Synthesis of new benzimidazolium salts and their application in the asymmetric arylation of aldehydes

Wei-Ping He, Bi-Hui Zhou, Ya-Li Zhou, Xiang-Rong Li, Li-Mei Fan, Hao-Wen Shou, Jie Li

PII: S0040-4039(16)30683-9
DOI: http://dx.doi.org/10.1016/j.tetlet.2016.06.023
Reference: TETL 47750

To appear in: *Tetrahedron Letters*

Received Date: 1 April 2016
Revised Date: 3 June 2016
Accepted Date: 6 June 2016

Please cite this article as: He, W-P., Zhou, B-H., Zhou, Y-L., Li, X-R., Fan, L-M., Shou, H-W., Li, J., Synthesis of new benzimidazolium salts and their application in the asymmetric arylation of aldehydes, *Tetrahedron Letters* (2016), doi: http://dx.doi.org/10.1016/j.tetlet.2016.06.023

Graphical Abstract

To create your abstract, type over the instructions in the template box below.
Fonts or abstract dimensions should not be changed or altered.

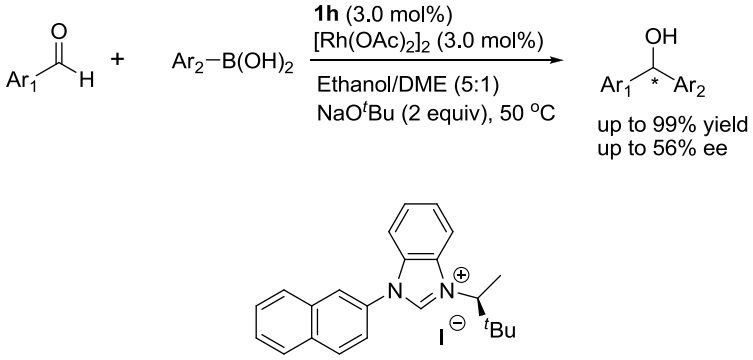
Synthesis of new benzimidazolium salts and their application in the asymmetric arylation of aldehydes

Leave this area blank for abstract info.

Wei-Ping He[a,b], Bi-Hui Zhou[a,b], Ya-Li Zhou[a], Xiang-Rong Li[a], Li-Mei Fan[a], Hao-Wen Shou[a], and Jie Li[a,*]

[a] *School of Medicine, Zhejiang University City College, No. 48, Huzhou Road, Hangzhou 310015, PR China*

[b] *College of Pharmaceutical Sciences, Zhejiang university, Hangzhou 310058, China*



Tetrahedron Letters
journal homepage: www.elsevier.com

Synthesis of new benzimidazolium salts and their application in the asymmetric arylation of aldehydes

Wei-Ping He[a,b], Bi-Hui Zhou[a,b], Ya-Li Zhou[a], Xiang-Rong Li[a], Li-Mei Fan[a], Hao-Wen Shou[a], and Jie Li[a,*]

[a] *School of Medicine, Zhejiang University City College, No. 48, Huzhou Road, Hangzhou 310015, PR China*
[b] *College of Pharmaceutical Sciences, Zhejiang university, Hangzhou 310058, China*

ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
N-Heterocyclic carbene
Benzimidazolium salt
Rh-catalyzed
Diarylmethanol

ABSTRACT

A series of novel chiral benzimidazolium salts, the precursor of *N*-heterocyclic carbene ligands, were designed and synthesized from 1,2-dibromobenzene. In situ prepared corresponding carbenes were tested in asymmetric Rh-catalyzed arylation of aromatic aldehydes, affording chiral diarylmethanols with high yields and moderate enantioselectivities.

