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CuCl-Catalyzed Hydroxylation of *N*-Heteroarylcarbazole Bromide: Approach for the Preparation of *N*-Heteroarylcarbazolyl Phenols and Its Application in the Synthesis of Phosphorescent Emitters

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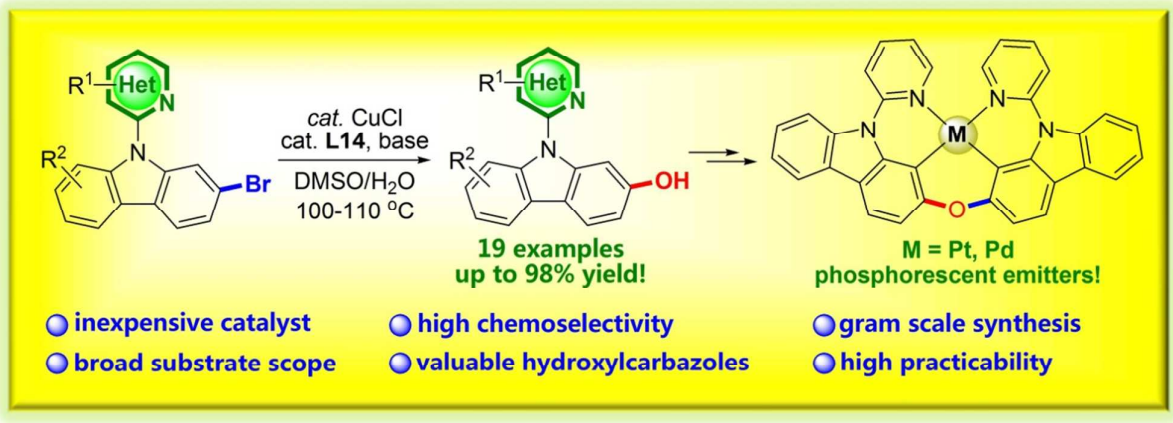


An efficient and practical CuCl-catalyzed hydroxylation of *N*-heteroarylcarbazole bromide for the preparation of *N*-heteroarylcarbazolyl phenols with broad functional group scope and yield up to 98% was developed. It was found that both the ligand and base played critical roles in the functional group transformation, and different products could be generated by changing the base for some substrates. *t*-BuONa was demonstrated to be a better base for the catalytic system to avoid the formation of the ether byproduct. In addition, this approach was suitable for large-scale preparation and was successfully applied in gram-scale synthesis of phosphorescent emitters **PtNON** and **PdNON**, demonstrating its practicability in organic synthesis methodology and material science. Furthermore, X-ray crystal diffraction, DFT calculation and photophysical properties were also investigated for the metal complexes.

■ INTRODUCTION

Hydroxyl carbazoles are very important synthetic intermediates and structural constituents for numerous pharmaceuticals, materials and natural products.[1-7] Moreover, *N*-heteroarylcarbazolyl phenols and their derivatives are wildly utilized in the organic light-emitting diodes (OLEDs) fields, especially, in the synthesis of phosphorescent tetradentate platinum(II) complexes (Figure 1)[8-13], which have attracted significant attention from both academia and industry owing to their promising commercial application for energy efficient full-colour displays and solid-state lighting.[14-17] However, many challenges still remain in the development of such phosphorescent emitters to meet commercial requirements. One of which is the efficient and economical large-scale synthesis of the complexes to promote their further development in OLED technology.

