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New symmetrical N^N^N palladium(II) pincer complexes: synthesis, characterization and catalytic evaluation in the Suzuki-Miyaura cross-coupling reaction

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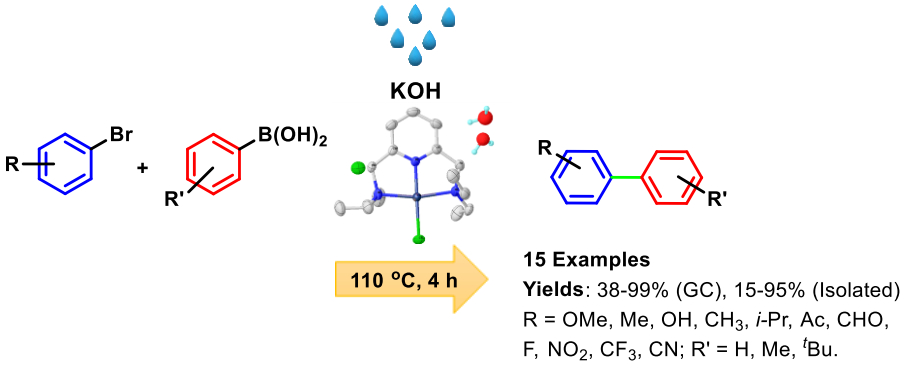
Abstract

Owing to their activity, versatility and ease of synthesis, N^N^N complexes with a central pyridine unit are of significance in organic synthesis. However, these complexes are relatively uncommon in comparison to their benzene analogues. In addition, neutral complexes of this pincer type ligand that consists of a pyridine core are rare. In view of this, a series of cationic palladium(II) N^N^N pincer complexes derived from neutral ligands that are based on a rigid pyridine backbone were synthesized, characterized and then evaluated as pre-catalysts in the Suzuki-Miyaura cross coupling reaction. At a catalyst loading of 0.1 mol%, the complexes were found to be effective pre-catalysts in the cross-coupling reactions under aqueous conditions. The scope, structure-activity relationships and limitations of these complexes are discussed.



Keywords: Suzuki-Miyaura, N^N^N pincer complexes, nitrogen-based ligands, catalysis

Introduction

The Suzuki-Miyaura reactions are significant in the formation of new C-C bonds through cross-coupling reaction of alkyl/phenyl halide with an organoboron compound under basic conditions. It is the most common cross-coupling reaction since it has higher catalytic capabilities and it is not only limited to the synthesis of biaryl systems, but conjugated dienes and high polyene systems can also be accessed. In addition, the coupling of deactivated alkyl/phenyl halides has also added value to the applications of this reaction.[1–3] Furthermore, this coupling procedure generally uses mild reaction conditions, produces non-toxic products and the organoboronic acids used in this reaction are easily accessible, thermally stable and do not react with moisture or oxygen.[4] Due to the presence of biaryls in the natural/synthetic products, the Suzuki-Miyaura reaction has been widely used in medicinal chemistry and other applications (**Figure 1**).[5–8] In this regard, many pre-catalysts, some of which contain the biaryl moiety such as pincer complexes have been developed for this reaction.[9]

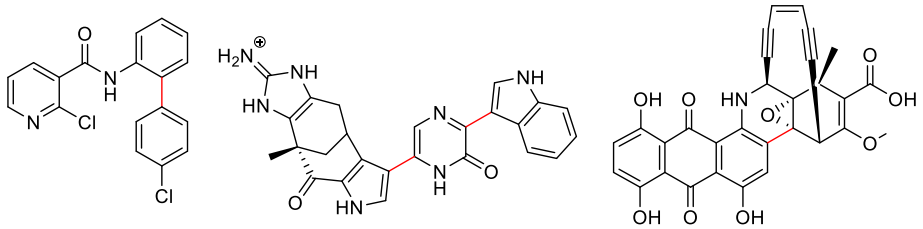


Figure 1. Examples of some commercially available drugs whose synthesis involve the Suzuki reaction as a major step.[5]

Pincers are a class of monoanionic tridentate ligands that prefer to conform to a meridional geometry upon complexation to a metal.[10] Pincer complexes have amassed a considerable amount of interest as alternative catalysts due to their unique balance between stability and reactivity.[11] Unsurprisingly, pincer complexes of certain transition metals have gained favor as catalysts in certain reactions *i.e*. palladium pincer complexes in cross-coupling.[12–14] Phosphine based palladium pincer complexes of the type P^C^P are the most commonly encountered palladium-based pincer complexes. However, the methods that are used to access these complexes are at times prone to degradation *via* oxidation or cleavage of the phosphorus-carbon bond.[14,15] This, combined with the fact that seemingly small modifications that are done to pincer complexes bring about noticeable changes in activity, led to our exploration of alternative donor atoms. New classes of pincer complexes such as N^C^N, S^C^S, Se^C^Se and other D^C^D type complexes were then developed. Unfortunately, the lack of a universal method to synthesize these D^C^D pincer complexes, especially those of the N^C^N type, due to regioselectivity led to the use of alternative central donors such as nitrogen.[15,16] Pincer complexes with a nitrogen atom as an anchor instead of the commonly employed carbon atom have also been synthesized giving rise to, for example, N^N^N, C^N^C, P^N^P, S^N^S, and O^N^O type of complexes.

Nitrogen donors differ from phosphorus donors, in several ways. Tolman's cone angles, which gauge steric bulkiness indicated that their steric effects are different.[17] Moreover, nitrogen donors generally form strong bonds with metals. This interaction is largely due to σ-donation since the π-back-donation is small or insignificant in these donors. Due to this, the ionic character of a nitrogen-metal bond is greater in comparison to that of a phosphorus-metal bond.[17]

Complexes that consist of nitrogen donating ligands typically display high reactivities. As such, they have gained much attention in homogenous catalysis over the years. Depending on the nature of the backbone utilized, a pincer complex having a covalent bond between an anionic nitrogen and the metal center or a

chelation between the anchoring neutral nitrogen atom and the metal center can be achieved, thus tailoring the electronic nature around the metal center. In accordance, a few of pincer complexes of the N^N^N type, particularly, those prepared from the corresponding anionic ligands have been developed and are well studied. Some of the well-known classes of N^N^N pincer ligands, which give rise to complexes that exhibit great potential in catalysis include 2,6-bis(oxazolinyl)pyridines or Pybox (**4**), 2,6-bis(imino)pyridines (**5**) and terpyridines (**6**). (**Figure 2)**.[18–20]

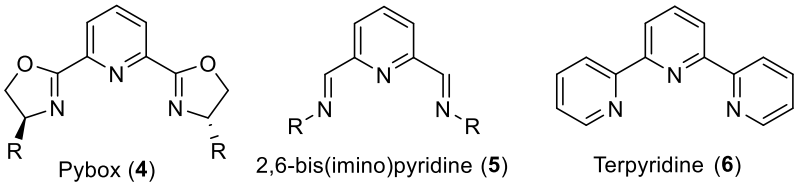
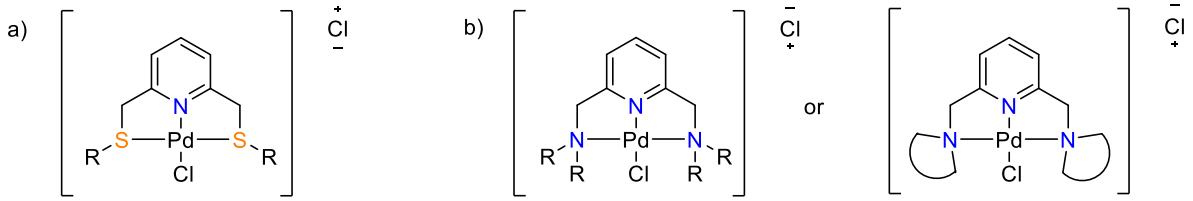