* Corresponding author. Tel.: +86 571 88016565; fax: +86 571 88018442; e-mail: lijie@zucc.edu.cn (J. Li)

Introduction

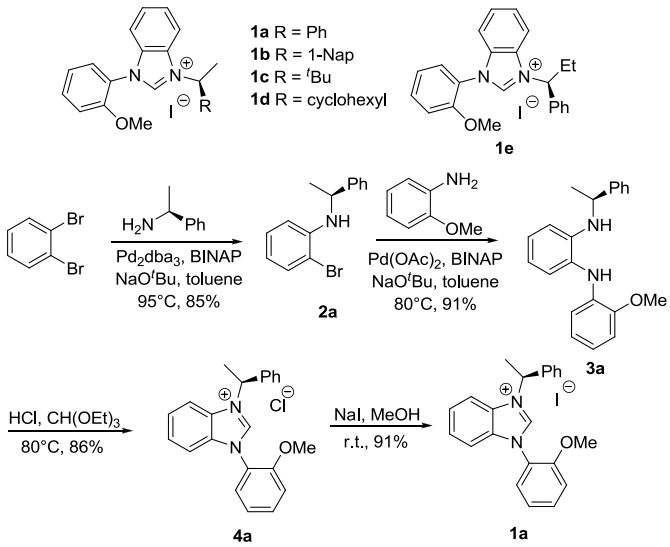
Chiral diarylmethanols are structural core involved in a variety of pharmacologically significant compounds and therefore represent important synthetic targets.[1] Besides asymmetric hydrogenation of diarylketones, catalytic asymmetric addition of aryl organometallic reagents to aldehydes provides a direct route for synthesis of enantiomerically enriched diarylmethanols.[2] Arylboronic acids are among the most convenient reagents due to their low toxicity, compatibility to a broad range of functional groups and high stability in water and air.[3] Since Miyaura first reported the Rh-catalyzed asymmetric addition of organoboronic acids to aldehydes in 1998,[4] much attention has shifted to a practical strategy: either to improve enantioselectivity or accelerate the reaction by using new catalyst systems.[5]

During the past 20 years, complexes with *N*-heterocyclic carbenes (NHCs) have gathered considerable interests from the organic chemistry community and have been widely used in homogeneous metal catalysis.[6] A logical extension of this development is the application of these ligands in stereoselective catalysis, the easy introduction of chiral elements into NHCs and the facile preparation of their precursors have made chiral NHCs promising chiral ligands in metal-based asymmetric catalysis.[7] In 2005, Bolm reported the synthesis of a variety of chiral imidazolium salts and their application in the asymmetric arylation of aldehydes.[8] However, the ligand did not show satisfactory enantioselectivity (38% ee). This study was followed by those of the groups of Shi and Ma, but only moderate enantioselectivities were obtained.[9] Obviously, it is still desirable to develop or find more active chiral catalysts and efficient catalytic systems for 1,2-addition of organoboronic acids to aldehydes. Herein, we wish to report the synthesis a series of new chiral benzimidazolium salts and their application in asymmetric Rh-catalyzed arylation of aromatic aldehydes.

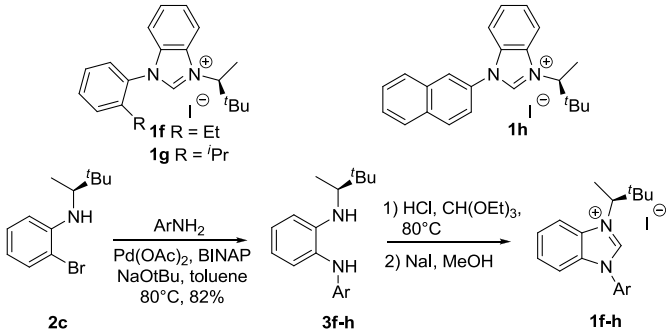
Results and discussion

Synthesis of benzimidazolium salts. The synthesis of the benzimidazolium salt **1a** as N-heterocyclic carbene precursor is representatively shown in Scheme 1. Buchwald-Hartwig coupling of 1,2-dibromobenzene with (*S*)-α-methylbenzylamine gave the monosubstituted product **2a** in 85% yield. A second Buchwald-Hartwig coupling proceeded well with this substituted aniline, producing the differentially substituted diamine **3a** in an excellent 91% yield. Finally, treatment of diamine with HCl in $CH(OEt)_3$ gave the benzimidazolium salt **4a** in 89% yield. The hygroscopic chloride salt **4a** which became gels on exposure to the atmosphere was difficult to handle on the benchtop, but this problem was solved by anion metathesis with NaI to give **1a**. Other benzimidazolium salts **1b−e** were prepared in the same manner. All of the benzimidazolium salts **1a−e** were purified and fully characterized by NMR and mass spectrometry.

