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Axially chiral C_2-symmetric *N*-heterocyclic carbene (NHC) palladium complexes-catalyzed asymmetric arylation of aldehydes with arylboronic acids

Rui Zhang [a], Qin Xu [a], Xiuchun Zhang [a], Tao Zhang [a], Min Shi [a,b,*]

[a] *Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 Mei Long Lu, Shanghai 200 237, China*

[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200 032, China*

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ABSTRACT

Chiral C_2-symmetric *N*-heterocyclic carbene (NHC) palladium diaquo complexes **5a–c** and the chiral C_2-symmetric NHC-palladium complexes **5d** and **5e** prepared from (*R*)-BINAM or H_8-(*R*)-BINAM could be used as the catalysts for the enantioselective arylation of arylaldehydes with arylboronic acids in which NHC-Pd complex **5a** was found to be fairly effective in this reaction to give the corresponding adducts in moderate enantioselectivities along with moderate to good yields.

1. Introduction

Chiral diarylmethanols are important intermediates in most pharmacologically and biologically active compounds and therefore represent significant synthetic targets.[1] With regards to the synthesis of chiral diarylmethanols, the catalytic asymmetric arylation of arylaldehydes with arylboronic acids in the presence of chiral transition metal complexes has attracted much attention due to its safe and mild conditions. Upon carrying out a survey in the literature, it was found that Oi and Inoue first reported the rhodium-catalyzed arylation of ketones and aldehydes with arylstannanes under mild conditions in 1997;[2] then Miyaura et al. reported the Rh complex-catalyzed 1,2-addition to aldehydes with arylboronic acids to give diarylmethanols in high yields in 1998.[3] Many synthetic methods on the transition metal-catalyzed arylation of aldehydes with arylboronic acids have since been disclosed.[4] Among these synthetic methods, Zhou et al. developed several novel and effective chiral Rh-spiromonophosphite complexes for this reaction, achieving 62–87% ees along with good yields for representative aromatic aldehydes.[5] More recently, Miyaura et al. have developed an interesting Me-bipam ligand system for the enantioselective ruthenium-catalyzed arylation of aldehydes with arylboronic acids, affording the corresponding diarylmethanols in good yields and ees.[6] Hayashi et al. also have developed effective tbf ligands for the rhodium-catalyzed asymmetric arylation of aldehydes, giving chiral diarylmethanols in high yields and ees.[7] However, unlike Rh and Ru catalysts, using chiral Pd catalysts in the arylation of aldehydes has not been very successful and usually gave the adducts in lower enantioselectivities.[8] These results promoted us to explore new chiral Pd catalysts for these asymmetric addition reactions, since we envisioned that with the development of novel chiral ligands, chiral Pd complexes could work as efficient catalysts in this reaction as well. Herein, we report several chiral C_2-symmetric *N*-heterocyclic carbene (NHC) palladium catalysts in the enantioselective arylation of aldehydes with arylboronic acids under mild conditions.

2. Results and discussion

Chiral C_2-symmetric *N*-heterocyclic carbene (NHC) palladium diaquo complexes **5a–c** in addition to chiral C_2-symmetric NHC-palladium complexes **5d** and **5e** were synthesized from (*R*)-BINAM or (*R*)-H_8-BINAM, respectively, according to our previous literature (Scheme 1).[9] Notably, the structure of new chiral NHC-Pd complex **5e** was determined by X-ray diffraction (Fig. 1).[10] In the comparison of the dihedral angles of the two naphthalene rings between NHC-Pd(II) complexes **5a** and **5e**, we found that **5e** is 84.6° and **5a** is 78.2°,[9] which may cause the difference in the chiral induction.

Initial examinations using 4-nitrobenzaldehyde **6a** and phenylboronic acid **7a** as the substrates in the presence of chiral C_2-symmetric *N*-heterocyclic carbene (NHC) palladium diaquo complex **5a** and 4 Å MS (20 mg) in $CHCl_3$ were aimed at determining the optimal conditions and the results of these experiments are summarized in Table 1. It was found that no reaction occurred in the absence of base, even when the reaction was carried out at 60 °C (Table 1, entries 1–3). Base screening for the reaction revealed that using KOH (1.0 equiv) as the base afforded **8aa** in 48% ee and >99% yield in $CHCl_3$ and increasing or decreasing the employed amount of KOH did not improve the yield of **8aa** (Table 1, entries 4–6). The other bases such as KF, K_3PO_4, H_2O, KO^{t}Bu, Cs_2CO_3, Ag_2CO_3, and NaOH did not give **8aa** in good yields (Table 1, entries 7–13).

* Corresponding author.
E-mail address: Mshi@mail.sioc.ac.cn (M. Shi).

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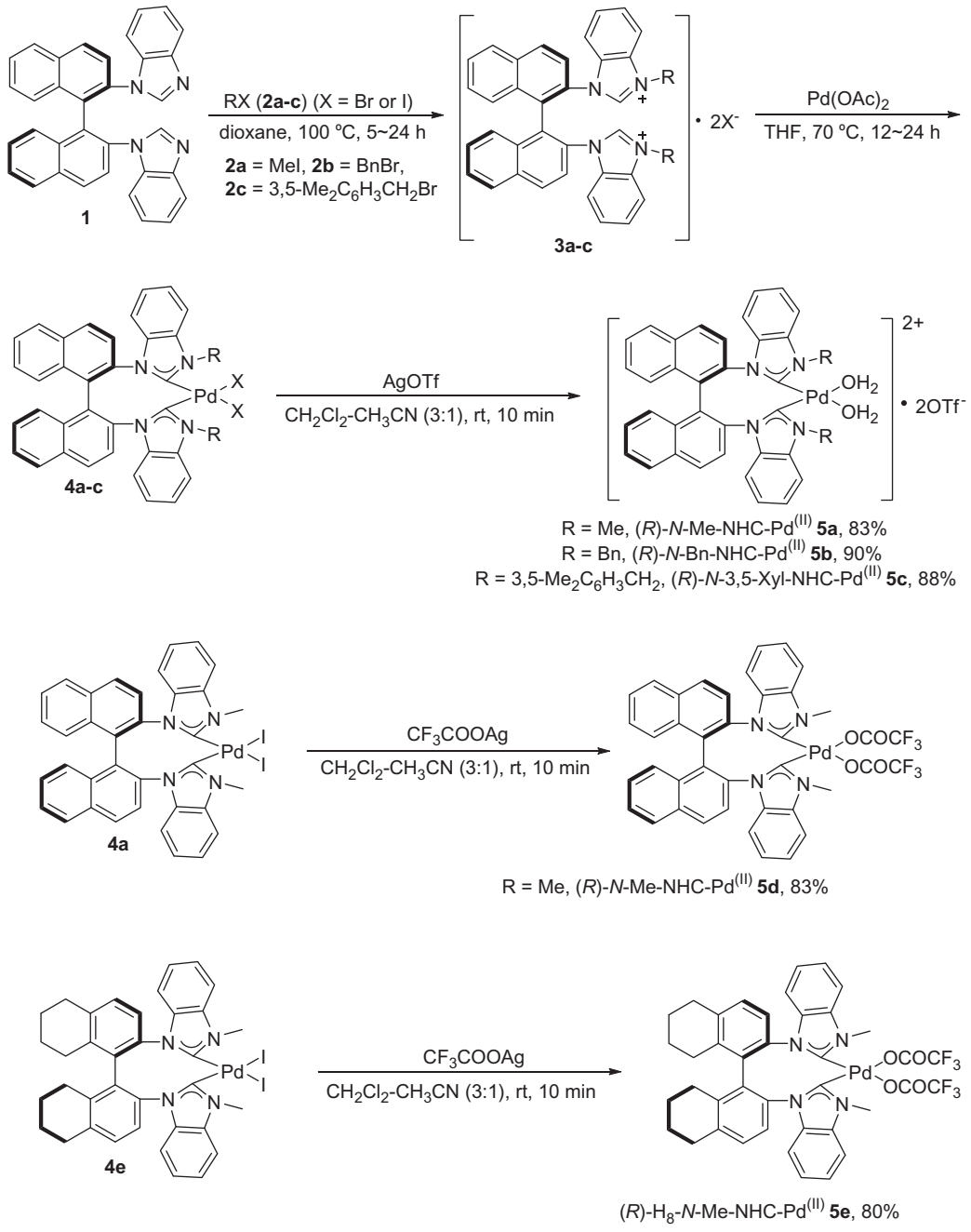


