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# Multifunctional PNN-Ni<sup>II</sup> pincer catalyst for C–C and C–N bond formation *via* alkylation, cross-coupling, and hydroamination reactions†

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Ligand  $\{(o\text{-PPh}_2)\text{C}_6\text{H}_4\text{C}(\text{O})\text{N}(\text{H})\text{CH}_2(\text{C}_5\text{H}_4\text{N})\}$  (**1**) upon reaction with  $[\text{NiCl}_2(\text{DME})]$  afforded  $[\text{NiCl}\{\{\text{PNN}\}-\kappa^3\text{-P}, \text{N}, \text{N}\}\}$  (**2**), while its oxide derivative  $\{(o\text{-}(\text{O})\text{PPh}_2)\text{C}_6\text{H}_4\text{C}(\text{O})\text{N}(\text{H})\text{CH}_2(\text{C}_5\text{H}_4\text{N})\}$  (**3**) yielded Ni<sup>III</sup> pincer  $[\{\text{NiCl}(\mu\text{-Cl})_2\text{NiCl}\}\{\{\text{P}(\text{O})\text{NN}\}_2\text{-}\kappa^3\text{-O}, \text{N}, \text{N}\}\}$  (**4**). Complex **2** catalyzes diverse transformations, including  $\alpha$ -alkylation of ketones, *N*-alkylation of anilines, and Suzuki–Miyaura cross-coupling of aryl chlorides. Notably, complex **2** promotes the hydroamination of styrene to selectively afford the anti-Markovnikov product, acting as an efficient and versatile catalyst, operating under mild conditions at low loadings (0.5–1 mol%) and delivering high yields (80–99%).

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## Introduction

Transition metal-catalyzed activation of inert bonds is central to modern catalysis.<sup>1–3</sup> Pincer complexes, with their rigid tridentate ligands and meridional geometry, offer a versatile platform for such transformations.<sup>4–8</sup> Their tunable steric and electronic properties, along with adaptive behavior upon metal coordination, enable broad catalytic applicability.<sup>9–12</sup> While noble metal complexes have traditionally dominated this field,<sup>13</sup> recent efforts have focused on developing catalysts based on earth-abundant, cost-effective alternatives.<sup>14</sup> Nickel, in particular, stands out due to its accessibility, biocompatibility, and ability to access multiple oxidation states (0, +1, +2, +3 and +4), which supports diverse catalytic cycles.<sup>15–17</sup> Its capacity for oxidative addition and its characteristically slow  $\beta$ -hydride elimination-attributable to the high rotational barrier of Ni–C bonds-further augment its catalytic utility.<sup>18–23</sup> Herein, we present a PNN-Ni pincer complex **2** that functions as an efficient and versatile catalyst for key transformations, including  $\alpha$ -alkylation, *N*-alkylation, Suzuki–Miyaura cross-coupling, and hydroamination reactions.

## Results and discussion

Ligand 2-(diphenylphosphaneyl)-*N*-(pyridine-2-ylmethyl) benzamide,  $\{(o\text{-PPh}_2)\text{C}_6\text{H}_4\text{C}(\text{O})\text{N}(\text{H})\text{CH}_2(\text{C}_5\text{H}_4\text{N})\}$  (**1**), (hereafter referred to as “PN(H)N” and its anionic form as “PNN”), was

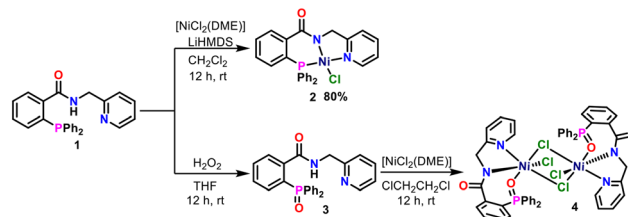
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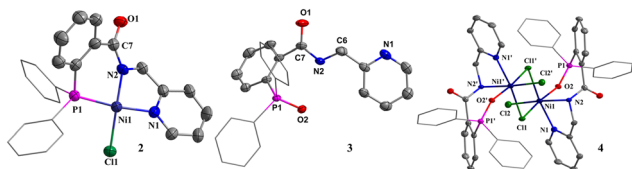
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synthesized according to the previously published procedure.<sup>24</sup> Ligand **1** upon reacting with  $[\text{NiCl}_2(\text{DME})]$  in the presence of LiHMDS afforded the pincer complex  $[\{\text{NiCl}\}\{\{\text{PNN}\}-\kappa^3\text{-P}, \text{N}, \text{N}\}\}$  (**2**), which exhibited a singlet at 13.1 ppm in  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. Ligand **1** reacts with excess  $\text{H}_2\text{O}_2$  to yield oxide derivative **3**, which upon treatment with  $[\text{NiCl}_2(\text{DME})]$  in dichloroethane yielded the dimeric Ni<sup>III</sup> pincer complex  $[\{\text{NiCl}(\mu\text{-Cl})_2\text{NiCl}\}\{\{\text{P}(\text{O})\text{NN}\}_2\text{-}\kappa^3\text{-O}, \text{N}, \text{N}\}\}$  (**4**) (Scheme 1).

