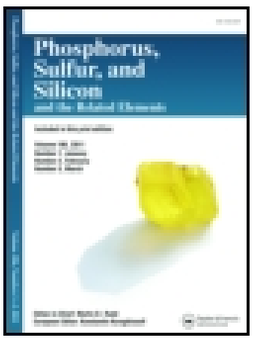

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Catalytic activity of chiral chelating *N*-heterocyclic carbene palladium complexes towards asymmetric allylic alkylation

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ABSTRACT

The catalytic activity of a series of chiral heteroaryl coordinated chelating *N*-heterocyclic carbene (NHC) palladium complexes towards asymmetric allylic alkylation (AAA) were presented here. The effects of different *N*-substituents, NHC backbones and chelate rings on the catalytic activity and the enantioselectivity of the alkylation of (*E*)-1,3-diarylallyl acetates with dialkyl malonate were investigated. The results showed that, under the optimized conditions, complexes **3a**, **3b**, and **3i** carrying the pyridinyl-coordinated five-membered chelate ring showed high catalytic activity and chiral induction efficiency. The corresponding alkylated products were obtained in high yields with moderate ee. Furthermore, it was found that the substituents of (*E*)-1,3-diarylallyl acetates and the type of the nucleophile affect the results as well.

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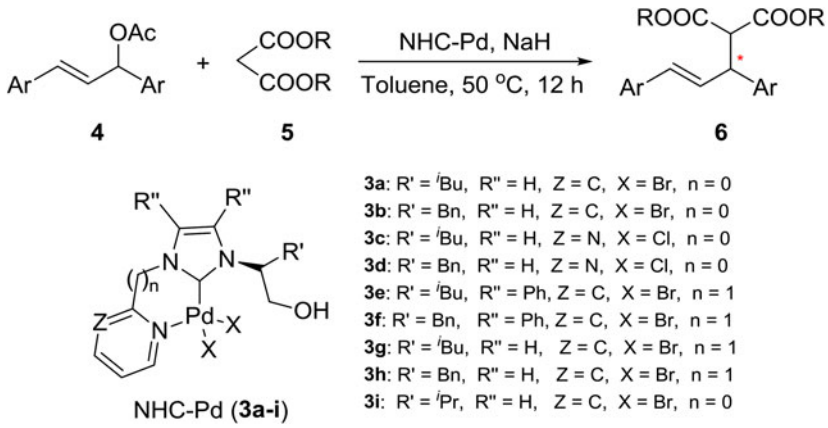
KEYWORDS
N-heterocyclic carbene; chiral; chelating; palladium; asymmetric allylic alkylation

GRAPHICAL ABSTRACT



Introduction

N-Heterocyclic carbenes (NHCs) have been recognized as a class of very powerful ligands in organic chemistry due to their inherent characteristics of strong σ-donor and comparatively weak π-acceptor abilities, and facilely modifiable steric and electronic properties.[1] One of the most important steps in the development of functionalized NHC ligands is their chiral modification for asymmetric reactions.[2] Many strategies have been developed for the introduction of chirality into NHC ligands, including introduction of chiral biaryl units, inclusion of chiral backbone in the heterocycle, and introduction of chiral alkyl side chains at *N*-substituent, etc.[3] Introduction of donor containing chiral *N*-substituent at NHC provides chelating NHC ligand, which is expected to acts as a polydentate ligand upon coordination to a metal center, and then offer a key structure for the construction of efficient stereodirecting group. Based on this, chelating NHC ligands carrying P, S, N, O, *etc.* donor containing *N*-substituents have been synthesized, characterized, and investigated in different kinds of asymmetric catalytic reactions.[4]

The transition-metal-catalyzed allylic substitution reaction is known as an efficient synthetic tool for the construction of carbon-carbon or carbon-heteroatom bonds.[5] Since the first palladium-catalyzed enantioselective allylic substitution process described by Trost in 1977,[6] palladium-catalyzed asymmetric allyl alkylation (AAA) reaction has developed into one of the most important method for the elaboration of enantioselective carbon–carbon or carbon-heteroatom bonds for the synthesis of pharmaceuticals and bulk materials.[7] Meanwhile, chiral NHC-palladium catalyzed AAA began to attract quite extensive research interest in recent

