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Unique CuI-pyridine based ligands catalytic systems for *N*-arylation of indoles and other heterocycles

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ABSTRACT

Two pyridine-based ligands (*N*-((pyridin-2-yl) methyl) pyridin-2-amine) **L1** and (*N*-((pyridin-2-yl) methylene) pyridin-2-amine) **L2** are explored in present work which are inexpensive, effective and environmentally benign in their properties. These have been utilized for C-N cross coupling reaction resulting in *N*-arylation. The *N*-arylation of indole, imidazole and triazole have been successfully carried out with different aryl and heteroaryl halides using these ligands.

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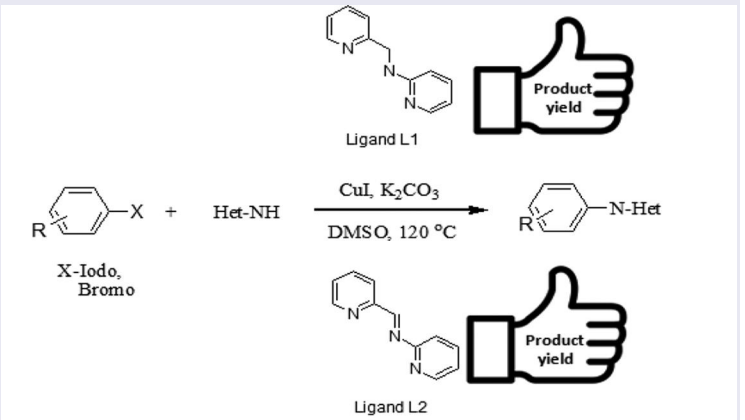
KEYWORDS
C-N Cross coupling; **L1** (*N*-((pyridin-2-yl) methyl) pyridin-2-amine); **L2** (*N*-((pyridin-2-yl) methylene) pyridin-2-amine); pyridine-based ligands-arylation

GRAPHICAL ABSTRACT



CuI-Base-Pyridine Based Ligands (L1/ L2) Catalytic System for N-Arylation

Introduction

The C-N bond formation has enormous importance as structural motif in wide range of synthetic organic reactions. In the same genre, *N*-aryl heterocycles are regarded as one of the most important modules in pharmaceutical and medicinal research,[1] agrochemicals,[2] biological,[3] and material sciences.[4] Moreover, C-N bond formation provides advance synthetic pathways to facilitate pharmaceutical and other chemical industries.[1–4] But, harsh reaction conditions *i.e.*, high temperature, sophisticated instrumentation, minimal yields invoke modern researcher to search for alternative

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methodology. Attractive new methodology may facilitate the synthesis of *N*-aryl heterocycles through high yield and easy isolation of the products.[5] During the last decade, significant advances have been reported in the cross-coupling methodology for indole, indole derivatives, imidazole, and triazoleetc.[5]

However structural and critical view point on *N*-aryl heterocycles suggests, poor nucelophilicity of the amine nitrogen atom induced by neighboring heteroatom or heteroaryl amines have historically been viewed as challenging substrates for *N*-arylation.[6] Classical Alchemists have employed different strategies on *N*-arylation of heterocyclic compounds for enhancement of the yields. The classical methods such as nucleophilic substitution,[7] reductive amination,[8] Ullmann-type amination,[9] Pd-catalyzed amination have been the subject of extensive study since the pioneering works of Buchwald,[10] Hartwig,[11] Nicolaou,[12] Liebeskind,[13] and Ma.[14] Copper catalyzed based zeolite were also used for amination.[15] Transition metal such as palladium[16] catalyzed method for C-N cross coupling reactions was however expensive and moisture–sensitive. The toxic nature of palladium compounds also limits their use in synthetic procedures.