Asymmetric arylation of aldehydes in the presence of 1. With the novel benzimidazolium salts **1a−e** in hand, we turned our attention to their application in Rh-catalyzed asymmetric additions of arylboronic acids to aromatic aldehydes. We began to screen benzimidazolium salts **1a−e** in enantioselective phenylation of 2-naphthaldehyde (**5a**) with $PhB(OH)_2$ (**6a**). The results are shown in Table 1. At first, reactions were carried out with the use of $Rh(OAc)_2$ in DME/H_2O (5:1) according to Fürstner's procedure (Table 1, entries 1-5).[10] Diarylmethanol **7aa** was obtained in high yield with each of the benzimidazolium salts **1a−e** (90-99%), **1c** possessing a *t*-butyl group as R substituent gave 23% enantioselectivity. We hypothesized that the bulky *t*-butyl group of catalyst **1c** resulted in better enantioselectivity. Thus, three additional benzimidazolium salts (**1f−h**) were prepared with different ortho positions of the *N*-bound aryl rings. As shown in Scheme 2, the precursors **1f−h** were prepared by applying the same three-step sequence to **1a−e** with **2c** as the starting materials (Scheme 2). To compare catalysts **1f−h** to catalyst **1c**, Rh-catalyzed asymmetric additions of $PhB(OH)_2$ to 2-naphthaldehyd using these catalysts were performed under above-described conditions. All three of the new catalysts reached similar conversions and **1h** performed the best enantioselectivity (37% ee).

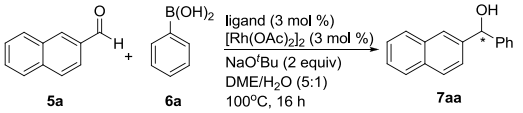


Scheme 1. Representative synthesis of benzimidazolium salts



Scheme 2. Synthesis of benzimidazolium salts **1f-h**

Table 1. Comparison of NHC precursors



Entry[a]	Ligand	Yield (%)[b]	ee (%)[c]
1	**1a**	92	3
2	**1b**	93	1
3	**1c**	99	23
4	**1d**	99	13
5	**1e**	90	6
6	**1f**	99	28
7	**1g**	95	21
8	**1h**	99	37

[a] Reaction condition: $[Rh(OAc)_2]_2$ (3 mol %), ligand (3 mol %), NaO^tBu (2 equiv), arylboronic acids (2 equiv), N_2, DME/H_2O (5:1), 100 °C, 16 h.

[b] Isolated yields.

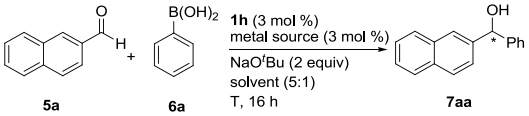
[c] Determined by chiral HPLC (CHIRALCEL OD Column) analysis.

We then optimized the experimental conditions using **1h** as ligand, a number of parameters were varied using phenylboronic acid and 2-naphthaldehyde as model substrates. In place of NaO^tBu, KO^tBu, LiO^tBu and LiOH gave same results. Probing of solvents revealed that EtOH/DME (5:1) is better than other solvents (Table 2, entry 7). Different rhodium sources were also investigated with **1h** (Table 2, entries 10−12), $[Rh(OAc)_2]_2$ emerged as the best choice of catalyst precursors. Further screen

of reaction temperature indicated that lower temperature can afford the desired product with higher enantioselectivity. Upon lowering the reaction temperature to 50 °C, a 98% conversion and 43% ee were observed, and 50% ee was obtained at 30 °C (Table 2, entry 13−14). However, the reaction did not proceed at all when the temperature was lowered to 0 °C (Table 2, entry 15).