Scheme 1. General procedure for the synthesis of chiral C_2-symmetric *N*-heterocyclic carbene cationic Pd(II) diaquo complexes **5a**–**c** as well as chiral C_2-symmetric NHC-Pd(II) complexes **5d** and **5e**.

With these tentatively optimized conditions in hand, we next attempted to use catalysts **5b**–**e** in the reaction under identical conditions as shown in entry 4 of Table 1. Catalyst **5d** (3 mol %) had similar catalytic ability to that of **5a**, giving the desired product **8aa** in excellent yield (>99%) and 45% ee after 36 h (Table 2, entry 3). Other NHC-Pd complexes **5b** and **5c** as well as **5e** having a chiral H_8-binaphthyl scaffold were not as effective as catalyst **5a** (Table 2, entries 1–4). Using chiral catalyst **5a**, we also examined solvent effect in this catalytic asymmetric addition reaction with toluene, tetrahydrofuran (THF), dichloromethane, DMSO, and DMF, but no improvement could be observed in these solvents (Table 2, entries 5–9). Using **5d** as the catalyst, we also carried out the reaction in $CHCl_3$, THF, toluene, and CH_2Cl_2 combined with 0.1 mL of water in the absence of 4 Å MS, but no improvement could be observed either (Table 2, entries 10–13). Lowering the reaction temperature to 15 °C or 4 °C did not improve the reaction outcome if using the NHC-Pd(II) complex **5d** as the catalyst in $CHCl_3$ (Table 2, entries 14 and 15).

Having optimized the reaction conditions, we next examined the substrate scope with various arylaldehydes and arylboronic acids; the results of these experiments are summarized in Table 3. The arylation of either the electron-rich or the electron-deficient arylaldehydes with a variety of arylboronic acids proceeded smoothly to afford the corresponding diarylmethanols in excellent yields using **5a** as the catalyst (Table 3, entries 1–7, 9–14, and 16–20). In the case of 4-nitrobenzaldehyde **6a**, good enantioselectivities were achieved using naphthalen-2-ylboronic acid **7e** or biphenyl-4-ylboronic acid **7f** as the arylation reagent (Table 3, entries 4 and 5). As for

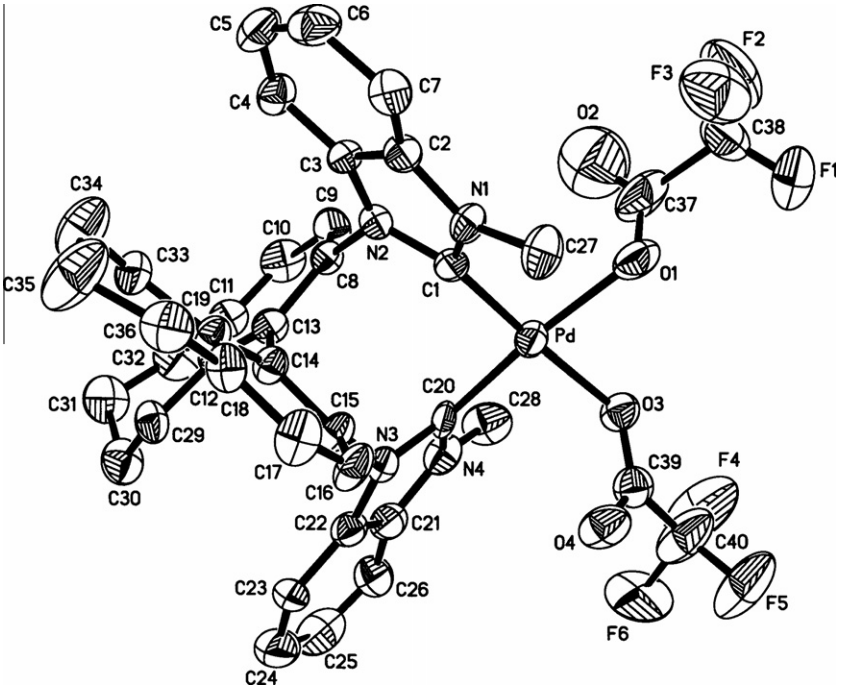
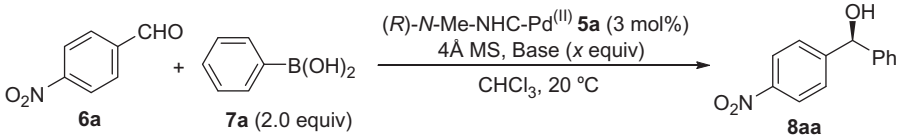


Figure 1. ORTEP drawing of Bis(NHC)-Pd(II) complex **5e** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (°): Pd–C_1 = 1.907 (10), Pd–C_{20} = 1.944 (10), Pd–O_1 = 2.802 (10), Pd–O_3 = 2.096 (7), C_1–Pd–C_{20} = 94.5 (4), C_1–Pd–O_1 = 90.8 (4), O_1–Pd–O_3 = 85.9 (3), O_3–Pd–C_{20} = 88.8 (3), C_{20}–Pd–O_1 = 173.4 (4), C_1–Pd–O_3 = 176.6 (4).