On this problem, till now most reliable approach available is coupling of aryl halide with hetero-aryl amines which employs 25–100% Cu and DMEDA (*N,N′*-dimethylethylenediamine) to provide moderate to good yields.[17]

Recently, Copper-based catalyst systems have been generating huge attention because of the use of Cu based catalyst in milder reaction conditions and high yields.[10] So far, many efficient ligands have been used with copper such as CuI,[18] CuI/metformin,[19] CuI/picolinic acid,[20] CuI/Benzotriazol-1-ylmethanol,[21] Cu_2O,[22] CuI/PPAPM,[23] CuI/amino acid,[24] CuBr/Dpphen,[25] $Cu(OAc)_2.H_2O$,[26] CuI/diamine,[27] CuI/IL,[28] CuI/Nhydroxyimide,[29] $Cu(OAc)_2$/MW,[30] $CuSO_4$/PyridineN-oxide,[31] Cu_2O(NPPA-O),[32] CuO,[33] CuI/hydrazone,[34] Cu(II)TMHD,[35] and other catalysts.[36] In recent years, transition metals such as $[Cu_2(pda)_3(ReO_4)_2]$,[37] [Fe]/[Cu],[38] $Cd(OAc)_2.2H_2O$,[39] have also been reported as the catalyst for this C-N coupling reaction.

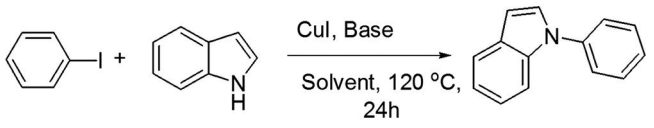
It has been also found that, the incorporation of ligands with catalytic amounts of copper made reactions methodologies milder and elegant with source ranging from 10 mol%.[16] Incorporation of ligands in Cu catalyzed reactions improvises the reaction mechanism through easy removal of halide and efficient C-N bond formation which reflect in terms of comparatively high yield and less time. It also prevents the aggregation of Cu salts in the progress of reaction, and subsequently enhances the reactivity by increasing the electron density on the catalytic species. Moreover ligands incorporation in catalysis attracted much attention due to cost effectiveness and time of reaction process.[16]

Present work mainly focused on minimization of harsh reaction conditions and yields occurring in C-N coupling reactions. Incorporation of ligands **L1** and **L2** addresses the issue arised during C-N coupling reaction methodology. In view of this scenario, two cost-effective pyridine-based new ligands **L1** [N-((pyridin-2-yl) methyl) pyridin-2-amine] and **L2** [N-((pyridin-2-yl) methylene) pyridin-2-amine] have been developed and utilized for Ullmann-type C-N coupling reactions of aryl iodide/aryl bromide with various ***N*-heterocyles.**

Results and discussion

Initially, to improve the C-N coupling reaction conditions for better yields, the reaction of iodobenzene **(1a)** (1 mmol), 1H-indole **(2a)** (1.2 mmol), CuI (0.1 mmol), base (2 mmol)

Table 1. Reaction scheme and optimization of reaction conditions.



1a 2a 3a

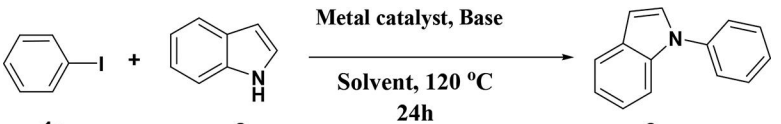
Entry	Catalyst	Base	Solvent	Time (h)	Yield (%)[a,b]
1	CuI	K_2CO_3	DMSO	24	42
2	CuI	DIPEA	Glycerol:DMSO(9:1)	24	20
3	CuI	K_2CO_3	Glycerol:Ethyl acetate(9:1)	24	Trace
4	CuI	$NaHCO_3$	DMSO	24	28
5	CuI	$NaHCO_3$	DMSO:water(9:1)	24	15
6	CuI	DIPEA	DMSO	24	18
7	CuI	CS_2CO_3	DMSO	24	32

[a]Reaction conditions: Iodobenzene (1.0 mmol), indole (1.2 mmol), CuI (0.1 mmol), Base (2.0 mol), (10 volume) solvent.
[b]Results isolated and analyzed on the basis of LC-MS analysis.

has been carried out in different solvent systems at 120 °C for 24 h. In first case, the reaction of **1a** and **2a**, in presence of CuI, base (K_2CO_3) in DMSO; gave 1-phenyl-1H-indole **(3a)** with an highest elevated yield up to 42% (Table 1, Entry 1).To further improve the yield of present synthetic approach, various bases (DIPEA, $NaHCO_3$, and Cs_2CO_3) and co-solvent system such as Glycerol:DMSO, Glycerol:Ethyl acetate, DMSO: Water and DMSO have been utilized. However, observed yield of product **3a** was very low in each case ranging from 15–32% (Entry 2–**7** in Table 1). These observations accounted for optimization of reaction yields and conditions, which clearly point out that Entry 1 in Table 1 work smoothly but yield was not adequate.