Having established the optimal catalytic condition, various substrates with different steric and electronic properties were examined in the asymmetric arylation of aromatic aldehydes using **1h** as catalyst. The results are summarized in Table 3. In most cases, the reaction proceeded with notable efficiency (up to 99% isolated yield) and moderate enantioselectivity. The best enantioselectivity was obtained starting from 4-(trifluoromethyl)benzaldehyde (56% ee, entry 12).

Table 2. Optimization of the reaction conditions



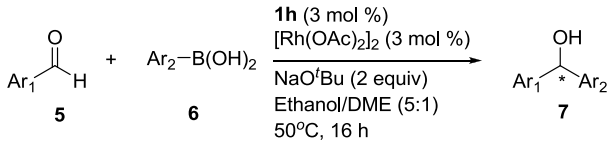
Entry[a]	Solvent	Metal source	Temperature	Yield (%)[b]	ee (%)[c]
1	Dioxane	$[Rh(OAc)_2]_2$	100 °C	57	25
2	DME	$[Rh(OAc)_2]_2$	100 °C	37	14
3	DME/H_2O (10:1)	$[Rh(OAc)_2]_2$	100 °C	99	34
4	DME/ H_2O (5:1)	$[Rh(OAc)_2]_2$	100 °C	99	37
5	DME/ H_2O (3:1)	$[Rh(OAc)_2]_2$	100 °C	96	31
6	MeOH	$[Rh(OAc)_2]_2$	100 °C	93	26
7	MeOH/DME (5:1)	$[Rh(OAc)_2]_2$	100 °C	36	41
8	Ethanol/DME (5:1)	$[Rh(OAc)_2]_2$	100 °C	99	40
9	Ethanol	$[Rh(OAc)_2]_2$	100 °C	94	37
10	Ethanol/DME (5:1)	$RhCl_3·3H_2O$	100 °C	95	35
11	Ethanol/DME (5:1)	$[Rh(COD)Cl]_2$	100 °C	92	3
12	Ethanol/DME (5:1)	$[Rh(C_2H_4)_2Cl]_2$	100 °C	90	5
13	Ethanol/DME (5:1)	$[Rh(OAc)_2]_2$	50 °C	98	43
14	Ethanol/DME (5:1)	$[Rh(OAc)_2]_2$	30 °C	98	50
15	Ethanol/DME (5:1)	$[Rh(OAc)_2]_2$	0 °C	–	–

[a] Reaction condition: $[Rh(OAc)_2]_2$ (3 mol %), **1h** (3 mol %), NaO^{t}Bu (2 equiv), arylboronic acids (2 equiv), N_2, 16 h.

[b] Isolated yields.

[c] Determined by chiral HPLC (CHIRALCEL OD Column) analysis.