Complex **4** displays a  $\nu_{\text{CO}}$  at  $1706\text{ cm}^{-1}$ , notably higher than that observed for the analogous Ni<sup>II</sup> complex **2** ( $1615\text{ cm}^{-1}$ ), along with a  $\nu_{\text{PO}}$  stretch at  $1165\text{ cm}^{-1}$ . The molecular structures of compounds **2–4** were confirmed by single-crystal X-ray analysis, as shown in Fig. 1. Selected bond lengths, bond angles, and crystallographic data are summarized in Table S1.† Complex **2** adopts a distorted square planar geometry around the Ni<sup>II</sup> center, while complex **4** features a Ni<sup>III</sup> center in a distorted octahedral geometry, incorporating two seven- and two five-membered metallacycles, one terminal chloride, and one bridging chloride ligand.

Cyclic voltammetry (CV) studies were performed to investigate the redox behaviour of complexes **2** (Ni<sup>II</sup>) and **4** (Ni<sup>III</sup>). Complex **2** exhibited two quasi-reversible reduction

Scheme 1 Synthesis of **2–4**.



**Fig. 1** Molecular structure of compounds 2–4. All hydrogen atoms and solvent molecules have been omitted for clarity. Displacement ellipsoids are drawn at 50% probability level.

waves corresponding to sequential Ni<sup>III</sup>/Ni<sup>I</sup> and Ni<sup>I</sup>/Ni<sup>0</sup> redox couples, typical of square planar Ni<sup>II</sup> complexes. In contrast, complex 4 displayed three distinct redox events, attributed to successive Ni<sup>III</sup>/Ni<sup>II</sup>, Ni<sup>II</sup>/Ni<sup>I</sup>, and Ni<sup>I</sup>/Ni<sup>0</sup> (Fig. S121†). The additional redox wave supports the presence of a higher oxidation state (Ni<sup>III</sup>) and the possibility of electron delocalization or redox activity across the dimeric core. These results confirm the multivalent redox nature of the Ni centers and support the potential for multielectron redox processes relevant to catalysis.

### $\alpha$ -Alkylation reaction between various ketones and benzyl alcohol derivatives promoted by nickel pincer complex 2

Carbon–carbon bond formation is a fundamental goal in synthetic organic chemistry.<sup>25,26</sup>  $\alpha$ -Alkylation of ketone enolates with alkyl halides is a classical method but is often hindered by the toxicity of halide reagents and the generation of stoichiometric inorganic waste.<sup>27</sup> In contrast, alcohols offer a more sustainable alternative due to their low toxicity, wide availability, and water as the sole byproduct.<sup>28–30</sup>  $\alpha$ -Alkylation *via* hydrogen-borrowing strategies has been widely explored using noble metals (Ir,<sup>31</sup> Rh,<sup>32</sup> Ru,<sup>33</sup> Pd<sup>34</sup>) and more abundant metals (Mn,<sup>35</sup> Fe,<sup>36</sup> Co,<sup>37</sup> and Cu<sup>38</sup>), though these often require harsh conditions and high catalyst loadings.<sup>39–41</sup> Despite these developments, the application of earth-abundant, non-precious metals such as nickel remains limited.<sup>40,42–44</sup> Compared to existing methods, complex 2 catalyzes the  $\alpha$ -alkylation of ketones under mild conditions with low catalyst loadings, enabling efficient synthesis of both linear and branched ketones and providing a practical, sustainable alternative to traditional approaches.

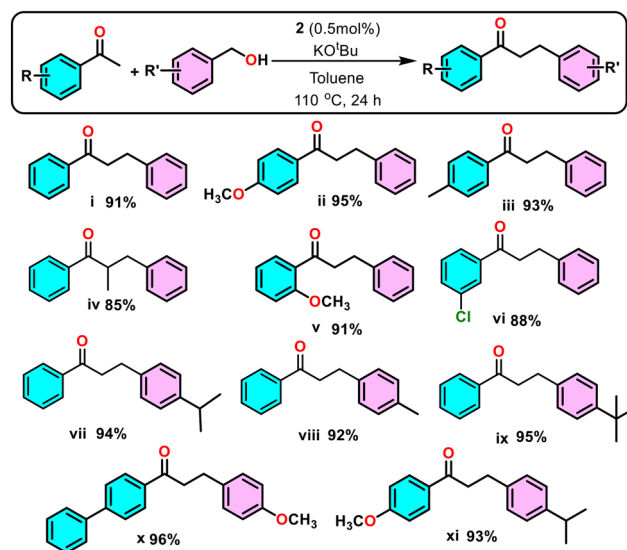
The  $\alpha$ -alkylation of acetophenone with benzyl alcohol was used as a model reaction to optimize conditions (Table 1). Using catalyst 2 with NaOH in toluene gave 86% yield (entry 1). Changing the base to KO<sup>t</sup>Bu improved the yield to 99% (entry 6), while other bases gave lower conversions (entries 2–5). Toluene was the optimal solvent, with other solvents being less effective (entries 7–9). No product formed with nickel salts (entries 10–11), and lower temperature or omission of the catalyst or base suppressed the reaction (entries 12–14). Under optimized conditions, various substituted acetophenones and benzyl alcohols gave the desired products in good yields (85–99%) (Scheme 2).

Based on literature precedents,<sup>45,46</sup> a plausible mechanism is proposed and outlined in Scheme 3.

