DOI: 10.1002/adsc.201000111

Development of Diphenylamine-Linked Bis(imidazoline) Ligands and Their Application in Asymmetric Friedel–Crafts Alkylation of Indole Derivatives with Nitroalkenes

Han Liu[b] and Da-Ming Du[a,b,*]

[a] School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081, People's Republic of China
Fax: (+86)-010-6891-4985; e-mail: dudm@bit.edu.cn
[b] Beijing National Laboratory for Molecular Sciences (BNLMS), College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Pepublic of China

Received: February 10, 2010; Published online: April 26, 2010

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201000111.

Abstract: The new diphenylamine-linked bis(imidazoline) ligands were prepared through Kelly-You's imidazoline formation procedure mediated by Hendrickson's reagent in good yields. The novel ligands were tested in the asymmetric Friedel–Crafts alkylation of indole derivatives with nitroalkenes. In most cases, good yields (up to 97%) and excellent enantioselectivities (up to 98%) can be achieved. The optimized bis(imidazoline) ligand with *trans*-diphenyl substitution on the imidazoline ring gave better enantioselectivity than the corresponding bis(oxazoline) ligand.

Keywords: asymmetric catalysis; bis(imidazoline)s; diphenylamine; Friedel–Crafts alkylation; indoles; nitroalkenes

As an important member of five-membered heterocycle systems, 2-imidazoline has attracted the attention from chemists in the fields of organic synthesis, medicinal chemistry, and homogeneous catalysis.[1] Natural and artificial compounds containing the 2-imidazoline moiety have been investigated for their biological activity.[2] Since the first report on the use of a chiral imidazoline ligand in rhodium-catalyzed asymmetric hydrogenation,[3] many chiral mono- and bis(imidazoline) ligands have been synthesized and tested in different types of asymmetric transformations.[1c,4] The substituents on the nitrogen atom provide more chance to tune the electronic effect of the ligands orthogonally to the steric effect, and thus provide more space for catalyst optimization. However, compared with its structural analogues 2-oxazoline[5] and 2-thiazoline[6] which have been widely used in asymmetric catalysis, the application of 2-imidazoline as chiral ligands is still less developed.

In 2002 and 2004, Guiry et al.[7] and our group[8] developed the diphenylamine-linked bis(oxazoline) ligands, and investigated their applications in the asymmetric Henry reaction,[8a,b] the asymmetric Nozaki–Hiyama–Kishi reaction,[7b,d] the asymmetric Micheal addition of nitroalkanes to nitroalkenes,[8c] and the asymmetric Friedel–Crafts alkylation of electron-rich heteroaromatics with nitroalkenes.[7c,8d–g] Later, Nishiyama's group applied these ligands in the asymmetric hydrosilylation of prochiral ketones.[9] As a rational extension of our project, we designed the diphenylamine-linked bis(imidazoline) ligands **1a–f**, as illustrated in Figure 1. Herein, we would like to document

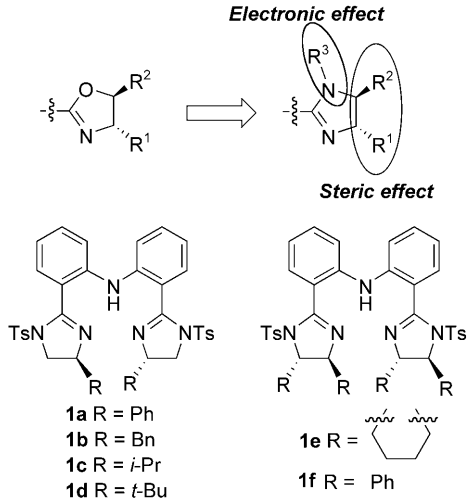


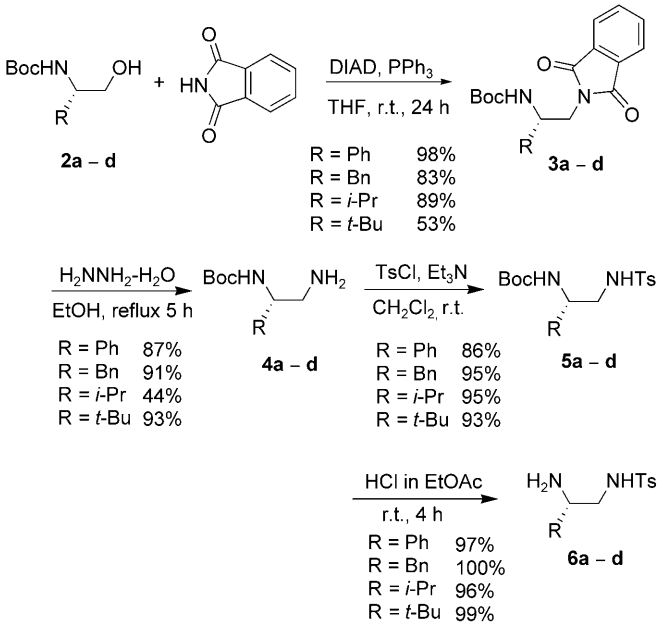
Figure 1. Design of diphenylamine-linked bis(imidazoline) ligands.