Table 3. Scope of methodology



Entry[a]	Ar_1	Ar_2	Yield (%)[b]	ee (%)[c]
1	2-Naphthyl **5a**	4-FPh **6b**	90 **7ab**	47
2	2-Naphthyl **5a**	2-MePh **6c**	87 **7ac**	27
3	2-Naphthyl **5a**	4-MeOPh **6d**	99 **7ad**	41
4	1- Naphthyl **5b**	Ph **6a**	87 **7ba**	54
5	1- Naphthyl **5b**	4-FPh **6b**	88 **7bb**	53
6	1- Naphthyl **5b**	2-MePh **6c**	99 **7bc**	40
7	1- Naphthyl **5b**	4-MeOPh **6d**	99 **7bd**	50
8	2-MeOPh **5c**	Ph **6a**	94 **7ca**	50
9	2-MeOPh **5c**	4-FPh **6b**	81 **7cd**	52
10	2-MeOPh **5c**	2-MePh **6c**	69 **7cc**	34
11	2-MeOPh **5c**	4-MeOPh **6d**	88 **7cd**	43
12	4-CF_3Ph **5d**	Ph **6a**	98 **7da**	56
13	4-CF_3Ph **5d**	4-FPh **6b**	67 **7db**	47
14	4-CF_3Ph **5d**	2-MePh **6c**	45 **7dc**	19
15	4-CF_3Ph **5d**	4-MeOPh **6d**	85 **7dd**	37
16	Ph **5e**	4-MeOPh **6d**	97 **7ed**	44
17	3,4-diMePh **5f**	Ph **6a**	99 **7fa**	51
18	4-EtPh **5g**	Ph **6a**	63 **7ga**	52
19	4-NO_2Ph **5h**	Ph **6a**	81 **7ha**	46
20	2-FPh **5i**	Ph **6a**	99 **7ia**	52
21	3,5-diFPh **5j**	Ph **6a**	99 **7ja**	35
22	4-ClPh **5k**	Ph **6a**	99 **7ka**	53
23	2-Furyl **5l**	Ph **6a**	99 **7la**	31
24	2-Thienyl **5m**	Ph **6a**	99 **7ma**	28

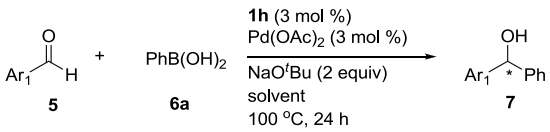
[a] Reaction condition: $[Rh(OAc)_2]_2$ (3 mol %), **1h** (3 mol %), NaO^{t}Bu (2 equiv), arylboronic acids (2 equiv), N_2, 50 °C, 16 h.

[b] Isolated yields.

[c] Determined by chiral HPLC (CHIRALCEL OD and AD Column) analysis.

Extension of **1h** as NHC precursor for palladium-catalyzed addition of phenylboronic acid to aromatic aldehyde was also examined. As in previous reports,[11] the use of $CHCl_3$ as additive is crucial for this Pd-catalyzed arylation, and the survey of solvents revealed that toluene was the only suitable solvent for this reaction. In the next step, four substrates with different electronic properties were applied in the reaction with salt **1h** as catalyst precursor. As shown in Table 4, these aryl aldehydes can be transformed to the corresponding diarylmethanols in moderate yield (34-48%) but inferior ee values.

Table 4. Palladium-catalyzed reaction of phenylboronic acid to aromatic aldehydes



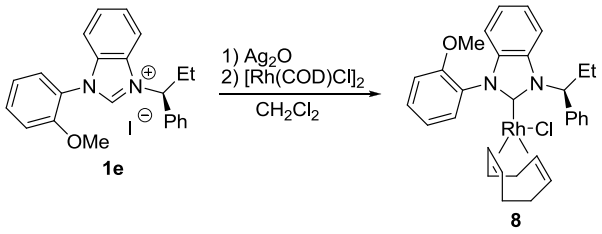
Entry[a]	Ar_1	Solvent	additive	Yield (%)[b]	ee (%)[c]
1	1-Naphthyl **5b**	Toluene	–	–	–
2	1-Naphthyl **5b**	Toluene	$CHCl_3$	48 **7ba**	5
3	1-Naphthyl **5b**	DME	$CHCl_3$	–	–
4	1-Naphthyl **5b**	CH_2Cl_2	$CHCl_3$	–	–
5	1-Naphthyl **5b**	THF	$CHCl_3$	–	–
6	1-Naphthyl **5b**	Xylene	$CHCl_3$	trace	–
7	2-Naphthyl **5a**	Toluene	$CHCl_3$	37 **7aa**	4
8	2-MeOPh **5c**	Toluene	$CHCl_3$	39 **7ca**	7
9	4-CF_3Ph **5d**	Toluene	$CHCl_3$	34 **7da**	6

[a] Reaction condition: $Pd(OAc)_2$ (3 mol %), ligand (3 mol %), NaO^{t}Bu (2 equiv), arylboronic acids (2 equiv), N_2, 100 °C, 24 h.