**Table 1** Optimization of the reaction condition for  $\alpha$ -alkylation reaction

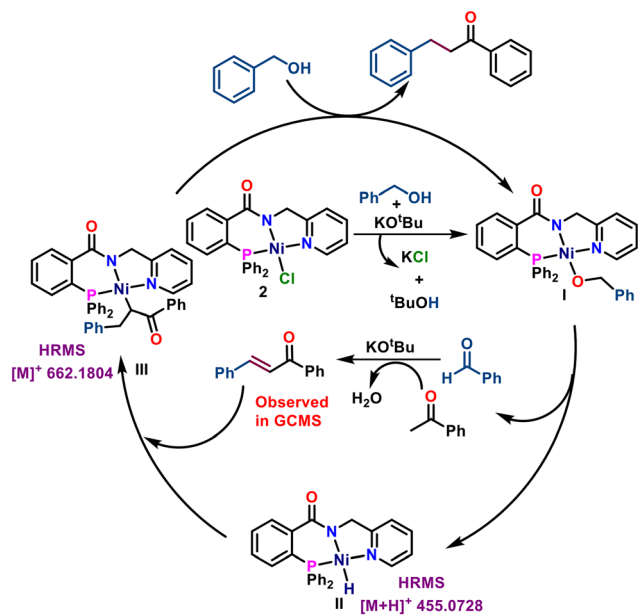
Entry	Catalyst	Solvent	Base	Yield <sup>a</sup> (%)
1	2	Toluene	NaOH	86
2	2	Toluene	KOH	78
3	2	Toluene	Cs <sub>2</sub> CO <sub>3</sub>	67
4	2	Toluene	K <sub>3</sub> PO <sub>4</sub>	24
5	2	Toluene	LiOH	64
6	2	Toluene	KO <sup>t</sup> Bu	99
7	2	THF	KO <sup>t</sup> Bu	84
8	2	Benzene	KO <sup>t</sup> Bu	87
9	2	Dioxane	KO <sup>t</sup> Bu	92
10	NiCl <sub>2</sub> (DME)	Toluene	KO <sup>t</sup> Bu	0
11	Ni(OAc) <sub>2</sub> ·4H <sub>2</sub> O	Toluene	KO <sup>t</sup> Bu	0
12 <sup>b</sup>	2	Toluene	KO <sup>t</sup> Bu	74
13	2	Toluene	No base	0
14	No catalyst	Toluene	KO <sup>t</sup> Bu	0

<sup>a</sup> Yield determined by GC-MS. Acetophenone (0.50 mmol), benzyl alcohol (0.55 mmol), base (0.75 mmol), 2 (0.5 mol%) and solvent (2 mL), 110 °C. <sup>b</sup> Reaction temp = 80 °C.



**Scheme 2** Substrate scope for  $\alpha$ -alkylation reaction. General reaction conditions: acetophenone (0.50 mmol), benzyl alcohol (0.55 mmol), KO<sup>t</sup>Bu (0.75 mmol), toluene 2 mL, 110 °C, and catalyst 2 (0.5 mol%). All are isolated yields.

The reaction begins with the formation of Ni-alkoxide species **I** from complex 2 and benzyl alcohol in the presence of base.  $\beta$ -Hydride elimination yields Ni–H species **II** and an aldehyde, which undergoes base-promoted aldol condensation with a ketone to form an  $\alpha,\beta$ -unsaturated ketone (detected by GC-MS). Insertion of the C=C bond into Ni–H species **II** gives intermediate **III**, which undergoes alcoholysis with benzyl alcohol to regenerate species **I** and release the  $\alpha$ -alkylated ketone.

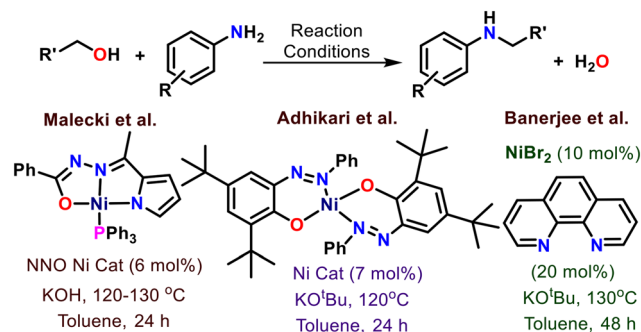
Scheme 3 Proposed mechanism for  $\alpha$ -alkylation reaction.

### *N*-Alkylation reaction between various anilines and benzyl alcohol derivatives promoted by nickel pincer complex 2

*N*-Alkylation of amines is a key transformation in pharmaceuticals, materials science, and agrochemicals. Traditional methods such as nucleophilic substitution, Buchwald–Hartwig coupling, Ullmann reactions, and hydroamination, often face issues like low selectivity, over-alkylation, and poor yields, highlighting the need for more efficient and sustainable approaches.<sup>47</sup> Transition metal-catalyzed *N*-alkylation *via* the borrowing hydrogen strategy has emerged as a highly atom-economical and environmentally benign approach, utilizing alcohols as both alkylating agents and hydrogen source.<sup>48,49</sup> While noble metal catalysts (*e.g.*, Ru,<sup>50</sup> Ir,<sup>51</sup> Rh,<sup>52</sup> and Pd<sup>53</sup>) have demonstrated high efficacy, nickel-based catalysts present an earth-abundant and cost-effective alternative. In heterogeneous catalysis, Yus has demonstrated effective hydrogen transfer using nickel nanoparticles,<sup>54</sup> while Barta and co-workers developed a heterogeneous Ni(COD)<sub>2</sub>-derived nickel oxide cluster for *N*-alkylation. However, homogeneous nickel catalysts remain less explored.<sup>55,56</sup>

Recent advances in *N*-alkylation reactions typically rely on protocols that require high catalyst loadings and elevated temperatures, affording moderate to high yields (50–90%) (Scheme 4).<sup>57–59</sup> Given these limitations, we report catalyst 2 that facilitates efficient *N*-alkylation across a broad range of alcohols, operates under mild conditions with minimal catalyst loading, and achieves high yields (85–96%) of the desired *N*-alkylated products.