our recent results on their synthesis and application as chiral catalysts.

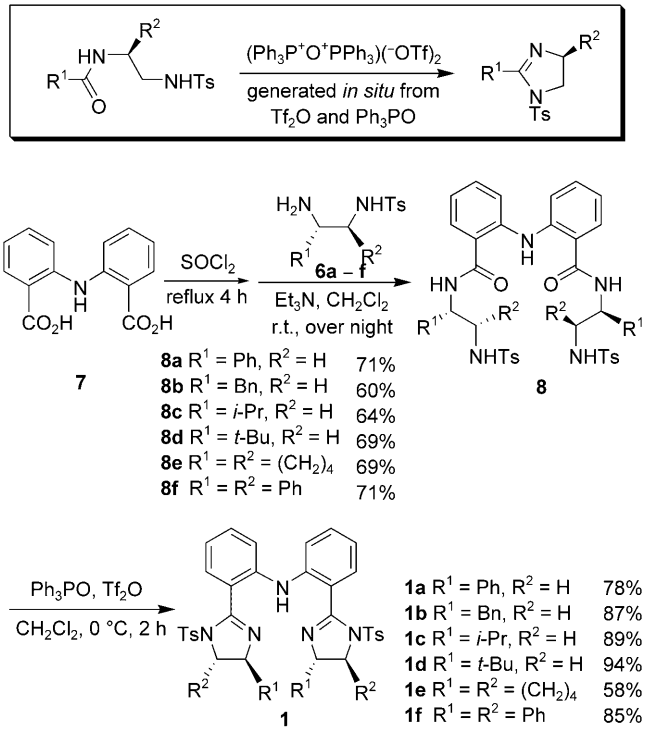
The strategy for the synthesis of chiral imidazoline ligands can be classified into two main types on the basis of the source of the nitrogen atom: from a chiral diamine,[10] or from a chiral β-hydroxyamide and another molecule of amine.[11] Unfortunately, the diphenylamine-linked bis(β-hydroxyamide)s failed to afford the imidazoline ring, and we had to use the other type of methods. The chiral diamines **6a–d** can be synthesized from Boc protected β-amino alcohols **2a–d** *via* Mitsunobu reaction, hydrazinolysis, sulfonamide formation, and deprotection of Boc group, in reasonable yields (Scheme 1). The other two diamines **6e** and **6f** can be prepared conveniently from corresponding C_2-symmetrical diamines following the literature procedure.[12]

With the chiral diamines in hand, the bis(β-sulfonamidoamide) intermediates **8a–f** were prepared in moderate yields (Scheme 2). We chose Kelly-You's imidazoline formation procedure[13] for the critial ring-closing step. The reaction was mediated by Hendrickson's reagent[14] $(Ph_3P^+O^+PPh_3)(^-OTf)_2$ which was generated *in situ* from 2 equivalents of Ph_3PO and 1 equivalent of Tf_2O at 0 °C. The desired products **1a–f** can be obtained smoothly within 2 h in moderate to good yields.

With the desired bis(imidazoline) ligands **1a–f** in hand, we tested their catalytic reactivity in the asymmetric Friedel–Crafts alkylation of indole **9a** with β-nitrostyrene **10a** at room temperature.[15] The results are summarized in Table 1. Compared with our former report, both the reactivtity and the enantioselectivity of bis(imidazoline) ligands are more sensitive

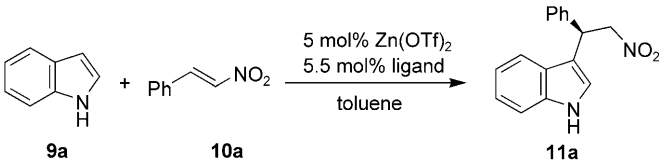


Scheme 1. Synthesis of mono-Ts protected chiral diamines.



