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ARTICLE

Chiral Linker - Bridged Bis-N-Heterocyclic Carbenes: Design, Synthesis, Palladium Complexes, and Catalytic Property†

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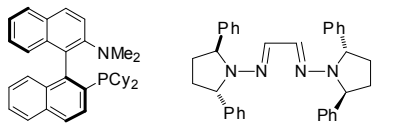
A series of chiral bis(benzimidazolium) salts **10**-**19** with (1*R*,2*R*)-cyclohexene, (1*R*,2*R*)-diphenylethylene and (a*R*)-binaphthylene linker have been designed and synthesized in 30-94 % yield. Ten chiral bis(NHC) palladium complexes **20**-**28** have been synthesized and characterized by NMR, HRMS, elemental analysis and further confirmed by X-ray single crystal analysis. These bis(NHC)-Pd complexes showed obviously different catalytic properties in the asymmetric Suzuki-Miyaura coupling reactions. The (1*R*,2*R*)-cyclohexene-bridged bis(NHC)-Pd complex (*R,R*)-**23** achieved the highest yield of 90%, while complex (*aR*)-**28**, with a binaphthylene linker, showed the best enantioselectivity of 60 ee%. The structural analysis of these complexes suggested that such difference of catalytic performance has the close relationships with their coordination surroundings around metal centres.

Introduction

The palladium-catalyzed asymmetric Suzuki-Miyaura coupling of aryl boronic acids and aryl halides to axially chiral biaryls continues to be an area of high research interest due to the wide existence of biaryl cores in numerous natural products and chiral ligands.[1] A typical Pd-catalyzed coupling with good enantioselectivity usually results from its suitable chiral auxiliary ligand that was first believed to govern the spatial configuration of the palladium active center. Thus, much effort has been devoted to search for more efficient ligands that can produce unique palladium catalytic systems. Several kinds of chiral ligands, including chiral mono- or diphosphine ligands under homogeneous or heterogeneous conditions,[2,3] bishydrazone or phosphine–hydrazone chiral ligands,[4] chiral diene ligands,[5] or a pyridylmethylamine ligand with a stereogenic center,[6] have been designed for palladium-catalyzed asymmetric Suzuki–Miyaura reactions, and some of them showed evident asymmetric induction activity. For most excellent chiral ligands, the suitable steric effect of the substituent near the chiral moiety was thought to be the first factor that influences ee values of the obtained biaryl compounds. For example, The well-known chiral phosphine ligand **I** (Figure 1), later called (*S*)-KenPhos afforded the highest ee value of up to 94 % for the coupling reaction between aryl boronic acid and aryl bromide incorporating phosphonate ester, amide and phosphine oxide substituents in the ortho-position.[2b] Furthermore, the interaction of the two aryl moieties in antiparallel between chiral ligands and substrates, existing in the oxidative addition and transmetalation intermediates can enhance the enantioselectivity of the coupling reaction. On this basis, the palladium catalyst with bis-hydrazones ligand **II** (Figure 1) indeed provided excellent enantioselectivities of up to >98% ee in the asymmetric coupling of substituted naphthylene bromides with aryl boronic acid at room temperature.[4a] Besides, the chiral biaryl backbone of phosphine-containing ligands seemed to be a great benefit to the high ee values of biaryl products due to its template effect.[2]



I Buchwald et al [2b] II Fernandez & Lassaletta et al [4a]

Figure 1. Two representative examples of chiral ligands in Pd-catalyzed asymmetric Suzuki-Miyaura coupling

As strong σ donor ligands, *N*-heterocyclic carbenes (NHCs) have received much attention in the field of metal based asymmetric catalysis.[7] The easy introduction of chiral elements and the facile preparation of their precursors have made them promising chiral auxiliary ligands in catalytic reactions with high enantioselectivity. Although several research groups have engaged in the study during the past few years, the use of chiral NHC ligands (**III**-**VI**, Figure 2) in asymmetric Suzuki–Miyaura coupling reactions is rare and only limited progress has been made.[8-11] In 2010 Labande et al. firstly

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† Electronic Supplementary Information (ESI) available: The characterization data for bis-benzimidazoles (*R,R*)-**1b-d**, (*R,R*)-**4** and relevant compounds (*R,R*)-**1d'**, (*R,R*)-**1d''**, (*R,R*)-**2b-d**, (*R,R*)-**3b-d**, (*R,R*)-**5a-b**, (*R,R*)-**6**, **7a-b and** (*R*)-**7c,** the ^{1}H and ^{13}C NMR full spectra of all new compounds (PDF), and Crystallographic data (CIF). See DOI: 10.1039/x0xx00000x

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reported a kind of planar chiral ferrocenyl phosphine-NHC ligand **III** supported palladium catalysts that gave an enantioselectivity of up to 46% ee for the Suzuki-Miyaura coupling.[8a] Notably, the best ee value of 80% was achieved from a type of PEPPSI-Pd catalysts bearing chiral bulky monodentate NHC ligand **IV** by Kündig et al. in 2014.[9] Although this result did not reach the levels of literature precedent, chiral NHCs no doubt revealed their promising prospects of application in the Pd-catalyzed Suzuki-Miyaura coupling reaction.

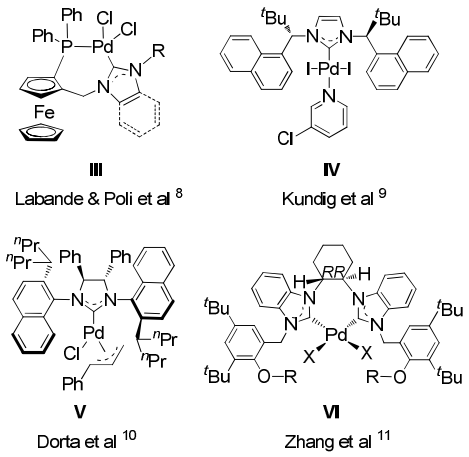

Figure 2. Chiral NHC palladium complexes reported in asymmetric Suzuki-Miyaura coupling reactions

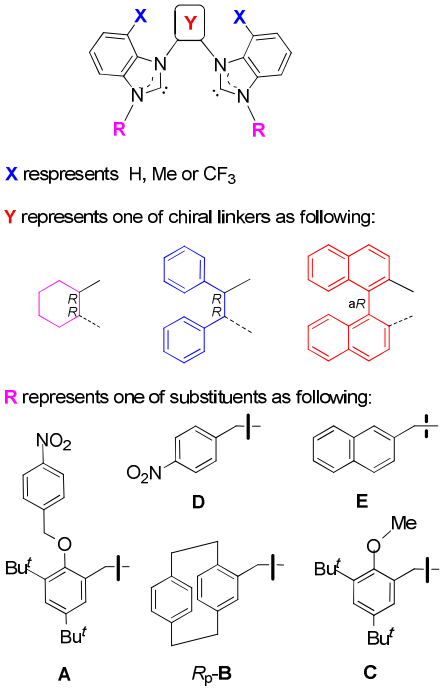

Figure 3. Targeted chiral linker - bridged bis(NHC) Ligands.

We are currently interested in the design and application of NHCs to the synthesis of early and late transition metal catalysts.[11,12] Recently, we presented a series of chiral cyclohexane-1,2-bridged bis(NHC)-Pd pre-catalysts (*R*,*R*)-**VI** (Figure 2) that was able to catalyse the asymmetric Suzuki-Miyaura couplings between 1-halido-2-R-naphthalene and naphthylboronic acid in good yields and moderate enantioselectivities.[11] To further understand the structural effect of chiral bis(NHC) ligands on the asymmetric catalysis, we undertook the modification of above bis(NHC) ligand (Figure 3) by increasing steric hindrance and electronic effect on X positions adjacent to the chiral source bridge, changing the chiral cyclohexane-1,2-linker with (*R*,*R*)-diphenylethylene-1,2-linker at the Y position, and introducing more chiral element, such as R_p-cyclophane group on R substituents. Moreover, considering that the axially chiral biaryl bridged bis(NHC) ligand, reported Shi et al. has good catalytic activity in metal-catalyzed enantioselective reactions,[13] we prepared a similar (a*R*)-binaphthylene bridged bis(NHC) palladium catalyst for comparison's sake. We herein describe the design, synthesis of these novel chiral bis(NHC) ligands and their palladium complexes, as well as their behaviours in Suzuki–Miyaura coupling reactions.

Results and discussion

Synthesis of Chiral Bis-Benzimidazoles

We first attempted to synthesize (1*R*,2*R*)-cyclohexene-bridged bis-benzimidazoles, with one or two alkyl substituents on the X positions of benzimidazolium moieties, respectively (Figure 3). According to an improved literature method for (*R*,*R*)-**1a**,[11] the reaction of (1*R*,2*R*)-diaminocyclohexane (DACH) L-tartrate with 2-fluoro-1-R-3-nitrobenzene (R = Me, CF_3) in the presence of 4 equiv of K_2CO_3 at 80 °C for 24 h afforded nitrobenzene derivatives **2b** and **2d**, which were smoothly reduced by hydrogen gas at atmosphere pressure using Pd/C as catalyst to give tetraamines **3b** and **3d** in almost quantitative yields (Scheme 1 & 2). Similar methods could be adopted in the synthesis of the unsymmetrical compounds **2c** and **3c** using two different 2-fluoro-1-R-3-nitrobenzenes (R = H, Me etc). Compounds **3b, 3c** and **3d** underwent cyclization to produce the corresponding 1,2-cyclohexene-bridged bis-benzimidazoles (*R*,*R*)-**1b, 1c** and **1d** in 60-80 % yield using excess triethyl orthoformate. It should be noted that, besides **1d**, two by-products **1d'** and **1d''** usually were found in the reaction mixture by TLC. They could then be conveniently separated from each other by gel chromatography and further identified by NMR and high-resolution mass spectra (HRMS).

