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Asymmetric Allylic Amination of Morita–Baylis–Hillman Adducts with Simple Aromatic Amines by Nucleophilic Amine Catalysis

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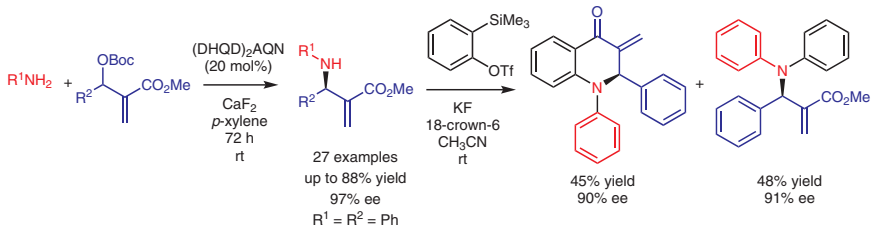

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Abstract Asymmetric allylic amination of Morita–Baylis–Hillman (MBH) adducts with simple aromatic amines is successfully realized by nucleophilic amine catalysis. A range of substituted α-methylene-β-arylamino esters is accessed in moderate to high yields (up to 88%) and with excellent enantioselectivities (up to 97% ee). Inorganic fluorides are found to be able to improve the enantioselectivity of the allylic amination reaction. A pyrrole-2-carboxylate and a cyclic imide are also compatible with this catalytic system. A chiral 2,3-dihydroquinolin-4-one derivative is easily obtained from the allylic amination product.

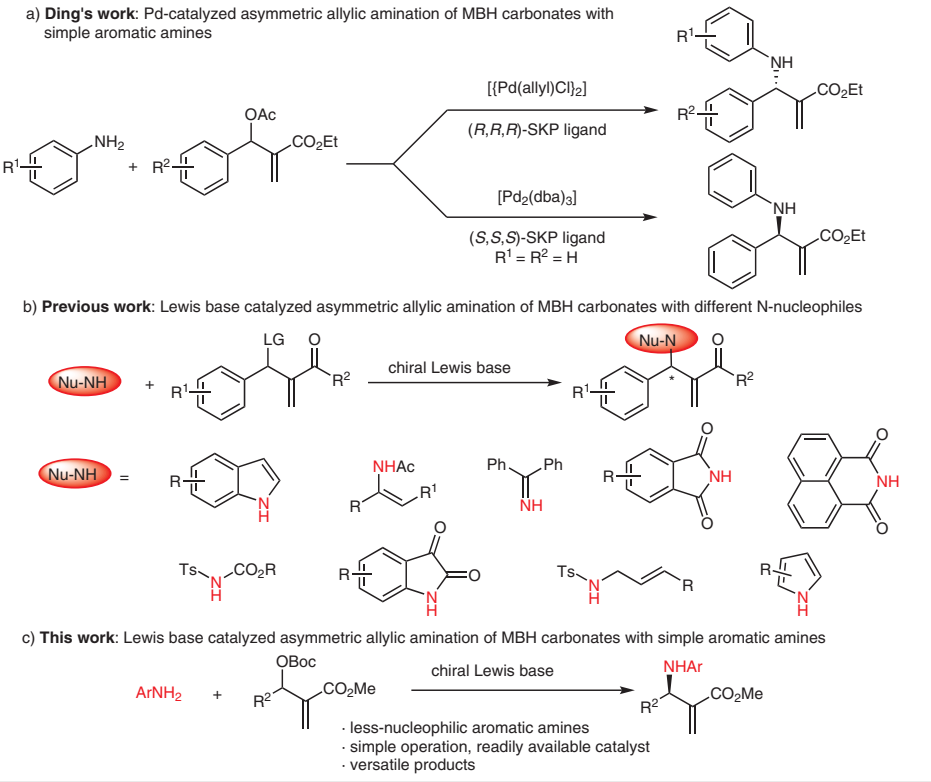
Key words MBH adducts, aromatic amines, asymmetric allylic amination, nucleophilic amine catalysis, inorganic fluorides

Optically active α-alkylidene-β-amino carbonyl compounds and their derivatives represent one type of highly valuable synthons, which have broad applications in the synthesis of complex natural products and medicinally relevant molecules,[1] and especially in the synthesis of chiral β-lactam derivatives.[2] Traditional strategies to access these building blocks include asymmetric aza-Morita–Baylis–Hillman (MBH) reactions between electron-deficient olefins and activated aldimines such as *N*-tosyl and *N*-mesyl aldimines.[3] However, aza-MBH reactions of electron-rich aldimines, such as N-alkyl or N-aromatic imines, can be difficult to realize.[4] In contrast, asymmetric allylic substitution reactions of MBH carbonates[5] with various N-nucleophiles under catalysis by transition metal complexes[1e,2a,2c,6] or organocatalysts[7] is another straightforward strategy for the synthesis of α-alkylidene-β-amino carbonyl compounds. Ding and co-workers have developed a palladium-catalyzed asymmetric allylic amination of MBH carbonates with simple aromatic amines.[2a,6d] Both enantiomers of optically active α-methylene-β-arylamino esters were afforded with excellent regio- and enantioselectivities by using aromatic spiroketal-based bisphosphine ligands (Scheme 1a). Ezetimibe was also easily accessed from the corresponding allylic amination product.