Table 1
Optimization of the reaction conditions in the asymmetric arylation of 4-nitrobenzaldehyde and phenylboronic acid[a]

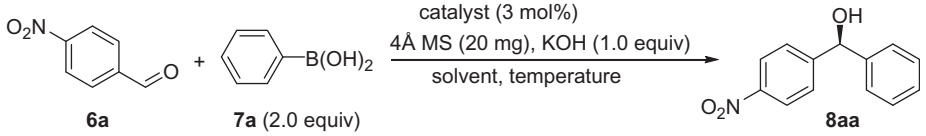


Entry	Base	X	Time (h)	Yield[b] (%)	ee[c] (%)
1[d]	—	—	24	n.r.[e]	n.d.
2	—	—	24	n.r.	n.d.
3[f]	—	—	24	n.r.	n.d.
4	KOH	1.0	24	>99	48 (*S*)
5	KOH	2.0	24	90	43 (*S*)
6	KOH	0.5	24	79	39 (*S*)
7	KF	1.0	24	53	42 (*S*)
8	$K_3PO_4{\cdot}3H_2O$	1.0	24	56	37 (*S*)
9	KO^{t}Bu	1.0	24	<10	2 (*S*)
10	Cs_2CO_3	1.0	24	<10	13 (*S*)
11	Ag_2CO_3	1.0	24	<10	n.d.
12	NaOH	1.0	24	10	20 (*S*)
13	K_2CO_3	1.0	24	65	40 (*S*)

[a] Reaction conditions: phenylboronic acid (**7a**, 0.5 mmol), 4-nitrobenzaldehyde (**6a**, 0.25 mmol), NHC-Pd(II) **5a** (3 mol %, 0.0075 mmol), 4 Å MS (20 mg), $CHCl_3$ (1.0 mL), and the reaction was carried out at 20 °C for 24 h.
[b] Isolated yields.
[c] The ee value was determined by HPLC using a Chiralcel AD-H column. The absolute configuration of the products was assigned by comparison with that of the literature compounds.
[d] H_2O (0.1 mL) was used as the additive in the absence of 4 Å MS.
[e] No reaction.
[f] This reaction was carried at 60 °C.

2,4-dichlorobenzaldehyde **6d**, good enantioselectivities were obtained using phenylboronic acid **7a** and 3- or 4-methylphenylboronic acid **7c** or **7d** as the arylation reagents (Table 3, entries 10–14). However, in the reactions of **6a** with **7b**–**d**, 3-nitrobenzaldehyde **6b** with **7e** and **7f**, and 4-cyanobenzaldehyde **6c** with **7f** as well as **6d** with **7b** and **7f**, the corresponding adducts were obtained in 10–23% ee's (Table 3, entries 1–3, 6–7, 9, 11 and 14). Using electron-rich arylaldehydes **6e** and **6f** in this reaction with **7f** afforded the corresponding adducts **8ef** and **8ff** in 0–1% ee's (Table 3, entries 16 and 17). In the reaction of 2- or 4-chlorobenzaldehyde with **7f** or **7a** and the reaction of 2-nitrobenzaldehyde with **7f**, the corresponding adducts **8ga**, **8ha**, and **8if** were also obtained in low enantiomeric

Table 2
Optimization of the reaction conditions in the asymmetric arylation of 4-nitrobenzaldehyde and phenylboronic acid[a]

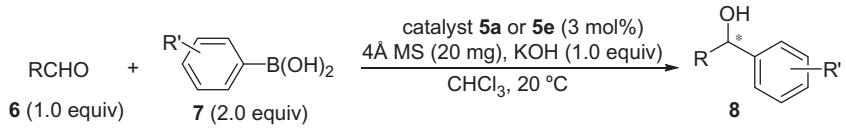


6a **7a** (2.0 equiv) **8aa**

Entry	Catalyst	Base	Solvent	Temp (°C)	Time (h)	Yield[b] (%)	ee[c] (%)
1	**5b**	KOH	$CHCl_3$	20	24	>99	9 (*S*)
2	**5c**	KOH	$CHCl_3$	20	24	96	30 (*S*)
3	**5d**	KOH	$CHCl_3$	20	36	>99	45 (*S*)
4	**5e**	KOH	$CHCl_3$	20	24	80	20 (*S*)
5	**5a**	KOH	Toluene	20	36	>99	43 (*S*)
6	**5a**	KOH	THF	20	24	>99	3 (*S*)
7	**5a**	KOH	CH_2Cl_2	20	24	75	43 (*S*)
8	**5a**	KOH	DMSO	60	24	n.r.[e]	n.d.
9	**5a**	KOH	DMF	60	24	<10	3 (*S*)
10[d]	**5d**	KOH	$CHCl_3/H_2O$	20	24	>99	47 (*S*)
11[d]	**5d**	KOH	THF/H_2O	20	24	30	3 (*S*)
12[d]	**5d**	KOH	$Toluene/H_2O$	20	36	80	43 (*S*)
13[d]	**5d**	KOH	CH_2Cl_2/H_2O	20	24	>99	47 (*S*)
14	**5d**	KOH	$CHCl_3$	15	24	75	43 (*S*)
15	**5d**	KOH	$CHCl_3$	4	48	n.r.	n.d.

[a] Reaction conditions: phenylboronic acid (**7a**, 0.5 mmol), 4-nitrobenzaldehyde (**6a**, 0.25 mmol), NHC-Pd(II) **5a** (3 mol %, 0.0075 mmol), 4 Å MS (20 mg), and $CHCl_3$ (1.0 mL).
[b] Isolated yields.
[c] The ee value was determined by HPLC using a Chiralcel AD-H column. The absolute configuration of the products was assigned by comparison with that of the literature compounds.
[d] H_2O (0.1 mL) as the additive and in the absence of 4 Å MS.
[e] No reaction.