Next we tried to prepare similar bis-benzimidazoles from (1*R*,2*R*)-diphenylethylenediamine (DPEN) using the aforementioned method (Scheme 3). As expected, the chiral bis-benzimidazole (*R*,*R*)-**4** was successfully obtained from *o*-fluoro-nitrobenzene through three continuous steps in high yield. However, when 2-fluoro-1-CF_3-3 -nitrobenzene was used as starting material, the result was not in line with our prediction. The simple and environmental friendly reduction of

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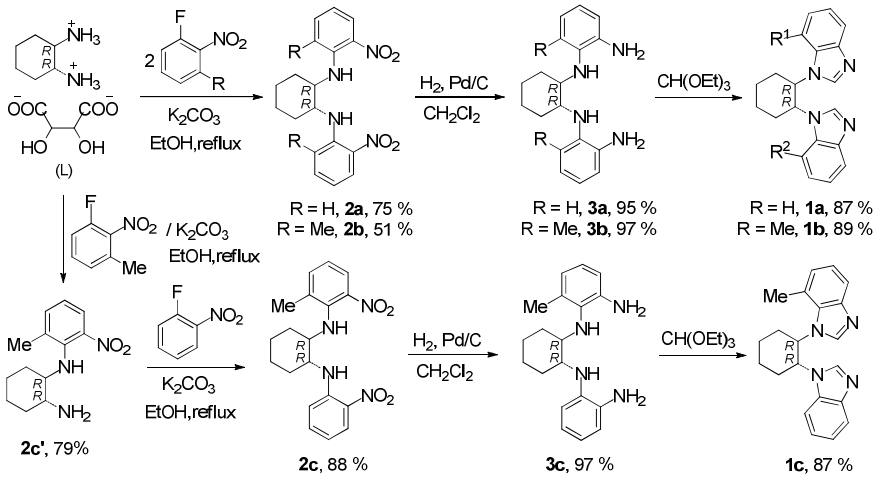
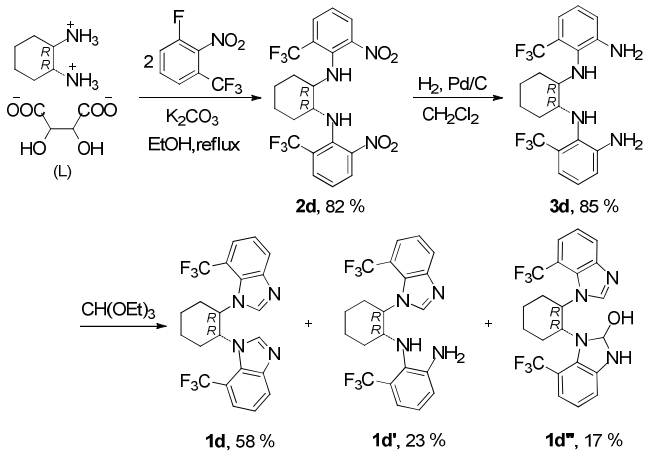
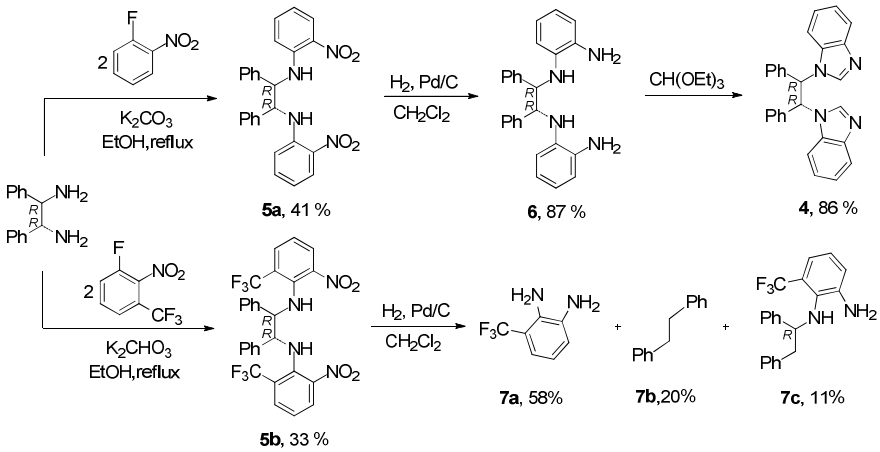
5b with H_2 gas failed to give the desired CF_3 substituted tetraamine product which is similar to **6**; several broken fragments **7a**, **7b** and **7c** were isolated and identified by NMR and HRMS after workup. Moreover, the axially chiral binaphthylene-linked bis-benzimidazole (*aR*)-**8** was prepared from (a*R*)-[1,1'-binaphthalene]-2,2'-diamine according to the literature method.[13]



Scheme 1. Synthesis of (1*R*,2*R*)-cyclohexene-bridged bis-benzimidazoles **1a-c**



Scheme 2. Synthesis of (1*R*,2*R*)-cyclohexene-bridged bis-benzimidazole **1d**



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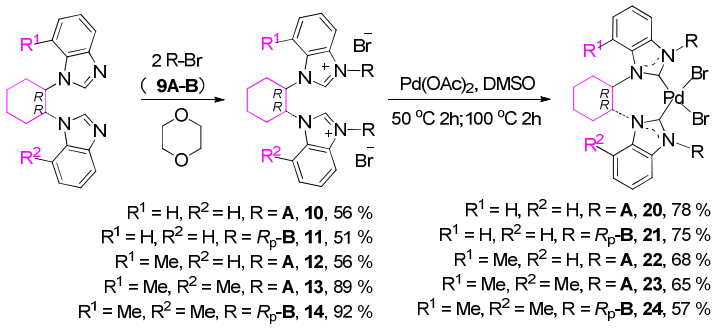
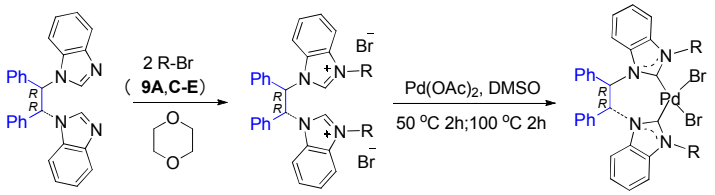
Scheme 3. Synthesis of (1*R*,2*R*)-diphenylethylene-bridged bis-benzimidazole **4**



R^1 = H, R^2 = H, R = **A**, **10**, 56 %
R^1 = H, R^2 = H, R = R_p-**B**, **11**, 51 %
R^1 = Me, R^2 = H, R = **A**, **12**, 56 %
R^1 = Me, R^2 = Me, R = **A**, **13**, 89 %
R^1 = Me, R^2 = Me, R = R_p-**B**, **14**, 92 %

R^1 = H, R^2 = H, R = **A**, **20**, 78 %
R^1 = H, R^2 = H, R = R_p-**B**, **21**, 75 %
R^1 = Me, R^2 = H, R = **A**, **22**, 68 %
R^1 = Me, R^2 = Me, R = **A**, **23**, 65 %
R^1 = Me, R^2 = Me, R = R_p-**B**, **24**, 57 %

Scheme 4. Synthesis of (1*R*,2*R*)-cyclohexene-bridged bis(benzimidazolium) salts **10-14** and their palladium complexes **20-24**

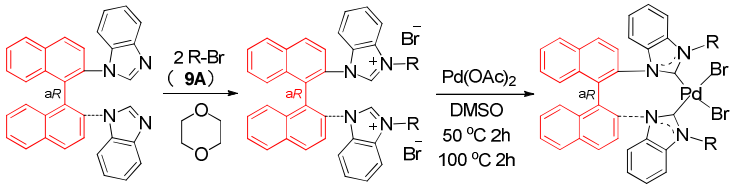


4

R = **A**, **15**, 94 %
R = **C**, **16**, 85 %
R = **D**, **17**, 80 %
R = **E**, **18**, 75 %

R = **A**, **25**, 59 %
R = **C**, **26**, 50 %
R = **D**, **27**, 55 %

Scheme 5. Synthesis of (1*R*,2*R*)-diphenylethylene-bridged bis-benzimidazolium salts **15-18** and their palladium complexes **25-27**



8

R = **A**, **19**, 78 %

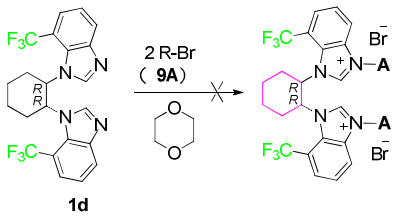
R = **A**, **28**, 55 %

Scheme 6. Synthesis of (a*R*)-binaphthylene-bridged bis(benzimidazolium) salt **19** and its palladium complex **28**

Synthesis of Chiral Bis(Benzimidazolium) Salts.

Chiral bis(benzimidazolium) salts (*R,R*)-**10** - **14**, **15** - **18** and **19** have been efficiently synthesized through direct alkylation reactions of the bis-benzimidazoles with different benzyl bromides (Scheme 4-6). It is worthy to note that the reaction should be carried out under an inert atmosphere and the solvent 1,4-dioxane must be dried by standard method. Otherwise the reaction was not clean and more by-products were found. A mixture of the bis-imidazole (**1b-c**, **4** and **8**) and 2.2 equiv. of R-Br (**9A**, R_p-**9B**, or **9C-E**) was refluxed for 18 hours in 1,4-dioxane to afford the crude imidazolium salts. After purification by silica gel column chromatography, these bis(benzimidazolium) salts were isolated as white solids in high yields. All these bis(benzimidazolium) salts were characterized by ^{1}H and ^{13}C NMR and HRMS.

However, we have been bothered with the synthesis of CF_3-containing bis(benzimidazolium) salt (Scheme 7) for a long time. We ever tried to increase the amount (up to 5 equiv. to **1d**) of R-Br (9**A**) or extend the reaction time to a week; the yield (less than 5%) is still very low and no satisfied NMR could be obtained. The reason for this was attributed to the two CF_3 groups that greatly decrease the nucleophilicity of nitrogen atoms of bis-imidazoles. Moreover, the common purification of the crude by gel chromatograph made thing worse and more unidentified impurities appeared after workup.