In addition, asymmetric allylic aminations of racemic MBH adducts mediated by nucleophilic Lewis bases have been successfully developed with various N-nucleophiles including indole, imines, enamines, imides, aliphatic amines and pyrroles (Scheme 1b).[7] However, the asymmetric allylic amination of racemic MBH adducts using less-nucleophilic aromatic amines mediated by Lewis bases still remains undeveloped.[8] Considering the broad application of optically active α-alkylidene-β-amino carbonyl compounds, and our interest in developing novel and practical asymmetric transformations,[9] we herein present an asymmetric allylic amination of MBH carbonates with simple aromatic amines by nucleophilic amine catalysis (Scheme 1c). Excellent enantioselectivities (up to 97% ee) were achieved for a wide range of MBH carbonates and aromatic amines. In addition, a pyrrole-2-carboxylate and a cyclic imide were also compatible with this catalytic system. A chiral multifunctional tetrahydroquinoline derivative can be easily afforded from the corresponding allylic amination product.

The initial study was undertaken with aniline (**2a**) and MBH carbonate **3a** in xylene at room temperature for 72 hours. A series of cinchona alkaloids and their derivatives were screened as the nucleophilic amine catalysts (Figure 1),[7] and the results are outlined in Table 1. Unmodified cinchona alkaloids **1a–d** were found to be able to catalyze the allylic amination reaction, giving the desired products in low yields and with moderate ee values (Table 1, entries 1–4). Among them, quinidine **1c** gave the best results. Analogs of **1c** with blocked hydroxy groups (**1e**,**f**) did not afford the desired products (Table 1, entries 5 and 6). Hydrogenated analogs **1g**,**h** and β-isocupreidine (β-ICD) (**1i**) gave lower ee values than **1c** (Table 1, entries 7–9). Next, the cinchona alkaloid dimers **1j–l** were tested as the catalysts (Table 1, entries 10–12). To our delight, the allylic amination product was obtained with 89% ee and in 52% yield when $(DHQD)_2AQN$ (**1k**) was used (Table 1, entry 11). Next, the effect of the solvent on the reaction was carefully studied with catalyst **1k** (see the Supporting Information) and *p*-xylene was found to be the best (Table 1, entry 13). To increase the yield of the reaction, higher concentrations of the sub-

strates were applied in this catalytic system. When the concentration of **2a** was increased from 0.05 M to 0.1 M, the yield of the reaction was greatly improved, whereas the ee value was almost unchanged (Table 1, entry 14). A decreased ee value was observed when the concentration of the substrates was further increased to 0.2 M, although the yield was improved as expected (Table 1, entry 15). Subsequently, several additives were investigated. When pyridine was used, a sharp decrease in the yield and ee were observed (Table 1, entry 16). Inorganic fluorides, especially