Table 3
Asymmetric arylation of arylaldehydes with various arylboronic acids under optimal conditions[a]



6 (1.0 equiv) **7** (2.0 equiv) **8**

Entry	RCHO	R′B(OH)$_2$	Time (h)	Yield[b] (%)	ee[c] (%)
1	4-NO_2–C_6H_4CHO, **6a**	2-Me-PhB(OH)$_2$, **7b**	24	80	**8ab**, 10 (+)
2	4-NO_2–C_6H_4HO, **6a**	3-Me-PhB(OH)$_2$, **7c**	24	90	**8ac**, 21 (+)
3	4-NO_2–C_6H_4CHO, **6a**	4-Me-PhB(OH)$_2$, **7d**	24	90	**8ad**, 23 (+)
4	4-NO_2–C_6H_4CHO, **6a**	2-Naphthalenyl-B(OH)$_2$, **7e**	36	70	**8ae**, 48 (+)
5	4-NO_2–C_6H_4CHO, **6a**	4-Biphenyl-B(OH)$_2$, **7f**	24	90	**8af**, 57 (+)
6	3-NO_2–C_6H_4CHO, **6b**	2-Naphthalenyl-B(OH)$_2$, **7e**	24	60	**8be**, 20 (−)
7	3-NO_2–C_6H_4CHO, **6b**	4-Biphenyl-B(OH)$_2$, **7f**	24	95	**8bf**, 15 (+)
8[d]	3-NO_2–C_6H_4CHO, **6b**	4-Biphenyl-B(OH)$_2$, **7f**	24	70	**8bf**, 29 (+)
9	4-CN–C_6H_4CHO, **6c**	4-Biphenyl-B(OH)$_2$, **7f**	24	85	**8cf**, 20 (+)
10[e]	2,4-Dichloro-C_6H_3CHO, **6d**	PhB(OH)$_2$, **7a**	24	85	**8da**, 65 (*S*)
11[e]	2,4-Dichloro-C_6H_3CHO, **6d**	2-Me-PhB(OH)$_2$, **7b**	24	75	**8db**, 20 (−)
12[e]	2,4-Dichloro-C_6H_3CHO, **6d**	3-Me-PhB(OH)$_2$, **7c**	24	80	**8dc**, 50 (+)
13[e]	2,4-Dichloro-C_6H_3CHO, **6d**	4-Me-PhB(OH)$_2$, **7d**	24	80	**8dd**, 40 (+)
14[e]	2,4-Dichloro-C_6H_3CHO, **6d**	4-Biphenyl-B(OH)$_2$, **7f**	24	90	**8df**, 20 (−)
15[d]	2,4-Dichloro-C_6H_3CHO, **6d**	4-Biphenyl-B(OH)$_2$, **7f**	24	75	**8df**, 40 (−)
16	4-MeO–C_6H_4CHO, **6e**	4-Biphenyl-B(OH)$_2$, **7f**	24	70	**8ef**, 1 (−)
17	4-Me-C_6H_4CHO, **6f**	4-Biphenyl-B(OH)$_2$, **7f**	24	75	**8ff**, 0
18	2-Chloro-C_6H_4CHO, **6g**	4-Biphenyl-B(OH)$_2$, **7f**	24	95	**8gf**, 6 (+)
19	4-Chloro-C_6H_4CHO, **6h**	PhB(OH)$_2$, **7a**	24	80	**8ha**, 13 (*S*)
20	2-NO_2–C_6H_4CHO, **6i**	4-Biphenyl-B(OH)$_2$, **7f**	24	85	**8if**, 5 (+)

[a] Reaction conditions: arylboronic acid (**7**, 0.5 mmol), arylaldehyde (**6**, 0.25 mmol), NHC-Pd(II) **5a** (3 mol %, 0.0075 mmol) and 4 Å MS (20 mg).
[b] Isolated yields.
[c] The ee value was determined by HPLC using a Chiralcel column. The absolute configuration of the products was assigned by comparison with that of the literature compounds.
[d] Reaction conditions: phenylboronic acid (**7**, 0.5 mmol), arylaldehyde (**6**, 0.25 mmol), NHC-Pd(II) **5e** (3 mol %, 0.0075 mmol), and 4 Å MS (20 mg).
[e] The reaction was carried out at 60 °C.

excesses (Table 3, entries 18–20). These results suggest that arylaldehydes and arylboronic acids have very subtle electronic and steric effects on the reaction outcome and the achieved enantiomeric excesses are dependent on the substrates employed. Since chiral NHC-Pd(II) complex **5e** is a new catalyst, we also used it in the reaction of **6b** and **6d** with biphenyl-4-ylboronic acid **7f**, affording the corresponding adducts **8bf** and **8df** in 29% and 40% ee's and good yields (Table 3, entries 8 and 15).

3. Conclusion

In conclusion, chiral C_2-symmetric *N*-heterocyclic carbene (NHC) palladium diaquo complexes **5a–c** and chiral C_2-symmetric NHC-palladium complexes **5d** and **5e** prepared from (*R*)-BINAM or H_8-(*R*)-BINAM could be used as catalysts for the enantioselective arylation of arylaldehydes with arylboronic acids to give the corresponding adducts in moderate enantioselectivities along with moderate to good yields. The NHC-Pd(II) complex **5a** is a fairly effective catalyst in this reaction to give the adduct in up to 65% ee and high yield. In this catalytic asymmetric reaction, arylaldehydes and arylboronic acids have very subtle electronic and steric effects on the reaction outcome. Efforts are currently underway to elucidate the mechanistic details of this asymmetric addition reaction in the presence of a chiral NHC-Pd(II) catalyst and to disclose the exact structure of the active species in this catalytic system.

4. Experimental

4.1. General methods

Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. Optical rotations were determined in a solution of $CHCl_3$, CH_2Cl_2, or acetone at 20 °C by using a Perkin–Elmer-241 MC polarimeter; $[\alpha]_D$-values are given in units of 10^{-1} deg cm^2 g^{-1}. Infra-red spectra were measured on a spectrometer. ^{1}H NMR spectra were recorded for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; ^{31}P NMR spectra were recorded at 121 MHz for a solution in $CDCl_3$ with 85% H_3PO_4 as the external reference. *J*-Values are in hertz. Mass spectra were recorded with an HP-5989 instrument and HRMS was measured by a Finnigan MA+ mass spectrometer. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All the reactions were monitored by TLC with Huanghai 60F_{254} Silica Gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure. All asymmetric addition reactions were performed under argon using standard Schlenk techniques. The enantiomeric purities of adducts were determined by HPLC analysis using a chiral stationary phase column (column, Daicel Co. Chiralcel AD and OD) and the absolute configuration of the major enantiomer was assigned according to the sign of the specific rotation.

4.2. General procedure for the synthesis of C_2-symmetric *N*-heterocarbene palladium complexes 5a–e

4.2.1. General procedure for the synthesis of imidazolium salts 3a–c

Compounds **1** (485 mg, 0.4 mmol) and **2a–c** (0.5 mmol) (**2a**: MeI, **2b**: BnBr, **2c**: 3,5-$Me_2C_6H_3CH_2Br$) in dioxane (10 mL) were stirred at reflux for 5–24 h. After cooling down to room temperature (20 °C), the volatiles were removed under reduced pressure and the solid compound obtained was used for the next reaction without any further purification.