1d

Scheme 7. Attempt to alkylation of CF_3-containing bis-benzimidazole **1d** with benzyl bromide **9A**

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Synthesis of Chiral Bis(NHC) Palladium Complexes

With the expected bis(benzimidazolium) salts in hand, the metalation reactions were attempted to prepare the corresponding chiral palladium carbene complexes. Previously we have found that the coligands, including Br^-, Cl^-, AcO^-, CF_3COO^-, and water, have little influence on the catalytic results of this kind of bis(NHC)-Pd catalysts in Suzuki-Miyaura coupling reactions.[11b] Accordingly, only neutral halide complexes (for example, Scheme 4, (*R,R*)-**20**) were taken into account in the synthesis of metal carbene compounds. The in-situ deprotonation of imidazolium salts by $Pd(OAc)_2$ proved to be a reliable synthetic pathway for these chelating bis(NHC) palladium complexes. The synthetic route for chiral 1,2-cyclohexene-bridged bis(NHC) palladium complexes is depicted in Scheme 4. Treatment of the above bis(NHC) precursors with 1.0 equivalent of $Pd(OAc)_2$ in DMSO at 50 °C for 2 h and 100 °C for another 3 h afforded the desired NHC metal complexes (*R,R*)-**21** - **24** in moderate to high yields. Following this route, the synthesis of chiral 1,2-diphenylethylene- and binaphthylene-bridged bis(NHC)-Pd complexes (*R,R*)-**25**-**27** and (*aR*)-**28** have been also developed (Scheme 5-6). The purification of these NHC palladium complexes was performed by gel chromatograph and recrystallization from a mixture of dichloromethane and hexane. However, the reaction of 1,2-diphenylethylene-bis(benzimidazolium) salt (*R,R*)-**18** with $Pd(OAc)_2$ gave a completely insoluble solid, which hindered us to characterize it further.

The obtained bis(NHC) palladium complexes **20 - 28** are air- and moisture-stable in the solid state and even in common organic solvents. The introduction of bulky *t*-Bu groups greatly improved the solubility of NHC metal compounds, which brings convenience to their characterization and the follow-up catalytic application. For example, the palladium complexes with R groups A or C (Figure 3) more easily dissolve in organic solvents (for example, THF, CH_2Cl_2 and CH_3Cl) than others do. Especially, no satisfied ^{13}C NMR data could be obtained for complexes **21** and **24** with two paracyclophane (R_p-**B**) substituents.

All palladium NHC complexes were fully characterized by NMR, HRMS and elemental analysis. The selected ^1H & ^{13}C NMR and HRMS data of bis(benzimidazolium) salts and corresponding palladium complexes are listed in Table 1. In the NMR spectra of these bis(NHC)-Pd(II) complexes the signals of the NC*H*N protons at 11.37 - 13.38 ppm for the bis(imidazolium) salts disappeared completely, while the characteristic peaks of carbene carbon (Pd-*C*) were observed at 169.6 - 177.3 ppm. Notably, from their ^{13}C NMR spectra there existed two types of carbene carbon atoms in these cyclometalated palladium complexes except complex **28** (δ 175.9 ppm) with a chiral binaphylene linker. For example, the signals for the C_{NHC}-Pd of compounds **23** and **25** appear at 177.3, 170.7 ppm and 175.8, 170.4 ppm, respectively. The result indicates that these complexes are C_1-symmetric and two distinct ligand resonances could be found in their ^1H NMR spectra, which is similar to the chiral *trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-diyl (DEA) bridged bis-NHC palladium complex reported by Veige et al.[15d]

All bis(NHC) palladium complexes were in good agreement with the results by HRMS (Table 1). Although no peak was observed at the position corresponding to the parent molecule M, there was a dominant fragment ion $[M - Br]^+$ that showed the most dominant intensity (100%) as the base peak in their mass spectra. In some case, the fragment ion formed by bond cleavage between the alkyl carbon and nitrogen could be observed.

Structural Analysis of Chiral Linker - Bridged Bis(NHC) Palladium Complexes

Crystals of complexes **23** and **24** (Figure S64 and Table S1) suitable for X-ray structure determination were developed from dichloromethane/hexane solution. As shown in Figure 4, complex **23** features a distorted square planar coordination of the palladium with the two carbene carbon atoms in a cis disposition, which is a good orientation for Suzuki-Miyaura coupling reactions. The seven-membered palladacycle adopted a pseudo-boatlike conformation (Figure 5), and the selected bond lengths, angles and dihedral angles of **23** are denoted in the caption of Figure 4, which fall comfortably within the range found other chelating or cis bis(NHC)-Pd(II) complexes.[11,13-15]

Table 1. Selected ^1H and ^{13}C NMR and HRMS data of bis(benzimidazolium) salts **10-19** and bis(NHC) palladium complex **20-28**

Bis(benzimidazolium) Salt	^1H (NC*H*N) [a]	Bis(NHC)-Pd Complex	^{13}C ($C_{carbene}$-Pd) [b]	*m/z* ([M-Br]$^+$) [c]	
				Calcd.	Found
10	11.96	**20**	175.6, 169.8	1209.3892	1209.3929
11	12.49	**21**	N.D. [d]	943.2414	943.2434
12	12.81,12.59	**22**	176.1, 169.7	1223.4024	1223.4094
13	11.90	**23**	177.3, 170.7	1237.4205	1237.4226
14	9.79 [e]	**24**	N.D. [d]	971.2727	971.2734
15	13.38	**25**	175.8, 170.4	1307.4024	1307.4128
16	13.06	**26**	176.5, 171.5	1065.3721	1065.3736
17	13.29	**27**	175.4, 169.6 [e]	871.0707	871.0726
19	11.37	**28**	175.9	1379.4024	1379.4031

[a] In ppm (400 MHz) in $CDCl_3$ at 20 °C. [b] In ppm (100.5MHz) in $CDCl_3$ at 20 °C. [c] HRMS (positive ions). [d] Not determined due to its low solubility. [e] In DMSO-d_6.

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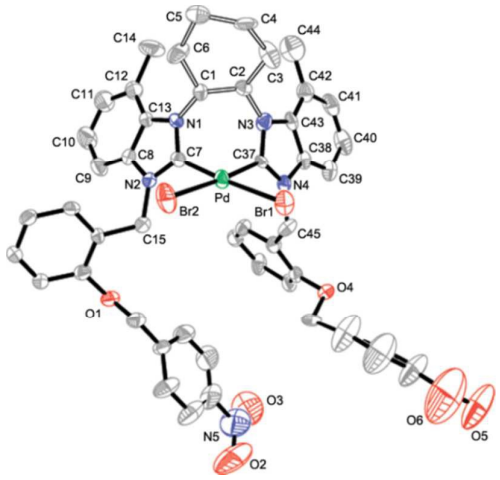

Figure 4. Molecular structure of complex (*R,R*)-**23** with ellipsoids drawn at the 50% probability level. All hydrogen atoms and *tert*-butyl groups are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Pd – C(7) = 1.960(8), Pd – C(37) = 2.004(7), Pd – Br(2) = 2.4683(18), Pd – Br(1) = 2.4517(19), C(7) – Pd – C(37) = 85.5(3), C(37) – Pd – Br(1) = 89.1(2), C(7) – Pd – Br(2) = 91.3(2), Br(1) – Pd – Br(2) = 94.04(5), C(7) – Pd – Br(1) = 174.5(2), C(37) – Pd – Br(2) = 175.8(2). Dihedral angels (deg): NHC(C7)/NHC (C37) = 92.7, NHC(C7)/P(Pd)* = 61.9, NHC(C37)/P(Pd)* = 63.9 (Pd). *Note: P(Pd)* represents the palladium coordination plane defined by [PdC(7)C(37)Br(1)Br(2)].*

Previously crystal structures of cyclohexane-1,2-based bis(NHC) palladium complexes (*R,R*)-**29** [11a] and (*R,R*)-**30** [11b] (Figure 5) have been determined by X-ray diffractions. By comparing **23** with them, we can draw some findings listed as follows: (1) The introduce of methyl group on the fragment of NHC ligands has led to the obvious structural change of bis(NHC)-Pd(II) complexes (**23** vs **29**). The cyclohexane-1,2-linker shows a boat conformation in **23** but a chair conformation in complexes **29** and **30** without methyl groups. Among the three dihedral angles of two carbene rings [NHC (C7) and NHC(C37)] and the PdC(7)C(37)Br(1)Br(2) coordination plane around palladium [for short, P(Pd)], the NHC(C7)/P(Pd) dihedral angle [61.9°] is much smaller than that [71.3°] in **29**, while the other two are similar to each other (92.7° and 63.9° for **23**, 92.5° and 64.4° for **29**). Moreover, the C-Pd-C bite angle [85.53°] in **23** is bigger than that [83.2(4)°] in **29**. (2) Although the R substituent on N-atom of NHCs has little effect on the bond distances, their influence on bond angles and dihedral angles is significant (**30** vs **29**, Figure 4). The C-Pd-C bite angle is decreased from 84.3(3)° in **30** to 83.2(4)° in **29**, while the Br-Pd-Br bite angles is increased from 92.51(4)° in **30** to 94.52(6)° in **29** along with the increase of the volume augmentation of the R groups. At the same time one of the NHC/P(Pd) dihedral angles radically enlarged nearly ten degrees (from 62.3° in 30 to 71.3° in 29) for the same reason. Moreover, the weak co-ligands (such as H_2O molecule) can reinforce the bonding of carbene carbon with the metal center, which shorten the two Pd-C bonds to ca. 1.96 Å.[11b]

Asymmetric Suzuki–Miyaura Coupling using Chiral Bis(NHC)-Pd Complexes

An initial screening revealed that complex (*aR*)-**28** performed best in the asymmetric coupling of 1-bromo-2-methoxynaphthalene and naphthylboronic acid (Figure 6). Optimization of the reaction conditions revealed a toluene solution associated with Cs_2CO_3 as base and 2 mol % of (*R,R*)-**20** to be an efficient combination for this reaction. On the whole, these chiral bis(NHC)-Pd complexes were able to sufficiently catalyse the Suzuki–Miyaura coupling: the (1R,2R)-cyclohexene-bridged bis(NHC)-Pd complex (*R,R*)-**23** achieved the highest yield of 90%, while complex (*aR*)-**28**, with a binaphthylene linker, showed the best enantioselectivity of 60 ee%.