Scheme 1 Asymmetric allylic substitution of MBH adducts

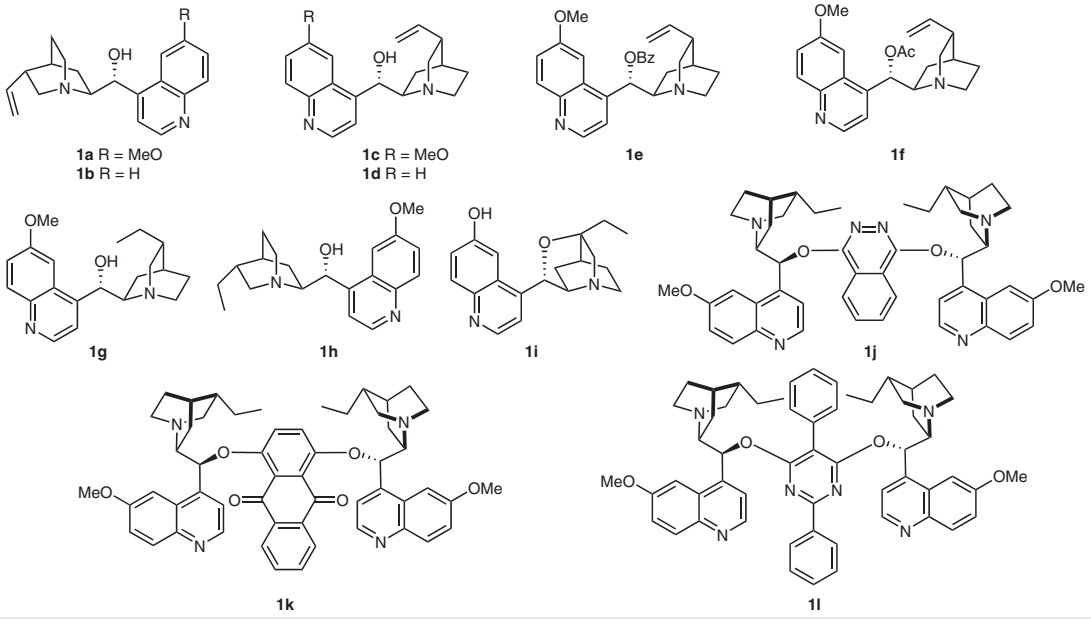
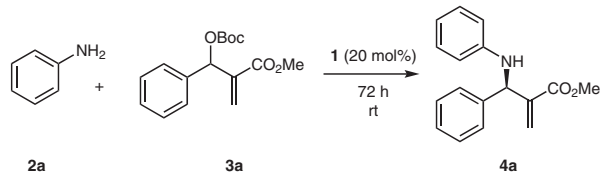


Figure 1 The chiral nucleophilic amine catalysts screened

CaF_2, were found to be effective in improving the ee values of the reaction (Table 1, entries 19–22).[10] Thus, the optimized conditions for the asymmetric allylic amination are as follows: **1k** (20 mol%) in *p*-xylene (0.1 M) with 5 equivalents of CaF_2 at room temperature for 72 hours (Table 1, entry 19).

Table 1 Optimization of the Reaction Parameters



2a **3a** **4a**

Entry[a]	1	Solvent	Additive	Yield (%)[b]	ee (%)[c]
1	**1a**	xylene	–	15	61
2	**1b**	xylene	–	14	47
3	**1c**	xylene	–	27	74
4	**1d**	xylene	–	24	5
5	**1e**	xylene	–	trace	ND
6	**1f**	xylene	–	trace	ND
7	**1g**	xylene	–	65	61
8	**1h**	xylene	–	23	68
9	**1i**	xylene	–	64	43
10	**1j**	xylene	–	13	17
11	**1k**	xylene	–	52	89
12	**1l**	xylene	–	28	52
13	**1k**	*p*-xylene	–	56	90
14[d]	**1k**	*p*-xylene	–	78	89
15[e]	**1k**	*p*-xylene	–	81	87
16[d]	**1k**	*p*-xylene	Py[f]	56	44
17[d]	**1k**	*p*-xylene	$CaCl_2$[f]	75	81
18[d]	**1k**	*p*-xylene	$MgCl_2$[f]	74	81
19[d]	**1k**	*p*-xylene	CaF_2[f]	80	92
20[d]	**1k**	*p*-xylene	MgF_2[f]	79	91
21[d]	**1k**	*p*-xylene	SrF_2[f]	78	90
22[d]	**1k**	*p*-xylene	BaF_2[f]	80	91

[a] Unless otherwise noted, the reaction was carried out with **2a** (0.05 mmol), **3a** (0.1 mmol), and **1** (0.01 mmol) in 1 mL of solvent at room temperature.
[b] Yield of isolated product.
[c] Determined by HPLC. ND = not determined
[d] The reaction was carried out in 0.5 mL of *p*-xylene.
[e] The reaction was carried out with **2a** (0.1 mmol), **3a** (0.2 mmol), and **1k** (0.02 mmol) in 0.5 mL of *p*-xylene at room temperature.
[f] 500 mol% of additive was used.

With optimized reaction conditions in hand, we next examined the substrate scope of the asymmetric allylic amination reaction.[11] As shown in Scheme 2, a variety of substituted MBH carbonates and aromatic amines were well tolerated using this catalytic system, providing the desired products in moderate to high yields (up to 88%) and with excellent enantioselectivities (up to 97% ee). The position and electronic properties of the substituents on the aromatic ring of MBH carbonates **3** had little influence on the enantioselectivity (**4ab–an**). When *ortho*-substituted substrates were used, decreased yields were observed, probably due to steric hindrance (**4ab**, **4ah**, **4ak**). Comparable results were obtained when the phenyl ring of MBH carbonate **3** was replaced with naphthyl (**4ao**) and thienyl (**4ap**) substituents.