Figure 2: General examples of some well-known N^N^N pincer ligands

Owing to their activity, versatility and ease of synthesis, N^N^N complexes with a central pyridine unit are of some significance in synthesis.[16,21] However, these complexes are relatively uncommon in comparison to their benzene analogues. In addition, neutral complexes of this pincer type are even more rare with one of the earliest neutral complexes being reported by Spivak and co-workers in 2002.[16] Hence, inspired by our recent report on the successful synthesis of simple S^N^S pincer palladium(II) complexes **7a-d** and their catalytic applications in the Suzuki-Miyaura cross-coupling reaction,[22] we herein report the two-step-synthesis and characterization of a series of N^N^N palladium(II) complexes **8** (**Figure 3**) and their catalytic evaluation in the Suzuki-Miyaura cross-coupling reaction. These complexes were synthesized from the corresponding neutral palindromic ligands possessing a rigid pyridine backbone.



7a R = Ph
7b R = *p*-Br-C_6H_4
7c R = 4-*t*-C_6H_4
7d R = *s*-Bu

8 R = alkyl

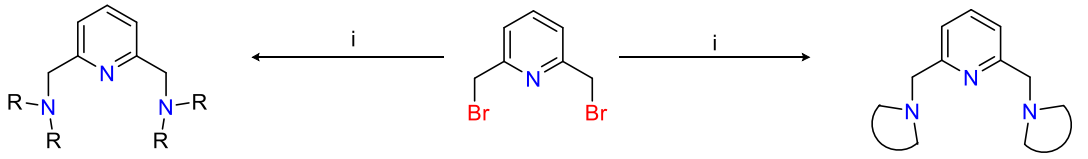
Figure 3. (a) Our previously reported S^N^S palladium(II) pincer complexes **7** as pre-catalysts in the Suzuki–Miyaura cross-coupling;[22] b) Proposed N^N^N palladium(II) pincer complexes **8.**

Results and Discussion

The preparation of the N^N^N pincer ligands **10a-10d** was carried out through the use of protocols from existing literature.[23] The formation of these N^N^N pincer ligands **10a-10d** was through S_N2 reaction of 2,6-bis(bromomethyl)pyridine (**9**) with the appropriate secondary amine in the presence of K_2CO_3 as shown in **Scheme 1**. Ligands **10a, 10b, 10c** and **10d** were isolated in yields of 78%, 80%, 98% and 88%, respectively.

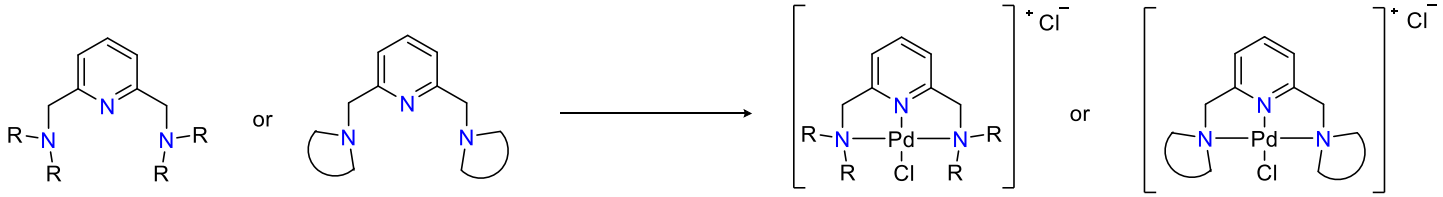
The structural elucidation of the synthesized ligands was then done using NMR as well as FT-IR spectroscopy. In the ^{1}H NMR spectrum of **10a**, the appearance of the pyridyl and the benzylic protons as a triplet, doublet and singlet in a 1:2:4 ratio, resonating at δ_H 7.61, 7.29 and 3.61, respectively, confirmed the palindromic and symmetrical nature of the ligand. The signals belonging to the methylene and methyl protons of the ethyl fragment appearing as a quartet (8H) and a triplet (12H) which resonated at δ_H 2.50 and 0.99,

respectively, confirmed that the diethylamine moiety had been incorporated into the ligand. Similarly, the ^{13}C NMR also supported the proposed structure by exhibiting the signals of the pyridyl and the benzyl linker carbons at δ_C 159.6, 136.5, 120.6 and 59.6, respectively, while the carbons of the ethyl groups resonated at δ_C 47.3 and 11.8, effectively confirming their incorporation into the ligand. The infrared spectrum of **10a** showed strong bands in the range of 1589.3 cm^{-1} to 1575.8 cm^{-1} which are characteristic of (C=N) stretching vibrations of the pyridyl moiety. The C-H functional groups belonging to any alkyl fragments in the ligand were found between 2802.5 cm^{-1} and 2966.5 cm^{-1} as this region is commonly associated with the asymmetrical and symmetrical stretching vibrations belonging to this functional group. Furthermore, the C-C stretches belonging to the pyridyl group in the ligand appeared around 1454.3 cm^{-1}. In the same fashion, ligands **10b**-**10d** were prepared and characterized in order to investigate the effect of steric and electronic factors of the ligands in the catalytic application of the corresponding complexes (*vide infra*).



Scheme 1. The synthesis of the symmetrical pincer ligands **10a-10d**. (i) Secondary amine (2.2 equiv.), K_2CO_3 (2.5 equiv.), CH_3CN, rt, 15 h.

Having the ligands in hand, our attention turned to the synthesis of the corresponding Pd(II) pincer complexes. All the corresponding complexes **8a-8d** were synthesized by treating the appropriate ligands **10a-10d** with 1 equivalent of a pre-formed metal precursor, $[PdCl_2(MeCN)_2]$, in dry DCM for 24 h at room temperature.[13] The resulting complexes usually precipitated out of the solution and were easily isolated by centrifugation. These N^N^N Pd(II) pincer complexes were formed with ease, probably due to the high affinity of the ligand's nitrogen donor atoms for the palladium metal, which allowed for the effortless displacement of the labile acetonitrile groups from the $[PdCl_2(MeCN)_2]$ precursor.[17,24] This afforded all the desired complexes in moderate to high yields as demonstrated in **Scheme 2**. The successful synthesis of these complexes was then determined by various analytical techniques such as NMR, FT-IR, HRMS and single crystal X-ray diffraction for **8a**.



Scheme 2. Synthesis of the N^N^N complexes **8a-8d** from the corresponding ligands **10a-10d**. Reaction conditions: $[PdCl_2(MeCN)_2]$ (1 equiv.), DCM, rt, 24 h.