Scheme 2. Synthesis of diphenylamine-linked bis(imidazoline) ligands.

Table 1. Screening of ligands and reaction temperature.[a]



Entry	Ligand	Temperature [°C]	Yield [%][b]	*ee* [%][c]
1	**1a**	20	96	11
2	**1b**	20	88	59
3	**1c**	20	40	−4
4	**1d**	20	trace	nd
5	**1e**	20	94	88
6	**1f**	20	97	92
7	**1f**	−20	89	98

[a] All data were obtained using 0.5 mmol substrates under the catalysis of 5 mol% ligand-Zn(OTf)$_2$ complex in 3 mL toluene for 24 h.
[b] Isolated yields.
[c] Determined by HPLC using a Chiracel OD-H column with hexane/2-propanol 70:30 as eluent.

to the substituents on the imidazoline ring. Good yields can be obtained for ligands **1a** and **1b** with relatively smaller substituents (entries 1 and 2), while the yields decreased dramatically with the bulkier isopropyl and *tert*-butyl substituents (entries 3 and 4). In accrodance with our former observation, ligands **1e** and

1f with *trans* substituents on the 4,5-positions of the imidazoline ring gave good yields and enantioselectivities (entries 5 and 6), which indicates the critical role of the substitutions on the 5-position. For ligand **1f**, better enantioselectivity was achieved than with the corresponding bis(oxazoline) ligand (92% *ee vs.* 89% *ee*).[8f] The enantioselectivity can be further improved to 98% *ee* [96% *ee* was obtained using the corresponding bis(oxazoline) ligand] when the reaction was performed at −20 °C. The slightly lower yield may be attributed to the weaker coordination ability of the imidazoline moiety caused by the electron-withdrawing nature of the tosyl group.

Having obtained the optimized reaction conditions, more indole derivatives and nitroalkenes were examined in this reaction. As illustrated in Table 2, excellent enantioselectivities can be achieved for the aromatic nitroalkenes with both electron-donating and electron-withdrawing groups on the *para* or *meta* positions of the phenyl ring (entries 1–6). When the *ortho* substitution exists, the enantioselectivity decreased due to the disfavored steric repulsion (entries 7 and 8). Aromatic nitroalkenes with heterocycles (entries 9 and 10) and an aliphatic nitroalkene (entry 11) are also suitable substrates in this reaction. Indole derivatives with substituents on the 5 and 1 positions were successfully involved (entries 12–15), while lower yields were obtained for electron-deficient 5-chloroindole (entry 14) and less active 1-methylindole (entry 15). Compared with the *ee* values in parentheses which were obtained when the bis(oxazoline) ligand was used,[8f] the diphenylamine-linked bis(imidazoline) ligand **1f** gave higher enantioselectivities than the corresponding bis(oxazoline) ligand in most cases.

Table 2. Asymmetric Friedel–Crafts alkylation of indole derivatives with nitroalkenes.[a]

Entry	R^1	R^2	R^3	Yield [%][b]	*ee* [%][c]
1	H	H	Ph (**11a**)	89	98 (96)[d]
2	H	H	4-MeC_6H_4 (**11b**)	88	95 (93)
3	H	H	4-$MeOC_6H_4$ (**11c**)	83	88 (90)
4	H	H	4-ClC_6H_4 (**11d**)	89	96 (95)
5	H	H	3-BrC_6H_4 (**11e**)	74	97 (95)
6	H	H	3-$NO_2C_6H_4$ (**11f**)	93	95 (94)
7	H	H	2-$MeOC_6H_4$ (**11g**)	90	87 (87)
8	H	H	2-ClC_6H_4 (**11h**)	71	45 (72)
9	H	H	2-furyl (**11i**)	86	89 (80)
10	H	H	2-thienyl (**11j**)	87	91 (87)
11	H	H	$PhCH_2CH_2$ (**11k**)	93	96 (91)
12	Me	H	Ph (**11l**)	92	97 (97)
13	MeO	H	Ph (**11m**)	97	96 (97)
14	Cl	H	Ph (**11n**)	67	95 (88)
15	H	Me	Ph (**11o**)	67[e]	91 (97)[d]

[a] All data were obtained using 0.5 mmol substrates under the catalysis of 5 mol% ligand-$Zn(OTf)_2$ complex in 3 mL of toluene for 24 h.
[b] Isolated yields.
[c] Determined by HPLC using Chiracel OD-H and Chiralcel IA column with hexane/2-propanol as eluent. The *ee* values in parentheses which were obtained when an oxazoline ligand was used are cited from our former report[8f] for comparison.
[d] The absolute configuration of the product was determined to be *R* through comparison of optical rotation and retension time on HPLC.
[e] Performed for 48 h.