The *N*-alkylation of benzyl alcohol with aniline using 0.5 mol% of catalyst 2 was selected as a benchmark reaction to optimize C–N bond formation. The optimized reaction conditions are mentioned in Table 2. A high yield of 87% in the initial test reaction prompted further investigation of

Scheme 4 *N*-Alkylation reaction using various catalysts.

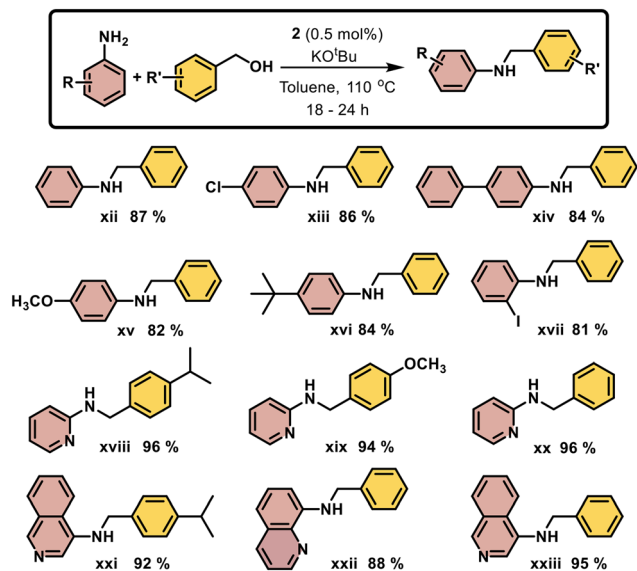
key catalytic parameters, including base, solvent, and temperature. Among the bases tested (KO<sup>t</sup>Bu, NaOH, KOH, Cs<sub>2</sub>CO<sub>3</sub>), KO<sup>t</sup>Bu proved the most effective in activating the catalyst (entries 1–4). Lower reaction temperatures resulted in moderate yields (entry 10), while nonpolar solvents significantly enhanced the alkylation process (entries 4–7). Control experiments confirmed that both the catalyst and base were essential, as the reaction did not proceed in their absence (entries 12–13). Ultimately, toluene and KO<sup>t</sup>Bu at 110 °C were identified as the optimal reaction conditions (entry 4), and were subsequently applied to assess the substrate scope (Scheme 5).

Interestingly, aniline derivatives bearing electron-donating substituents (4-methoxy and 4-<sup>t</sup>butyl) and electron-withdrawing substituents (4-chloro, 2-iodo, and 4-biphenyl) proved to be effective coupling partners, affording the corresponding products in good yields 81–86% (xiii–xvii). Notably, 2-aminopyridine exhibited excellent conversion when coupled with different benzyl alcohol derivatives, affording products in 94–96% yield (xviii–xx). Similarly,

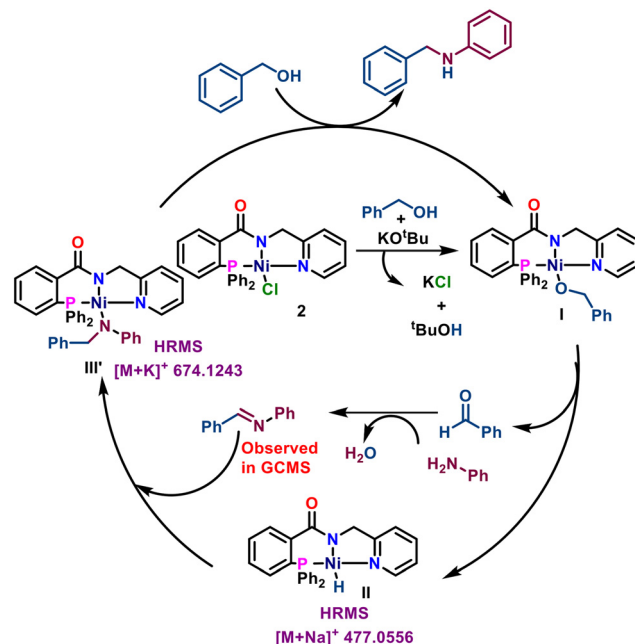
Table 2 Optimization of the reaction condition for *N*-alkylation reaction