We next investigated the scope of the aromatic amine (Scheme 2). The presence of substituents on the aniline **2** had a slight influence on the enantioselectivity of the products **4ba–bi**. However, decreased yields were observed when anilines bearing *m*-Me (**4bb**), *p*-Me (**4bc**), *o*-F (**4bd**) or *p*-Cl (**4bg**) substituents were used. This might be due to the lower reactivities of these anilines, with studies showing that significant amounts of the substrates were still present in the reaction mixtures after 72 hours under the optimized conditions. When the aniline was replaced with 2-naphthylamine, the desired product **4bj** was obtained in high yield and with excellent enantioselectivity. It was noteworthy that product **4bk**, a key synthetic intermediate en route to the drug ezetimibe, could also be obtained in moderate yield and with high enantioselectivity.[2a,12]

The absolute configurations of products **4** were determined by comparing the optical rotation value of **4aa** {$[\alpha]_D^{28}$ = –91.1 (*c* 0.7, $CHCl_3$)} with those reported in the literature {$[\alpha]_D^{20}$ = –175.2 (*c* 1.0, $CHCl_3$) for *R*-**4aa** in reference 2c}.[2a,2c,6c] Thus products **4** were assigned the *R* configuration.

Based on experimental observations and literature reports,[7h,13] a plausible transition state is proposed in Figure 2. Michael addition to the vinylic moiety of the MBH carbonate by nucleophilic amine **1k** gave the intermediate, which would be probably formed as the *E* isomer and stabilized by π-π stacking between the quinoline moiety and the phenyl ring of the MBH carbonate. As the *si* face of the complex is effectively blocked by the left half of the quinoline moiety, the N-nucleophile would presumably approach the *re* face in the preferable S_N2'/*anti*-elimination manner to give the final product.

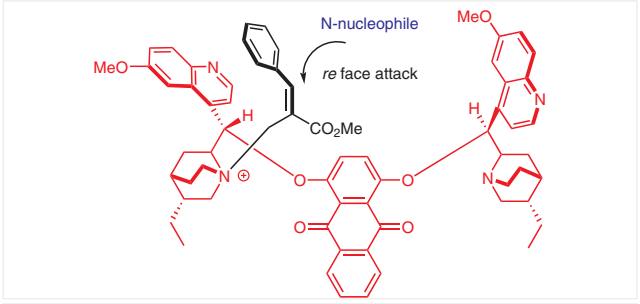
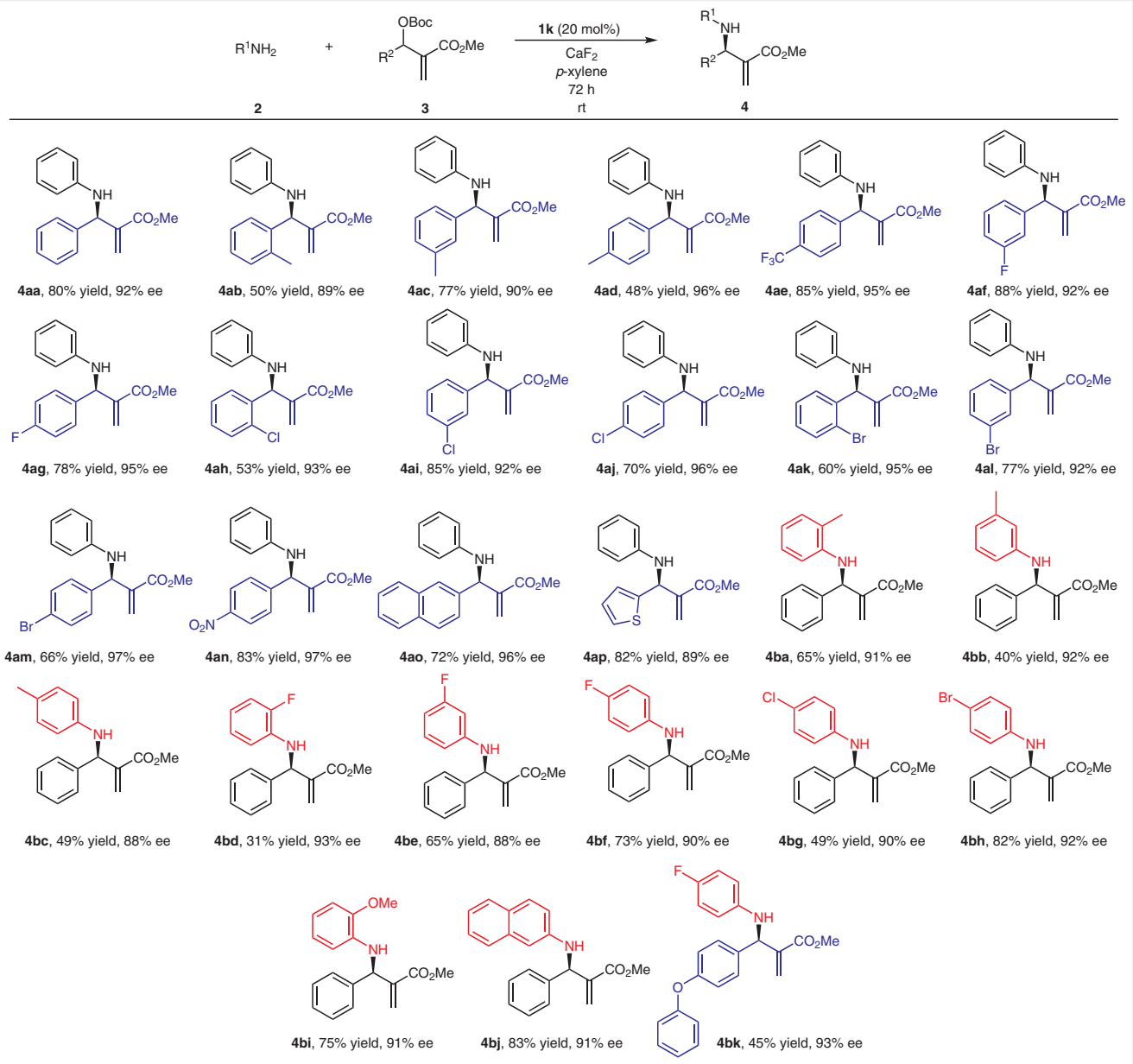