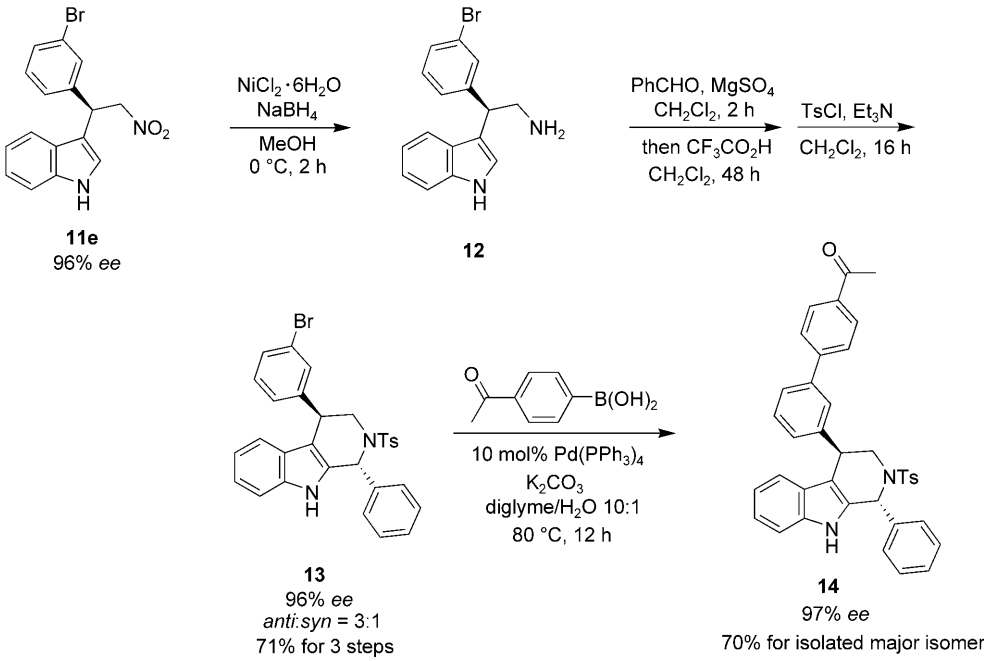
To indicate the applicability of the asymmetric Friedel–Crafts methodology, the chiral adduct **11e** derived from 3-Br-substituted nitrostyrene was transformed to chiral 1,2,3,4-tetrahydro-β-carboline following Akiyama's procedure.[15h] The bromine in the compound provides the active site for further derivation. The tosylated Pictet–Spengler product was formed in good yield without erosion of enantiomeric excess as an *anti*/*syn* 3:1 mixture. Suzuki–Miyaura coupling with 4-acetylphenylboronic acid gave the desired product smoothly (Scheme 3). The major isomer can be isolated as the pure diastereomer in 70% yield. The asymmetric Friedel–Crafts methodology thus provides a method for the construction of a chiral 1,2,3,4-tetrahydro-β-carboline library.

In conclusion, the diphenylamine-linked bis(imidazoline) ligands were synthesized through Kelly-You's imidazoline formation mediated by Hendrickson's reagent efficiently. In the asymmetric Friedel–Crafts alkylation of indole derivatives with nitroalkenes, the complex of ligand **1f** with $Zn(OTf)_2$ gave good reactivity and excellent enantioselectivity in most cases, better than the corresponding bis(oxazoline) ligand we developed before. The chiral adduct can be derived to useful heterocyclic compounds efficiently without loss of the enantiomeric excess. Further investigations on the application of the novel bis(imidazoline) ligands are currently underway in our laboratory.