[b] Isolated yields.

[c] Determined by chiral HPLC (CHIRALCEL OD Column) analysis.

The X-ray crystal structure of NHC−Rh. We attempted to prepare rhodium(I) complex of **1e** using a mild transmetalation method developed by Wang and Lin.[12] Reaction of benzimidazolium precursors with Ag_2O in CH_2Cl_2 at room temperature in the darkness gave rather unstable silver complexes, observed by NMR spectroscopy, which decomposed too quickly to be isolated. Direct addition of $[Rh(COD)Cl]_2$ to a freshly prepared solution of silver complexes yielded upon workup the corresponding chiral complex **8**, which were purified by chromatography on silica gel (Scheme 3). The complex **8** is air stable in solid state and X-ray-quality crystals of **8** was easily grown by layering a CH_2Cl_2 solution of **8** with hexane. The structure of the new chiral NHC−Rh complex **8** was confirmed by X-ray diffraction (Fig. 1).



Scheme 3. Synthesis of NHC-Rh complex **8**

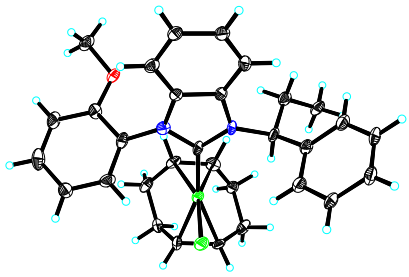


Figure 1. ORTEP diagram of **8**. Selected bond lengths (Å) and angles (°): Rh(1)-C(8) 2.003(14), Rh(1)-C(2) 2.098(12), Rh(1)-C(3) 2.113(11), Rh(1)-C(9) 2.201(11), Rh(1)-C(1) 2.234(15), Rh(1)-Cl(1) 2.394(3); C(8)-Rh(1)-C(2) 94.1(5), C(8)-Rh(1)-C(3) 89.9(5), C(2)-Rh(1)-C(3) 38.7(6), C(2)-Rh(1)-C(9) 82.1(5), C(3)-Rh(1)-C(9) 98.6(5), C(2)-Rh(1)-C(1) 89.2(6), C(3)-Rh(1)-C(1) 81.2(6), C(9)-Rh(1)-C(1) 38.2(5), C(8)-Rh(1)-Cl(1) 90.0(4), C(2)-Rh(1)-Cl(1) 162.1(4), C(3)-Rh(1)-Cl(1) 158.9(4), C(9)-Rh(1)-Cl(1) 88.2(4), C(1)-Rh(1)-Cl(1) 92.4(5).

Conclusion

In conclusion, a series of new chiral benzimidazolium salts have been prepared and the single-crystal X-ray diffraction result further confirmed the molecular structure of NHC−Rh complex **8**. Their applicability in the asymmetric additions of arylboronic acids to aromatic aldehydes has been demonstrated, and the corresponding diarylmethanols were obtained with high yields and moderate enantiomeric excesses (up to 56%). It is worth mentioning that the palladium complex catalyst was also active in this reaction by addition of a catalytic amount of chloroform to the reaction mixture. Further work is in progress to utilize these benzimidazolium salts in asymmetric Rh-catalyzed 1,2-addition reactions of arylboronic acids with ketones.

Acknowledgments

We are grateful to the National Natural Science Foundation of China (81302668) and Hangzhou Science and Technology Information Institute of China (20150633B45).