Further, to delineate and to improvise the yield of reaction (between **1a** and **2a**), efficacy of catalyst for the synthesis of C-N coupling (*i.e.*, **3a**) several reactions have been investigated through different reaction medium shown in Table 2. The catalysts such as KI, ZnI and NiBr were found to be inactive in present conditions (Entry 1, 3 and 4 in Table 2). The catalysts like CuBr, CuCl, $CuSO_4$, CuO and Cu afforded trace to very low yields. In Table 2

Table 2. Reaction scheme and conditions for **1a** and **2a** with respect to catalyst and base.



1a **2a** **3a**

Entry	Catalyst	Base	Solvent	Temperature (°C)	Time (h)	Yield(%)[a,b]
1	KI	K_2CO_3	Acetonitrile	Reflux	24	0%
2	CuBr	DIPEA	DMSO	120	24	Trace
3	ZnI	K_2CO_3	DMSO	120	24	0
4	NiBr	K_2CO_3	DMSO	120	24	0
5	CuBr	$NaHCO_3$	DMSO	120	24	40
6	CuCl	$NaHCO_3$	DMSO	120	24	Trace
7	Cu(SO4)	$NaHCO_3$	DMSO	120	24	30
8	Cu	$NaHCO_3$	DMSO	120	24	25
9	CuO	K_2CO_3	Methanol	Refluxed	24	30
10	–	K_2CO_3	DMSO	120	24	Trace

[a]Reaction conditions: Iodobenzene (1.0 mmol), indole (1.2 mmol), **metal catalyst** (0.1 mmol), Base (2.0 mol), (10 volume) solvent.
[b]Results isolated and analyzed on the basis of LCMS analysis.

Entry 5, CuBr introduced in combinations with inorganic weak base *i.e.*, $NaHCO_3$ showed reasonable yield. In Entry 6, CuCl used in combination with $NaHCO_3$ yields traces of product. Upon careful inspection of Entry 7–9, it can be seen that $Cu(SO_4)$, Cu and CuO gave 25–30% yield of the product. On contrary, without catalyst same reaction yields trace amount of product shown in Entry 10.

In accordance with the observations in Table 2, plausible reason behind the low yields of product can be explained on the basis of increase in activation energy in the transition state during complex formation between base-Cu catalyst and reactant. Probably, this complex formation in each case in Table 2 elevates activation energy so that it effectively hampered reaction yield. On the basis of above observations it can be stated that, no significant effect on the yield of the product was observed.[40] Therefore, in order to increase the yield, easy isolation of product with innovative reaction methodology in consideration, in the present work two ligands **L1** (*N*-((pyridin-2-yl) methyl) pyridin-2-amine) and **L2** (*N*-((pyridin-2-yl) methylene) pyridin-2-amine)have been designed which facilitate reaction mechanism in such a way that it could create practical catalyst system CuI-base-L1/L2 for the C-N coupling reactions.[18,41]

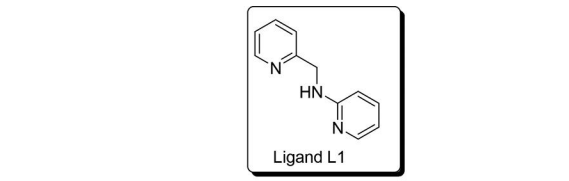
Ligands L1 and L2 as a member of CuI-Base-L1/L2 catalyst system for various C-N coupling reactions