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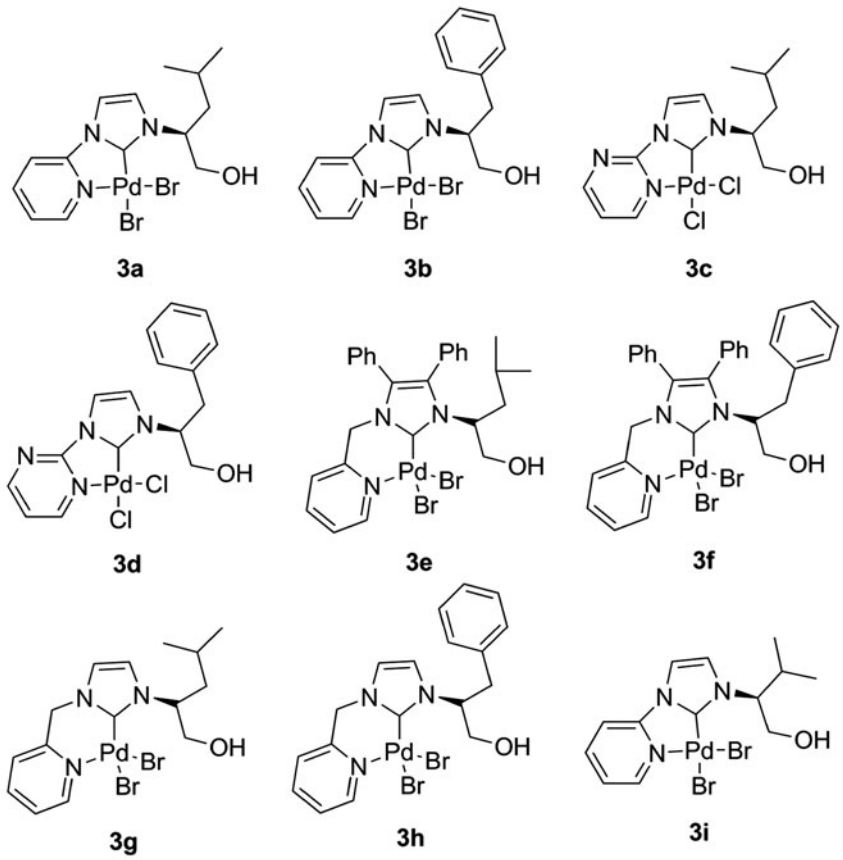


Figure 1. NHC palladium complexes used in this paper.

years.[8] Douthwaite et al. synthesized imine-functionalized NHCs containing neutral donor *N* atoms, by using which a maximum *ee* of 92% was achieved in the palladium-catalyzed AAA reaction of 1,3-diphenylprop-3-en-1-yl acetate with dimethyl malonate.[9] Fernández et al. developed a palladium complex with a chelating neutral thioether/NHC ligand, and tested the complex in the AAA reaction. Good yields of product and moderate to good *ee* values were obtained.[10] Sakaguchi et al. synthesized anionic amidate/NHC-Pd(II) complexes and tested the complexes in AAA reaction of 1,3-diphenylprop-3-en-1-yl acetate with $NaCH(CO_2Me)_2$. 88% *ee* was achieved under optimized conditions.[8b]

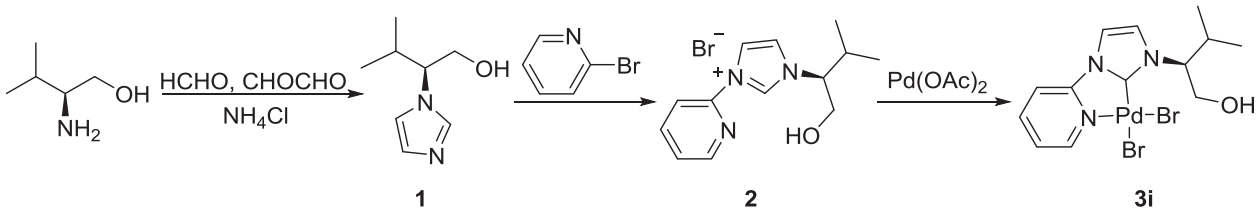
Recently, we synthesized and characterized a series of heteroaryl coordinated chelating chiral NHC palladium complexes **3a**-**h** featuring different *N*-substituents, chelate rings or NHC backbones (Figure 1).[11] The preliminary research proved their efficient catalytic activity towards the 2-arylation of (benzo)oxazoles,[11a] Suzuki cross-coupling in water,[11b] and regioselective phosphorylation of coumarins.[11c] Here, the catalytic performance of these chiral chelating NHC palladium complexes towards the asymmetric allylic substitution reaction of *rac*-(*E*)-1,3-diaryl-2-propenyl acetate and dialkyl malonate was examined. To investigate the chiral induction efficiency of the chiral chelating NHC palladium complexes and establish the relationship between the structure and the activity and enantioselectivity, compound **3i** was synthesized and structurally characterized in addition to the reported complexes **3a**-**h.**[11]