Supplementary Material

Supplementary data associated with this article can be found, in the online version, at http://

References and notes

1. (a) Meguro, K.; Aizawa, M.; Sohda, T.; Kawamatsu, Y.; Nagaoka, A. *Chem. Pharm. Bull*. **1985**, *33*, 3787−3797; (b) Casy, A. F.; Drake, A. F.; Ganellin, C. R.; Mercer, A. D.; Upton, C. *Chirality* **1992**, *4*, 356−366; (c) Spencer, C. M.; Foulds, D.; Peter, D. H. *Drugs* **1993**, *46*, 1055−1080; (d) Stanev, S.; Rakovska, R.; Berova, N.; Snatzke, G. *Tetrahedron: Asymmetry* **1995**, *6*, 183−198; (e) Botta, M.; Summa, V.; Corelli, F.; Pietro, G. D.; Lombardi, P. *Tetrahedron: Asymmetry* **1996**, *7*, 1263−1266; (f) Seto, M.; Aramaki, Y.; Imoto, H.; Akikawa, K.; Oda, T.; Kanzaki, N.; Iizawa, Y.; Baba, M.; Shiraishi, M. *Chem. Pharm. Bull.* **2004**, *52*, 819−829; (g) Bolshan, Y.; Chen, C. Y.; Chilenski, J. R.; Gosselin, F.; Mathre, D. J.; O'Shea, P. D.; Roy, A.; Tillyer, R. D. *Org. Lett*. **2004**, *6*, 111−114.
2. (a) Dosa, P. I.; Ruble, J. C.; Fu, G. C. *J. Org. Chem.* **1997**, *62*, 444−445; (b) Ji, J.-X.; Wu, J.; Au-Yeung, T. T.-L.; Yip, C.-W.; Haynes, R. K.; Chan, A. S. C. *J. Org. Chem.* **2005**, *70*, 1093−1095; (c) Bolm, C.; Hermanns, N.; Hildebrand, J. P.; Mun˜iz, K. *Angew. Chem., Int. Ed.* **2000**, *39*, 3465−3467; (d) Bolm, C.; Kesselgruber, M.; Hermanns, N.; Hildebrand, J. P.; Raabe, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 1488−1490; (e) Tomita, D.; Wada, R.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2005**, *127*, 4138−4139; (f) Umeda, R.; Studer, A. *Org. Lett.* **2008**, *10*, 993−996.
3. (a) Suzuki, A. *Acc. Chem. Res*. **1982**, *15*, 178−184; (b) Miyaura, N.; Suzuki, A. *Chem. Rev*. **1995**, *95*, 2457−2483; (c) Suzuki, A. *J. Organomet. Chem*. **1998**, *576*, 147−168; (d) Darses, S.; Genet, J. P. *Eur. J. Org. Chem.* **2003**, 4313−4327; (e) Batey, R. A.; Thadani, A. N.; Smil, D. V. *Tetrahedron Lett.* **1999**, *40*, 4289−4292; (f) Chambers, R. D.; Clark, H. C.; Willis, C. J. *J. Am. Chem. Soc*. **1960**, *82*, 5298−5301.
4. Sakai, M.; Ueda, M.; Miyaura, N. *Angew. Chem., Int. Ed.* **1998**, *37*, 3279−3281.
5. (a) Focken, T.; Rudolph, J.; Bolm, C. *Synthesis* **2005**, *3*, 429−436; (b) Shintani, R.; Inoue, M.; Hayashi, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 3353−3356; (c) Duan, H. F.; Xie, J. H.; Qiao, X. C.; Wang, L. X.; Zhou, Q. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 4351−4353; (d) Morikawa, S.; Michigami, K.; Amii, H. *Org. Lett*. **2010**, *12*, 2520−2523; (e) Yamamoto, Y.; Kurihara, K.; Miyaura, N. *Angew. Chem., Int. Ed*. **2009**, *48*, 4414−4416; (f) Nishimura, T.; Kumamoto, H.; Nagaosa, M.; Hayashi, T. *Chem. Commun*. **2009**, *38*, 5713−5715; (g) Tian, P.; Dong, H. Q.; Lin, G. Q. *ACS Catal*. **2012**, *2*, 95−119; (h) Shintani, R.; Takatsu, K.; Hayashi, T. *Chem. Commun*. **2010**, *46*, 6822−6824; (i) Zhang, R.; Xu, Q.; Zhang, X. C.; Zhang, T.; Shi, M. *Tetrahedron: Asymmetry* **2010**, *21*, 1928−1935; (j) Liu, Z.; Gu, P.; Shi, M.; McDowell, P.; Li, G. G. *Org. Lett*. **2011**, *13*, 2314−2317.