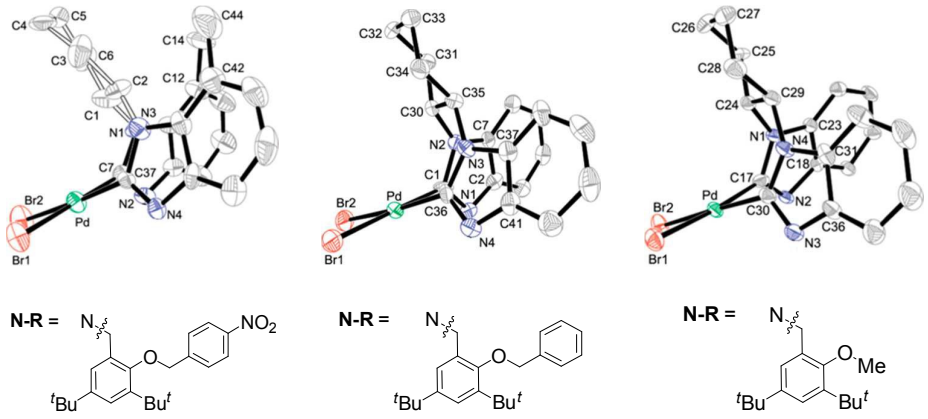

Figure 5. The side views of (1*R*,2*R*)-cyclohexane-bridged bis(NHC) palladium complex (*R,R*)-**23** (left) and compounds (*R,R*)-**29** [11a] (middle), and (*R,R*)-**30** [11b] (right).

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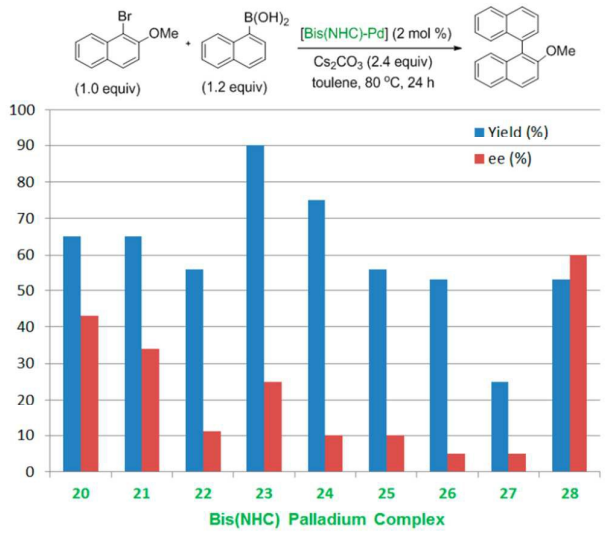
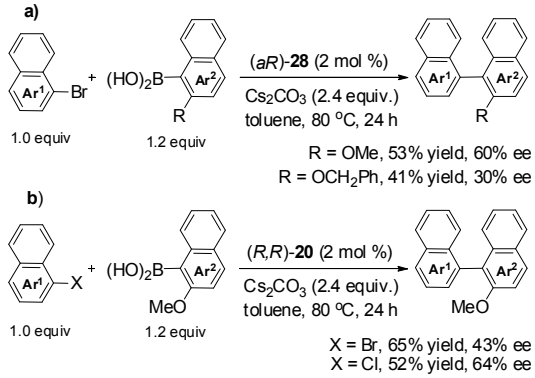


Figure 6. Suzuki–Miyaura coupling using chiral bis(NHC)-Pd complexes **20**-**28**

As shown in Figure 6, the structure characteristics of these chiral bis(NHC)-Pd complexes significantly affected their catalytic behaviours. Complexes (*R,R*)-**23** and (*R,R*)-**24** with two Me groups on the NHC fragments near to the chiral linker showed slightly higher yields but lower ee values than their analogues (*R,R*)-**20** and (*R,R*)-**21**. Considering that complex **20** has a similar structure and catalytic property to **29** [11a], it is acceptable to draw a direct comparison of their coordination surroundings around palladium centres in **23** and **29**. The biggest difference is that in **23**, one of the NHC/P(Pd) dihedral angles (61.9°) is much smaller than that (71.3°) in complex **29**. For this particular reaction, the latter is benefit to good enantioselectivity of the produced biaryls while the former ready access to high yield of couplings. In addition to the aforementioned chiral linker-related efforts, the planar chiral R_p-cyclophane group has also been used to modify bis(NHC) ligands on their *N*-positions [(*R,R,R*$_p$,*R*$_p$)-**21** and (*R,R,R*$_p$,*R*$_p$)-**24**] for the sake of the high ee values; unfortunately, the effect in practice is not as exception.

We anticipated that a bulkier substituent at the 2-position of the aryl boronic acid would lead to higher selectivities. As such, the use of 2-benzyloxyl-naphthylboronic acid was investigated (Scheme 8a). The benzyloxyl group set close to the Ar^1–Ar^2 bond generates more steric hindrance in the transition state in comparison to the previously used methoxy group. This hypothesis proved correct; only 30 % ee value could be obtained using complex (*aR*)-**28** under the previously optimized conditions. Besides, these bis(NHC)-Pd catalysts were sensitive to aryl halide (Scheme 8b). Using chloronaphthalene to replace its bromide analogue as a coupling partner led to an improved selectivity from 43 % to 64 % ee, a slightly low yield of 52% was observed for complex (*R,R*)-**20**. Based on this result, we explored other bis(NHC) palladium complexes in mediating the coupling of aryl boronic acids with low active aryl chlorides. These palladium complexes revealed a high isolated yield (66-93%) of biaryls at elevated temperature of 110 °C (Figure S65), which suggested that they are high stabilities to the harsh reaction conditions.



Scheme 8. Asymmetric Suzuki–Miyaura Coupling Using **20** and **28**

Conclusions

In conclusion we have designed and prepared a series of novel chiral-linker bridged bis(bebzimidazolium) salts by changing the chiral bridged linker, increasing steric hindrance and introducing more chiral elements. The formed chiral bis(NHC) palladium complexes have been full characterized by ^{1}H & ^{13}C NMR and HRMS, and further confirmed by X-ray single crystal analysis. These palladium complexes could sufficiently catalyze the Suzuki–Miyaura coupling reactions of aryl halides with substituted arylboronic acids in good yields (up to 90 %) and moderate enantioselectivities (up to 60 % ee), depending on their structure characteristics. Compared with the higher ee % value of other palladium catalytic systems, such as chiral monophosphines, the enantioselectivity produced by bi(NHC) palladium system has plenty of room to move up.

Experimental

General Methods

All manipulations were performed under an inert atmosphere of dry argon by using vacuum line and Schlenk tube techniques. The solvents were dried and distilled prior to use by literature methods. All chemical reagents were purchased from commercial sources (Acros, Aldrich, Alfa Aesar, or Fluka) and used as received unless otherwise indicated.

Starting Materials and Reagents

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Bis(NHC) palladium complex (*R,R*)-**20**,[11b] bis-benzimidazole (*aR*)-**8**,[13] benzyl bromides **9A**,[11b] R_p-**9B**,[16] **9C**,[11b] **9D**,[11b] **9E**[11b] and compounds (*R,R*)-**1a**,[11a] (*R,R*)-**2a**,[11a] (*R,R*)-**3a**[11a] were synthesized following literature procedures. Bis-benzimidazoles (*R,R*)-**1b-d**, (*R,R*)-**4** and relevant compounds (*R,R*)-**1d'**, (*R,R*)-**1d''**, (*R,R*)-**2b-d**, (*R,R*)-**3b-d**, (*R,R*)-**5a-b**, (*R,R*)-**6**, **7a-b and** (*R*)-**7c** were prepared and their characterization data, including NMR full spectra were list in Supporting Information.

Characterizations

^{1}H and ^{13}C NMR spectra were recorded on JEOL ECA-400 and Bruker AV500 spectrometers. ^{1}H and ^{13}C chemical shifts (δ) are given in ppm (the residual peak of deuterated solvents was used as reference). Elemental and high-resolution mass spectral (HRMS) analyses were carried out by the Analysis Center, Fudan University. Optical rotations were measured in a 100 mm cell with a Perkin-Elmer 241 photopolarimeter. Flash column chromatography was performed on silica gel (300–400 mesh). Analytical HPLC was performed using an Agilent 1100 series chromatograph with a JASCO PU-980 pump and Agilent 1100 Series detection system, together equipped with a Chiralcel OJ-H column. GC chromatograms were recorded on a HP 4890A GC equipped with a DB-5 MS UI capillary column, and the products were identified by comparison with authentic samples.

X-ray Crystallographic Studies

Single crystals of **23** and **24** suitable for X-ray analysis were sealed into a glass capillary, and the intensity data of the single crystals were collected on the CCD Bruker Smart APEX system. Data obtained with the ω−2θ scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. The structures were solved using direct methods, while further refinement with full-matrix least squares on F^2 was obtained with the SHELXTL program package.[17] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

Crystal Data for ***23***: $C_{66}H_{78}Br_2N_6O_6Pd$, Mr = 1317.56, colorless lamellar crystal, 0.18 × 0.10 × 0.01 mm, monoclinic, space group P 21/c, a = 20.197(17) Å, b = 18.197(15) Å, c = 18.417(15) Å, β = 96.093(14)°, V = 6730(10) Å^3, Z = 4, ρ_{calcd} = 1.300 g cm^{-3}, μ = 1.514 mm^{-1}, F(000) =2720, T = 293(2) K; I > 2σ(I), R_1 = 0.0690 and wR_2 = 0.1446; all data, R_1 = 0.1766 and wR_2 = 0.1612; GOF 0.925, 11844 independent reflections (2θ ≤ 50.02°) and 768 parameters, 206 restraints. The CCDC file 1447381 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via ccdc.cam.ac.uk/products/csd/request.

General Procedure for the Synthesis of Chiral Linker-Bridged Bis(Benzimidazolium) Salts.

A mixture of bis-imidazole (0.50 mmol) and benzyl bromide (1.33 mmol) was stirred at 100 °C in 1,4-dioxane (5.0 mL) for 18 h. Then the solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatography (eluent: EtOAc/CH_2Cl_2/CH_3OH/Et_3N = 8/2/1/0.2) to afford the bis(benzimidazolium) salt.

