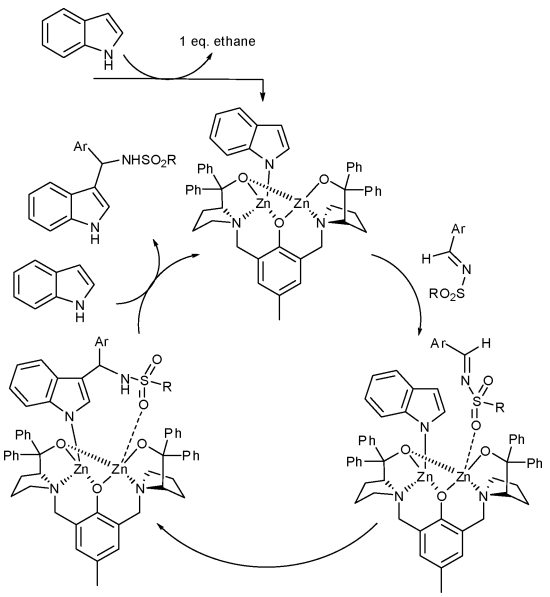
Entry	Indoles (R^1, R^2)	Aldimines (R^3, Ar)	Product	Yield (%)[b]	er[c,d]
1	R^1, R^2 = H (**2a**)	Ts[e], C_6H_5 (**3a**)	**4a**	95	92 : 8
2	R^1, R^2 = H (**2a**)	Ts, *p*-FC_6H_4 (**3b**)	**4b**	97	90 : 10
3	R^1, R^2 = H (**2a**)	Ts, *p*-ClC_6H_4 (**3c**)	**4c**	98	74 : 26
4	R^1, R^2 = H (**2a**)	Ts, *p*-BrC_6H_4 (**3d**)	**4d**	98	86 : 14 (*R*)
5	R^1, R^2 = H (**2a**)	Ts, *p*-$MeOC_6H_4$ (**3e**)	**4e**	90	92 : 8
6	R^1, R^2 = H (**2a**)	Ts, *p*-MeC_6H_4 (**3f**)	**4f**	98	78 : 22
7	R^1, R^2 = H (**2a**)	Ts, *p*-$CF_3C_6H_4$ (**3g**)	**4g**	98	94 : 6 (*R*)
8	R^1, R^2 = H (**2a**)	Ts, *o*-ClC_6H_4 (**3h**)	**4h**	98	92 : 8
9	R^1, R^2 = H (**2a**)	Ts, *o*-FC_6H_4 (**3i**)	**4i**	96	82 : 18
10	R^1, R^2 = H (**2a**)	Ts, *o*-BrC_6H_4 (**3j**)	**4j**	97	84 : 16
11	R^1, R^2 = H (**2a**)	Ts, *o*-$MeOC_6H_4$ (**3k**)	**4k**	98	90 : 10
12	R^1, R^2 = H (**2a**)	Ts, *m*-MeC_6H_4 (**3l**)	**4l**	92	88 : 12
13	R^1, R^2 = H (**2a**)	Ts, *m*-ClC_6H_4 (**3m**)	**4m**	98	76 : 24
14	R^1, R^2 = H (**2a**)	Ts, 2,4-$Cl_2C_6H_3$ (**3n**)	**4n**	98	95 : 5
15	R^1, R^2 = H (**2a**)	Ts, 1-Naphthyl (**3o**)	**4o**	96	85 : 15
16	R^1, R^2 = H (**2a**)	Ts, 2-Naphthyl (**3p**)	**4p**	90	78 : 22
17	R^1, R^2 = H (**2a**)	Ts, thiophen-2-yl (**3q**)	**4q**	85	81 : 19
18	R^1 = 5-CH_3, R^2 = H (**2b**)	Ts, C_6H_5 (**3a**)	**4r**	94	72 : 28
19	R^1 = 5-Br, R^2 = H (**2c**)	Ts, C_6H_5 (**3a**)	**4s**	98	70 : 30
20	R^1 = 7-CH_3, R^2 = H (**2d**)	Ts, C_6H_5 (**3a**)	**4t**	90	85 : 15
21	R^1 = 7-CH_3, R^2 = H (**2d**)	Ts, *o*-ClC_6H_4 (**3h**)	**4u**	91	87 : 13
22	R^1, R^2 = H(**2a**)	Bs[f], C_6H_5 (**3r**)	**4v**	87	85 : 15
23	R^1, R^2 = H(**2a**)	*p*-ClC_6H_4, C_6H_5 (**3s**)	**4w**	Trace	—
24	R^1 = H, R^2 = CH_3 (**2e**)	Ts, C_6H_5 (**3a**)	**4x**	Trace	—