Figure 2 A plausible transition state model in the asymmetric allylic amination reactions

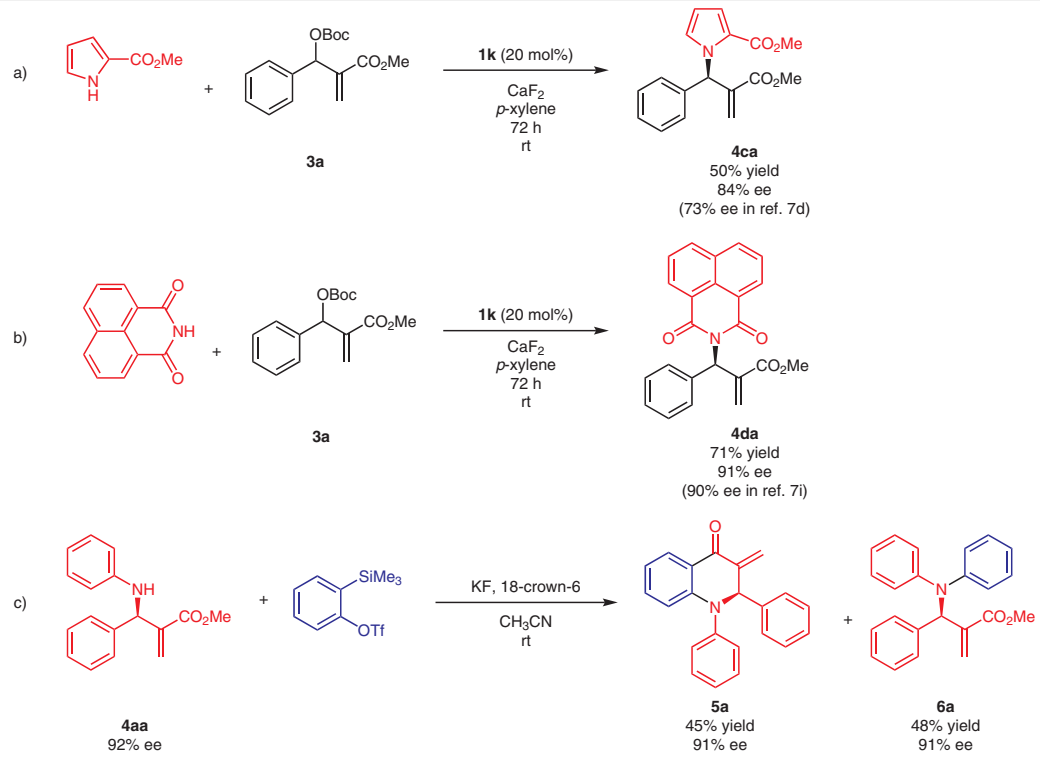


Scheme 2 Substrate scope of the asymmetric allylic amination reaction. *Reaction conditions*: **2** (0.05 mmol), **3** (0.1 mmol), **1k** (0.01 mmol), *p*-xylene (0.5 mL), CaF_2 (0.25 mmol), room temperature, 72 hours. Yields of isolated products are reported. The ee values were determined by HPLC

To demonstrate the utility of the developed methodology, asymmetric allylic amination reactions of MBH carbonate **3a** with other N-nucleophiles were conducted. To our delight, methyl pyrrole-2-carboxylate and 1,8-naphthalimide were well tolerated in this catalytic system. The desired allylic amination products **4ca** and **4da** were afforded in moderate yields and with higher enantioselectivities than those reported in the literature (Scheme 3, eqs a and b).[7d,7i]

The chiral α-methylene-β-arylamino ester **4aa** is widely recognized as a versatile synthetic intermediate.[1] We found that the allylic amination product **4aa** reacted with the aryne precursor 2-(trimethylsilyl)aryl triflate through a cascade sequence involving an insertion/cyclization process, as reported by He in 2016.[1g] Chiral 2,3-dihydroquinolin-4-one derivative **5a** and insertion product **6a** were produced with high enantioselectivities (Scheme 3, eq c).