4.2.1.1. (*R*)-2,2′-Di (1*H*-benzo[*d*]imidazol-1-yl)-1,1′-binaphthyl 1. This is a known compound.[9] White solid; mp 294.5–294.8 °C; $[\alpha]_D^{20} = +516.7$ (*c* 0.97, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.06 (d, *J* = 8.8 Hz, 4H), 7.67–7.63 (m, 2H), 7.55–7.48 (m, 6H), 7.43 (d, *J* = 8.8 Hz, 2H), 6.99 (s, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.50 (t, *J* = 7.6 Hz, 2H), 6.11 (d, 2H, *J* = 8.0 Hz).

4.2.2. General procedure for the synthesis of NHC-Pd(II) complexes 4a–c

Compounds **3a–c** (0.2 mmol) and $Pd(OAc)_2$ (44.8 mg, 0.2 mmol) were refluxed in THF (10 mL) for 16–30 h. The volatiles were then removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 2:1 to 0:1) to give **4a–c** as yellow solids.

4.2.2.1. (*R*)-NHC-Pd(II) complex 4a. This is a known compound.[9] A yellow solid; mp >300 °C (dec); $[\alpha]_D^{20} = +270.0$ (*c* 0.086, $CHCl_3$), ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 8.10–8.03 (m, 4H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.25–7.19 (m, 2H), 6.94–6.87 (m, 4H), 6.85–6.82 (m, 2H), 6.78–6.74 (m, 4H), 6.68 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 6H).

4.2.2.2. (*R*)-NHC-Pd(II) complex 4b. This is a known compound.[9] Pale-yellow solid; mp >300 °C (dec); $[\alpha]_D^{20} = +45.0$ (*c* 0.245, $CHCl_3$); IR (CH_2Cl_2) ν 3060, 2961, 2926, 2855, 1474, 1389, 1335, 1261, 1101, 1032, 804 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.30–7.27 (m, 6H), 6.94–6.85 (m, 10H), 6.77–6.71 (m, 8H), 5.39 (d, *J* = 15.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 170.9, 136.3, 135.3, 134.6, 133.0, 132.7, 132.1, 131.4, 130.5, 128.5, 128.1, 128.0, 127.8, 127.7, 127.4, 126.7, 124.5, 123.6, 123.1, 112.3, 111.5, 55.6.

4.2.2.3. NHC-Pd(II) complex 4c. This is a known compound.[9] Pale-yellow solid; mp >300 °C (dec); $[\alpha]_D^{20} = +132.0$ (*c* 0.195, $CHCl_3$); IR (CH_2Cl_2) ν 3057, 2920, 2845, 1736, 1720, 1607, 1475, 1389, 1251, 1175, 1032, 853, 830, 743 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.27–7.21 (m, 8H), 7.05–6.85 (m, 10H), 6.73 (d, *J* = 8.7 Hz, 2H), 6.60 (d, *J* = 8.1 Hz, 2H), 6.55 (d, *J* = 15.6 Hz, 2H), 5.29 (d, *J* = 15.6 Hz, 2H), 2.38 (s, 12H).

4.2.3. General procedure for the synthesis of cationic NHC-Pd(II) diaquo complexes 5a–c

Complexes **4a–c** (0.20 mmol) were suspended in a mixture of CH_2Cl_2 (15 mL) and CH_3CN (5 mL). Next, AgOTf (108 mg, 0.42 mmol) was added and the mixture was stirred at room temperature for 10 min. The resulting suspension was filtered from the precipitated AgX (X = Br or I) through Celite and the solvent was removed under reduced pressure to give **5a–c** as a white powder.

4.2.3.1. Cationic NHC-Pd(II) diaquo complex 5a. This is a known compound.[9] White solid; mp 289 °C (dec); $[\alpha]_D^{20} = +43.0$ (*c* 0.315, $CHCl_3$); IR (CH_2Cl_2) ν 3223, 2925, 2847, 1580, 1511, 1395, 1290, 1168, 1029, 751 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 8.14 (s, 4H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.30–7.27 (m, 2H), 7.05–6.91 (m, 8H), 6.84–6.77 (m, 4H), 3.93 (s, 6H), 2.16 (br s, 4H). ^{19}F NMR (282 MHz, $CDCl_3$, CF_3CO_2H): δ −83.8 (s).

4.2.3.2. Cationic NHC-Pd(II) diaquo complex 5b. This is a known compound.[9] White solid; mp 259 °C (dec); $[\alpha]_D^{20} = +66.0$ (*c* 0.22, $CHCl_3$); IR (CH_2Cl_2) ν 2956, 2924, 2854, 1580, 1464, 1379, 1250, 1170, 1030, 745 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.35–7.32 (m, 8H), 7.03–6.89 (m, 6H), 6.84–6.72 (m, 10H), 5.84 (d, *J* = 16.2 Hz, 2H), 5.65 (d, *J* = 16.2 Hz, 2H), 4.13 (br s, >4H). ^{19}F NMR (282 MHz, $CDCl_3$, CF_3CO_2H): δ −83.6 (s).

4.2.3.3. Cationic NHC-Pd(II) diaquo complex 5c. This is a known compound.[9] White solid; mp >250 °C (dec); $[\alpha]_D^{20} = +95.0$ (*c* 0.22, $CHCl_3$); IR (CH_2Cl_2) ν 2958, 2925, 2852, 1581, 1487, 1339, 1258, 1172, 1030, 745 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.78 (d, *J* = 7.8 Hz, 2H), 7.44–7.34 (m, 4H), 6.97–6.73 (m, 18H), 6.66–6.63

(m, 4H), 5.72 (d, J = 9.9 Hz, 2H), 5.37 (br s, 4H), 2.27 (s, 12H). ^{19}F NMR (282 MHz, $CDCl_3$, CF_3CO_2H): δ −83.6 (s).

4.2.3.4. NHC-Pd(II) complex 5d. At first, NHC-Pd(II) complex **5d** was prepared by a similar procedure using (*R*)-2,2′-di (1*H*-benzo-[*d*]imidazol-1-yl)-1,1′-binaphthyl as the starting material. This is a known compound.[9] White solid; mp >250 °C (dec); $[\alpha]_D^{20}$ = −33.0 (*c* 0.395, $CHCl_3$); IR (CH_2Cl_2) ν 2957, 2925, 2854, 1735, 1466, 1379, 1260, 1174, 1031, 747 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.09 (s, 4H), 7.73 (d, J = 7.8 Hz, 2H), 7.28–7.23 (m, 2H), 6.98–6.83 (m, 10H), 6.78–6.76 (m, 2H), 3.88 (s, 6H). ^{19}F NMR (282 MHz, $CDCl_3$, CF_3CO_2H) δ −74.9 (s).