Ligands L1

Documented results in Table 1 and 2 point out that reaction between aryl halide and 1H-indole in absence of **L1** in reaction system gave very less or trace of the desired product *i.e.*,1-phenyl-1H-indole (**3a**) in each case. Therefore, for enhancement of reaction yield and to examine versatility of ligand **L1** and **L2**, various types of indole and halo benzene have been examined in present study. Ligand **L1** (10 mol %) was screened for *N*-arylation of indole with aryl halide using CuI (10 mol %), K_2CO_3in DMSO at 120 °C temperature for 16 and 24 h (Table 3). After careful examination, it has been observed that when ligand **L1** was used for *N*-arylation of indole comparatively better results have been obtained in each case with respect to yields and reaction time (Table 3, Entry 1–5).[42] Entry 1 and 2 in Table 3, clearly showed 78 and 72% yields of product in C-N coupling reactions. Enhanced yield of products have been achieved by the introduction of CuI-base-**L1** catalytic system. Results obtained showed that neutral and electron donating reactant moieties producing significant effect on overall reactivity and yields of reaction in CuI-base-**L1** system (Table 3 Entry 1–4). Enhanced reactivity and yields of C-N coupling reaction have been reflected in 78, 72, 80, and 88% yields respectively in the reaction. However effect of nature of indole on the overall reaction and subsequent reactivity of methyl indole has been examined in the reaction (Entry 5). Surprisingly, about 80% yield in CuI-base-**L1** system indicate that neither neutral, electron withdrawing nor electron donating alteration in the reactant counterpart showed adverse effect on C-N coupling reaction.

Proportional yields obtained in the present reaction condition (*i.e.*, in presence of ligand **L1**) compared to earlier findings indicate that ligand **L1** played pivotal role in enhancement of catalytic activity of CuI-base-**L1** through complex formation.[27(a),43] Complex formation in present reaction condition may facilitate accurate exposure of reactant moieties for the catalyzation, which probably reflects in the enhancement of the yields.

Table 3. Reaction scheme and amplification of reaction with respect to catalyst and Ligand **L1**.

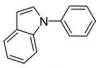
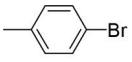
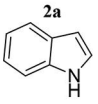
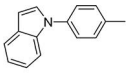
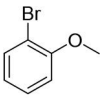
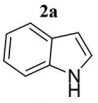
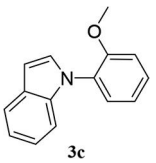
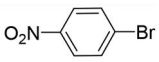
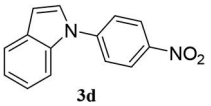
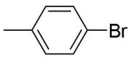
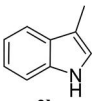
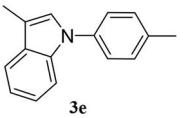


X-Iodo,Bromo

1a: R-H
1b: R-4-Me
1c: R-2OMe
1d: R-NO_2

2a: 1H-indole

2b:3-Methyl-1-H-indole

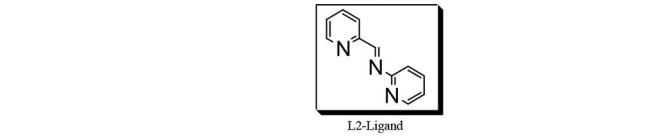
Entry	Aryl halide	Amines	Product	Ligands	Time (h)	Yield (%)[a,b]
1	 1a	 2a	 3a	L1	24	78
2	 1b	 2a	 3b	L1	24	72
3	 1c	 2a	 3c	L1	24	80
4	 1d	 2a	 3d	L1	16	88
5	 1b	 2b	 3e	L1	16	80

[a]Reaction conditions: **Aryl halide** (1.0 mmol), indole (1.2 mmol), CuI (0.1 mmol), Base (2.0 mol), (10 volume) solvent, all reactions are carried at 120 °C temperature.
[b]Results isolated and analyzed on the basis of ($^{13}C/^{1}H$) NMR and LC-MS analysis.