In summary, we have described a highly efficient asymmetric allylic amination reaction of MBH carbonates with simple aromatic amines by employing a readily available nucleophilic amine catalyst. A series of chiral α-methylene-β-arylamino esters has been accessed in moderate to high yields and with excellent enantioselectivities. Methyl pyr-



Scheme 3 (a) Asymmetric allylic amination of MBH carbonate **3a** with methyl pyrrole-2-carboxylate. (b) Asymmetric allylic amination of MBH carbonate **3a** with 1,8-naphthalimide. (c) Synthesis of chiral 2,3-dihydroquinolin-4-one derivative **5a** from allylic amination product **4aa** and the aryne precursor 2-(trimethylsilyl)aryl triflate

role-2-carboxylate and 1,8-naphthalimide were well tolerated in this catalytic system and gave the desired products with improved enantioselectivities. In addition, a chiral 2,3-dihydroquinolin-4-one derivative was obtained with retained enantiopurity. We believe that the methodology presented herein is a good complement to the palladium-catalyzed allylic amination reaction and might have applications in the synthesis of natural products and biologically relevant compounds.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611740.

References and Notes

(1) (a) Basavaiah, D.; Rao, A. J.; Satyanarayana, T. *Chem. Rev.* **2003**, *103*, 811. (b) Sorbetti, J. M.; Clary, K. N.; Rankic, D. A.; Wulff, J. E.; Parvez, M.; Back, T. G. *J. Org. Chem.* **2007**, *72*, 3326. (c) Declerck, V.; Toupet, L.; Martinez, J.; Lamaty, F. *J. Org. Chem.* **2009**, *74*, 2004. (d) Galeazzi, R.; Martelli, G.; Mobbili, G.; Orena, M.; Rinaldi, S. *Org. Lett.* **2004**, *6*, 2571. (e) Nemoto, T.; Fukuyama, T.; Yamamoto, E.; Tamura, S.; Fukuda, T.; Matsumoto, T.; Akimoto, Y.; Hamada, Y. *Org. Lett.* **2007**, *9*, 927. (f) Murru, S.; McGough, B.; Srivastava, R. S. *Org. Biomol. Chem.* **2014**, *12*, 9133. (g) Reddy, R. S.; Lagishetti, C.; Kiran, I. N. C.; You, H.; He, Y. *Org. Lett.* **2016**, *18*, 3818. (h) Pathak, R.; Madapa, S.; Batra, S. *Tetrahedron* **2007**, *63*, 451. (i) Gowrisankar, S.; Lee, H. S.; Kim, J. M.; Kim, J. N. *Tetrahedron Lett.* **2008**, *49*, 1670.

(2) (a) Wang, X.; Meng, F.; Wang, Y.; Han, Z.; Chen, Y.-J.; Liu, L.; Wang, Z.; Ding, K. *Angew. Chem. Int. Ed.* **2012**, *51*, 9276. (b) Zhou, P.; Liang, Y.; Zhang, H.; Jiang, H.; Feng, K.; Xu, P.; Wang, J.; Wang, X.; Ding, K.; Luo, C.; Liu, M.; Wang, Y. *Eur. J. Med. Chem.* **2018**, *144*, 817. (c) Liu, J.; Han, Z.; Wang, X.; Wang, Z.; Ding, K. *J. Am. Chem. Soc.* **2015**, *137*, 15346. (d) Zhou, P.; Liu, Y.; Zhou, L.; Zhu, K.; Feng, K.; Zhang, H.; Liang, Y.; Jiang, H.; Luo, C.; Liu, M.; Wang, Y. *J. Med. Chem.* **2016**, *59*, 10329. (e) Benfatti, F.; Cardillo, G.; Gentilucci, L.; Mosconi, E.; Tolomelli, A. *Org. Lett.* **2008**, *10*, 2425.

(3) (a) Masson, G.; Housseman, C.; Zhu, J. *Angew. Chem. Int. Ed.* **2007**, *46*, 4614. (b) Declerck, V.; Martinez, J.; Lamaty, F. *Chem. Rev.* **2009**, *109*, 1. (c) Basavaiah, D.; Reddy, B. S.; Badsara, S. S. *Chem. Rev.* **2010**, *110*, 5447.