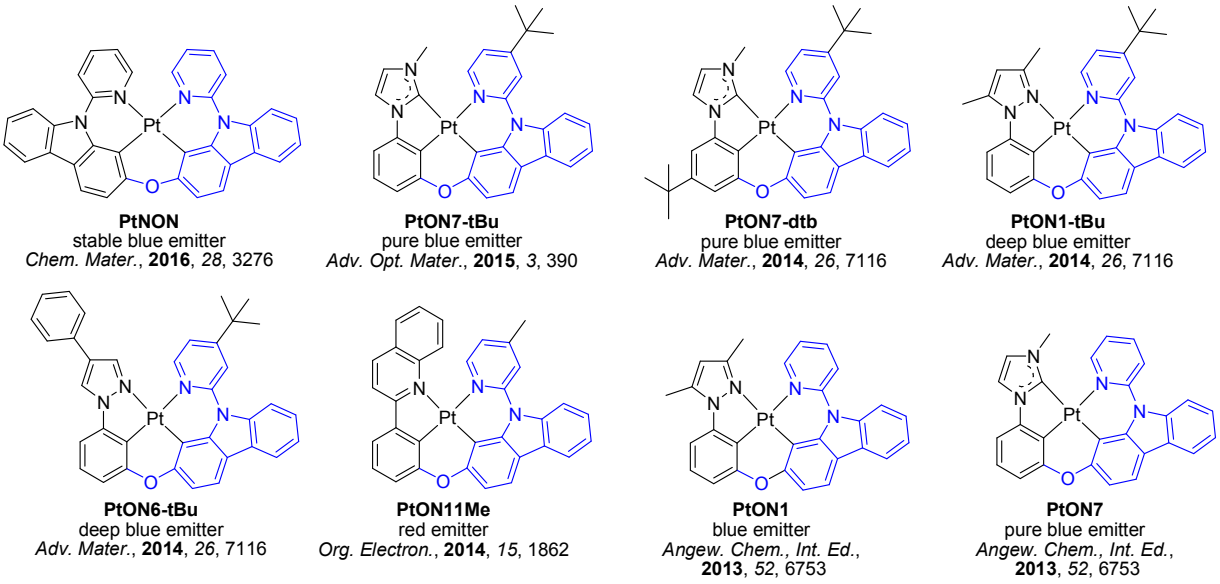


Figure 1. Selected tetradentate platinum-based phosphorescent emitters containing 2-oxy-9-(pyridin-2-yl)-9*H*-carbazole skeleton

Generally, hydroxyl group can be introduced into molecules through nucleophilic substitution of activated aryl halides[18], borylation/oxidation[19-21] or directly hydroxylation of aryl halide. The first two routes usually suffer from substrate limitation or complicated operation process.[22] Thanks to excellent work of Buchwald[23,24], Beller[25,26], You[27], Ma[28-30] and other groups[29,30], remarkable progress has been made for the Pd- and Cu-catalyzed hydroxylation of aryl halide.[31-32] However, the synthetic application of the Pd-catalyzed hydroxylation of aryl halide was limited, particularly for large-scale preparation due to the

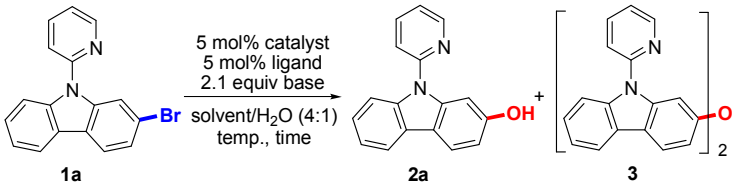
high cost of Pd catalysts and phosphine ligands. Consequently, the development of the Cu-catalyzed hydroxylation attracted plenty of attention, and it had been demonstrated that a variety of bidentate ligands could successfully promote the transformation in recent years.[27-30,34-46] Especially, Ma and co-workers recently developed a CuI-mediated hydroxylation of (hetero)aryl halides under mild conditions promoted by a bis-oxalamide ligand and realized direct hydroxylation of aryl chlorides.[28] In addition, 2-hydroxylcarbazoles could be prepared through intermolecular ring-closure via nitrene intermediate[47], Pd(II)-catalyzed C-H bond activation[48], or Pummerer reaction of sulfinyl compounds[49]. However, to the best of our knowledge, the Cu-catalyzed hydroxylation of *N*-heteroarylcarbazole bromide to synthesis *N*-heteroarylcarbazolyl phenols is not reported.

■ RESULTS AND DISCUSSION

N-heteroarylcarbazolyl phenols are critical intermediates and wildly used for the synthesis of the *N*-(pyridin-2-yl)carbazole based phosphorescent emitters,[8-13] like PtNON[9,50], PtON7-dtb[12], all of which demonstrated inspiring device performances. So far, mainly two synthetic routes were employed to make the *N*-heteroarylcarbazolyl phenols (See Figure S2). One route is to utilize 2-nitroiodobenzene and 4-methoxyphenylboronic acid as starting materials through $Pd(PPh_3)_4$-catalyzed C-C bond coupling, $P(OEt)_3$-promoted cyclization reaction at 165 ^oC, $Pd_2(dba)_3$-induced C-N bond cross-coupling, and demethylation reaction in the presence of excess pyridine hydrochloride at 200 ^oC.[11] The other is via hydroxyl protection of expensive 2-hydroxylcarbazole (about $110/5g), $Pd_2(dba)_3$-catalized C-N bond cross-coupling, and removal of protective group. Both of these routes have many disadvantages, such as the use of expensive Pd catalysts and phosphine ligands, high reaction temperature, or employing expensive starting material, which limited their application in the field of material science. Recently, we developed an efficient and economical approach to synthesize 2-bromo-*N*-heteroarylcarbazole derivatives employing inexpensive CuCl, *N*-methylimidazole and 2-bromocarbazole (about $740/1kg) as catalyst, ligand and starting material respectively.[51] We envision that direct hydroxylation of the

2-bromo-*N*-heteroarylcarbazole derivatives catalyzed by cheap copper salts will benefit to their application in organic synthesis and material field.