Results and discussion

The catalysts used in this paper have been reported except complex **3i** (Figure 1).[11] Complex **3i** was synthesized through a procedure similar to the literature by using *L*-valinol as starting material (Scheme 1).[11,12] The condensation reaction of *L*-valinol, formaldehyde, glyoxal, and ammonium chlorides in methanol afforded imidazole alcohol **1** in high yields (85%). The following neat reaction of imidazole alcohol **1** with excess 2-bromopyridine at 150 °C afforded the pyridine hydroxyalkyl di-functionalized imidazolium salt **2**. Direct metalation of imidazolium salt **2** by $Pd(OAc)_2$ in dichloromethane at room temperature lead to the formation of the chelating NHC palladium complex **3i**, which was purified by column chromatography and characterized by NMR and elemental analysis data.

Having the catalysts in hands, the allylic alkylation substitution reaction of *rac*-(*E*)-1,3-diphenyl-2-propenyl acetate **4a** and diethyl malonate **5a** was chosen as a model reaction to test the performance (Table 1). The results showed that the pyridinyl-coordinated complexes (**3a**, **3b**) showed better catalytic activity than the pyrimidinyl-coordinated analogs (**3c**, **3d**) (Table 1, entries 1–4). High yields and moderate *ee* were obtained with complex **3a** (yield 96%, 56% *ee*) and complex **3b** (yield 96%, 60% *ee*). The dominant configuration is determined to be (*R*) by comparison of the retention time under similar HPLC conditions with the literature reports.[13]

In addition, the complexes (**3a, 3b,** or **3i**) containing pyridinyl-coordinated five-membered chelate ring showed better



Scheme 1. Synthesis of complex **3i**.

results than the analogs (**3e, 3f, 3g,** or **3h**) containing six-membered chelate ring (Table 1, entries 1–2, and 5–9). This may be attributed to the high rigidity of the five-membered chelate ring, which favors for catalytic activity and enantioselectivity. In the five-membered chelating pyridinyl-coordinated complexes (**3a, 3b,** or **3i**), the *N*-substituent did not show significant effect on the catalytic results. While in the six-membered chelating pyridinyl-coordinated complexes (**3e, 3f, 3g,** or **3h**), the *N*-substituent affected the catalytic results significantly, with those carrying benzyl-substituent showing much higher yields and better *ee* values than the *iso*-butyl substituted analogs (Table 1, entries 5–8). Introduction of phenyl substituents on the backbone of the NHC lead to the inversion of the preferential configuration of the products. When using **3e** or **3f** as catalyst, the dominant configuration of the product is determined to be (*S*). This may be attributed to the steric effects of the phenyl group, which makes the favorable attack reversal.

Based on the above analysis, using complex **3a** as catalyst, the effect of solvent, base, and temperature on the reaction was investigated (Table 2). High yield with moderate *ee* was obtained when using NaH as base (Table 2, entry 1). The presence of other bases, such as NaOH, Na_2CO_3, KOAc, or KOAc/BSA, resulted in very low yields or nearly no reaction at all (Table 2, entries 2–5). When screening different solvents such as toluene, DMF, THF, MeCN, CH_2Cl_2, diethyl ether, or DMSO, we found that toluene exhibited the best performance. When using DMF or DMSO as solvent, the dominant configuration of the product became (*S*). Decreasing the reaction temperature to 40 °C resulted in a drastic drop of the reaction yield, while no obvious improvement on the *ee* (Table 2, entry 12). From the above discussion, the optimal reaction conditions were determined to employ **3a** (2.5 mol%) as catalyst, NaH (2.5 equiv.) as base, and toluene as solvent at 50 °C for 12 h.