When the ^1H NMR spectra of the ligands were compared with those of their corresponding complexes, downfield shifts were observed for all the protons of the ligands upon complexation. The protons had shifted by $\Delta\delta_H$ 0.4-0.8 and this shift was attributed to the deshielding effect of the palladium metal center. For ligand **10a**, the pattern and integration of all the signals apart from those of the methylene protons belonging to the alkyl amine, was retained in the complex. These methylene protons formed an AB-system due to restricted rotation which resulted from the formation of the palladacycles, confirming that complexation had occurred. The $^{13}C\{^1H\}$ NMR spectrum also supported the proposed structure of **8a** by exhibiting the same number of

signals shown in ligand **10a**, which had now shifted slightly downfield due to the same deshielding effect of the palladium center. This retention in the arrangement of the signals in both the proton and carbon NMR spectra suggested that the palindromic and symmetrical nature had also been retained in the complex. Furthermore, IR studies revealed that bands in the range of 1572.0 cm^{-1} to 1589.0 cm^{-1}, which are characteristic of (C=N) stretching vibrations of the pyridyl moiety in the ligands had shifted to 1577.8 cm^{-1} and 1602.9 cm^{-1} in the complexes. Moreover, the mass spectra of the complexes were recorded in the positive mode. Only the m/z ratios of the cationic fragments were expressed with high accuracy since the experimental values were closely correlated with the calculated ones. The chloride counter ions were not observed as they had combined with H^+ from the instrument to form neutral HCl molecules that could not be detected.

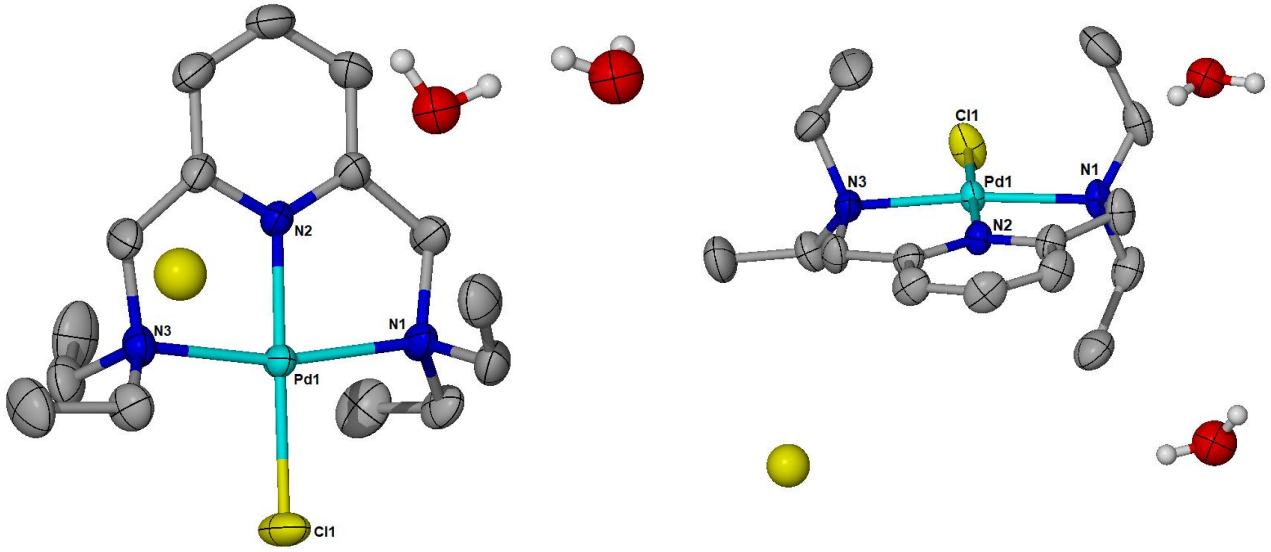


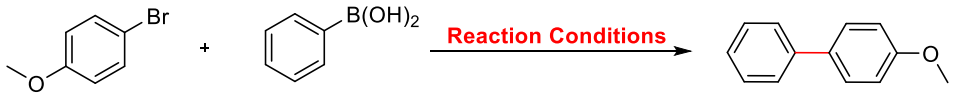
Figure 4. The crystal structure of **8a**. Pd(light blue), N(dark blue), Cl(yellow), O(red), C(grey), H(light grey). Selected bond lengths and angles Pd1---N2(1.9409 Å), Pd1---N1(2.0824 Å), Pd1---N3(2.0848 Å), Pd1--Cl(2.3026 Å), N1---Pd1---N2(83.31˚), N2---Pd1---N3(83.77˚), N1---Pd1---Cl1(95.94˚), N3---Pd1---Cl1 (96.98˚).

The successful synthesized complex **8a** was confirmed using single crystal X-ray diffraction (SCD) as shown in **Figure 4**. Single crystals were grown using slow evaporation of a saturated solution of **8a** in acetonitrile. The complex **8a** crystallizes in the monoclinic crystal system with space group P21/n. The coordination sphere around Pd(II) adopts a square planar geometry with marginally distortion. It is also revealed that palladium center is coordinated to neutral N^N^N tridentate with a pyridyl core, two identical amine groups that were trans to each other in both terminal arms and a chloride atom that was trans to the core. Using mercury, the calculated contact surface is 9.6 % (probe radius 1.5) which is occupied by the uncoordinated chloride anion and two water molecules which contribute to stabilize the complex. The N1---Pd1---N2 bond angle of 83.31˚as well as the N2---Pd1---N3 bond angle of 83.77˚slightly deviate from the optimal angle of 90º and are quite similar to those reported by Markies *et al*. for a related complex.[25] The bond angles of N1---Pd1---Cl1 (95.94˚) and N3---Pd1---Cl1 (96.98˚) are also fairly similar. This suggested the symmetry equivalent of the two pincer arms. The difference in bond lengths between the central Pd1---N2 (1.9409 Å), Pd1---N1 (2.0824 Å) and Pd1---N3 (2.0848 Å) is lower than 0.15 Å, which is unique for N^N^N pincer architectures. It clearly confirms that geometric constrains of complex **8a** could be considered rather than electronic effects.

After the successful synthesis of the complexes, they were evaluated for their catalytic activity in the Suzuki-Miyaura cross-coupling reaction. Here, 4-bromoanisole (**11a**) and phenyl boronic acid (**12a**) were used as the model substrates. Complex **8a** was used as the pre-catalyst to establish the optimum reaction

conditions. The results obtained for the optimization reactions are summarized in **Table 1**. Preliminary solvent variation studies with 1 mol% of **8a** at 140 °C, with K_2CO_3 as the base revealed that the desired biphenyl product **13a** was formed in high yields of 91% and 92% in toluene and H_2O, respectively (**Table 1**, entries 1 and 2). Other solvents resulted in inferior yields, hence, H_2O was selected as the optimum solvent over toluene as it is safer (non-toxic and non-flammable), easily accessible, cheap and boronic acids are known to be stable in aqueous medium.[26,27] Three inorganic and two organic bases were screened in this reaction (**Table 1**, entries 6-9). When the inorganic bases were used, the reaction formed some insoluble black residue. This was not the case with the organic bases as the reactions remained homogenous throughout. No obvious trends were observed in terms of yield. Pyridine, the weakest base, gave the lowest yield of 62% (**Table 1**, entries 6) and the highest yield of 98% was observed with NEt_3 (**Table 1**, entries 7). Comparable results were observed with the inorganic bases, however, K_3PO_4 was the exception (**Table 1**, entries 1,8-9). According to Amatore *et al*.[28–30] the high conversions observed with these inorganic bases was due to the formation of the hydroxide anion in the presence of water, which plays a crucial role in the transmetalation and reductive elimination steps of the catalytic cycle. Although, palladium black was observed with potassium hydroxide, this base was selected over NEt_3 as it was the cheaper alternative.