[a] Photographs: i before reaction and ii after reaction for entry 1. [b] Isolated yields. [c] Determined on a chiralcel OD-H column. [d] Absolute configuration was determined by comparison of the optical rotation with known compounds in the literature.[4b,5,6] [e] Ts = *p*-$MeC_6H_4SO_2$, [f] Bs = $C_6H_5SO_2$.

thiophen-2-yl groups were also suitable for this transformation to give the desired products **4o–q** in high yields and moderate enantioselectivities (entries 15–17). The indole derivatives **2b–c** bearing 5-CH_3 and 5-Br groups were also investigated for the reaction to provide the corresponding products **4r–s** in high yields (94% and 98%) and modest er (72 : 28 and 70 : 30) (entries 18–19). By comparison, the reactions of the indole derivative **2d** bearing a 7-CH_3 group with **3a** and **3h**, respectively, led to the desired products in slightly lower yields but with better enantiomeric ratios (85 : 15 and 87 : 13) (entries 20–21). Furthermore, when N-Bs aryl aldimine **3r** was used in the reaction with indole **2a**, the reaction ran smoothly with high yield and good enantiomeric ratio (entry 22). In addition, the reactions of indole **2a** with aldimine **3s** and N-methyl indole **2e** with **3a** were subsequently tested, affording essentially only trace amounts of the products after prolonged reaction time of 36 h (entries 23–24).

Based on Ding's single-crystal X-ray analysis for the bis-ProPhenol zinc complex[10a] and the mechanism of Friedel–Crafts alkylation of pyrroles with nitroalkenes proposed by Trost,[8e] the mechanism of this reaction is speculated to be that one zinc atom coordinates to nitrogen atom of an indole through the deprotonation by the formation of one equivalent of ethane, and another zinc atom coordinates to the oxygen atom of sulfonyl group. Then the Friedel–Crafts amidoalkylation of the indoles with aldimines occurs. Finally, the exchange of proton with another indole promotes the catalytic cycle and regenerates the active catalysts (Scheme 2).

In conclusion, we have developed one new approach to synthesis of 3-indolyl methanamine derivatives through the asymmetric Friedel–Crafts amidoalkylation of indoles with N-sulfonyl aldimines, catalyzed by the intramolecular dinuclear zinc catalysts. The corresponding adducts have been obtained



Scheme 2 Proposed catalytic cycle.[8e]

in good to excellent yields (up to 98%) with moderate to high enantioselectivities (up to 95 : 5 er). It should be noted that this transformation stereoselectively produces the desired 3-indolyl methanamines without the bis- and tris-indolylmethanes (BIMs and TIMs) being generated. Studies into the detailed mechanism and more substrates for this reaction are ongoing in our laboratory.

Experimental section

General procedure for the catalytic Friedel–Crafts amidoalkylation

Under an argon atmosphere, a solution of diethylzinc (50 μL, 1.0 M in toluene, 0.05 mmol) was added to a stirred and cooled solution of **L4** (0.025 mmol) in toluene (0.5 mL) at 0 °C. After the addition, the cold bath was removed and the resulting solution was allowed to stir at rt for 30 min. Then a solution of N-sulfonyl imine **3** (0.25 mmol) and **2** (1.25 mmol) in 1.0 mL toluene were added. The corresponding mixture was stirred for another 2 h at rt. After the reaction was complete (monitored by TLC), 10% $NaHCO_3$ (3 mL) was added. The mixture was extracted with ethyl acetate (3 × 10 mL). The organic layer was washed by H_2O (5 mL), brine (5 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography to afford the desired products.

Acknowledgements

We are grateful for the financial support from National Natural Science Foundation of China (21072145), Foundation for the Author of National Excellent Doctoral Dissertation of PR China (200931), Natural Science Foundation of Jiangsu Province of China (BK2009115).

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