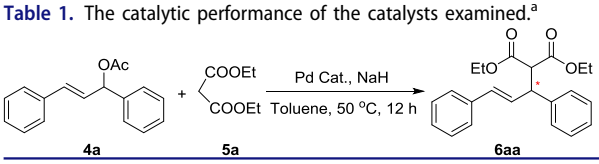
To investigate the catalytic efficiency of complexes **3a** and **3i** further, a series of (*E*)-1,3-diarylallyl acetates **4a-h** bearing differently substituted phenyl groups were synthesized *via* aldol condensation, reduction, and esterification according to literature report.[14] Both diethyl malonate and dimethyl malonate were utilized as nucleophile for the substitution reaction. As shown in Table 3, under the optimized reaction conditions, when using diethyl malonate as nucleophile, the substrates with *ortho*-, or *meta*- substituent all provided moderate to high yields and enantioselectivities. The electron-withdrawing group substituted substrates produced better results than the electron-donating group substituted ones (Table 3, entries 2–6, 18–20). When using dimethyl malonate as nucleophile, the substrates with *ortho*-, or *meta*- substituent produced slightly lower yields and enantioselectivities than those using diethyl malonate as nucleophile (Table 3, entries 9–14, and 25–30). While for *para*-bromo-substituted (*E*)-1,3-diarylallyl acetates, lower yields and enantioselectivities were obtained when using diethyl malonate as a nucleophile (Table 3, entries 7, 23). In the reaction of *para*-methoxyl-substituted substrate, nearly no products were obtained either using diethyl malonate or dimethyl malonate as a nucleophile (Table 3, entries 8, 16, 24, or 36). From above discussion, it can be concluded that in the NHC-palladium catalyzed asymmetric allylic alkylation system here, both the substituents of (*E*)-1,3-diarylallyl acetates and the type of the nucleophile affect the results obviously.

At this stage, we had no experimental evidence to explain the reaction mechanism. Based on above results and literature reports,[15] we proposed the following model to explain the formation of the major enantiomer (Scheme 2). The key intermediate of the enantioselective allylic substitution is the formation of square-planar palladium-allyl complex, which gives two possible orientations: M-type and W-type. To relieve the steric hindrance between the substituents on the NHC ligand and the aryl group of the substrates, M-type intermediate is favored.[16] Concerning the *trans*-effect, the carbon atom situated *trans*- to NHC-carbon would be more susceptible to the incoming nucleophile attack due to the larger *trans*- influence of the NHC moiety compared to the pyridine *N* in these system.[11a] Hence, the nucleophilic substitution occurred at the allylic carbon *trans*- to the NHC-carbon, the prevailing enantiomer originated from the M-type isomer and provided the (*R*)-product. As reported in literature,[8b] the hydroxyl group in the NHC would be converted into sodium alcoholate under the reaction conditions. The interaction between the sodium alcoholate and nucleophile would assist the approach of the nucleophile to the π-allyl palladium center.

Conclusions

In conclusion, the catalytic activity and chiral induction efficiency of a series of heteroaryl coordinated chelating NHC palladium complexes towards the asymmetric allylic alkylation were investigated. The relationship between the activity and the structure was tentatively established. The pyridinyl-coordinated NHC complexes carrying the highly rigid five-membered chelate ring showed higher catalytic activity and chiral induction efficiency. The reaction of different substituted (*E*)-1,3-diarylallyl acetates with diethyl/dimethyl malonates were tested. The results showed that the substituents of (*E*)-1,3-diarylallyl acetates and the type of the nucleophile affect the results as well. Studies on the performance of the chiral chelating NHC palladium complexes towards other asymmetric organic transformations are currently in progress in our lab.

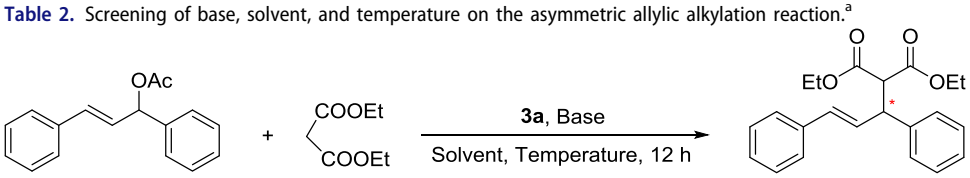
Table 1. The catalytic performance of the catalysts examined.[a]



Entry	Pd Cat.	Yield[b] (%)	ee[c] (%)
1	**3a**	96	56 (*R*)
2	**3b**	96	60 (*R*)
3	**3c**	10	52 (*R*)
4	**3d**	15	11 (*R*)
5	**3e**	16	13 (*S*)
6	**3f**	84	27 (*S*)
7	**3g**	20	13 (*R*)
8	**3h**	96	35 (*R*)
9	**3i**	99	70 (*R*)
10	**Pd(PPh$_3$)$_4$**	94	0 (*R*)