(4) (a) Liu, X.; Chai, Z.; Zhao, G.; Zhu, S. *J. Fluorine Chem.* **2005**, *126*, 1215. (b) Shi, M.; Ma, G.-N.; Gao, J. *J. Org. Chem.* **2007**, *72*, 9779. (c) Liu, X.; Zhao, J.; Jin, G.; Zhao, G.; Zhua, S.; Wang, S. *Tetrahedron* **2005**, *61*, 3841.

(5) For some recent developments on catalytic transformation of MBH adducts, see: (a) Jiang, F.; Luo, G.-Z.; Zhu, Z.-Q.; Wang, C.-S.; Mei, G.-J.; Shi, F. *J. Org. Chem.* **2018**, *83*, 10060. (b) Cheng, Y.; Han, Y.; Li, P. *Org. Lett.* **2017**, *19*, 4774. (c) Zhan, G.; Shi, M.-L.; He, Q.; Lin, W.-J.; Ouyang, Q.; Du, W.; Chen, Y.-C. *Angew. Chem. Int. Ed.* **2016**, *55*, 2147.

(6) (a) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921. (b) Lu, Z.; Ma, S. *Angew. Chem. Int. Ed.* **2008**, *47*, 258. (c) Wang, Y.; Zhang, T.; Liu, L.; Wang, D.; Chen, Y. *Chin. J. Chem.* **2012**, *30*, 2641. (d) Wang, X.; Guo, P.; Han, Z.; Wang, X.; Wang, Z.; Ding, K. *J. Am. Chem. Soc.* **2014**, *136*, 405. (e) Rajesh, S.; Banerji, B.; Iqbal, J. *J. Org. Chem.* **2002**, *67*, 7852. (f) Wang, Y.; Liu, L.; Wang, D.; Chen, Y.-J. *Org. Biomol. Chem.* **2012**, *10*, 6908. (g) Mei, G.-J.; Li, D.; Zhou, G.-X.; Shi, Q.; Cao, Z.; Shi, F. *Chem. Commun.* **2017**, *53*, 10030. (h) Lu, Y.-N.; Lan, J.-P.; Mao, Y.-J.; Wang, Y.-X.; Mei, G.-J.; Shi, F. *Chem. Commun.* **2018**, *54*, 18527. (i) Li, M.-M.; Wei, Y.; Liu, J.; Chen, H.-W.; Lu, L.-Q.; Xiao, W.-J. *J. Am. Chem. Soc.* **2017**, *139*, 14707. (j) Wang, Y.-N.; Wang, B.-C.; Zhang, M.-M.; Gao, X.-W.; Li, T.-R.; Lu, L.-Q.; Xiao, W.-J. *Org. Lett.* **2017**, *19*, 4094. (k) Mei, G.-J.; Bian, C.-Y.; Li, G.-H.; Xu, S.-L.; Zheng, W.-Q.; Shi, F. *Org. Lett.* **2017**, *19*, 3219.

(7) (a) Rios, R. *Catal. Sci. Technol.* **2012**, *2*, 267. (b) Liu, T.-Y.; Xie, M.; Chen, Y.-C. *Chem. Soc. Rev.* **2012**, *41*, 4101. (c) Wei, Y.; Shi, M. *Chem. Rev.* **2013**, *113*, 6659. (d) Cui, H.-L.; Feng, X.; Peng, J.; Lei, J.; Jiang, K.; Chen, Y.-C. *Angew. Chem. Int. Ed.* **2009**, *48*, 5737. (e) Zhang, H.; Zhang, S.-J.; Zhou, Q.-Q.; Dong, L.; Chen, Y.-C. *Beilstein J. Org. Chem.* **2012**, *8*, 1241. (f) Huang, J.-R.; Cui, H.-L.; Lei, J.; Sun, X.-H.; Chen, Y.-C. *Chem. Commun.* **2011**, *47*, 4784. (g) Lu, H.; Lin, J.-B.; Liu, J.-Y.; Xu, P.-F. *Chem. Eur. J.* **2014**, *20*, 11659. (h) Lin, A.; Mao, H.; Zhu, X.; Ge, H.; Tan, R.; Zhu, C.; Cheng, Y. *Chem. Eur. J.* **2011**, *17*, 13676. (i) Zhang, S.-J.; Cui, H.-L.; Jiang, K.; Li, R.; Ding, Z.-Y.; Chen, Y.-C. *Eur. J. Org. Chem.* **2009**, 5804. (j) Pei, C.-K.; Zhang, X.-C.; Shi, M. *Eur. J. Org. Chem.* **2011**, 4479. (k) Zhao, M.-X.; Chen, M.-X.; Tang, W.-H.; Wei, D.-K.; Dai, T.-L.; Shi, M. *Eur. J. Org. Chem.* **2012**, 3598. (l) Sun, W.; Ma, X.; Hong, L.; Wang, R. *J. Org. Chem.* **2011**, *76*, 7826. (m) Huang, L.; Wei, Y.; Shi, M. *Org. Biomol. Chem.* **2012**, *10*, 1396. (n) Cho, C.-W.; Kong, J.-R.; Krische, M. J. *Org. Lett.* **2004**, *6*, 1337. (o) Pellissier, H. *Tetrahedron* **2017**, *73*, 2831. (p) Zhang, T.-Z.; Dai, L.-X.; Hou, X.-L. *Tetrahedron: Asymmetry*. **2007**, *18*, 1990.