4.2.3.5. NHC-Pd(II) complex 4e. This is a known compound.[9] Pale-yellow solid; mp >300 °C (dec); $[\alpha]_D^{20}$ = +53 (*c* 0.24, $CHCl_3$); IR (CH_2Cl_2): ν 3054, 2930, 2306, 1480, 1436, 1340, 1132, 897, 740, 705, 557 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.60 (d, J = 8.1 Hz, 2H), 7.24–7.22 (m, 3H), 7.20–7.18 (m, 1H), 7.15–7.11 (m, 4H), 6.89 (d, J = 8.1 Hz, 2H), 3.92 (s, 6H), 2.66–2.56 (m, 2H), 2.31–2.20 (m, 2H), 1.91–1.81 (m, 2H), 1.64–1.55 (m, 4H), 1.41–1.17 (m, 6H).

4.2.3.6. NHC-Pd(II) complex 5e. NHC-Pd(II) complex **5e** was prepared by a similar procedure using (*R*)-1,1′-(4a,5,5′,6,6′,7,7′,8,8a,8′-decahydro-1,1′-binaphthyl-2,2′-diyl)bis(1*H*-benzo[*d*]imidazole) as the starting materials. White solid; mp >290 °C (dec); $[\alpha]_D^{20}$ = +54.0 (*c* 0.162, $CHCl_3$); IR (CH_2Cl_2) ν 3450, 3016, 2970, 1738, 1439, 1366, 1228, 1217, 1130, 1085, 897, 838, 747, 724 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.68 (d, J = 8.0 Hz, 2H), 7.30–7.24 (m, 4H), 7.20–7.13 (m, 4H), 6.90 (d, J = 8.0 Hz, 2H), 3.96 (s, 6H), 2.65–2.60 (m, 2H), 2.32–2.26 (m, 2H), 2.01–1.93 (m, 2H), 1.77–1.72 (m, 2H), 1.44–1.40 (m, 2H), 1.29–1.22 (m, 4H), 0.44–0.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 166.7, 161.7 (q, J = 35.3 Hz), 139.9, 137.6, 135.4, 134.5, 133.8, 133.7, 129.7, 124.9, 124.1, 123.8, 116.0 (q, J = 289.6 Hz), 112.6, 109.8, 34.9, 29.2, 27.2, 21.9, 21.5. ^{19}F NMR (282 MHz, $CDCl_3$, CF_3CO_2H): δ −74.6 (s). MS (ESI) *m/z*: 741.2 (M^+−CF_3COO, 100). HRMS (ESI) calcd for $C_{38}H_{34}N_4O_2F_3Pd$ requires: 741.1669. Found: 741.1653. Anal. Cald for 4[$C_{40}H_{34}F_6N_4O_4Pd$]·CH_2Cl_2: C, 55.16; H, 3.97; N, 6.39. Found: C, 55.08; H, 4.22; N, 6.39. Crystals that were suitable for X-ray diffraction analysis were grown from solutions in CH_2Cl_2/hexane (2:1).

4.2.4. General procedure for the asymmetric arylation of arylaldehydes and arylboronic acids

At first, NHC-Pd^{II} catalyst **5a** (3 mol %, 7.5 μmol), KOH (1.0 equiv, 0.25 mmol, 14 mg), and 20 mg activated 4 Å molecule sieves were dissolved in $CHCl_3$ (1.0 mL) in a flame-dried Schlenk tube equipped with a septum and stirring bar and the mixture was stirred under argon at room temperature (20 °C) for 10 min. Arylboronic acid **7** (2.0 equiv, 0.5 mmol) was added followed by the addition of the corresponding arylaldehyde **6** (0.25 mmol). After that, the reaction mixture was stirred at 20 °C for 24 h, and then saturated aqueous solution of $NaHCO_3$ (5 mL) was added into the reaction mixture. The organic phase was separated and the resulting aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic phases were filtered through a thin-layer of Celite. The filtrate was washed with brine (5 mL), dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography on silica gel (eluent: EtOAc/petroleum ether = 1:8) to yield the corresponding pure product **8**.

4.2.4.1. (*S*)-(4-Nitrophenyl)(phenyl)methanol 8aa. A known compound,[11,12] 99% yield, a yellow oil. $[\alpha]_D^{20}$ = +14.0 (*c* 1.715, $CHCl_3$), 48% ee [HPLC conditions: Chiracel AD-H column, hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, t_{minor} = 12.52 min and t_{major} = 15.47 min]. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.18 (d, J = 8.8 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 7.36–7.31 (m, 5H), 5.91 (s, 1H), 2.49 (br s, 1H).

4.2.4.2. (+)-(4-Nitrophenyl)(*o*-tolyl)methanol 8ab. A known compound,[12] 80% yield, a yellow oil, $[\alpha]_D^{20}$ = +6.8 (*c* 1.06, $CHCl_3$), 10% ee [HPLC conditions: Chiracel AD-H column, hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, t_{minor} = 10.39 min and t_{major} = 13.13 min]. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.14 (d, J = 7.8 Hz, 2H), 7.49 (d, J = 10.2 Hz, 2H), 7.32–7.29 (m, 1H), 7.25–7.15 (m, 3H). 6.05 (s, 1H), 2.70 (br s, 1H), 2.28 (s, 3H).

4.2.4.3. (+)-(4-Nitrophenyl)(*m*-tolyl)methanol 8ac. A known compound,[13] 90% yield, yellow oil. $[\alpha]_D^{20}$ = +13.5 (*c* 0.24, $CHCl_3$), 21% ee [HPLC conditions: Chiracel AD-H column, hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, t_{minor} = 10.51 min and t_{major} = 14.09 min]. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.16 (d, J = 8.8 Hz, 2H), 7.55 (d, J = 8.8 Hz, 2H), 7.25–7.22 (m, 1H), 7.13–7.11 (m, 3H), 5.85 (s, 1H), 2.56 (br s, 1H), 2.33 (s, 3H).

4.2.4.4. (+)-(4-Nitrophenyl)(*p*-tolyl)methanol 8ad. A known compound,[12] 90% yield, yellow oil. $[\alpha]_D^{20}$ = +11.1 (*c* 1.03, $CHCl_3$), 23% ee [HPLC conditions: Chiracel AD-H column, hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, t_{minor} = 12.94 min and t_{major} = 15.89 min]. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.16 (d, J = 8.8 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 5.86 (s, 1H), 2.53 (br s, 1H), 2.33 (s, 3H).

4.2.4.5. (+)-Naphthalen-2-yl(4-nitrophenyl)methanol 8ae. A known compound,[8b] 70% yield, yellow oil, $[\alpha]_D^{20}$ = +2.0 (c 0.58 $CHCl_3$), 48% ee [HPLC conditions: Chiracel AD-H column, hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, t_{minor} = 20.72 min and t_{major} = 24.95 min].^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.20 (d, J = 8.8 Hz, 2H), 7.85 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.51 (t, J = 3.6 Hz, 2H), 7.39 (dd, J = 1.6, 8.4 Hz, 1H), 6.09 (s, 1H), 2.50 (br s, 1H).