Ligands L2

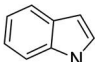
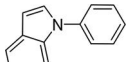
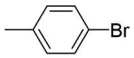
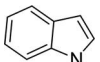
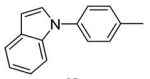
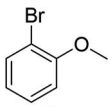
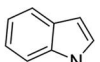
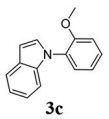
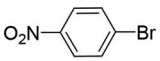
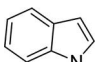
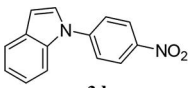
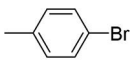
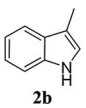
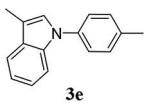
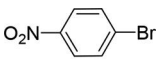
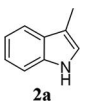
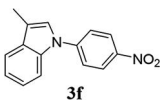
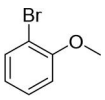
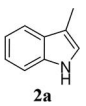
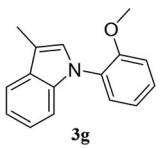
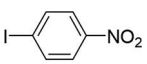
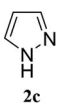
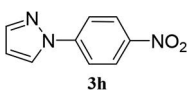
To validate our claim of superiority and sustainability of ligand **L2**, CuI-base-**L2** system has been examined through various reactant derivatives. Ligands **L2** (10 mol %) was screened for *N*-arylation of 1H-indole with aryl halide using CuI (10 mol %), K_2CO_3 in DMSO at 120 °C temperature for 4 and 16 h (Table 4). When ligand **L2** was used for *N*-arylation of 1H-indole, unexpectedly excellent results have been observed in each case (Table 4, Entry 1–5). Entry 1 and 2 in Table 4 showed 97 and 93% yields for C-N coupling reaction in comparatively less reaction time *i.e.*, 4–5 h to that of earlier reports.[38] These increase in reaction yield were probably due to enhanced catalytic effect of CuI-base-**L2** system. Results obtained showed that neutral and electron donating moieties in reactants propagate negligible effect on overall reactivity of reaction in CuI-base-**L2** system which was also

Table 4. Various reaction counterparts to validate accountability of reaction conditions containing CuI-base-**L2** system.



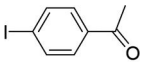
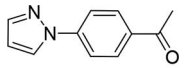
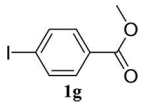
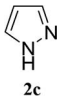
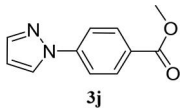
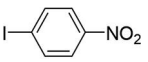
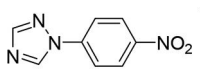
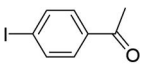
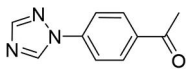
1a: R-H
1b: R-4Me
1c: R-2OMe
1d: R-4NO2
1e: R-4NO2
1f: R-1-(4-iodophenyl)ethanone
1g: R-methyl 4-iodobenzoate

2a:1*H*-indole
2b: 3-methyl-1*H*-indole
2c: 1*H*-pyrazole
2d: 1*H*-1,2,4-triazole

Entry	Aryl halide	Amines	Product	Ligands	Time(h)	Yield (%)[a,b]
1	 **1a**	 **2a**	 **3a**	L2	4	97
2	 **1b**	 **2a**	 **3b**	L2	5	93
3	 **1c**	 **2a**	 **3c**	L2	16	86
4	 **1d**	 **2a**	 **3d**	L2	16	96
5	 **1b**	 **2b**	 **3e**	L2	16	88
6	 **1d**	 **2a**	 **3f**	L2	16	90
7	 **1c**	 **2a**	 **3g**	L2	16	84
8	 **1e**	 **2c**	 **3h**	L2	16	93

(*Continued*)

Table 4. Continued.

Entry	Aryl halide	Amines	Product	Ligands	Time(h)	Yield (%)[a,b]
9	 1f	 2c	 3i	L2	16	97
10	 1g	 2c	 3j	L2	16	89
11	 1e	 2d	 3k	L2	16	97
12	 1f	 2d	 3l	L2	16	93

[a]Reaction condition: **Aryl halide** (1.0 mmol), indole (1.2 mmol), CuI (0.1 mmol), Base (2.0 mol), (10 volume) solvent, all reactions are carried at 120 °C temperature.
[b]Results isolated and analyzed on the basis of (13C/1H) NMR and LC-MS analysis.

shown by 97, 93, 86, and 96% yields of the products (Table 4 Entry 1–4). Similarly to examine nature of different indoles on the overall reaction, reactivity of methyl indole has been studied (Entry 5). About 88% yield in CuI-base-**L2** system has been seen in case of altercation in indole moiety. Entry 6 and 7 showed 90 and 84% yields for electron withdrawing and electron donating reactant moieties (Aryl halide), which clearly point out that catalytic effect of ligand **L2** plays dominant factor over electron withdrawing/donating reactants.