(R,R,R_p*,*R_p*)-**11**. Compound **11** was prepared from (*R,R*)-**1a** (158 mg, 0.50 mmol) and R_p-**9B** (400 mg, 1.33 mmol) as a white solid. Yield: 234 mg (51 %). Anal. Calcd for $C_{54}H_{54}Br_2N_4$ (M = 918.8414 g mol^{-1}): C, 70.59; H, 5.92; N, 6.10; Found: C, 70.44; H, 5.75; N, 6.12. HRMS (positive ions): *m/z* 839.3524, 757.4270 (calcd for $[M–Br]^+$ 839.3511, $[M–2Br-H]^+$ 757.4261). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.50 (s, 2H, NCHN), 8.94 (s, 2H, ArH), 7.57(s, 2H, ArH), 7.26 - 7.23(m, 4H, ArH), 6.89 - 6.81 (m, 14H, ArH), 6.47 - 6.33 (m, 2H, CH), 5.60 (d, J = 15.0 Hz, 2H, CH_2), 5.20 (d, J = 14.1 Hz, 2H, CH_2), 3.13 - 2.92 (m, 6H, CH_2), 2.69 (m, 4H, CH_2), 2.49 - 2.39 (m, 8H, CH_2), 2.08 (s, 4H, CH_2), 1.80(s, 2H, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 141.4 ($CH_{imidazolium}$), 139.4 (C_{Ar}), 139.0 (C_{Ar}), 138.2 (C_{Ar}), 135.7 (C_{Ar}), 134.2 (C_{Ar}), 134.1 (C_{Ar}), 133.2 (C_{Ar}), 132.4 (CH_{Ar}), 131.7 (CH_{Ar}), 130.3 (CH_{Ar}), 129.3 (CH_{Ar}), 128.0 (CH_{Ar}), 127.4 (CH_{Ar}), 114.7 (CH_{Ar}), 113.5 (CH_{Ar}), 60.5 (CH), 51.8 (CH_2), 46.2 (CH_2), 35.1 (CH_2N), 34.8 (CH_2), 34.4 (CH_2), 34.1 (CH_2), 24.3 (CH_2).

*(R,R)-**12***. Compound **12** was prepared from (*R,R*)-**1c** (158 mg, 0.50 mmol) and benzyl bromide **9A** (577 mg, 1.33 mmol) as a white solid. Yield: 534 mg (89 %). Anal. Calcd for $C_{65}H_{78}Br_2N_6O_6$ (M = 1199.1549 g mol^{-1}): C, 65.10; H, 6.56; N, 7.01; Found: C, 64.99; H, 6.48; N, 7.05. HRMS (positive ions): *m/z* 1119.5165, 1037.5905 (calcd for $[M–Br]^+$ 1119.5146, $[M–2Br-H]^+$ 1037.5917). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.81 (s, 1H, NCHN), 12.59 (s, 1H, NCHN), 9.27 (d, J = 7.2 Hz, 1H, ArH), 8.27 (d, J = 12.8 Hz, 4H, ArH), 7.73 (t, J = 8.4 Hz, 4H, ArH), 7.62 (t, J = 8.0 Hz, 1H, ArH), 7.40 (t, J = 8.0 Hz, 1H, ArH), 7.33 – 7.26 (m, 6H, ArH), 7.16 (t, J = 4.8 Hz, 1H, ArH), 6.94 (d, J = 2.4 Hz, 1H), 6.79 (br, 1H), 6.67 – 6.61 (m, 1H), 6.12 (d, J = 14.8 Hz, 1H), 5.99 – 5.93 (m, 1H), 5.82 (d, J = 14.8 Hz, 1H, CH_2), 5.71 (d, J = 14.8 Hz, 1H, CH_2), 5.54 (d, J = 14.8 Hz, 1H, CH_2), 5.17 (t, J = 12.8 Hz, 1H, CH_2), 5.06 – 4.99 (m, 2H), 3.18(s, 3H), 2.68 – 2.63 (m, 1H), 2.94 – 2.31 (m, 3H), 2.17 – 2.05 (m, 7H), 1.40 (s, 18H, CH_3), 0.92 (d, J = 13.2 Hz, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0 (C_{Ar-O}), 152.9 (C_{Ar-O}), 148.2 (C_{Ar-NO2}), 148.0 (C_{Ar-NO2}), 147.6 (C_{Ar-NO2}), 143.8 (C_{Ar-CH2}), 143.7 (C_{Ar-CH2}), 142.7 (C_{Ar-CH3}), 141.9 (C_{Ar}), 141.6 (C_{Ar}), 131.7 (C_{Ar-But}), 131.2 (C_{Ar-But}), 130.8, 130.3 (C_{Ar-But}), 130.0 (C_{Ar-But}), 128.3 (CH_{Ar}), 127.7 (CH_{Ar}), 127.5 (CH_{Ar}), 127.2 (CH_{Ar}), 127.1 (CH_{Ar}), 126.0 (C_{Ar-CH3}), 125.9 (CH_{Ar}), 125.4 (CH_{Ar}), 125.1 (CH_{Ar}), 124.4 (CH_{Ar}), 124.2 (CH_{Ar}), 124.0 (CH_{Ar}), 115.0 ($CH_{Ar-NO2-m}$), 113.3 (CH_{Ar}), 111.1 (CH_{Ar}), 75.9 (CH_2O), 75.8 (CH_2O), 63.0 (CH), 60.0 (CH), 46.8 (CH_2N), 46.7 (CH_2N), 35.9 (C_{But}), 35.5 (C_{But}), 34.9 (C_{But}), 31.0 ($CH_{3\ But}$), 29.7 (CH_2), 24.1 (CH_2), 21.1 (CH_3).

*(R,R)-**13***. Compound **13** was prepared from (*R,R*)-**1b** (172 mg, 0.50 mmol) and **9A** (577 mg, 1.33 mmol) as a white solid. Yield: 558 mg (92 %). Anal. Calcd for $C_{66}H_{80}Br_2N_6O_6$ (M = 1213.1860 g mol^{-1}): C, 65.34; H, 6.65; N, 6.93; Found: C, 65.33; H, 6.63; N, 7.00. HRMS (positive ions): *m/z* 1133.5327, 1051.6071 (calcd for $[M–Br]^+$ 1133.5302, $[M–2Br–H]^+$ 1051.6061). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 12.06 (s, NCHN, 2H),

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8.26 (d, *J* = 8.8 Hz, 4H, ArH), 7.68 (d, *J* = 8.8Hz, 4H, ArH), 7.39-7.33 (m, *J* = 8.4 Hz, 4H, ArH), 7.27 (2H, ArH), 7.23 (d, *J* = 2.0 Hz, 2H, ArH), 6.78 (d, *J* = 2.4 Hz, 2H, ArH), 6.21 (dd, *J* = 9.2, 4.4 Hz, 2H, CH_{Cy}), 5.96 (d, *J* = 14.8 Hz, 4H, CH_2), 5.75 (d, J = 14.8 Hz, 4H, CH_2), 5.10 (d, J = 14.0 Hz, 4H, CH_2), 4.96 (d, *J* = 14.0 Hz, 4H, CH_2), 3.34 (s, 6H, CH_3), 2.93 (m, 2H, CH_2), 1.46 (m, 2H, CH_2), 2.04 - 1.93 (m, 4H, CH_2), 1.38 (s, 18H, CH_3), 0.82 (s, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9 ($C_{Ar\text{-}O}$), 147.8 ($C_{Ar\text{-}NO2}$), 147.6 ($C_{Ar\text{-}NO2}$), 143.8 ($C_{Ar\text{-}CH2}$), 142.6 ($C_{Ar\text{-}CH3}$), 140.5 (C_{Ar}), 131.7 ($C_{Ar\text{-}But}$), 131.1 ($C_{Ar\text{-}But}$), 130.0 ($C_{Ar\text{-}But}$), 127.7 (CH_{Ar}), 127.1 (CH_{Ar}), 126.3 ($C_{Ar\text{-}CH3}$), 125.6 (CH_{Ar}), 125.5 (CH_{Ar}), 124.2 (CH_{Ar}), 123.9 (CH_{Ar}), 111.8 (CH_{Ar}), 111.1 (CH_{Ar}),75.8 (CH_2O), 61.1 (CH), 46.5 (CH_2N), 36.1 (C_{But}), 35.5 (C_{But}), 34.3 (C_{But}), 31.2 ($CH_{3\ But}$), 31.0 (CH_2), 23.9 (CH_2), 21.0 (CH_3).

*(R,R,R$_p$,R$_p$)-**14***. Compound **14** was prepared from (*R*,*R*)-**1b** (172 mg, 0.50 mmol) and *R$_p$*-**9B** (400 mg, 1.33 mmol) as a white solid. Yield: 142 mg (30%). Anal. Calcd for $C_{56}H_{58}Br_2N_4$ (M = 946.8945 g mol^{-1}): C, 71.03; H, 6.17; N, 5.92; Found: C, 70.94; H, 6.11; N, 6.03. HRMS (positive ions): *m/z* 865.3850, 785.4596 (calcd for [M – Br]$^+$ 865.3845, [M–2Br-H]$^+$ 785.4583.) ^{1}H NMR (400 MHz, $(CD_3)SO$): δ 9.78 (s, 2H, NCHN), 7.72 (d, *J* = 8.40 Hz, 2H, ArH), 7.60 - 7.56 (m, 2H, ArH), 7.42 (d, *J* = 7.44 Hz, 2H, ArH), 6.70 - 6.68 (m, 2H, ArH), 6.43 - 6.42 (m, 4H), 6.25 (d, *J* = 7.0 Hz, 2H), 5.85 - 5.84 (m, 2H, CH), 5.40 (d, *J* =1 4.8 Hz, 2H, CH_2), 5.18 (d, *J* = 14.4 Hz, 2H, CH_2), 2.93 - 2.69 (m, 18H), 2.50 - 2 .41 (m, 4H, CH_2), 1.67 - 1.62 (m, 2H, CH_2). ^{13}C NMR (100MHz, $(CD_3)SO$): δ 141.0 ($CH_{imidazolium}$), 139.6 (C_{Ar}), 139.2 (C_{Ar}), 138.4 (C_{Ar}), 135.7 (C_{Ar}), 134.8 (C_{Ar}), 133.7 (C_{Ar}), 133.3 (C_{Ar}), 132.6 (C_{Ar}), 132.0 (C_{Ar}), 131.9 (C_{Ar}), 130.8 (CH_{Ar}), 129.9 (CH_{Ar}), 129.7 (CH_{Ar}), 127.6 (CH_{Ar}), 125.3 (CH_{Ar}), 114.5 (CH_{Ar}), 60.6 (CH), 49.7 (CH_2N), 34.9 (CH_2), 34.7 (CH_2), 34.1 (CH_2), 24.2 (CH_2), 19.2 (CH_3).