[a]The reaction was conducted with **4a** (1.0 mmol) and **5a** (2.5 mmol) in the presence of NaH (2.5 mmol) in toluene (3 mL), using complexes **3a-3i**, or **Pd(PPh$_3$)$_4$** as catalyst for 12 h.
[b]Isolated yield.
[c]Determined by HPLC analysis of the products using a Chiralcel AD-H column with n-hexane/2-propanol (90:10, 1.0 mL/min) as eluent. The absolute configuration was determined by comparison of the retention time under similar HPLC conditions with the literature reports.[13]

Table 2. Screening of base, solvent, and temperature on the asymmetric allylic alkylation reaction.[a]



Entry	Base	Solvent	Temp (°C)	Yield[b] (%)	ee[c] (%)
1	NaH	Toluene	50	96	56 (*R*)
2	NaOH	Toluene	50	5	30 (*R*)
3	Na_2CO_3	Toluene	50	Trace	—
4	KOAc	Toluene	50	Trace	—
5	OKAc/BSA	Toluene	50	Trace	—
6	NaH	DMF	50	20	16 (*S*)
7	NaH	THF	50	Trace	—
8	NaH	MeCN	50	Trace	—
9	NaH	CH_2Cl_2	50	5	13 (*R*)
10	NaH	Diethyl ether	50	25	64 (*R*)
11	NaH	DMSO	50	9	15 (*S*)
12	NaH	Toluene	40	14	51 (*R*)
13	NaH	Toluene	30	Trace	—

[a]The reaction was conducted with **4a** (1.0 mmol) and **5a** (2.5 mmol) in the presence of base (2.5 mmol) in solvent (3 mL), using catalyst **3a** (2.5mol%) for 12 h.
[b]Isolated yield.
[c]Determined by HPLC analysis of the products using a Chiralcel AD-H column with n-hexane/2-propanol (90:10, 1.0 mL/min) as eluent. The absolute configuration was determined by comparison of the retention time under similar HPLC conditions with the literature reports.[13]

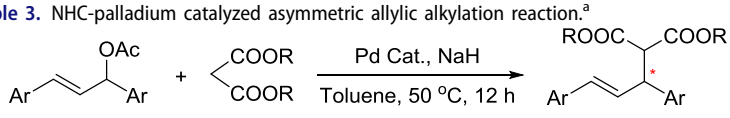
Experimental

Unless otherwise noted, all reactions were carried out under Ar or N_2 using standard Schlenk and vacuum line techniques. The NHC palladium complexes were prepared by our group.[11] Other reagents were obtained from commercial sources and used as received without further purification. NMR Spectra (^{1}H and ^{13}C) were recorded at 25 °C on a Bruker 400 MHz spectrometer. Chemical shifts (δ in ppm, coupling constant J in Hz) were referenced to internal Me_4Si.

General procedure for the synthesis of complex 3i

Synthesis of imidazole alcohol (**1**): *L*-valinol (60 mmol, 7.5 mL) and ammonium chloride (60 mmol, 3.21 g) were dissolved in MeOH (120 mL), and the mixture was put into an ice bath. Aqueous HCHO solution (36%, 60 mmol, 11.7 mL) and aqueous CHOCHO solution (40%, 60 mmol, 14.8 mL) were then added dropwise before the mixture was heated to 60 °C for 5 h. The mixture was then cooled to room temperature and the solvent was removed by evaporation. The residue was dispersed in NaOH solution (150 mL, 2 M), and then extracted by CH_2Cl_2 (3 × 20 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated. Purification of the residue by flash chromatography (silica, CH_3COOEt/EtOH, 10/1, *v/v*) afforded the pure product as white crystals (7.86 g, yield 85%). ^{1}H NMR (DMSO, 400 MHz): δ 7.59 (s, 1H, CH in imidazole), 7.16 (s, 1H, CH in imidazole), 6.88 (s, 1H, CH in imidazole), 4.97 (t, J = 4.80 Hz, 1H, CH_2OH), 3.79–3.71 (m, 3H, NC*H*, CH_2OH), 2.08–2.04 (m, 1H, C*H*$(CH_3)_2$), 0.93 (d, J = 6.40 Hz, 3H, CH$(CH_3)_2$), 0.63 (d, J = 6.80 Hz, 3H,