To elaborate present results in the direction of medicinal studies, 1-iodo-4-nitrobenzene, 1-(4-iodophenyl) ethanone and methyl 4-iodo benzoate with 1H-pyrazole were studied in Entry 8–10. The yields of 93, 97, and 89% respectively, proved that CuI-base-**L2** system can be considered as useful prospect in the synthesis of medicinal molecules. In similar approach, 1-iodo-4-nitrobenzene, 1-(4-iodophenyl) ethanone were studied with 1*H*-1,2,4-triazole in Entry 11 and 12 and about 97 and 93% yields were obtained with CuI-base-**L2** system.

From observed results in Table 4, it can be concluded that **L2** ligand can be regarded as more superior ligand as compared to **L1** for C-N coupling reaction. If we carefully observe the structural differences between two ligands **L1** and **L2** (Fig. 1), it can be seen that

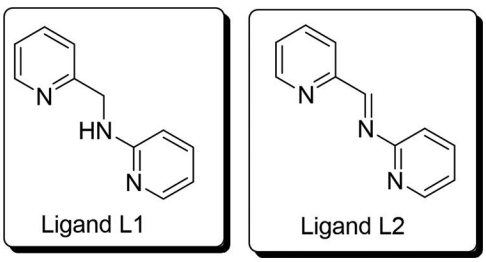


Figure 1. Representative structures of ligands **L1** (*N*-((pyridin-2-yl) methyl) pyridin-2-amine) and **L2** (*N*-((pyridin-2-yl) methylene) pyridin-2-amine).

presence of unsaturation in the structure of ligand **L2** may be playing additional catalyzation by holding metal for longer period and stabilization role for transition state of C-N coupling reaction of various *N*-heterocycles.[25,30]

Conclusions

In conclusion, present reaction methodology containing ligand **L1** and **L2** provided viable option for the synthesis of C-N coupling reaction in terms of yield enhancement effect. Present observations on the basis of C-N coupling reaction can be applicable to various sluggish coupling reactions for enhancement of the yields. Easy reaction methodology and enhancement in yield and economic viability projects the presented two ligands as capable alternative option in organic synthesis.

Experimental

All starting materials were of the highest commercially available grade and used without further purification. All solvents used in the reactions were of good quality. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Compound purified by column chromatography using 100–200 silica gel. ^{13}C and ^{1}H NMR (200 and 400 MHz, respectively) spectra were recorded in $CDCl_3$ and DMSO-d_6. ^{1}H-NMR chemical shifts are reported in ppm (**δ**) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard (CDCl3 and DMSO, **δ** 7.26 and 2.6 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet). ^{13}C-NMR chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (CDCl3, **δ** 77.0 ppm). Chemical yields refer to pure isolated substances.

Synthesis of ligands L1 and L2

Ligand **L1** and **L2** are synthesized in laboratory through economical and simple synthetic procedure.

A typical procedure for the preparation of (N-((pyridin-2-yl) methyl) pyridin-2-amine)

Synthesis procedure of ligand L1:[43c]

For synthesis of ligand **L1**, to a solution of pyridin-2-ylmethanamine (1.2 mmol) in acetonitrile (10 volume), *N,N*-diisopropylethylamine (3 mmol) was added drop-wise which was then followed by addition of 2-bromopyridine (1 mmol) to the reaction mixture. Then reaction mixture was heated at 80 °C temperature for 16 h. Isolated product was then subjected to workup and subsequent purification by column chromatography. The purified product was then used as ligand **L1** in exploration of its activity in catalyzing *N*-arylation reactions.