Table 1. Establishment of the optimum reaction conditions for the Suzuki-Miyaura cross-coupling reaction using **8a** as the pre-catalyst.



11a **12a** **13a**

Entry	Solvent	Base	Cat.	Cat. Load (mol %)	Temp. (°C)	Time	Yield[a]
Solvent effects							
1	**H_2O**	K_2CO_3	**8a**	1	140	6	92%
2	Toluene	K_2CO_3	**8a**	1	140	6	91%
3	DMF	K_2CO_3	**8a**	1	140	6	33%
4	DMA	K_2CO_3	**8a**	1	140	6	33%
5	CH_3CN	K_2CO_3	**8a**	1	140	6	25%
Optimization of base							
6	H_2O	Pyridine	**8a**	1	140	6	62%
7	H_2O	NEt_3	**8a**	1	140	6	98%
8	H_2O	K_3PO_4	**8a**	1	140	6	73%
9	H_2O	**KOH**	**8a**	1	140	6	92%
Temperature effects							
10	H_2O	KOH	**8a**	1	120	6	94%
11	H_2O	KOH	**8a**	1	**110**	6	94%
12	H_2O	KOH	**8a**	1	100	6	86%
13	H_2O	KOH	**8a**	1	80	6	76%
Conversion as a function of time							
14	H_2O	KOH	**8a**	1	110	**4**	96%
15	H_2O	KOH	**8a**	1	110	2	84%

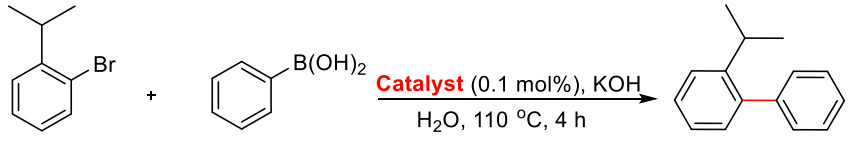
16	H_2O	KOH	**8a**	1	110	1	83%
17	H_2O	KOH	**8a**	1	110	0.5	73%
Catalyst Loading							
18	H_2O	KOH	**8a**	0.5	110	4	95%
19	H_2O	KOH	**8a**	0.25	110	4	93%
20	H_2O	KOH	**8a**	**0.1**	110	4	92%
21	H_2O	KOH	**8a**	0.05	110	4	78%
22	H_2O	KOH	**8a**	0	110	4	0%
Catalyst Screening							
23	H_2O	KOH	**8b**	0.1	110	4	95%
24	H_2O	KOH	**8c**	0.1	110	4	97%
25	H_2O	KOH	**8d**	0.1	110	4	97%
Mercury Drop Test							
26	H_2O + Hg	KOH	**8b**	0.1	110	4	52 %

Conditions: Catalyst loading (0.05-1 mol%), **11a** (0.703 mmol), **12a** (1.11 mmol), base (1.41 mmol), solvent (4 mL), 80-140 °C, 0.5-6 h, *n*-decane internal standard. All reactions were monitored by GC and yield of biphenyl is an average of two experiments. [**a**] GC yield.

In pursuit of a milder reaction condition, the reaction was performed at temperatures below 140 °C. Upon decreasing the temperature to 120 °C, the yield of the biphenyl slightly increased to 94%, and this yield was maintained when the temperature was further decreased to 110 °C (**Table 1**, entries 10 and 11). An appreciable decrease of the yield was only observed when the temperature was decreased to 100 °C and below as the GC chromatogram revealed that the aryl halide was not completely consumed (**Table 1**, entries 12 and 13). This trend could be attributed to the decrease in the solubility of **8a** in water as the temperature decreased. Therefore, the optimum temperature was chosen to be 110 °C. At a reaction time of 6 h, the GC chromatograms showed that all the aryl halide substrate had been consumed. Furthermore, to observe if the reaction had completed earlier than this time, reactions were performed for 4 h, 2 h, 1 h and 0.5 h (**Table 1**, entries 14-17). After 4 h, the 4-bromoanisole (**11a**) had been completely converted into 4-methoxy biphenyl (**13a**). However, a gradual decline in conversion was observed when the reaction times were decreased from 2 h all the way to 0.5 h, thus all the experiments that followed were carried out for 4 h.

Employing a catalyst load of 1 mol% of **8a** was sufficient to achieve the complete conversion of the aryl halide **11a** to the desired biphenyl product **13a**. In order to be more economic, the coupling reaction was performed with **8a** at lower catalyst loads. As the catalyst load was decreased from 1 to 0.1 mol%, substrate conversion barely decreased (**Table 1**, entries 18-20). A noticeable decline in conversion was only observed when the catalyst load was dropped to 0.05 mol% (**Table 1**, entries 21).

Table 2. Screening of the best complex for the Suzuki-Miyaura cross-coupling reaction were 1-bromo-2-isopropylbenzene (**11f**) was used as the aryl halide



11f **12a** **13f**

Entry	Solvent	Base	Cat.	Cat. Load (mol %)	Temp. (°C)	Time	Yield[a]

1	H_2O	KOH	**8a**	0.1	110	4	11%
2	**H_2O**	**KOH**	**8b**	**0.1**	**110**	**4**	**38%**
3	H_2O	KOH	**8c**	0.1	110	4	23%
4	H_2O	KOH	**8d**	0.1	110	4	22%

Conditions: Catalyst loading (0.1 mol%), **11f** (0.703 mmol), **12a** (1.11 mmol), KOH (1.41 mmol), H_2O (4 mL), 80 -140 °C, 0.5-6 h, *n*-decane internal standard. All reactions were monitored by GC and yield of biphenyl is an average of two experiments. [**a**] GC yield.

Once the optimum conditions were established with **8a,** the other complexes **8b**, **8c** and **8d** were then evaluated as pre-catalysts in the cross-coupling reaction, to observe the effect of varying the alkylamine groups. Initially, all the complexes gave nearly identical conversions when 4-bromo anisole (**11a**) was used as the aryl halide. Therefore, a more challenging substrate **11f** was used to effectively differentiate the proficiency of each complex in this reaction (**Table 2**). Complex **8b**, was found to be almost twice as active as the other complexes. This indicated that having bulky groups on the nitrogen donors of the pincer complex resulted in an enhanced catalytic activity. A similar observation where a bulkier catalyst resulted in a higher activity had been made by Szilvási and Veszprémi.[31] Their results showed that steric attraction and other favorable π-interactions occurred between the bulky groups of the catalyst and the aryl halide substrate. This indicated that bulkiness not only played an essential role in the reductive elimination step, but also in the oxidative addition in the catalytic cycle of the reaction. Hence, both these steps are accelerated when bulky catalysts are used.