Experimental Section

General Procedure for Synthesis of Diphenylamine-Linked Bis(imidazoline) Ligands 1a–f

2,2′-Bis[(*S*)-1-(4-methylbenzenesulfonyl)-4-phenylimidazolin-2-yl]-1,1′-diphenylamine (1a): To a flame-dried Schlenk



Scheme 3. Derivation of the Friedel–Crafts adduct.

tube were added triphenylphosphine oxide (1.596 g, 5.74 mmol) and CH_2Cl_2 (10 mL). The solution was cooled to 0 °C and trifluoromethanesulfonic anhydride (0.472 mL, 2.87 mmol) was added in one portion. The mixture was stirred at 0 °C for 0.5 h, then the solution of bis(β-sulfonamidoamide) **8a** (766 mg, 0.956 mmol) in CH_2Cl_2 (10 mL) was added slowly *via* syringe. After the completion of the addition, the mixture was stirred at 0 °C for 2 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution. The organic phase was separated, and the water phase was extracted with CH_2Cl_2 (2×10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum. The residue was purified by silica gel (buffered with Et_3N) column chromatography using CH_2Cl_2 as eluent. The desired ligand was obtained as a white solid; yield: 570 mg (78%); mp 164–166 °C; $[\alpha]_D^{20}$: +121.5 (*c* 0.54 g/100 mL, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.76 (s, 1H), 7.69 (d, *J* = 7.5 Hz, 2H), 7.37–7.55 (m, 8H), 7.08–7.17 (m, 6H), 7.02 (d, *J* = 8.4 Hz, 6H), 6.72 (d, *J* = 7.2 Hz, 4H), 4.46 (t, *J* = 9.6 Hz, 2H), 4.09 (t, *J* = 10.5 Hz, 2H), 3.49 (t, *J* = 10.5 Hz, 2H), 2.28 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.7, 144.5, 141.9, 141.3, 134.5, 132.1, 131.3, 129.8, 128.3, 127.4, 126.3, 119.4, 119.2, 117.0, 68.3, 55.9, 21.5; IR (neat): ν = 3028, 2923, 1630, 1596, 1579, 1513, 1450, 1364, 1306, 1270, 1169, 1089, 992 cm^{-1}; HR-ESI-MS: *m*/*z* = 766.25005, calcd. for $C_{44}H_{40}N_5O_4S_2$ (M+H): 766.25217.

2,2′-Bis[(4*S*,5*S*)-4,5-diphenyl-1-(4-methylbenzenesulfonyl)-imidazolin-2-yl]-1,1′-diphenylamine (1f): Prepared according to general procedure from the corresponding bis(β-sulfonamidoamide) **8f** (1.348 g, 1.41 mmol). The desired product was obtained as a white solid; yield: 1.097 g (85%); mp 250–252 °C; $[\alpha]_D^{20}$: +151.0 (*c* 0.63 g/100 mL, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.35 (s, 1H), 8.04 (d, *J* = 7.5 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.24–7.39 (m, 14H), 7.13 (t, *J* = 7.5 Hz, 2H), 6.69–6.81 (m, 10H), 6.31 (d, *J* = 6.6 Hz, 4H), 4.70 (d, *J* = 3.9 Hz, 2H), 4.16 (s, 2H), 2.23 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.2, 144.3, 142.6, 142.5, 140.6, 133.7, 133.1, 131.4, 129.5, 128.9, 127.8, 127.5, 126.4, 126.1, 125.9, 119.6, 118.6, 78.1, 70.9, 21.5; IR (neat): ν = 3027, 1629, 1597, 1574, 1505, 1446, 1365, 1299, 1266, 1171, 1089, 1021 cm^{-1}; HR-ESI-MS: *m*/*z* = 918.31320, calcd. for $C_{56}H_{48}N_5O_4S_2$ (M+H): 918.31477.

Other ligands **1b**–**1e** were prepared in a similar manner.

General Procedure for Asymmetric Friedel–Crafts Reactions

To a flame-dried Schlenk tube were added $Zn(OTf)_2$ (9.3 mg, 0.025 mmol) and ligand **1f** (25.2 mg, 0.028 mmol) under nitrogen, followed by addition of toluene (3 mL). The mixture was stirred at room temperature for 2 h and 0.5 mmol of nitroalkene **10** were added. Then the mixture was stirred for another 10 min. and cooled to −20 °C. Indole derivative **9** (0.5 mmol) was added at −20 °C and the mixture was stirred at this temperature for 24 h. The mixture was separated directly by basic alumina (deactivated with 2% w/w water) column chromatography using petroleum ether-ethyl acetate 5:1 to 1:1 as eluent, and the product was obtained in pure form.

For products **11f** and **11o**, the purification was performed by silica gel flash chromatography using petroleum ether-ethyl acetate 5:1 and 20:1 v/v, as eluent, respectively.

Acknowledgements

We thank the National Natural Science Foundation of China (Grant No.20772006), the Development Program for Distinguished Young and Middle-aged Teachers of Beijing Institute

of Technology and the Program for New Century Excellent Talents in University (NCET-07-0011) for financial support.

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