Entry	Catalyst	Solvent	Base	Yield <sup>a</sup> (%)
1	2	Toluene	NaOH	73
2	2	Toluene	KOH	69
3	2	Toluene	Cs <sub>2</sub> CO <sub>3</sub>	54
4	2	Toluene	KO <sup>t</sup> Bu	87
5	2	<i>n</i> -Hexane	KO <sup>t</sup> Bu	71
6	2	Benzene	KO <sup>t</sup> Bu	83
7	2	Dioxane	KO <sup>t</sup> Bu	73
8	NiCl <sub>2</sub> (DME)	Toluene	KO <sup>t</sup> Bu	0
9	Ni(OAc) <sub>2</sub> ·4H <sub>2</sub> O	Toluene	KO <sup>t</sup> Bu	0
10 <sup>b</sup>	2	Toluene	KO <sup>t</sup> Bu	67
11 <sup>c</sup>	2	Toluene	KO <sup>t</sup> Bu	58
12	2	Toluene	No base	0
13	No catalyst	Toluene	KO <sup>t</sup> Bu	0

<sup>a</sup> Yield determined by GC-MS. Aniline (0.50 mmol), benzyl alcohol (0.55 mmol), base (0.75 mmol), catalyst 2 (0.5 mol%) and solvent (2 mL), 110 °C. <sup>b</sup> Reaction temp = 80 °C. <sup>c</sup> 2 (0.25 mol%).



**Scheme 5** Substrate scope for *N*-alkylation reaction. General reaction conditions: aniline (0.50 mmol), benzyl alcohol (0.55 mmol), KO<sup>t</sup>Bu (0.75 mmol), toluene 2 mL, 110 °C, and 2 (0.5 mol%). All are isolated yields.



**Scheme 6** Proposed mechanism for *N*-alkylation reaction.

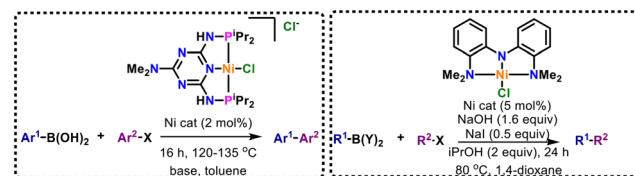
isoquinolin-4-amine and quinoline-8-amine displayed high reactivity, providing yields of 88–95% (xxi–xxiii).

A plausible catalytic mechanism for C–N bond formation is proposed based on experimental evidence and supported by literature precedents (Scheme 6).<sup>60,61</sup> The reaction begins with alcohol coordination to nickel in the presence of KO<sup>t</sup>Bu, forming Ni-alkoxide I. β-Hydride elimination produces an aldehyde and Ni-hydride intermediate II. The aldehyde condenses with an amine to form an imine (confirmed by GCMS), which inserts into the Ni–H bond and is reduced to intermediate III'. Reaction of III' with another alcohol regenerates Ni-alkoxide I, completing the catalytic cycle. Consistent with literature, attempts to isolate the unstable Ni-hydride intermediate were unsuccessful.<sup>58</sup>

### Suzuki–Miyaura cross coupling reaction between aryl chlorides and boronic acids promoted by nickel pincer complex 2

The Suzuki–Miyaura cross-coupling reaction is a widely utilized method for synthesizing substituted diphenyls, valued for its mild conditions and broad functional group tolerance.<sup>62</sup> Its popularity stems from the use of boronic acid nucleophiles, which are non-toxic, stable to air and moisture, and readily available.<sup>63,64</sup> Kirchner *et al.* demonstrated the use of a Ni<sup>II</sup> PNP complex<sup>65</sup> while Hu *et al.* employed [(MeN<sub>2</sub>-N)NiCl] complex, for alkyl–alkyl and alkyl–aryl couplings,<sup>66</sup> both methods required high catalyst loadings and additives (Scheme 7).

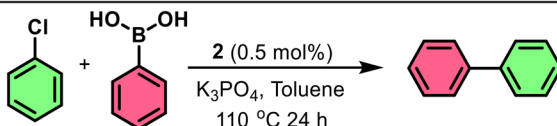
While aryl bromides and iodides are commonly employed under basic conditions with metal catalysts,<sup>67–69</sup> aryl chlorides are increasingly attractive due to their lower cost, commercial availability, and structural diversity.<sup>70,71</sup> However,



**Scheme 7** Suzuki–Miyaura cross coupling reaction using various catalysts.

their activation remains challenging, typically necessitating harsh conditions. To overcome these limitations, we sought to develop a highly efficient PNN-ligated Ni catalyst 2 capable of promoting Suzuki–Miyaura cross-coupling of aryl chlorides under mild conditions and with low catalyst loading.

The PNN Ni pincer complex 2 efficiently catalyzed the Suzuki–Miyaura cross-coupling reaction, affording the desired products in yields ranging from 85% to 99% under optimized conditions reported in Table 3. An initial assessment of the coupling reaction between chlorobenzene and phenylboronic acid in the absence of catalyst 2 showed no product formation (entry 1). Upon the addition of 0.25 mol% of the catalyst, a yield of 78% was observed (entry 2). Increasing the catalyst loading to 0.5 mol% significantly enhanced the yield to 96% (entry 3). A variety of bases, including K<sub>3</sub>PO<sub>4</sub>, KOH, NaO<sup>t</sup>Bu, and KO<sup>t</sup>Bu, were screened, with K<sub>3</sub>PO<sub>4</sub> demonstrating superior performance (entries 3–6). Similarly, the effect of different solvents—toluene, 1,4-dioxane, THF, and water, was investigated, with toluene proving to be the most effective medium for the reaction (entries 3, 7–9). Lowering the reaction temperature to 80 °C resulted in a reduced yield of 69% (entry 10), while decreasing the reaction time also led to diminished product formation, with an optimized reaction time of 24 h (entry