The insoluble black residues that were being formed under the optimum reaction conditions were suspected to be palladium black. Consequently, a homogeneity test of **8b** was performed with mercury to verify if this was the case (**Table 1**, entry 26). The cross-coupling reaction was performed with **8b** in the presence of excess mercury (>400 equiv.) under the optimum conditions using the model substrates **11a** and **12a**. The conversion was almost halved when mercury was present. This partial inhibition of the catalytic activity in the presence of mercury suggested that this catalytic process involved both homogenous and heterogenous routes with Pd(II) and Pd(0) species, respectively.[32] This is plausible as mercury forms an amalgamate with metal-particle heterogeneous catalysts such as Pd(0) species, which effectively poisons any processes arising from these metal-particles. If Pd(0) species were the sole catalysts in this reaction, then the presence of mercury should have completely suppressed the reaction. Hence, other homogenous species that could not be poisoned by the mercury must have been present as well.[32,33]

To evaluate the sustainability of this catalytic system, the reusability of the catalyst was investigated by coupling 4-bromoanisole (**11a**) with phenyl boronic acid (**12a**) under the established optimum reaction conditions with **8b**. After reaction completion, toluene was used to extract the unreacted organic substrates and the biphenyl product **13a** from the aqueous layer where the active catalyst is expected to remain. Thereafter, fresh coupling substrates were added to the aqueous phase to perform the next cycle. The aqueous layer showed that it could still catalyze the reaction for only one more cycle. Furthermore, a significant decline in activity was observed for the second cycle. This revealed that the catalyst could not be effectively reused. It is probable that the catalyst, while in its active form, was leaching away into the organic phase during extraction. Hence, the catalyst system could not preserve its activity for the following batch.[34]

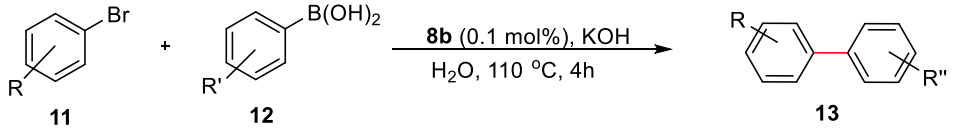
The substrate scope of the reaction with **8b** as the pre-catalyst, was expanded to study its functional group tolerance. Both the aryl bromides and aryl boronic acids were varied as outlined in **Table 3**. Generally good yields were observed when *para*-substituted substrates were reacted. The yield also improved when electron donating substituents were present on the aryl boronic acids. This is demonstrated in **Table 3** (entries 2-4) were the yield increased by 9% when 4-methylphenyl boronic acid (**12b**) was exchanged for 4-*t*-butylphenyl boronic acid (**12c**). In contrast to this, the yield decreases by 12% when 4-chlorophenyl boronic

acid (**12d**) is used in place of **12b**. Additionally, there was no conversion when 3-nitrophenyl boronic acid was used. Boronic acids are the nucleophilic components in this reaction, thus, an increase in the nucleophilicity of the boronic acid gives rise to faster transmetalation rates.[4,35] This supports the observation made for entries 2-4 in **Table 3** since *t*-butyl groups are more nucleophilic than methyl groups as the chloride and the nitro moieties are electron-withdrawing.

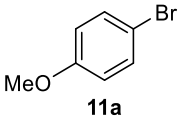
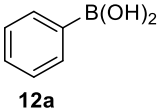
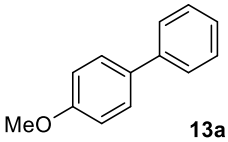
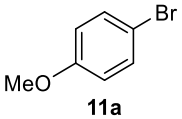
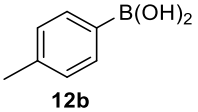
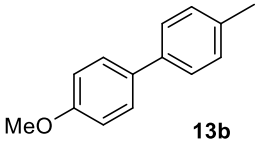
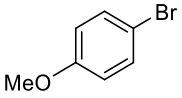
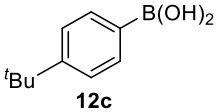
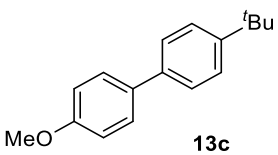
Entry 1 as well as entries 5-9 in **Table 3** show the effect of having electron-donating substituents on the aryl bromides. Generally, electron-donating substituents deactivate the aryl halide by strengthening the C-Br bond, which makes oxidative addition across this bond more challenging. The more donating effects of the substituents on the aryl halide, resulted in less activity in the coupling reactions. [36] Hence, 4-bromoanisole (**11a)** and 4-bromophenol (**11b)** were expected to result in lower product yields than 4-bromotoluene (**11c**), but the inverse was observed. This unusual observation could be attributed to the inferior solubility of **11c** in water when compared to **11a** and **11b**. Changing the position of the electron-donating group and moving it closer to the C-Br bond did not significantly affect the product yield (**Table 3**, entries 6-8). However, when the electron-donating group was bulkier and *para* to the C-Br bond, the product yield decreased drastically since sterically hindered substrates restrict access to the active site of the catalyst (**Table 3**, entry 9).[37]

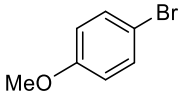
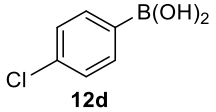
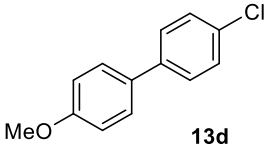
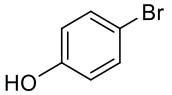
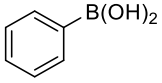
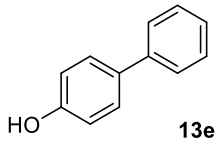
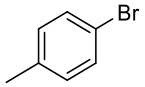
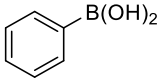
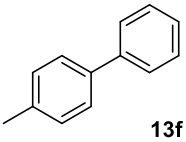
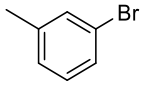
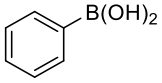
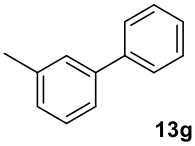
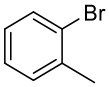
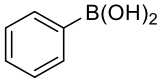
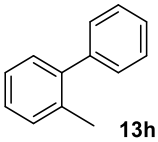
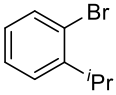
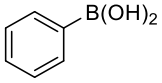
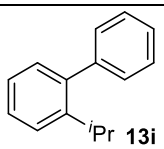
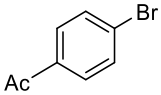
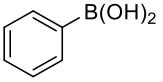
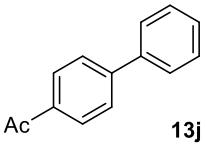
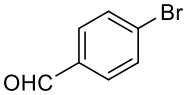
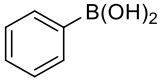
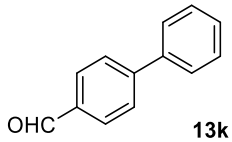
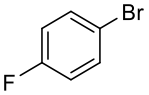
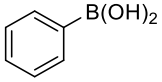
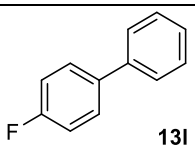
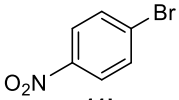
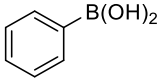
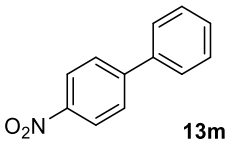
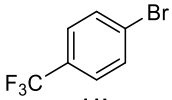
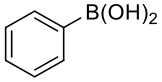
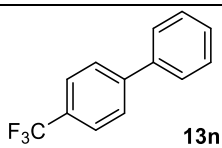
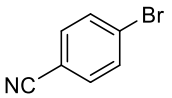
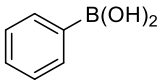
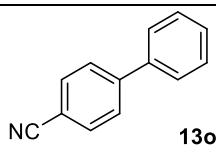
When electron-withdrawing groups are present on the aryl bromides, the bond dissociation energy of the C-Br bond is lowered and the oxidative addition of these substrates becomes less challenging.[36] The effect of these substituents on the aryl bromides is also presented in **Table 3** (entries 10-15). Conversions that were in the higher nineties were observed for all the aryl bromides bearing electron-withdrawing groups. However, the product yields of these substrates still differed due to the differences in their selectivity for the desired product. Moreover, an attempt to couple 1-chloro-4-nitrobenzene with phenylboronic acid did not yield any product. This indicated that our catalysts system was not capable of coupling aryl chlorides even when they are activated.