4.2.4.6. (+)-Biphenyl-4-yl(4-nitrophenyl)methanol 8af. 90% yield, white solid; mp 138.7.2–140.1 °C; $[\alpha]_D^{20}$ = +65.0 (*c* 0.35 $CHCl_3$), 57% ee [HPLC conditions: Chiracel OD-H column, hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, t_{minor} = 35.59 min and t_{major} = 40.19 min]. IR (CH_2Cl_2) ν 3534, 3106, 3074, 3029, 2920, 2876, 2844, 1731, 1715, 1602, 1511, 1486, 1346, 1286, 1189, 1170, 1106, 1042, 1007, 962, 878, 866, 825, 803, 763, 755, 731, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.19 (d, J = 8.8 Hz, 2H), 7.61–7.54 (m, 6H), 7.45–7.39 (m, 4H), 7.37–7.33 (m, 1H), 5.95 (s, 1H), 2.49 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 150.6, 147.2, 141.6, 141.4, 140.3, 128.8, 127.64, 127.56, 127.13, 127.06, 123.7, 75.3. MS (%) *m/z* 305.1 (M^+, 100), 241.1 (9), 181.1 (29), 155.1 (97), 77.0 (8). HRMS (EI) calcd for $C_{19}H_{15}NO_3$ requires: 305.1052. Found: 305.1051.

4.2.4.7. (−)-Naphthalen-2-yl(3-nitrophenyl)methanol 8be. 60% yield, yellow oil; $[\alpha]_D^{20}$ = −87 (*c* 0.215, $CHCl_3$), 20% ee [HPLC conditions: Chiracel OD-H column, hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, t_{minor} = 44.04 min and t_{major} = 50.66 min]. IR (CH_2Cl_2) ν 3419, 3056, 2922, 2853, 1731, 1601, 1528, 1349, 1267, 1164, 1122, 1093, 1036, 966, 901, 860, 812, 777, 746, 727, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.35 (s, 1H), 8.11 (d, J = 8.0 Hz, 1H), 7.86–7.81 (m, 4H), 7.73 (d, J = 8.0 Hz, 1H), 7.52–7.46 (m, 3H), 7.40 (dd, J = 1.6, 8.8 Hz, 1H), 6.07 (s, 1H), 2.56 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 148.4, 145.6, 140.0, 133.19, 133.13, 132.5, 129.4, 129.0, 128.1, 127.7, 126.6, 126.5, 125.6, 124.2, 122.5, 121.4, 75.5. MS (%) *m/z* 279.1 (M^+, 79), 215.1 (14), 202.1 (10), 155.0 (16), 150.0 (17),

129.1 (100), 104.0 (5), 77.0 (4). HRMS (EI) calcd for $C_{17}H_{13}NO_3$ requires: 279.0895. Found: 279.0897.

4.2.4.8. (+)-Biphenyl-4-yl(3-nitrophenyl)methanol 8bf. 70% yield, yellow solid; mp 89.6–91.1 °C, $[\alpha]_D^{20} = +8.0$ (*c* 0.35, $CHCl_3$), 29% ee [HPLC conditions: Chiracel OD-H column, hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, t_{minor} = 47.21 min and t_{major} = 83.52 min]. IR (CH_2Cl_2) *v* 3416, 3125, 1617, 1525, 1485, 1401, 1350, 1030, 1007, 846, 802, 764, 749, 724, 697, 477 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 8.32 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 8.0 Hz 1H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.2, 1H), 5.93 (s, 1H), 2.65 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 148.4, 144.9, 140.9, 140.6, 138.5, 133.5, 129.4, 128.8, 128.5, 127.41, 127.37, 127.3, 127.1, 124.8, 71.3. MS (%) *m/z* 305.1 (M^+, 100), 241.1 (8), 228.1 (7), 183.1 (18), 155.1 (89), 134.0 (3), 104.0 (3), 77.0 (8). HRMS (EI) calcd for $C_{19}H_{15}NO_3$ requires: 305.1052. Found: 305.1054.

4.2.4.9. (+)-4-(Biphenyl-4-yl(hydroxy)methyl)benzonitrile 8cf. 85% yield, white solid; mp 158.4–161.1 °C, $[\alpha]_D^{20} = +7.8$ (*c* 0.50, $CHCl_3$), 20% ee [HPLC conditions: Chiracel OD-H column, hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, t_{major} = 37.00 min and t_{minor} = 42.34 min]. IR (CH_2Cl_2) *v* 3467, 3029, 2927, 2852, 2232, 1731, 1606, 1485, 1406, 1275, 1228, 1191, 1122, 1060, 1017, 871, 828, 803, 770, 749, 733, 695, 624 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.57–7.52 (m, 6H), 7.44–7.32 (m, 5H), 5.88 (s, 1H), 2.46 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 148.8, 141.7, 141.2, 140.4, 132.3, 128.8, 127.53, 127.50, 127.1, 127.02, 127.00, 118.8, 111.2, 75.3. MS (%) *m/z* 285.1 (M^+, 100), 268.1 (9), 181.1 (21), 155.1 (94), 130.0 (25), 102.0 (14), 77.0 (16). HRMS (EI) calcd for $C_{20}H_{15}NO$ requires: 285.1154. Found: 285.1147.

4.2.4.10. (*S*)-(2,4-Dichlorophenyl)(phenyl)methanol 8da. A known compound,[8c,14] 85% yield, colorless oil, $[\alpha]_D^{20} = -4.6$ (*c* 0.91, acetone), 65% ee [HPLC conditions: Chiracel OD-H column, hexane/2-propanol = 95:5, flow rate = 1.0 mL/min, wavelength = 230 nm, t_{major} = 16.27 min and t_{minor} = 18.13 min]. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.58 (d, *J* = 8.4 Hz, 1H), 7.37–7.25 (m, 7H), 6.16 (s, 1H), 2.33 (s, 1H).

4.2.4.11. (−)-(2,4-Dichlorophenyl)(o-tolyl)methanol 8db. A known compound,[15] 75% yield, colorless oil. $[\alpha]_D^{20} = -4.6$ (*c* 0.75, $CHCl_3$), 20% ee [HPLC conditions: Chiracel OD-H column, hexane/2-propanol = 95:5, flow rate = 0.7 mL/min, wavelength = 230 nm, t_{minor} = 14.04 min and t_{major} = 25.37 min]. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.39 (d, *J* = 2.0 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.27–7.18 (m, 5H), 6.24 (s, 1H), 2.64 (br s, 1H), 2.31 (s, 3H).