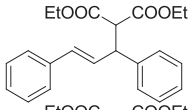
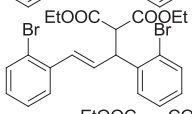
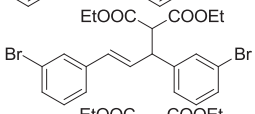
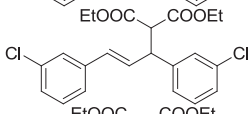
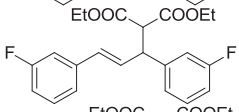
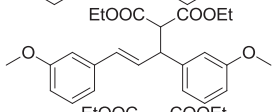
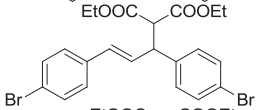
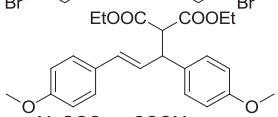
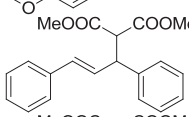
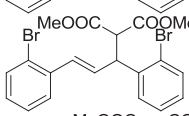
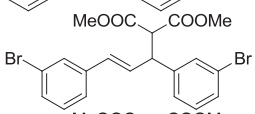
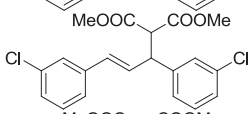
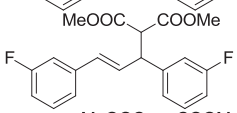
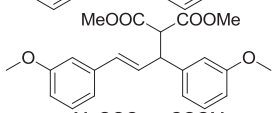
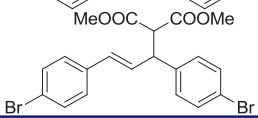
Table 3. NHC-palladium catalyzed asymmetric allylic alkylation reaction.[a]



4 **5** **6**

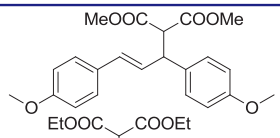
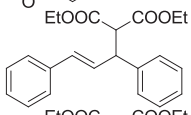
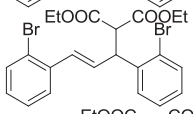
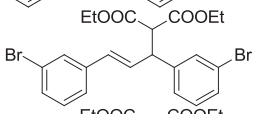
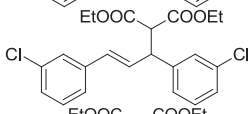
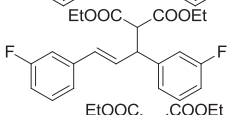
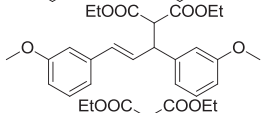
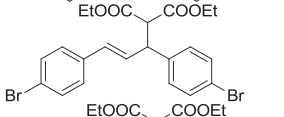
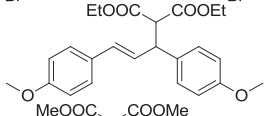
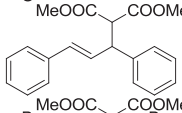
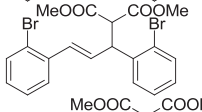
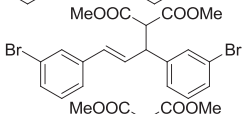
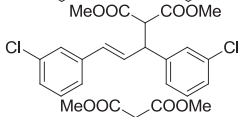
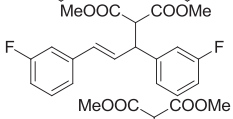
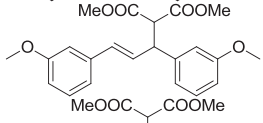
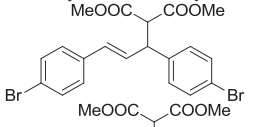
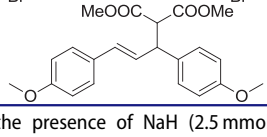
R = Et- (**a**), Me- (**b**).

Ar = C_6H_5- (**a**), *o*-Br-C_6H_4- (**b**), *m*-Br-C_6H_4- (**c**), *m*-Cl-C_6H_4- (**d**), *m*-F-C_6H_4- (**e**), *m*-MeO-C_6H_4- (**f**), *p*-Br-C_6H_4- (**g**), *p*-MeO-C_6H_4- (**h**).