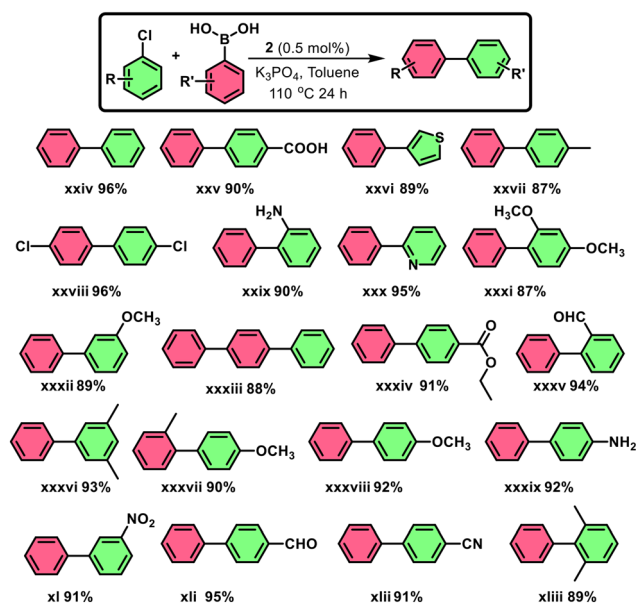
**Table 3** Optimization of the reaction condition for Suzuki–Miyaura cross coupling reaction


Entry	Catalyst [mol%]	Base	Solvent	Yield <sup>a</sup> [%]
1	No cat	K <sub>3</sub> PO <sub>4</sub>	Toluene	0
2	0.25	K <sub>3</sub> PO <sub>4</sub>	Toluene	78
3	0.5	K <sub>3</sub> PO <sub>4</sub>	Toluene	96
4	0.5	KOH	Toluene	62
5	0.5	NaO <sup>t</sup> Bu	Toluene	76
6	0.5	KO <sup>t</sup> Bu	Toluene	81
7	0.5	K <sub>3</sub> PO <sub>4</sub>	1,4-Dioxane	80
8	0.5	K <sub>3</sub> PO <sub>4</sub>	THF	56
9	0.5	K <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> O	0
10 <sup>b</sup>	0.5	K <sub>3</sub> PO <sub>4</sub>	Toluene	69
11 <sup>c</sup>	0.5	K <sub>3</sub> PO <sub>4</sub>	Toluene	77
12	0.5	No base	Toluene	0

<sup>a</sup> Aryl chloride (0.50 mmol), phenyl boronic acid (0.75 mmol), base (1 mmol), **2** (0.5 mol%) and solvent (2 mL), 110 °C, yield was determined by GCMS. <sup>b</sup> Temp, 80 °C. <sup>c</sup> Reaction time, 18 h.

11). Notably, no product formation was observed in the absence of a base (entry 12).

Using the optimized conditions (0.5 mol% catalyst **2**, K<sub>3</sub>PO<sub>4</sub>, toluene, 110 °C, 24 h) (Scheme 8), a broad range of aryl chlorides and phenylboronic acids underwent smooth coupling to afford biphenyl derivatives in excellent yields. The method showed broad functional group tolerance and outperformed or matched existing systems, highlighting the efficiency of catalyst.



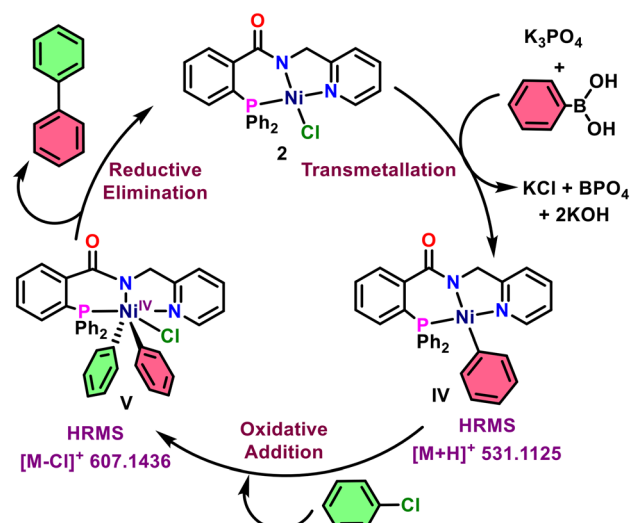
**Scheme 8** Substrate scope for Suzuki–Miyaura cross coupling reaction. General reaction conditions: aryl chloride (0.5 mmol), phenyl boronic acid (0.75 mmol), K<sub>3</sub>PO<sub>4</sub> (1 mmol), toluene 2 mL, 110 °C, and **2** (0.5 mol%). All are isolated yields.