Table 3. Investigation of the functional group tolerance of the Suzuki-Miyaura cross coupling reaction with **8b** as a pre-catalyst.



11 **12** **13**

Entry	Aryl Halide	Boronic Acid	Product	Yield %: GC (Isolated)
1	 **11a**	 **12a**	 **13a**	92 (88)
2	 **11a**	 **12b**	 **13b**	88 (55)
3	 **11a**	 **12c**	 **13c**	97 (67)

4	 **11a**	 **12d**	 **13d**	76 (74)
5	 **11b**	 **12a**	 **13e**	98 (89)
6	 **11c**	 **12a**	 **13f**	77 (74)
7	 **11d**	 **12a**	 **13g**	84 (69)
8	 **11e**	 **12a**	 **13h**	85 (76)
9	 **11f**	 **12a**	 **13i**	38 (15)
10	 **11g**	 **12a**	 **13j**	99 (84)
11	 **11h**	 **12a**	 **13k**	89 (80)
12	 **11i**	 **12a**	 **13l**	83 (79)
13	 **11j**	 **12a**	 **13m**	95 (95)
14	 **11k**	 **12a**	 **13n**	93 (83)
15	 **11l**	 **12a**	 **13o**	90 (86)

Conditions: 8b (0.1 mol%), ArX (0.703 mmol), $Ar(B(OH)_2)$ (1.11 mmol), KOH (1.41 mmol), H_2O (4 mL), 110 °C, 4 h, *n*-decane

internal standard. All reactions were monitored by GC and yield of biphenyl is average of two experiments.

Conclusions

Four N^N^N pincer ligands and their corresponding new cationic palladium(II) pincer complexes were successfully synthesized. The structures of the ligands and complexes were confirmed through the use of characterization techniques such as NMR, IR, HRMS and single crystal XRD. The cationic palladium pincer complexes **8a-8d** were evaluated as pre-catalysts in the Suzuki-Miyaura cross-coupling reaction on water. All the complexes exhibited excellent activity under the optimum conditions. At a low catalyst loading of 0.1 mol%, the reaction had completed in 4 h and required a temperature of 110 °C with KOH as a base. Moreover, this catalyst system did not require TBAB, as an additive as it is generally required in this reaction as a phase-transfer catalyst when aqueous conditions are used. The complex bearing the most sterically hindered ligand **8b** displayed improved conversions especially with sterically hindered substrates.

However, the catalyst system could not be effectively reused after aqueous work-up. Pincer complex **8b** could tolerate both electron-donating and electron-withdrawing substituents on the aryl bromides and aryl boronic acids. Slightly improved conversions were observed with electron-withdrawing substituents on the aryl bromides and electron-donating substituents on the aryl boronic acids. However, a poor conversion was observed with a sterically hindered aryl bromide and no conversion was observed with aryl chlorides suggesting a further improvement in the electronic and steric factors of the complexes. Partial inhibition in the presence of excess of mercury implied that the catalytic process occurred through a combination of a heterogenous Pd(0)/Pd(II) pathway and a homogenous Pd(II)/P(IV) pathway.

Experimental Section

Crystallographic aata

CCDC 1991901 (**8a**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/getstructures.

General procedure for the synthesis of ligands 10a-10d. K_2CO_3 (3.40 mmol) was suspended in dry acetonitrile (5 mL) in a two-necked round bottom flask and the appropriate dialkylamine (2.49 mmol) was added to the stirring suspension. After the mixture was stirred for a further 10-15 min, 2,6-Bis(bromomethyl)pyridine (1.13 mmol) was added to the suspension and the reaction was stirred at room temperature for 15 hours. Once the reaction had completed, it was quenched with H_2O and extracted with ethyl acetate (3 × 15 mL), concentrated *in vacuo* and analyzed without the need for any further purification.

***N,N'*-[Pyridine-2,6-diylbis(methylene)]bis(N-ethylethanamine) (10a).** Light yellow oil, Yield: 78%; ^{1}H NMR (500 MHz, CD_3CN): δ = 7.61 (t, *J* 7.5 Hz, 1H), 7.29 (d, *J* 7.6 Hz, 2H), 3.61 (s, 4H), 2.50 (q, *J* 7.0 Hz, 8H), 0.99 (t, *J* 7.1 Hz, 12H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 159.6, 136.5, 120.6, 59.6, 47.3, 11.8; FTIR (υ_{max} /cm^{-1}): 1589.3-1575.8 (C=N, stretch), 1068.6 (C-N, stretch). Spectroscopic data was in agreement with the reported data.[38]

2,6-Bis(piperidin-1-ylmethyl)pyridine (10b). Light yellow oil, Yield: 98%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 (t, *J* 7.7 Hz, 1H), 7.21 (d, *J* 7.6 Hz, 2H), 3.53 (s, 4H), 2.36 (s, 8H), 1.58 – 1.47 (m, 8H), 1.45 – 1.35 (m, 4H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 158.4, 136.4, 120.9, 65.3, 54.7, 25.9, 24.2; FTIR (υ_{max} /cm^{-1}): 1589.3-1573.9 (C=N, stretch), 1066.6 (C-N, stretch). Spectroscopic data was in agreement with the reported data.[23,39,40]

2,6-Bis(pyrrolidin-1-ylmethyl)pyridine (10c). Light yellow oil, Yield: 88%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (t, *J* 7.7 Hz, 1H), 7.16 (d, *J* 7.7 Hz, 2H), 3.68 (s, 4H), 2.47 (t, *J* 5.5 Hz, 8H), 1.75 – 1.63 (m, 8H); ^{13}C {^{1}H} NMR (101

MHz, $CDCl_3$): δ = 158.5, 136.5, 120.7, 62.1, 54.1, 24.2; FTIR (υ_{max} /cm^{-1}): 1589.3-1573.9 (C=N, stretch), 1124.5 (C-N, stretch). Spectroscopic data was in agreement with the reported data.[23,38]