*(R,R)-**15***. Compound **15** was prepared from (*R*,*R*)-**4** (207 mg, 0.50 mmol) and **9A** (577 mg, 1.33 mmol) as a white solid (eluent: EtOAc/CH_2Cl_2/CH_3OH = 8/2/1). Anal. Calcd for $C_{72}H_{78}Br_2N_6O_6$ (M = 1283.2343 g mol^{-1}): C, 67.39; H, 6.13; N, 6.55; Found: C, 67.32; H, 6.10; N, 6.57. Yield: 603 mg (94 %). HRMS (positive ions): *m/z* 1203.5128, 1121.5905 (calcd for [M–Br]$^+$ 1203.5146, [M–2Br-H]$^+$1121.5911. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.37 (s, 2H, NCHN), 9.52 - 9.50 (d, *J* = 8.4 Hz ,2H, ArH), 8.46 (s, 2H, ArH), 8.28 - 8.20 (m, 8H, ArH), 7.72 - 7.68 (m, 6H, ArH), 7.50 - 7.42 (m, 4H, ArH), 7.27 - 7.21 (m, 6H, ArH), 7.15 - 7.11 (m, 2H, ArH), 7.04 (s, 2H, CH), 5.76 (d, *J* = 14.3 Hz, 2H, CH_2), 5.65 (d, *J* = 8.4 Hz, 2H, CH_2), 5.10 - 4.96 (m, 4H, CH_2), 1.40 (s, 18H, CH_3), 0.87(s, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9 ($C_{Ar\text{-}O}$), 147.3 ($C_{Ar\text{-}NO2}$), 146.7 ($C_{Ar\text{-}NO2}$), 142.6 (C_{Ar}), 141.5 ($CH_{imidazolium}$), 140.4 (C_{Ar}), 132.8 ($C_{Ar\text{-}But}$), 130.9 (CH_{Ar}), 129.4 (CH_{Ar}), 128.6 ($CH_{Ar\text{-}NO2\text{-}m}$), 127.7 ($CH_{Ar}$), 127.5 ($CH_{Ar}$), 126.8 ($CH_{Ar}$), 126.0 ($CH_{Ar}$), 125.0 ($C_{Ar\text{-}CH2}$), 124.3 ($CH_{Ar}$), 123.8 ($CH_{Ar}$), 123.1($CH_{Ar}$), 115.8 ($CH_{Ar}$), 111.8 ($CH_{Ar}$), 63.9 ($CH_2O$), 45.2 ($CH_2N$), 34.5 ($C_{But}$), 33.4 ($C_{But}$), 30.1 ($CH_{3\ But}$), 30.0 ($CH_{3\ But}$).

*(R,R)-**16***. Compound **16** was prepared from (*R*,*R*)-**4** (207 mg, 0.50 mmol) and **9C** (415 mg, 1.33 mmol) as a white solid (eluent: EtOAc/CH_2Cl_2/CH_3OH = 8/2/1). Yield: 442 mg (85%). Anal. Calcd for $C_{60}H_{72}Br_2N_4O_2$ (M = 1041.0473 g mol^{-1}): C, 69.22; H, 6.97; N, 5.38; Found: C, 69.16; H, 6.87; N, 5.43. HRMS (positive ions): *m/z* 961.4820, 879.5567 (calcd for [M–Br]$^+$ 961.4818, [M–2Br-H]$^+$ 879.5577). ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.05 (s, 2H, NCHN), 9.47 (d, *J* = 8.4 Hz , 2H, ArH), 8.54 (s, 2H, ArH), 8.26 (d, *J* = 7.4 Hz, 4H, ArH), 7.70 (t, *J* = 5.0 Hz, 2H, ArH), 7.57 (d, *J* = 4.4 Hz, 2H, ArH) 7.44 (t, *J* = 7.8 Hz, 2H, ArH), 7.30 - 7.20 (m, 8H, ArH), 7.16 - 7.14 (m, 2H, CH), 5.74 (d, *J* = 14.4 Hz, 2H, CH_2), 5.63 (d, *J* = 10.4 Hz, 2H, CH_2), 3.79 (s, 6H, CH_3), 1.21 (s, 18H, CH_3), 1.05 (s, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5 ($C_{Ar\text{-}O}$), 147.3 (C_{Ar}), 142.5 ($CH_{imidazolium}$), 133.6 (C_{Ar}), 129.5 (CH_{Ar}), 128.8 (CH_{Ar}), 128.1 (CH_{Ar}), 127.5 (CH_{Ar}), 125.9 (CH_{Ar}), 125.3 ($C_{Ar\text{-}CH2}$), 116.8 (CH_{Ar}), 113.1 (CH_{Ar}), 64.6 (CH), 64.0 (CH_2O), 47.4 (CH_2N), 35.1 (C_{But}), 34.4 (C_{But}), 31.2 ($CH_{3\ But}$), 30.9 ($CH_{3\ But}$).

*(R,R)-**17***. Compound **17** was prepared from (*R*,*R*)-**4** (207 mg, 0.50 mmol) and benzyl bromide **9D** (306 mg, 1.33 mmol) as a white solid (eluent: EtOAc/CH_2Cl_2/CH_3OH/PE = 8/2/1/2). Yield: 339 mg (80%). Anal. Calcd for $C_{42}H_{34}Br_2N_6O_4$ (M = 846.5652 g mol^{-1}): C, 59.59; H, 4.05; N, 9.93; Found: C, 59.55; H, 4.01; N, 10.02. HRMS (positive ions): *m/z* 765.1826, 685.2567 (calcd for [M–Br]$^+$ 765.1825, [M–2Br-H]$^+$ 685.2563). ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.27 (s, 2H, NCHN), 9.61 (d, *J* = 8.6 Hz, 2H, ArH), 8.35 (s, 2H, ArH), 8.26 (d, *J* = 7.5 Hz, 4H, ArH), 7.82 - 7.77 (m, 6H, ArH), 7.63 (t, *J* = 7.8 Hz, 2H, ArH), 7.47 (d, *J* = 8.4 Hz, 2H, ArH), 7.40 (d, *J* = 8.6 Hz, 4H, ArH), 7.34 - 7.30 (m, 4H, ArH), 7.25 (t, *J* = 7.4 Hz, 2H, CH), 5.85 (d, *J* = 15.2 Hz, 2H, CH_2), 5.66 (d, *J*=15.2 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1 ($C_{Ar\text{-}NO2}$), 141.8 ($CH_{imidazolium}$), 138.8 (C_{Ar}), 132.7 ($C_{Ar\text{-}CH2}$), 131.6 (C_{Ar}), 130.2 (C_{Ar}), 129.9 (C_{Ar}), 129.0 (C_{Ar}), 128.8 (CH_{Ar}), 128.7 (CH_{Ar}), 128.4 (CH_{Ar}), 124.2 (CH_{Ar}), 117.2 (CH_{Ar}), 112.0 (CH_{Ar}), 65.8 (CH), 50.1 (CH_2N).

*(R,R)-**18***. Compound **18** was prepared from (*R*,*R*)-**8e** (207 mg, 0.50 mmol) and **9E** (294 mg, 1.33 mmol) as a white solid (eluent: EtOAc/CH_2Cl_2/CH_3OH/PE = 8/2/1/2). Yield: 321 mg (75%). Anal. Calcd for $C_{50}H_{40}Br_2N_4$ (M = 856.6874 g mol^{-1}): C, 70.10; H, 4.71; N, 6.54; Found: C, 69.93; H, 4.65; N, 6.62. HRMS (positive ions): *m/z* 775.2450, 695.3216 (calcd for [M–Br]$^+$ 775.2436, [M–2Br-H]$^+$ 695.3175). ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.04 (s, 2H, NCHN), 9.62 (d, *J* = 8.6 Hz, 2H, ArH), 8.44 - 8.40(m, 4H, ArH), 7.77 (br s, 16H, ArH), 7.61 - 7.59 (m, 4H, ArH), 7.55 - 7.51 (m, 2H, ArH), 7.46 - 7.27 (m, 2H, ArH), 7.23 - 7.19 (m, 2H, ArH), 6.96 (d, *J* = 8.5 Hz, 2H, CH_2), 5.65 (d, *J* = 14.9 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6 ($CH_{imidazolium}$), 133.2 (C_{Ar}), 133.1 (C_{Ar}), 132.8 (C_{Ar}), 131.8 (C_{Ar}), 130.1 (C_{Ar}), 129.8 (C_{Ar}), 129.6 (C_{Ar}), 129.3 (C_{Ar}), 129.2 (C_{Ar}), 128.3 (CH_{Ar}), 128.0 (CH_{Ar}), 127.8 (CH_{Ar}), 127.6 (CH_{Ar}), 127.6 (CH_{Ar}), 127.0 (CH_{Ar}), 126.8 (CH_{Ar}), 124.2 (CH_{Ar}), 116.7(CH_{Ar}), 112.4 (CH_{Ar}), 65.7 (CH), 51.8 (CH_2N).