Aryl chlorides are typically challenging substrates due to the high bond dissociation energy of the C–Cl bond and their reluctance to undergo oxidative addition. The high catalytic efficiency observed with complex **2**, even with aryl chlorides, can be attributed to the strong electron-donating and rigid tridentate nature of the PNN ligand, which stabilizes the Ni<sup>II</sup> center and enhances its nucleophilicity. The square planar geometry enforced by the ligand framework is also conducive to oxidative addition. Additionally, the reaction conditions, including the presence of base and elevated temperature, likely facilitate this transformation. Literature reports support the formation of Ni<sup>IV</sup> species from Ni<sup>II</sup> *via* oxidative addition, particularly in pincer-ligated systems, suggesting that the transformation may proceed through a Ni<sup>II</sup>/Ni<sup>IV</sup> redox pathway under the employed conditions.<sup>17,72–75</sup>

A plausible catalytic mechanism for the reaction, supported by experimental data and literature (Scheme 9), involves an initial transmetalation step.<sup>58,76,77</sup> The PNN–Ni<sup>II</sup> complex **2** reacts with a boronic acid and base to form intermediate **IV**. This is followed by oxidative addition of an aryl halide, yielding the PNN–Ni<sup>IV</sup> complex (**V**). Subsequent reductive elimination affords the biphenyl product and regenerates the active Ni<sup>II</sup> catalyst, thereby completing the catalytic cycle.

#### Hydroamination reaction between various anilines and styrene derivatives promoted by nickel pincer complex **2**

Hydroamination is the atom-economical addition of an N–H bond across C–C multiple bonds, forming C–N and C–H bonds. It enables efficient amine synthesis from alkenes (*e.g.*, vinyl arenes, dienes, allenes, strained alkenes) and alkynes.<sup>78,79</sup> Hydroamination of alkenes is generally more challenging than that of alkynes due to their lower reactivity. The reaction can proceed *via* Markovnikov or anti-Markovnikov pathways, but achieving anti-Markovnikov



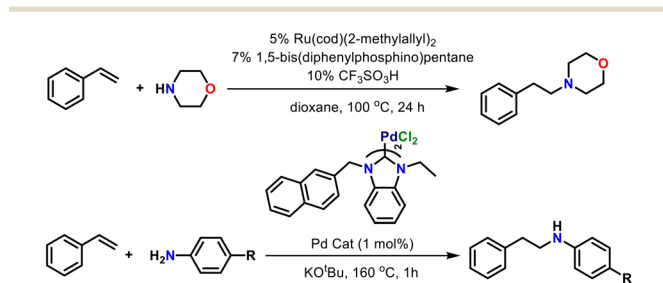
**Scheme 9** Proposed mechanism for Suzuki–Miyaura cross coupling reaction.

selectivity, especially in intermolecular reactions remains a major challenge.<sup>80</sup>

Previous studies have relied on expensive metals such as palladium and ruthenium, often under harsh conditions involving high temperatures,<sup>81</sup> acidic media, and high catalyst loadings (Scheme 10).<sup>82</sup> In contrast, our approach employs nickel, a much more economical alternative, under mild conditions with low catalyst loading, while still achieving high selectivity for the anti-Markovnikov product.

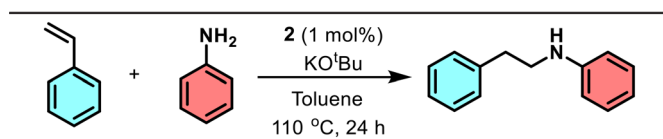
Styrene and aniline were selected as model substrates for this study. The optimized reaction conditions are provided in Table 4. In the presence of 0.5 mol% of the catalyst 2 at 110 °C in toluene with KO<sup>t</sup>Bu as the base, the reaction yielded 76% of the selective anti-Markovnikov product (entry 1). Increasing the catalyst loading to 1 mol% improved the selectivity to 88% (entry 2). Screening various bases identified KO<sup>t</sup>Bu as the most effective (entries 2–5). Lowering the reaction temperature to 80 °C reduced the yield to 64% (entry 8). Among the solvents tested, toluene provided the highest yield (entries 2, 6–7).

Optimized conditions (2 (1 mol%), KO<sup>t</sup>Bu, toluene, 110 °C) enabled efficient anti-Markovnikov hydroamination. Substrate scope studies (Scheme 11) showed that both electron-donating and electron-withdrawing groups on styrene or aniline were well tolerated, delivering excellent yields (88–94%, **xlv**–**I**).



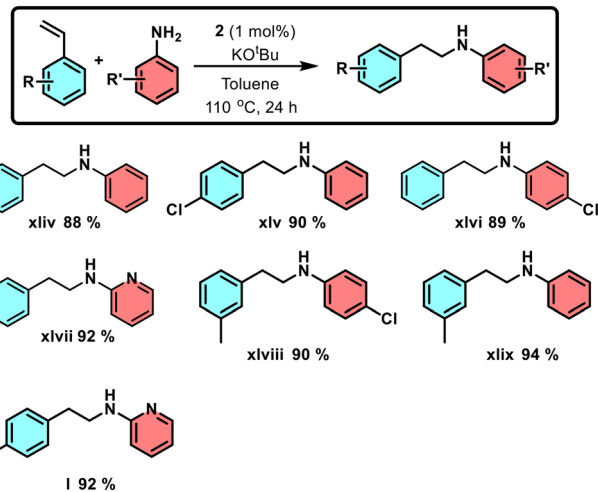
Scheme 10 Hydroamination reaction using Pd and Ru catalysts.