(8) (a) Lee, C. G.; Lee, K. Y.; Lee, S.; Kim, J. N. *Tetrahedron* **2005**, *61*, 1493. (b) Bakthadoss, M.; Srinivasan, J.; Selvakumar, R. *Aust. J. Chem.* **2014**, *67*, 295. (c) Ge, S.-Q.; Hua, Y.-Y.; Xia, M. *Synth. Commun.* **2010**, *40*, 1954. (d) Ge, S.-Q.; Hua, Y.-Y.; Xia, M. *Ultrason. Sonochem.* **2009**, *16*, 743.

(9) (a) Zhao, S.; Lin, J.-B.; Zhao, Y.-Y.; Liang, Y.-M.; Xu, P.-F. *Org. Lett.* **2014**, *16*, 1802. (b) Zhao, S.; Zhao, Y.-Y.; Lin, J.-B.; Xie, T.; Liang, Y.-M.; Xu, P.-F. *Org. Lett.* **2015**, *17*, 3206.

(10) (a) Su, W.; Raders, S.; Verkade, J. G.; Liao, X.; Hartwig, J. F. *Angew. Chem. Int. Ed.* **2006**, *45*, 5852. (b) Bugarin, A.; Connell, B. T. *Chem. Commun.* **2010**, *46*, 2644. (c) Zhu, B.; Yan, L.; Pan, Y.; Lee, R.; Liu, H.; Han, Z.; Huang, K.-W.; Tan, C.-H.; Jiang, Z. *J. Org. Chem.* **2011**, *76*, 6894.

(11) **Asymmetric Allylic Amination; General Procedure**A solution of amine **2** (0.05 mmol), MBH carbonate **3** (0.1 mmol), catalyst **1k** (0.01 mmol) and CaF_2 (0.25 mmol) in *p*-xylene (0.5 mL) was stirred at room temperature for 72 hours. Then the reaction mixture was directly purified by flash column chromatography (eluting with EtOAc/petroleum ether, 10:1) to afford the product **4**.

Methyl (*R*)-2-[Phenyl(phenylamino)methyl]acrylate (4aa) Colorless oil; 80% yield; 92% ee; $[\alpha]_D^{28}$ = –91.1 (*c* 0.7, $CHCl_3$). The enantiomeric excess was determined by HPLC analysis with an OD-H column (*n*-hexane/*i*-PrOH, 95:5), 1.0 mL/min, λ = 254 nm, t_R (major) = 8.57 min, t_R (minor) = 10.76 min. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.28 (m, 5 H), 7.20–7.14 (m, 2 H), 6.75–6.70 (m, 1 H), 6.58 (dd, *J* = 8.4 Hz, *J* = 0.9 Hz, 2 H), 6.40 (s, 1 H), 5.97 (t, *J* = 1.2 Hz, 1 H), 5.41 (s, 1 H), 4.16 (s, 1 H), 3.71 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 146.8, 140.7, 140.0, 129.3, 128.9, 128.0, 127.7, 126.4, 118.0, 113.5, 59.1, 52.1; HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{18}NO_2$: 268.1332; found: 268.1333.

(12) (a) Wu, G.; Wong, Y.; Chen, X.; Ding, Z. *J. Org. Chem.* **1999**, *64*, 3714. (b) Sasikala, C. H. V. A.; Padi, P. R.; Sunkara, V.; Ramayya, P.; Dubey, P. K.; Uppala, V. B. R.; Praveen, C. *Org. Process Res. Dev.* **2009**, *13*, 907.

(13) (a) Kim, J. N.; Lee, H. J.; Gong, J. H. *Tetrahedron Lett.* **2002**, *43*, 9141. (b) Baidya, M.; Remennikov, G. Y.; Mayer, P.; Mayr, H. *Chem. Eur. J.* **2010**, *16*, 1365.