***N,N*'-[Pyridine-2,6-diylbis(methylene)]bis(*N*-isopropylpropan-2-amine) (10d).** Light yellow oil (latter solidifies), mp 45-50 °C. Yield: 80%; ^{1}H NMR (500 MHz, DMSO): δ 7.67 (t, *J* 7.7 Hz, 1H), 7.34 (d, *J* 7.7 Hz, 2H), 3.68 (s, 4H), 3.10 - 2.90 (m, 4H), 0.99 (d, *J* 6.6 Hz, 24H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 162.7, 136.4, 119.0, 51.5, 48.8, 20.8; FTIR (υ_{max} /cm^{-1}): 1589.3-1573.9 (C=N, stretch), 1124. (C-N, stretch). Spectroscopic data was in agreement with the reported data.[38,41]

General procedure for the synthesis of Pd(II) N^N^N pincer complexes 8a-8d. To a 50 mL round bottom flask containing a solution of [$PdCl_2(MeCN)_2$] (0.44 mmol) in dry DCM (10 mL), the appropriate ligand (0.44 mmol) was added. The reaction mixture was stirred for 24 h at room temperature under an nitrogen atmosphere. The solvent was then removed by vacuum to afford the corresponding cationic palladium pincer complexes.

Chloro-2,6-bis[(diethylamino)methyl]pyridine palladium(II) chloride (8a). Yellow solid, mp 198-208 ^{o}C (Thermal decomposition observed at this temperature). Yield: 75%; ^{1}H NMR (500 MHz, CD_3CN): δ 8.03 (td, *J* 1.5, 9.5, 17.5 Hz, 1H), 7.44 (dd, *J* 1.0, 9.0 Hz, 2H), 4.40 (s, 4H), 3.25 - 3.13 (m, 4H), 2.70 - 2.60 (m, 4H), 1.61 (td, *J* 1.0, 8.5, 15.5 Hz, 12H); ^{13}C {^{1}H} NMR (126 MHz, CD_3CN): δ = 160.6, 140.9, 120.3, 66.6, 57.9, 12.5; FTIR (υ_{max}/cm^{-1}): 1602.9- 1577.8 (C=N, stretch), 1082.1 (C-N, stretch); HR-ESI-MS: $C_{15}H_{27}ClN_3Pd^+$ calcd. *m/z* 390.0923 [M-Cl] $^+$, found m/z = 390.0927 $[M\text{-}Cl]^+$.

Chloro-2,6-bis(piperidin-1-ylmethyl)pyridine palladium(II) chloride (8b). Yellow solid, mp 195-205 °C (Thermal decomposition observed at this temperature). Yield: 99%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (t, *J* 7.7 Hz, 1H), 7.88 (d, *J* 7.9 Hz, 2H), 4.88 (s, 4H), 3.73 (t, *J* 11.6 Hz, 4H), 3.36 (d, *J* 12.3 Hz, 4H), 1.94 (d, *J* 12.7 Hz, 4H), 1.73 (s, 2H), 1.51 (d, *J* 10.0 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 158.8, 141.2, 122.3, 66.3, 60.1, 22.9, 20.7; FTIR (υ_{max} /cm^{-1}): 1602.9- 1579.7 (C=N, stretch), 1099.4 (C-N, stretch); HR-ESI-MS: $C_{15}H_{27}ClN_3Pd^+$ calcd. *m/z* 416.0927 $[M\text{-}Cl]^+$, found m/z = 416.0923 $[M\text{-}Cl]^+$. Spectroscopic data was in agreement with the reported data.[39,42]

Chloro-2,6-bis(pyrrolidin-1-ylmethyl)pyridine palladium(II) chloride (8c)

Dark brown solid, mp 194-202 °C (Thermal decomposition observed at this temperature). Yield: 98%; ^{1}H NMR (500 MHz, DMSO): δ 8.17 (t, *J* 20.0 Hz, 1H), 7.60 (d, *J* 10.0 Hz, 2H), 4.54 (s, 4H), 3.59 – 3.43 (m, 4H), 3.18 – 2.99 (m, 4H), 2.0 – 1.85 (m, 8H); ^{13}C {^{1}H} NMR (101 MHz, DMSO): δ 158.9, 141.0, 121.8, 69.6, 60.1, 21.5; FTIR (υ_{max} /cm^{-1}): 1600.9-1577.8 (C=N, stretch), 1101.4 (C-N, stretch). HR-ESI-MS: $C_{15}H_{23}ClN_3Pd^+$ calcd. *m/z* 388.0614 $[M\text{-}Cl]^+$, found m/z = 388.0610 $[M\text{-}Cl]^+$.

Chloro-2,6-bis[(diisopropylamino)methyl]pyridine palladium(II) chloride (8d). Pale sandy solid, mp 217-222 °C (Thermal decomposition observed at this temperature). Yield: 69%; ^{1}H NMR (500 MHz, DMSO): δ 8.16 (t, *J* 16.0 Hz, 1H), 7.52 (d, *J* 8.0 Hz, 2H), 4.56 (s, 4H), 3.45 – 3.37 (m, 4H), 1.80 (d, *J* 6.5 Hz, 12H), 1.29 (d, *J* 6.5 Hz, 12H); ^{13}C {^{1}H} NMR (101 MHz, DMSO): δ = 162.4, 141.2, 119.1, 62.8, 59.7, 21.6, 18.5; FTIR (υ_{max} /cm^{-1}): 1604.8-1583.6 (C=N, stretch), 1105.2 (C-N, stretch); HR-ESI-MS: $C_{19}H_{35}ClN_3Pd^+$ calcd. *m/z* 448.1553 $[M\text{-}Cl]^+$, found m/z = 448.1551 $[M\text{-}Cl]^+$.

General experimental procedure of the Suzuki-Miyaura cross-coupling reaction. A suitable aryl halide (0.703 mmol), aryl boronic acid (1.11 mmol), KOH (1.41 mmol), 8b (0.1–1 mol%), internal standard (*n*-decane, 0.703 mmol) and H_2O (4 mL) were charged in a carousel tube (24 × 150 mm quick-thread glass). The reaction mixture was sealed and stirred at 110 °C for 4 h. After reaction completion, the mixture was cooled in an ice bath and extracted with DCM. The organic extract was then dried over anhydrous $MgSO_4$, filtered and analysed with Gas Chromatography (GC). Isolation of the desired biphenyls products was achieved *via* column chromatography using silica gel and 5-10 % EtOAc in hexane as an eluent. Further confirmation of the isolated

products was performed via ^{1}H and ^{13}C NMR characterisation as well as melting point determination for the solids.