Table 4 Optimization of the reaction condition for hydroamination reaction<sup>a,b</sup>



Entry	Catalyst	Solvent	Base	Yield (%)
1 <sup>c</sup>	2	Toluene	KO <sup>t</sup> Bu	76
2	2	Toluene	KO <sup>t</sup> Bu	88
3	2	Toluene	NaOH	55
4	2	Toluene	KOH	69
5	2	Toluene	CS <sub>2</sub> CO <sub>3</sub>	24
6	2	Benzene	KO <sup>t</sup> Bu	72
7	2	Dioxane	KO <sup>t</sup> Bu	60
8 <sup>d</sup>	2	Toluene	KO <sup>t</sup> Bu	64
9	2	Toluene	No base	0
10	No catalyst	Toluene	KO <sup>t</sup> Bu	0

<sup>a</sup> Yield determined by GC-MS. <sup>b</sup> Styrene (0.50 mmol), aniline (0.55 mmol), base (0.75 mmol), toluene 2 mL, 110 °C and catalyst 2 (1 mol%). <sup>c</sup> Ni cat 2 (0.5 mol%). <sup>d</sup> Reaction temp = 80 °C.

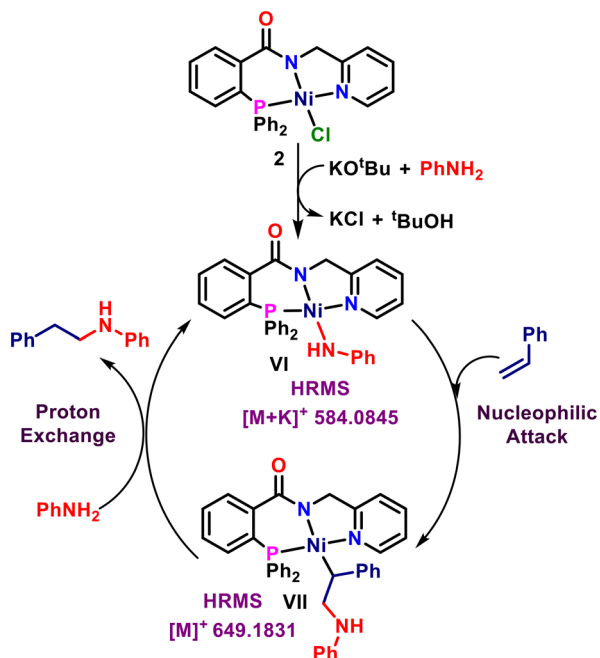


Scheme 11 Substrate scope for hydroamination reaction. General reaction conditions: styrene (0.50 mmol), aniline (0.55 mmol), KO<sup>t</sup>Bu (0.75 mmol), toluene 2 mL, 110 °C, and catalyst (1 mol%). All are isolated yields.

The catalytic cycle for the base-catalyzed hydroamination of alkenes begins with the deprotonation of the amine by a base, generating a metal amide species (**VI**).<sup>83</sup> This metal amide then acts as a nucleophile, facilitating the addition to the alkene. In our system, the nucleophilic attack preferentially occurs at the terminal carbon of the alkene, leading to exclusive formation of the anti-Markovnikov product. This regioselectivity can be attributed to the steric and electronic characteristics of the PNN-Ni<sup>II</sup> complex, which likely favour an outer-sphere nucleophilic pathway and disfavours attack at the more hindered internal carbon. The resulting highly reactive 2-aminoalkyl complex (**VII**) subsequently undergoes proton transfer with a fresh amine molecule, regenerating the active metal amide catalyst and yielding the hydroamination product (Scheme 12).

While a comprehensive kinetic investigation was beyond the scope of this study, preliminary mechanistic insights suggest that the rate-determining step varies depending on the transformation. In the  $\alpha$ -alkylation and *N*-alkylation reactions, the  $\beta$ -hydride elimination step, which generates the aldehyde and Ni–H intermediate, is likely the rate-determining step, consistent with established borrowing hydrogen mechanisms.<sup>59,84,85</sup> In the case of Suzuki–Miyaura cross-coupling, transmetalation is the rate determining step.<sup>86,87</sup> For the hydroamination reaction, nucleophilic attack of the metal-amido intermediate on the alkene likely constitutes the slowest step in the catalytic cycle.<sup>79,83,88</sup> To further support these mechanistic proposals, key intermediates were detected and characterized by high-resolution mass spectrometry.

Mechanistic studies, including mercury drop tests, confirmed the homogeneous nature of all the reactions. Gram-scale reactions under optimized conditions demonstrated the robustness of the system, delivering excellent yields across various transformations: 94% ( $\alpha$ -



Scheme 12 Proposed catalytic cycle for hydroamination reaction.

alkylation), 84% (*N*-alkylation), 91% (Suzuki–Miyaura), and 80% (hydroamination).

## Conclusions

In summary, the PNN Ni pincer complex 2 was synthesized and shown to catalyse diverse transformations, including  $\alpha$ -alkylation of ketones, *N*-alkylation of anilines, and Suzuki–Miyaura cross-coupling of aryl chlorides. It also enables selective anti-Markovnikov hydroamination of styrene under mild conditions with low loadings (0.5–1 mol%) and high yields (80–99%) across a broad substrate scope, underscoring its versatility and efficiency as a catalyst.

## Data availability

The data supporting this article have been included as part of the ESI† contents. Crystal structure determination, NMR and HRMS spectra of complexes, controlled experiments of reaction mechanism, NMR and mass spectra of catalytic products.

## Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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