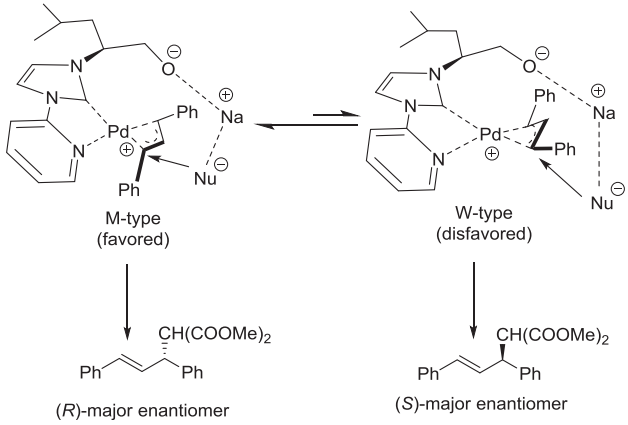
Entry	Cat	Product	Product	Yield[b] (%)	ee[c](%)
1	**3a**	**6aa**		96	56 (*R*)
2	**3a**	**6ba**		31	30 (*R*)
3	**3a**	**6ca**		81	69 (*R*)
4	**3a**	**6da**		90	69 (*R*)
5	**3a**	**6ea**		91	63 (*R*)
6	**3a**	**6fa**		75	59 (*R*)
7	**3a**	**6ga**		61	71 (*R*)
8	**3a**	**6ha**		Trace	—
9	**3a**	**6ab**		65	56 (*R*)
10	**3a**	**6bb**		Trace	—
11	**3a**	**6cb**		56	62 (*R*)
12	**3a**	**6db**		30	44 (*R*)
13	**3a**	**6eb**		50	50 (*R*)
14	**3a**	**6fb**		20	25 (*R*)
15	**3a**	**6gb**		52	59 (*R*)

(*continued*)

Table 3. Continued.

Entry	Cat	Product	Product	Yield[b] (%)	ee[c](%)
16	**3a**	**6hb**		Trace	—
17	**3i**	**6aa**		99	70 (*R*)
18	**3i**	**6ba**		56	54 (*R*)
19	**3i**	**6ca**		61	74 (*R*)
20	**3i**	**6da**		90	72 (*R*)
21	**3i**	**6ea**		99	6 (*R*)
22	**3i**	**6fa**		75	7 (*R*)
23	**3i**	**6ga**		20	54 (*R*)
24	**3i**	**6ha**		Trace	—
25	**3i**	**6ab**		90	50[d] (*R*)
26	**3i**	**6bb**		Trace	—
27	**3i**	**6cb**		39	54 (*R*)
28	**3i**	**6db**		15	54 (*R*)
29	**3i**	**6eb**		40	8 (*R*)
30	**3i**	**6fb**		21	0
31	**3i**	**6gb**		45	66 (*R*)
32	**3i**	**6hb**		Trace	—

[a]The reaction was conducted with **4** (1.0 mmol) and **5** (2.5 mmol) in the presence of NaH (2.5 mmol) in toluene (3 mL), using catalyst **3a** or **3i** (2.5 mol%) for 12 h.
[b]Isolated yield.
[c]Determined by HPLC analysis of the products using a Chiralcel AD-H column with n-hexane/2-propanol (90:10, 1.0 mL/min) as eluent. The absolute configuration was determined by comparison of the retention time under similar HPLC conditions with the literature reports.[13]
[d]Determined by HPLC analysis of the products using a Chiralcel OD-H column with n-hexane/2-propanol (100:1, 0.6 mL/min) as eluent. The absolute configuration was determined by comparison of the retention time under similar HPLC conditions with the literature reports.[13]



Scheme 2. Proposed mechanism for the formation of enantioselectivity.

$CH(CH_3)_2$) ppm. ^{13}C NMR (DMSO, 100 MHz): δ 137.4, 128.5, 118.1, 65.0, 57.8, 24.5, 23.5, 22.0 ppm. MS Calcd. for $C_8H_{14}N_2O$, 154.11. Found: ESI-MS (m/z): 155.12 $[M+H]^+$.