4-Methoxy-1,1'-biphenyl (13a). White solid, mp 86-88 °C; Yield: 88%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 – 7.52 (m, 4H), 7.45 (t, *J* 7.6 Hz, 2H), 7.33 (t, *J* 7.6 Hz, 1H), 7.01 (d, *J* 8.6 Hz, 2H), 3.88 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 159.1, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3. Spectroscopic data was in agreement with the reported data.[22,43,44]

4-Methoxy-4'-methyl-1,1'-biphenyl (13b). White solid, mp 105-108 °C; Yield: 55%; ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.55 (d, *J* 8.5 Hz, 2H), 7.49 (d, *J* 8.0 Hz, 2H), 7.26 (d, *J* 8.0 Hz, 2H), 7.00 (d, *J* 8.5 Hz, 2H), 3.88 (s, 3H), 2.42 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 158.9, 138.0, 136.3, 133.8, 129.4, 127.9, 126.5, 114.1, 55.3, 21.0. Spectroscopic data was in agreement with the reported data.[45]

4-(tert-Butyl)-4'-methoxy-1,1'-biphenyl (13c). White solid, mp 134-137 °C; Yield: 67%; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.58 – 7.36 (m, 6H), 6.99 – 6.92 (m, 2H), 3.83 (s, 3H), 1.35 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): *δ* 158.9, 149.5, 137.9, 133.6, 127.9, 126.3, 125.6, 114.1, 55.3, 34.4, 31.3. Spectroscopic data was in agreement with the reported data.[46]

4-Chloro-4'-methoxy-1,1'-biphenyl (13d). White solid, mp 109-112 °C; Yield: 74%; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.46 (dd, *J* 6.3, 8.4 Hz, 4H), 7.36 (d, *J* 8.4 Hz, 2H), 6.96 (d, *J* 8.6 Hz, 2H), 3.83 (s, 3H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): *δ* 159.3, 139.2, 132.6, 132.4, 128.8, 128.0, 127.9, 114.2, 55.3. Spectroscopic data was in agreement with the reported data.[47]

[1,1'-Biphenyl]-4-ol (13e). White solid, mp 160-163 °C; Yield: 89%; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.52 (d, *J* 7.7 Hz, 2H), 7.47 (d, *J* 8.5 Hz, 2H), 7.40 (t, *J* 7.6 Hz, 2H), 7.29 (t, *J* 7.3 Hz, 1H), 6.89 (d, *J* 8.5 Hz, 2H), 4.70 (s, 1H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 155.0, 140.7, 134.1, 128.7, 128.4, 126.7, 115.6. Spectroscopic data was in agreement with the reported data.[48]

4-Methyl-1,1'-biphenyl (13f). Clear solid, mp 42-44 °C; Yield: 74%; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.62 – 7.58 (m, 2H), 7.51 (d, *J* 8.2 Hz, 2H), 7.43 (t, *J* 7.6 Hz, 2H), 7.38 – 7.30 (m, 1H), 7.26 (d, *J* 8.0 Hz, 2H), 2.41 (s, 3H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): *δ* 141.1, 138.3, 136.9, 129.4, 128.6, 126.9, 126.9, 21.0. Spectroscopic data was in agreement with the reported data.[46]

3-Methyl-1,1'-biphenyl (13g). Clear oil. Yield: 69%; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.62 – 7.54 (m, 2H), 7.47 – 7.37 (m, 4H), 7.36 – 7.29 (m, 2H), 7.16 (d, *J* 7.3 Hz, 1H), 2.42 (s, 3H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): *δ* 141.3, 141.1, 138.3, 128.6, 128.6, 127.9, 127.1, 124.2, 21.0. Spectroscopic data was in agreement with the reported data.[47]

2-Methyl-1,1'-biphenyl (13h). Clear oil. Yield: 76%; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.35 – 7.15 (m, 9H), 2.19 (s, 3H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): *δ* 139.5, 138.5, 130.9, 130.74, 129.5, 128.6, 128.0, 126.9, 125.4, 120.9, 20.1. Spectroscopic data was in agreement with the reported data.[47]

2-Isopropyl-1,1'-biphenyl (13i). Clear oil. Yield: 15%; ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.47 – 7.25 (m, 7H), 7.18 (dtd, *J* 1.4, 7.6, 9.0 Hz, 2H), 3.12 – 2.90 (m, 1H), 1.14 (d, *J* 6.9 Hz, 6H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 146.3, 142.1, 141.1, 129.9, 129.3, 127.9, 127.6, 126.67, 125.5, 125.2, 29.3, 24.2. Spectroscopic data was in agreement with the reported data.[49]

1-([1,1'-Biphenyl]-4-yl)ethan-1-one (13j). White solid, mp 115-118 °C; Yield: 84%: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 8.02 (d, *J* 8.2 Hz, 2H), 7.64 (dd, *J* 7.8, 23.2 Hz, 4H), 7.42 (dt, *J* 7.2, 28.3 Hz, 3H), 2.62 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 197.6, 145.8, 139.9, 135.9, 128.9, 128.8, 128.2, 127.2, 127.2, 26.5. Spectroscopic data was in agreement with the reported data.[46]

[1,1'-Biphenyl]-4-carbaldehyde (13k). White solid, mp 55-58 °C; Yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 10.04 (s, 1H), 7.94 (d, *J* 8.0 Hz, 2H), 7.68 (d, *J* 7.6 Hz, 4H), 7.53 – 7.28 (m, 3H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): *δ* 191.8,

147.1, 139.6, 135.2, 130.2, 128.9, 128.4, 127.6, 127.3. Spectroscopic data was in agreement with the reported data.[44]

4-Fluoro-1,1'-biphenyl (13l). White solid, mp 69-72 °C; Yield: 79%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 – 7.57 (m, 1H), 7.53 (ddd, *J* 1.8, 4.3, 6.5 Hz, 3H), 7.47 – 7.39 (m, 3H), 7.37 – 7.29 (m, 1H), 7.11 (t, *J* 8.7 Hz, 1H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ = 162.5 (d, *J* 246.3 Hz), 140.7 (d, *J* 123.7 Hz), 137.3 (d, *J* 3.2 Hz), 128.7 (d, *J* 8.7 Hz), 128.6 (d, *J* 8.0 Hz), 127.2 (d, *J* 1.2 Hz), 127.1 (d, *J* 18.0 Hz), 115.6 (d, *J* 21.4 Hz). Spectroscopic data was in agreement with the reported data.[44]

4-Nitro-1,1'-biphenyl (13m). Cream white/Beige solid, mp 107-112 °C; Yield: 95%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (d, *J* 8.7 Hz, 2H), 7.72 (d, *J* 8.7 Hz, 2H), 7.61 (d, *J* 7.1 Hz, 2H), 7.46 (dt, *J* 7.0, 21.6 Hz, 3H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 147.6, 147.0, 138.7, 129.1, 128.9, 127.8, 127.3, 124.0. Spectroscopic data was in agreement with the reported data.[44]

4-Methoxy-4'-(trifluoromethyl)-1,1'-biphenyl (13n). White solid. mp 66-70 °C. Yield: 83%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 3H), 7.58 (d, *J* 8.0 Hz, 2H), 7.50 – 7.29 (m, 4H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.7, 139.8, 129.5, 129.1, 128.9, 128.8, 128.7, 128.1, 127.4, 127.2, 127.1, 125.7, 125.6, 122.9. Spectroscopic data was in agreement with the reported data.[47]

4'-Methoxy-[1,1'-biphenyl]-4-carbonitrile (13o). White solid, mp 84-87 °C; Yield: 86%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 – 7.62 (m, 4H), 7.62 – 7.52 (m, 2H), 7.52 – 7.37 (m, 3H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 144.7, 139.7, 129.4 (q, *J* 32.3 Hz), 128.9, 128.1, 127.4, 127.2, 125.7 (q, *J* 3.7 Hz), 122.9 (q, *J* 269.8 Hz). Spectroscopic data was in agreement with the reported data.[44]

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