4.2.4.12. (+)-(2,4-Dichlorophenyl)(m-tolyl)methanol 8dc. 80% yield, colorless oil, $[\alpha]_D^{20} = +3.6$ (*c* 1.95, $CHCl_3$), 50% ee [HPLC conditions: Chiracel OD-H column, hexane/2-propanol = 95:5, flow rate = 0.7 mL/min, wavelength = 230 nm, t_{minor} = 13.27 min and t_{major} = 14.29 min]. IR (CH_2Cl_2): *v* 3390, 3134, 2923, 1607, 1590, 1561, 1469, 1400, 1385, 1188, 1149, 1102, 1056, 1030, 846, 824, 794, 754, 696, 583, 455 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.56 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 2.0 Hz, 1H), 7.28–7.20 (m, 2H), 7.15–7.08 (m, 3H), 6.10 (s, 1H), 2.41 (br s, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 141.7, 139.6, 138.3, 133.7, 133.0, 129.2, 128.9, 128.8, 128.5, 127.5, 127.4, 123.9, 72.3, 21.4. MS (%) *m/z* 266.0 (M^+, 100), 251.0 (72), 213.0 (14), 173.0 (67), 119.0 (43), 93.1 (53), 77.0 (9). HRMS (EI) calcd for $C_{14}H_{12}Cl_2O$ requires: 266.0625. Found: 266.0624.

4.2.4.13. (+)-(2,4-Dichlorophenyl)(p-tolyl)methanol 8dd. A known compound,[16] 80% yield, colorless oil, $[\alpha]_D^{20} = +1.0$ (*c* 0.50, $CHCl_3$), 40% ee [HPLC conditions: Chiracel OD-H column, hexane/2-propanol = 95:5, flow rate = 0.7 mL/min, wavelength = 254 nm, t_{minor} = 14.28 min and t_{major} = 15.08 min]. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.58 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 2.0 Hz, 1H), 7.28–7.21 (m, 3H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.08 (s, 1H), 2.43 (br s, 1H), 2.32 (s, 3H).

4.2.4.14. (−)-Biphenyl-4-yl(2,4-dichlorophenyl)methanol 8df. 75% yield, white solid; mp 67.6–69.7 °C, $[\alpha]_D^{20} = -5.6$ (*c* 1.19, $CHCl_3$), 40% ee [HPLC conditions: Chiracel AD-H column, hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, t_{minor} = 11.63 min and t_{major} = 12.97 min]. IR (CH_2Cl_2): *v* 3468, 2956, 2924, 2854, 1737, 1590, 1562, 1486, 1468, 1376, 1270, 1229, 1217, 1178, 1095, 1057, 1030, 1008, 866, 828, 810, 753, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.64 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 4H), 7.46–7.43 (m, 4H), 7.39–7.31 (m, 3H), 6.22 (s, 1H), 2.44 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 140.9, 140.8, 140.6, 139.6, 133.9, 133.1, 129.3, 128.9, 128.8, 127.5, 127.4, 127.33, 127.30, 127.1, 72.1; MS (%) *m/z* 328 (M^+, 86), 311 (6), 275 (11), 239 (11), 228 (4), 183 (16), 173 (31), 155 (100), 110 (6) 77 (5). HRMS (EI) calcd for $C_{19}H_{14}Cl_2O$ requires: 328.0422. Found: 328.0421.

4.2.4.15. (−)-Biphenyl-4-yl(4-methoxyphenyl)methanol 8ef. A known compound,[17] 70% yield, white solid; mp 107.3–109.2 °C. $[\alpha]_D^{20} = -1.0$ (*c* 0.24, $CHCl_3$), 1% ee [HPLC conditions: Chiracel AD-H column, hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, t_{major} = 17.38 min and t_{minor} = 18.91 min]. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.59–7.56 (m, 4H), 7.46–7.41 (m, 4H), 7.35–7.32 (m, 3H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.87 (s, 1H), 3.80 (s, 3H).

4.2.4.16. Biphenyl-4-yl(p-tolyl)methanol 8ff. A known compound,[18] 75% yield, white solid; mp 108.5–110.2 °C. $[\alpha]_D^{20} = 0$ (*c* 0.24, $CHCl_3$), 0% ee [HPLC conditions: Chiracel OD-H column, hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, t_{minor} = 12.18 min and t_{major} = 13.68 min]. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.57–7.55 (m, 4H), 7.47–7.40 (m, 4H), 7.36–7.30 (m, 3H), 7.25–7.21 (m, 1H), 6.27 (s, 1H), 2.50 (br s, 1H), 2.16 (s, 3H).

4.2.4.17. (+)-Biphenyl-4-yl(2-chlorophenyl)methanol 8gf. A known compound,[19] 95% yield, colorless oil. $[\alpha]_D^{20} = +1.8$ (*c* 0.78, $CHCl_3$), 6% ee [HPLC conditions: Chiracel OD-H column, hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, t_{minor} = 13.15 min and t_{major} = 20.77 min]. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.66–7.63 (m, 1H), 7.57–7.54 (m, 4H), 7.46–7.40 (m, 4H), 7.36–7.29 (m, 3H), 7.24–7.20 (m, 1H), 6.26 (s, 1H), 2.44 (br s, 1H).

4.2.4.18. (*S*)-(4-Chlorophenyl)(phenyl)methanol 8ha. A known compound,[6] 80% yield, colorless oil. $[\alpha]_D^{20} = +3.0$ (*c* 0.15, $CHCl_3$), 13% ee [HPLC conditions: Chiracel AD-H column, hexane/2-propanol = 95:5, flow rate = 0.70 mL/min, wavelength = 254 nm, t_{minor} = 21.16 min and t_{major} = 18.82 min]. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.35–7.34 (m, 4H), 7.31–7.27 (m, 5H), 5.82 (s, 1H), 2.24 (br s, 1H).

4.2.4.19. (+)-Biphenyl-4-yl(2-nitrophenyl)methanol 8if. 85% yield, yellow oil, $[\alpha]_D^{20} = +2.4$ (*c* 0.545, $CHCl_3$), 5% ee [HPLC conditions: Chiracel OD-H column, hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, t_{minor} = 23.42 min and t_{major} = 19.51 min]. IR (CH_2Cl_2): *v* 3640, 3556, 3320, 3151, 3123, 2926, 1606, 1525, 1484, 1350, 1265, 1176, 1024, 855, 761, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.57–7.55 (m,

4H), 7.48–7.39 (m, 5H), 7.35 (d, J = 7.6 Hz, 1H), 6.48 (s, 1H), 2.63 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 148.3, 140.9, 140.5, 138.5, 133.5, 129.4, 129.0, 128.8, 128.5, 127.40, 127.37, 127.3, 127.1, 124.8, 71.3. MS (ESI) m/z: 344.1 (M^++K, 24). HRMS (ESI) calcd for $C_{19}H_{15}NO_3K$ requires: 344.0689. Found: 344.0687.

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