Synthesis of pyridine hydroxyalkyl di-functionalized imidazolium bromides (**2**): A Schlenk tube containing imidazole alcohol **1** (0.77 g, 5.0 mmol) and 2-bromopyridine (3.0 mL) was heated at 150 °C for 72 h. The mixture was then cooled to room temperature and added to diethyl ether (30 mL) dropwise. The deep yellow precipitate formed was then collected and purified by flash chromatography (silica, CH_2Cl_2/EtOH, gradient elution, 15/1–8/1, *v/v*) to obtain the pure product as a viscous oil (1.29 g, yield 83%). ^1H NMR (400 MHz, DMSO): δ 10.23 (s, 1H, CH in imidazole), 8.67–8.64 (m, 2H, CH in pyridine, CH in imidazole), 8.25–8.15 (m, 3H, CH in pyridine, CH in imidazole), 7.67–7.64 (m, 1H, CH in pyridine), 5.25 (bs, 1H, CH_2OH), 4.34–4.28 (m, 1H, NC*H*), 3.95–3.86 (m, 2H, CH_2OH), 2.34–2.25 (m, 1H, $CH(CH_3)_2$), 1.03 (d, 3H, $J=6.80$ Hz, $CH(CH_3)_2$), 0.79 (d, 3H, $J=6.80$ Hz, $CH(CH_3)_2$) ppm. ^{13}C NMR (100 MHz, DMSO): δ 149.6, 146.9, 141.0, 135.1, 125.7, 123.4, 119.8, 114.9, 69.8, 60.9, 29.1, 19.6, 19.4 ppm. MS Calcd. For $C_{13}H_{18}BrN_3O$, 311.06. Found: ESI-MS (m/z): 232.15 $[M\text{-}Br]^+$.

Synthesis of palladium complex (**3i**): A mixture of imidazolium salt **2** (0.31 g, 1.0 mmol), $Pd(OAc)_2$ (0.22 g, 1.0 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 12 h. The solvent was then evaporated and the residue was purified by column chromatography (silica, CH_2Cl_2/acetone, gradient elution, 15/1–4/1, *v/v*). NHC palladium complex **3i** was obtained as yellow solids (0.15 g, yield 30%). ^1H NMR (DMSO, 400 MHz): δ 9.46 (s, 1H, CH in pyridine), 8.47 (d, 1H, $J=2.24$ Hz, CH in imidazole), 8.40–8.36 (m, 1H, CH in pyridine), 8.18 (d, 1H, $J=8.0$ Hz, CH in pyridine), 7.76 (d, 1H, $J=2.3$ Hz, CH in imidazole), 7.62 (t, 1H, $J=6.6$ Hz, CH in pyridine), 6.02 (bs, 1H, NC*H*), 5.00 (t, 1H, $J=5.0$ Hz, CH_2OH), 3.84–3.75 (m, 2H, CH_2OH), 2.25–2.19 (m, 1H, $CH(CH_3)_2$), 1.05 (d, 3H, $J=6.6$ Hz, $CH(CH_3)_2$), 0.81 (d, 3H, $J=6.8$ Hz, $CH(CH_3)_2$). ^{13}C NMR (DMSO, 100 MHz): δ 151.9, 150.8, 143.4, 123.6, 122.4, 117.7, 112.8, 66.1, 61.3, 29.0, 19.6, 19.5 ppm. Anal Cald. for $C_{13}H_{17}Br_2N_3OPd$ (497.53): C, 31.38; H, 3.44; N, 8.45. Found: C, 31.30; H, 3.39; N, 8.48.

General procedure for the asymmetric allylic alkylation

To a flame-dried Schlenk tube under an argon atmosphere, NHC Pd-catalysts (2.5 mol%) and toluene (3 mL) were added. The solution was stirred at room temperature for 0.5 h, before (*E*)-1,3-diarylallyl acetates **4** (1.0 mmol) was added, followed by addition of malonate **5** (2.5 mmol) and NaH (2.5 mmol). The mixture was then heated to 50 °C and kept for 12 h. TLC showed the full conversion of the substrates. Water (10 mL) was added and the mixture was extracted with CH_2Cl_2 (2×10 mL). The organic layer was combined, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1, *v/v*) to afford the desired product **6**, which were characterized by ^1H NMR. The *ee* of **6ab** was determined by HPLC using a Chiralcel OD-H column (*n*-hexane/2-propanol =100:1; 0.6 mL/min) and detected at a UV wave length of 254 nm. The *ee* of other products were determined by HPLC using a Chiralcel AD-H column (*n*-hexane/2-propanol =90:10; 1.0 mL/min) and detected at a UV wave length of 254 nm. The yields and the *ee* of each case were listed in Table 3.

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