^{1}HNMR (400 MHz, CDCl3): **δ = 8.57(d, *J* = 4.7 Hz, 1H), 8.01 (dt, 2H), 7.80 (d, *J* = 2.7 Hz 1H), 7.68 (dt, 1H), 7.31(d, *J* = 7.8 Hz, 1H), 7.22(dd, *J* = 7 Hz, 1H), 5.92(s, 1H), 4.67(d, *J* = 4.6 Hz, 2H);** ^{13}C NMR (200 MHz, CDCl3): δ = 157.7, 156.9, 154.3, 148.9, 147.7, 136.6, 133.0, 132.5, 122.2, 121.8, 45.9 ppm; **IR (CHCl3): $\tilde{\nu}_{max}$ = 3391, 3059, 2926, 2854, 1718, 1654, 1638, 1617, 1592, 1524, 1404, 1147, 772 cm^{-1};** HRMS (ESI): m/z: calcd for $C_{11}H_{11}N_3$ $[M+H]^+$: 187.0987; found: 187.0991.

A typical procedure for the preparation N-((pyridin-2-yl) methylene)pyridin-2-amine

Synthesis procedure of ligand L2:[8]

To a solution of picolinaldehyde (3.0 g, 0.028 mmol) in methanol (40 mL) was added pyridin-2-amine (2 .89 g, 0.038 mmol) and catalytic amount of acetic acid. The reaction mixture was stirred at room temperature for 16 h. After consumption of starting material, methanol was removed under reduced pressure and crude product was dissolved in water and product was extracted in EtOAc (3 × 100 mL), separated organic layer was then passed over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford 4.5 g crude L2 ligand.

^{1}HNMR (400 MHz, CDCl3): **δ = 8.78(d, *J* = 5.5 Hz, 1H), 8.61(d, *J* = 4.7 Hz, 1H), 8.02–8.00 (m, 2H), 7.90 (d, *J* = 2.5 Hz, 1H), 7.71 (dt, 1H), 7.44–7.41 (m, 1H), 7.30–7.25 (m, 1H), 6.89 (t, *J* = 7.2 Hz, 1H);** ^{13}C NMR (200 MHz, CDCl3): δ = 157.1, 154.5, 153.1, 150.1, 148.8, 141.7, 137.4, 133.8, 132.8, 127.8, 123.5 ppm; **IR** (CHCl3): $\tilde{\nu}_{max}$ = 3059, 2926, 2854, 1718, 1654, 1638, 1626, 1617, 1592, 1524, 1404, 1147, 772 cm^{-1}; MS (EI, 70 eV): HRMS (ESI): m/z: calcd for $C_{11}H_9N_3$ [M+H]+: 185.0830;found: 185.0833.

A typical procedure for the preparation of 1-phenyl-1H-indole

General coupling procedure: In 50 mL round bottom flask equipped with a septum and magnetic stirrer bar, aryl halide (1.0 mmol), Amine (1.2 mmol), ligand (0.1 mmol), CuI (0.10 mmol), K_2CO_3 (2.0 mmol), and solvent (10 volume) .The mixture was stirred at 120 °C and checked by TLC until the starting material was finished (about 16–24 h). The reaction was cooled down to room temperature, quenched with water (5 mL), and then extracted with EtOAc (10 mL). The crude solution was dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified by column chromatography to afford the desired product.

1-Phenyl-1H-indole (3a).[42a]

The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the target compound **3a** (187.5 mg, 97%) as pale yellow oil.

^{1}HNMR (400 MHz, CDCl3): **δ = 7.70 (d, *J* = 7.8 Hz, 1H,), 7.57 (d, *J* = 7.48 Hz, 1H), 7.51–7.50 (m, 4H), 7.37–7.32 (m, 2H), 7.23(t, *J* = 7.0 Hz, 1H), 7.18 (t, *J* = 6.9 Hz, 1H), 6.68 (d, *J* = 32 Hz, 1H)**; ^{13}C NMR (200 MHz, CDCl3): δ = 137.5, 130.3, 129.6, 129.3, 128.0, 127.5, 126.5, 124.4, 122.4, 122.3, 121.2, 120.4, 110.5, 103.6 ppm; **IR (CHCl3): $\tilde{\nu}_{max}$ = 3053, 2931, 2857, 1598, 1516, 1498, 1457, 1349, 1332, 1234, 1016, 953, 695 cm^{-1};** MS (ESI): M/Z 194 [M+H]$^+$.

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