*(aR)-**19***. Compound **19** was prepared from (a*R*)-**8** (243 mg, 0.50 mmol) and **9A** (577 mg, 1.33 mmol) as a white solid (eluent: EtOAc/CH_2Cl_2/CH_3OH/PE = 8/2/1/1). Yield: 528 mg (78%). Anal. Calcd for $C_{78}H_{78}Br_2N_6O_6$ (M = 1355.2985 g mol^{-1}): C, 69.12; H, 5.80; N, 6.20; Found: C, 69.09; H, 5.75; N, 6.24. HRMS(positive ions): *m/z* 1275.5178, 1193.5917 (calcd for [M–Br]$^+$ 1275.5166, [M-2Br-H]$^+$ 1193.5905). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.37 (s,2H,NCHN), 8.22 (d, *J* = 8.4 Hz, 6H, ArH), 8.03 - 8.02 (m, 2H, ArH), 7.92 (d, *J* = 8.2, 2H, ArH), 7.76 (d, *J* = 7.8 Hz, 4H, ArH), 7.76 (d, *J* = 7.8 Hz, 4H, ArH), 7.53 -

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7.42 (m, 4H, ArH), 7.31 - 7.12 (m, 14 H, ArH), 5.47 (s, 4H, CH_2), 5.34 (d, *J* = 11.2 Hz, 2H, CH_2), 5.00 (d, *J* = 13.8 Hz, 2H, CH_2), 1.32 (s, 18H, CH_3), 1.18 (s, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9 (C_{Ar-O}), 147.5 (C_{Ar-NO2}), 144.5 (C_{Ar-NO2}), 143.0 (C_{Ar}), 142.0 ($CH_{imidazolium}$), 133.6 (C_{Ar-But}), 132.4 (C_{Ar-But}), 131.4 (C_{Ar}), 129.3 (C_{Ar}), 128.6 (CH_{Ar}), 128.1 (CH_{Ar}), 127.9 (CH_{Ar}), 127.6 (CH_{Ar}), 125.6 (C_{Ar-CH2}), 125.2 (C_{Ar-CH2}), 123.6 (CH_{Ar}), 115.1 (CH_{Ar}), 112.7 (CH_{Ar}), 77.9 (CH_2O), 77.3 (CH_2O), 76.8 (CH_2O), 74.9 (CH_2O), 47.8 (CH_2N), 35.3 (C_{But}), 34.6 (C_{But}), 31.4 ($CH_{3\ But}$), 30.9 ($CH_{3\ But}$), 29.6 ($CH_{3\ But}$).

General Procedure for the Synthesis of Chiral Linker-Bridged Bis(NHC) Palladium Complexes

A mixture of chiral bis(benzimidazolium) salt (0.2 mmol) and 98% $Pd(OAc)_2$ (44.8 mg, 0.2 mmol) in DMSO (3.0 mL) was stirred at 50 °C for 2 h and then at 110 °C for 3 h. After the solvent was removed by reduced pressure while heating, the residue was purified by silica gel column chromatography (eluent: 1/10 EtOAc/CH_2Cl_2) to afford a brown crude product. The crude product was then washed with toluene to afford the pure palladium complex

(R,R,Rp)-***21***. Complex **21** was prepared from (R,R)-**11** (167.8 mg, 0.2 mmol) as a light yellow solid. Yield: 153 mg (75%). Anal. Calcd for $C_{54}H_{52}Br_2N_4Pd$ (M = 1023.2455 g mol^{-1}): C, 63.38; H, 5.12; N, 5.48; Found: C, 63.25; H, 5.07; N, 5.60. HRMS (positive ions): *m/z* 943.2434 (calcd for $[M–Br]^+$ 943.2414). ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 7.81(d, *J* = 8.6 Hz, 1H, ArH), 7.74 (d, *J* = 8.2 Hz, 2H, ArH), 7.66 (d, *J* = 8.2 Hz, 1H, ArH), 7.46 - 7.43 (m, 1H, ArH), 7.38 - 7.35 (m, 1H, ArH), 7.30 - 7.25 (m, 2H, ArH), 7.07 - 7.05 (m, 1H, ArH), 6.88 - 6.86 (m, 2H, ArH), 6.70 (s, 3H), 6.85 - 6.39 (m, 8H), 6.32 (d, *J* = 7.7 Hz， 1H), 6.13 (s, 1H, CH), 5.70 - 5.52 (m, 4H, CH_2), 5.27 - 5.22 (m, 4H, CH_2), 3.81 - 3.78 (m, 1H, CH_2), 3.33 - 2.76 (m, 12H, CH_2), 2.54 - 2.35(m, 5H, CH_2), 2.13 (d, *J* = 12.44 Hz, 1H, CH_2), 1.94 (s, 2H, CH_2), 1.82 - 1.80 (m, 1H, CH_2), 1.66 (s, 1H, CH_2). No satisfied ^{13}C NMR spectrum could be obtained due to its low solubility.

(R,R)-***22***. Complex **22** was prepared from (*R,R*)-**12** (239.8 mg, 0.2 mmol) as a white solid. Yield: 177 mg (68%). Anal. Calcd for $C_{65}H_{76}Br_2N_6O_6Pd$ (M = 1303.5635 g mol^{-1}): C, 59.89; H, 5.88; N, 6.45; Found: C, 59.71; H, 5.75; N, 6.55. HRMS (positive ions): *m/z* 1223.4094 (calcd for $[M–Br]^+$ 1223.4024). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 – 8.11 (m, 5H, ArH), 7.89 (s, 1H, ArH), 7.69 - 7.55 (m, 6H, ArH), 7.25 – 7.18 (m, 3H, ArH), 6.99 (t, *J* = 8.0 Hz, 1H), 6.91 -6.87 (m, 2H), 6.61 (d, *J* = 8.0 Hz, 2H), 6.50 – 6.48 (m, 1H), 6.11 (brs, 1H), 5.30 – 4.97 (m, 4H), 4.62 (brs, 1H), 3.00 (s, 1H), 2.68 (s, 3H), 2.50 – 2.33 (m, 2H), 2.26 – 2.14 (m, 2H), 2.04 – 1.99 (m, 1H), 1.84 – 1.77 (m, 2H), 1.45 – 1.36 (m, 18H, CH_3), 0.88 (br, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1 (NCN), 169.7 (NCN), 153.1 (C_{Ar-O}), 153.0 (C_{Ar-O}), 147.5 (C_{Ar-NO2}), 147.4 (C_{Ar-NO2}), 146.6 (C_{Ar-NO2}), 144.6 (C_{Ar-CH2}), 144.4(C_{Ar-CH2}), 142.09 (C_{Ar-CH3}), 135.1 (C_{Ar}), 134.5 (C_{Ar}), 133.0 (C_{Ar}), 132.5 (C_{Ar}), 128.4 (CH_{Ar}), 128.0 (CH_{Ar}), 127.6 (CH_{Ar}), 127.5 (CH_{Ar}), 126.8 (CH_{Ar}), 124.2 (C_{Ar-CH3}), 124.1 (C_{Ar-CH3}), 123.8 (CH_{Ar}), 121.2 (CH_{Ar}), 112.9 (CH_{Ar}), 111.2 (CH_{Ar}), 111.0 (CH_{Ar}), 74.9 (CH_2O), 74.8 (CH_2O), 63.8 (CH), 62.1 (CH), 50.7 (CH_2N), 36.4 (C_{But}), 35.5 (C_{But}), 34.5 (C_{But}), 34.4 (C_{But}), 31.2 ($CH_{3\ But}$), 31.0 ($CH_{3\ But}$), 29.8 (CH_2), 25.7 (CH_2), 24.7 (CH_2), 20.0 (CH_3).

(R,R)-***23***. Complex **23** was prepared from (*R,R*)-**13** (239.8 mg, 0.2 mmol) as a white solid. Yield: 159 mg (65%). Anal. Calcd for $C_{66}H_{78}Br_2N_6O_6Pd$ (M = 1317.5901 g mol^{-1}): C, 60.16; H, 5.97; N, 6.38; Found: C, 60.13; H, 5.95; N, 6.41. HRMS (positive ions): *m/z* 1237.4226 (calcd for $[M–Br]^+$ 1237.4205). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (t, *J* = 11.2 Hz, 2H), 8.14 (t, *J* = 8.8 Hz, 2H), 7.82 (br s, 1H), 7.59 (br s, 2H), 7.23 (s, 1H), 7.18 (s, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.94 -6.87 (m, 3H), 6.48 (d, *J* = 8.0 Hz, 3H), 5.30 – 5.25 (m, 2H), 5.06 – 5.03 (m, 2H), 4.78 (brs, 1H), 3.00 (s, 1H), 2.81 (s, 3H), 2.76 (s, 3H), 2.56 – 2.46 (m, 3H), 2.19 (m, 2H), 1.77 (br s, 2H), 1.41 (s, 9H, CH_3), 1.37 (s, 9H, CH_3), 0.97 (s, 9H, CH_3), 0.76 (s, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3 (NCN), 170.7 (NCN), 153.0 (C_{Ar-O}), 152.9 (C_{Ar-O}), 147.5 (C_{Ar-NO2}), 147.4 (C_{Ar-NO2}), 147.0 (C_{Ar-NO2}), 146.6(C_{Ar-CH2}), 144.4 (C_{Ar}), 144.3(C_{Ar}), 135.6 (C_{Ar}), 134.3 (C_{Ar}), 132.9 (C_{Ar}), 132.3 (C_{Ar}), 128.2 (CH_{Ar}), 127.9 (CH_{Ar}), 127.6 (CH_{Ar}), 127.0 (CH_{Ar}), 124.1 (C_{Ar-CH3}), 123.9 (CH_{Ar}), 123.8 (CH_{Ar}), 123.7 (CH_{Ar}), 123.4 (CH_{Ar}), 120.7 (CH_{Ar}), 120.1 (CH_{Ar}), 110.8 (CH_{Ar}), 110.5 (CH_{Ar}), 74.8 (CH_2O), 74.6 (CH_2O), 64.8 (CH), 62.1 (CH), 50.7 (CH_2N), 42.8, 36.4 (C_{But}), 35.4 (C_{But}), 35.3 (C_{But}), 34.5 (C_{But}), 34.2 (C_{But}), 31.2 ($CH_{3\ But}$), 31.0 ($CH_{3\ But}$), 30.9 ($CH_{3\ But}$), 26.0 (CH_2), 24.7 (CH_2), 24.0 (CH_2), 20.0 (CH_3).