6. (a) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 2162−2187; (b) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev*. **2000**, *100*, 39−92; (c) Zinn, F. K.; Viciu, M. S.; Nolan, S. P. *Annu. Rep. Prog. Chem. Sect. B*. **2004**, *100*, 231−249; (d) Cavell, K. J.; McGuinness, D. S. *Coord. Chem. Rev*. **2004**, *248*, 671−681; (e) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev*. **2004**, *248*, 2239−2246; (f) Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev*. **2004**, *248*, 2247−2273; (g) Pugh, D.; Danopoulos, A. A. *Coord. Chem. Rev*. **2007**, *251*, 610−641; (h) Mata, J. A.; Poyatos, M.; Peris, E. *Coord. Chem. Rev*. **2007**, *251*, 841−859; (i) Sommer, W. J.; Weck, M. *Coord. Chem. Rev*. **2007**, *251*, 860−873; (j) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed*. **2008**, *47*, 3122−3172. (k) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. *Nature* **2014**, *510*, 485−496.
7. (a) Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry* **2003**, *14*, 951−961; (b) César, V.;Bellemin-Laponnaz, S.; Gade, L. H. *Chem. Soc. Rev*. **2004**, *33*, 619−636; (c) Douthwaite, R. E. *Coord. Chem. Rev*. **2007**, *251*, 702−717; (d) Gade, L. H.; Bellemin-Laponnaz, S. *Coord. Chem. Rev*. **2007**, *251*, 718−725; (e) Snead, D. R.; Seo, H.; Hong, S. *Curr. Org. Chem*. **2008**, *12*, 1370−1387; (f) Wang, F. J.; Liu, L. J.; Wang, W. F.; Li, S. K.; Shi, M. *Coord. Chem. Rev*. **2012** , *256*, 804−853.
8. Focken, M. T.; Rudolph, J.; Bolm, C. *Synthesis* **2005**, *3*, 429−436.
9. (a) Arao, T.; Sato, K.; Kondo, K.; Aoyama, T. *Chem. Pharm. Bull.* **2006**, *54*, 1576−1581; (b) Zhang, R.; Xu, Q.; Zhang, X.-C.; Zhang, T.; Shi, M. *Tetrahedron: Asymmetry* **2010**, *21*, 1928−1935; (c) Ma, Q.-S.; Ma, Y.-D.; Liu, X.; Duan, W.-Z.; Qu, B.; Song, C. *Tetrahedron: Asymmetry* **2010**, *21*, 292−298; (d) Duan, W. Z.; Ma, Y. D.; Qu, B.; Zhao, L.; Chen, J. Q.; Song, C. *Tetrahedron: Asymmetry* **2012**, *23*, 1369−1375; (e) Duan, W. Z.; Ma, Y. D.; He, F. Y.; Zhao, L.; Chen, J. Q.; Song, C. *Tetrahedron: Asymmetry* **2013**, *24*, 241−248; (f) Chen, J. Q.; Yang, S. B.; Chen, Z.; Song, C.; Ma, Y. D. *Tetrahedron: Asymmetry* **2015**, *26*, 288−295.
10. Fürstner, A.; Krause, H. *Adv. Synth. Catal.* **2001**, *343*, 343−350.
11. Yamamoto, T.; Ohta, T.; Ito, Y. *Org. Lett*. **2005**, *7*, 4153−4155.
12. Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972−975.

Highlights

- Several new chiral benzimidazolium salts were synthesized.
- These new ligands were highly effective catalysts for the arylation of aldehydes.
- Various chiral diarylmthanols were obtained in excellent yields and moderate ee.