(R,R,Rp,Rp)-***24***. Complex **24** was prepared from (*R,R,Rp,Rp*)-**14** (189.4 mg, 0.2 mmol) as a light yellow solid. Yield: 120 mg (57%). Anal. Calcd for $C_{56}H_{56}Br_2N_4Pd$ (M = 1051.2986 g mol^{-1}): C, 63.98; H, 5.37; N, 5.33; Found: C, 63.88; H, 5.33; N, 5.35. HRMS (positive ions): *m/z* 971.2734 (calcd for $[M–Br]^+$ 971.2727). ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 8.13 (s, 1H, ArH), 7.55 (s, 1H, ArH), 7.33 - 7.13 (m, 3H, ArH), 6.98 - 6.29 (m, 14H), 6.09 (s, 1H), 5.75 - 5.61 (m, 3H), 6.80 - 6.78 (m, 1H), 5.25 (m, 2H, CH_2), 3.69 (m, 2H, CH_2), 3.25 - 3.15 (m, 3H, CH_2), 3.06 - 2.70 (m, 17H, CH_2), 2.18 - 1.64 (m, 4H, CH_2), 1.33 - 1.22 (m, 4H, CH_2). No satisfied ^{13}C NMR spectrum could be obtained due to its low solubility.

(R,R)-***25***. Complex **25** was prepared from (*R,R*)-**15** (256.6 mg, 0.2 mmol) as a light yellow solid (eluent: EtOAc/CH_2Cl_2 = 1/10). Yield: 164 mg (59%). Anal. Calcd for $C_{72}H_{76}Br_2N_6O_6Pd$ (M = 1386.6384 g mol^{-1}): C, 62.32; H, 5.22; N, 6.06; Found: C, 62.23; H, 5.20; N, 6.10. HRMS (positive ions): *m/z* 1307.4128 (calcd for $[M–Br]^+$ 1307.4024). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.46 (d, *J* = 12.16 Hz, 4H), 8.48 (s, 2H, ArH), 8.18 - 8.11 (m, 6H, ArH), 7.90 (s, 2H, ArH), 7.66 (d, *J* = 11.2 Hz, 6H, ArH), 7.40 - 7.14 (m, 4H, ArH), 6.96 - 6.73 (m, 6H), 6.58 - 6.52 (m, 2H, CH_2), 6.17 - 6.01 (m, 2H, CH_2), 5.07 - 4.86 (m, 4H, CH_2), 1.41 (d, *J* = 10.8 Hz, 18H, CH_3), 0.74 (s, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.8 (NCN), 170.4 (NCN), 153.1 (C_{Ar-O}), 152.9 (C_{Ar-O}), 147.4 (C_{Ar-NO2}), 147.3 (C_{Ar-NO2}), 147.0 (C_{Ar-NO2}), 146.6 (C_{Ar}), 130.3 (C_{Ar}), 129.4 (C_{Ar}), 127.7 (CH_{Ar}), 124.1 (CH_{Ar}), 123.8 (CH_{Ar}), 123.7 (CH_{Ar}), 112.6 (CH_{Ar}), 112.2 (CH_{Ar}), 111.8 (CH_{Ar}), 111.0 (CH_{Ar}), 74.9 (CH), 65.3 (CH_2O), 62.0 (CH_2O), 50.2 (CH_2N), 48.0 (CH_2N), 35.3 (C_{But}), 34.2 (C_{But}), 31.0 ($CH_{3\ But}$), 30.9 ($CH_{3\ But}$), 30.5 ($CH_{3\ But}$), 29.6 ($CH_{3\ But}$).

(R,R)-***26***. Complex **26** was prepared from (*R,R*)-**16** (208.2 mg, 0.2 mmol) as a light yellow solid (eluent: EtOAc/CH_2Cl_2 = 1/10). Yield: 115 mg (50%). Anal. Calcd for $C_{60}H_{70}Br_2N_4O_2Pd$

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(M = 1145.4514 g mol^{-1}): C, 62.91; H, 6.16; N, 4.89; Found: C, 63.00; H, 6.10; N, 4.95. HRMS (positive ions): *m/z* 1065.3736 (calcd for $[M–Br^-]^+$ 1065.3721). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (d, *J* = 8.1 Hz, 2H, ArH), 8.48 (d, *J* = 7.4 Hz, 2H, ArH), 7.90 (d, *J* = 7.4 Hz, 2H, ArH), 7.64 (d, *J* = 8.4 Hz, 1H, ArH), 7.42 - 7.40 (m, 6H, ArH), 7.26 - 7.18 (m, 4H, ArH), 7.04 - 7.00 (m, 1H), 6.89 - 6.87 (m, 2H), 6.86 - 6.81 (m, 2H, CH), 6.78 - 6.61 (m, 2H, CH_2), 6.30 (s, 1H, CH_2), 6.16 (d, *J* = 16.3 Hz, 1H, CH_2), 5.94 (d, *J* = 15.5 Hz, 1H, CH_2), 5.64 (s, 1H, CH_2), 3.91 (s, 3H, CH_3), 3.59 (s, 3H, CH_3) ,1.443 (d, *J* = 5.2 Hz, 18H, CH_3), 0.74 (m, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4 (NCN), 171.7 (NCN), 155.4 (C_{Ar-O}), 155.2 (C_{Ar-O}), 146.2 (C_{Ar}), 145.7 (C_{Ar}), 141.8 (C_{Ar}), 141.4 (C_{Ar}), 140.3 (C_{Ar}), 130.2 (C_{Ar}), 129.7 (C_{Ar}), 129.4 (C_{Ar}), 129.2 (C_{Ar}), 129.0 (CH_{Ar}), 124.0 (C_{Ar-CH2}), 123.9 (CH_{Ar}), 123.6 (CH_{Ar}), 123.1 (CH_{Ar}), 122.9 (CH_{Ar}), 112.7 (CH_{Ar}), 112.5 (CH_{Ar}), 111.5 (CH_{Ar}), 110.7 (CH_{Ar}), 65,4 (CH), 62.9 (CH_2O), 62.5 (CH_2O), 62.0 (CH_2O), 50.1 (CH_2N), 47.4 (CH_2N), 35.2 (C_{But}), 34.2 (C_{But}), 34.2 (C_{But}), 31.0 ($CH_{3\ But}$), 31.0 ($CH_{3\ But}$), 29.6 ($CH_{3\ But}$).

(R,R)-***27***. Complex **27** was prepared from (*R,R*)-**17** (169.3 mg, 0.2 mmol) as a light yellow solid (eluent: EtOAc/CH_2Cl_2 = 1/10). Yield: 105 mg (55%). Anal. Calcd for $C_{42}H_{32}Br_2N_6O_4Pd$ (M = 950.9693 g mol^{-1}): C, 53.05; H, 3.39; N, 8.84; Found: C, 52.87; H, 3.53; N, 8.94. HRMS (positive ions): *m/z* 871.0726 (calcd for $[M–Br]^+$ 871.0707). ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 9.22 (s, 3H, ArH), 8.50 (s, 2H, ArH), 8.25 - 8.10(m, 6H, ArH), 7.61 - 7.10 (m, 17H, ArH), 6.26 - 6.18 (m, 2H, CH_2), 5.9 (d, *J* = 16.4 Hz, 1H, CH_2), 5.53 (s, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.4 (NCN), 169.8 (NCN), 147.7 (C_{Ar-NO2}), 147.6 (C_{Ar-NO2}), 143.6 (C_{Ar}), 142.8 (C_{Ar}), 136.8 (C_{Ar}), 129.5 (C_{Ar}), 129.4 (C_{Ar}), 129.3 (C_{Ar}), 129.1 (C_{Ar}), 128.9 (CH_{Ar}), 124.6 (CH_{Ar}), 124.3 (CH_{Ar}), 124.0 (CH_{Ar}), 113.0 (CH_{Ar}), 112.6 (CH_{Ar}), 112.4 (CH_{Ar}), 66.1 (CH), 60.6 (CH), 53.0 (CH_2N), 51.0 (CH_2N).

(aR)-***28***. Complex **28** was prepared from (*aR*)-**19** (255.3 mg, 0.2 mmol) as a light yellow solid (eluent: EtOAc/CH_2Cl_2 = 1/10). Yield: 160 mg (55%). Anal. Calcd for $C_{78}H_{76}Br_2N_6O_6Pd$ (M = 1459.7026 g mol^{-1}): C, 64.18; H, 5.25; N, 5.76; Found: C, 64.10; H, 5.21; N, 5.81. HRMS (positive ions): *m/z* 1379.4031 (calcd for $[M–Br^-]^+$ 1379.4024). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 8.4 Hz, 4H, ArH), 8.01 (d, *J* = 8.2 Hz, 2H, ArH), 7.66 - 7.55 (m, 6H, ArH), 7.26 - 7.22(m, 4H, ArH), 6.92 - 6.56 (m, 12H), 5.95 (d, *J* = 8.0 Hz, 2H), 5.14 (s, 4H), 4.83 (d, *J* = 15.7 Hz, 2H, CH_2), 1.49 (s, 18H, CH_3), 1.05 (s, 18H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1 (NCN), 152.6 (C_{Ar-O}), 133.0 (C_{Ar}), 132.5 (C_{Ar}), 131.6 (C_{Ar}), 130.0 (C_{Ar}), 127.9 (CH_{Ar}), 127.5 (CH_{Ar}), 127.2 (CH_{Ar}), 126.7 (CH_{Ar}), 124.4 (C_{Ar-CH2}), 123.8 (CH_{Ar}), 123.3 (CH_{Ar}), 112.6 (CH_{Ar}), 112.0 (CH_{Ar}), 111.6 (CH_{Ar}), 74.9 (CH_2O), 50.3 (CH_2N), 35.4 (C_{But}), 34.6 (C_{But}), 31.9 ($CH_{3\ But}$), 31.3 ($CH_{3\ But}$), 30.8 ($CH_{3\ But}$), 29.6 ($CH_{3\ But}$).

General Procedure for Asymmetric Suzuki–Miyaura Coupling Reactions

The desired aryl halides (0.2 mmol), the corresponding bis(NHC) palladium complex (0.006 mmol), the corresponding aryl boronic acid (0.3 mmol), and base (0.50 mmol) were introduced into an oven-dried Schlenk tube (25 mL). Deoxygenated solvent (2 mL) was added, the flask was sealed, and the mixture was stirred and heated at the indicated temperature. After the reaction mixture was heated to reflux (when THF was used as a reaction solvent) or maintained at 70 °C for 24 h, it was treated with distilled water (10 mL), extracted with CH_2Cl_2 (3 × 10 mL), dried ($MgSO_4$), and purified by flash chromatography (1/50 EtOAc/hexane) to give the corresponding product.

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Notes and references

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