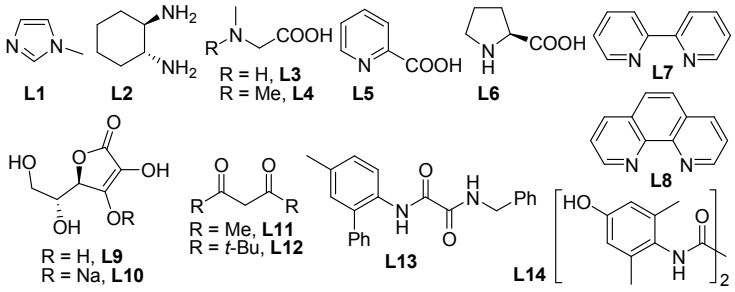
Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3

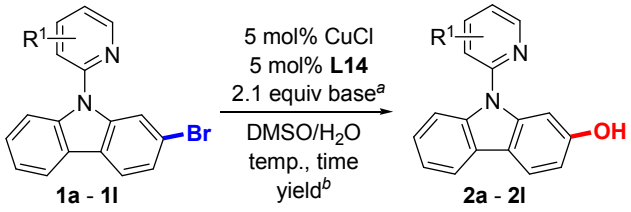
entry[a]	catalyst	ligand[e]	base	solvent	temp.	time	yield[b]/**2a**	yield[b]/**3**
1	CuCl	**L1**	$LiOH·H_2O$	DMSO	100 °C	24 h	NR[c]	
2	CuCl	**L2**	$LiOH·H_2O$	DMSO	100 °C	24 h	NR	
3	CuCl	**L3**	$LiOH·H_2O$	DMSO	100 °C	24 h	NR	
4	CuCl	**L4**	$LiOH·H_2O$	DMSO	100 °C	24 h	NR	
5	CuCl	**L5**	$LiOH·H_2O$	DMSO	100 °C	24 h	NR	
6	CuCl	**L6**	$LiOH·H_2O$	DMSO	100 °C	24 h	NR	
7	CuCl	**L7**	$LiOH·H_2O$	DMSO	100 °C	24 h	NR	
8	CuCl	**L8**	$LiOH·H_2O$	DMSO	100 °C	24 h	NR	
9	CuCl	**L9**	$LiOH·H_2O$	DMSO	100 °C	24 h	NR	
10	CuCl	**L10**	$LiOH·H_2O$	DMSO	100 °C	24 h	NR	
11	CuCl	**L11**	$LiOH·H_2O$	DMSO	100 °C	24 h	NR	
12	CuCl	**L12**	$LiOH·H_2O$	DMSO	100 °C	24 h	NR	
13	CuCl	**L13**	$LiOH·H_2O$	DMSO	100 °C	24 h	NR	
14	CuCl	**L14**	$LiOH·H_2O$	DMSO	100 °C	12 h	79%	trace
15	CuBr	**L14**	$LiOH·H_2O$	DMSO	100 °C	24 h	80%	trace
16	CuI	**L14**	$LiOH·H_2O$	DMSO	100 °C	24 h	80%	trace
17[d]	$Cu(OAc)_2$	**L14**	$LiOH·H_2O$	DMSO	100 °C	48 h	66%	trace
18	$CuSO_4·5H_2O$	**L14**	$LiOH·H_2O$	DMSO	100 °C	24 h	40%	trace
19	CuCl	**L14**	$LiOH·H_2O$	DMF	100 °C	24 h	43%	trace
20	CuCl	**L14**	$LiOH·H_2O$	Dioxane	100 °C	24 h	trace	
21	CuCl	**L14**	NaOH	DMSO	110 °C	24 h	88%	trace
22	CuCl	**L14**	KOH	DMSO	100 °C	24 h	83%	trace
23	CuCl	**L14**	K_3PO_4	DMSO	100 °C	24 h	30%	8%
24	CuCl	**L14**	K_2CO_3	DMSO	100 °C	24 h	25%	6%
25	CuCl	**L14**	Cs_2CO_3	DMSO	100 °C	24 h	65%	8%
26	CuCl	**L14**	*t*-BuOLi	DMSO	100 °C	24 h	88%	
27	CuCl	**L14**	*t*-BuONa	DMSO	100 °C	24 h	95%	
28	CuCl	**L14**	*t*-BuOK	DMSO	110 °C	24 h	92%	
29	CuCl	**L14**	MeONa	DMSO	110 °C	24 h	78%	trace
30	CuCl	**L14**	EtONa	DMSO	110 °C	24 h	88%	

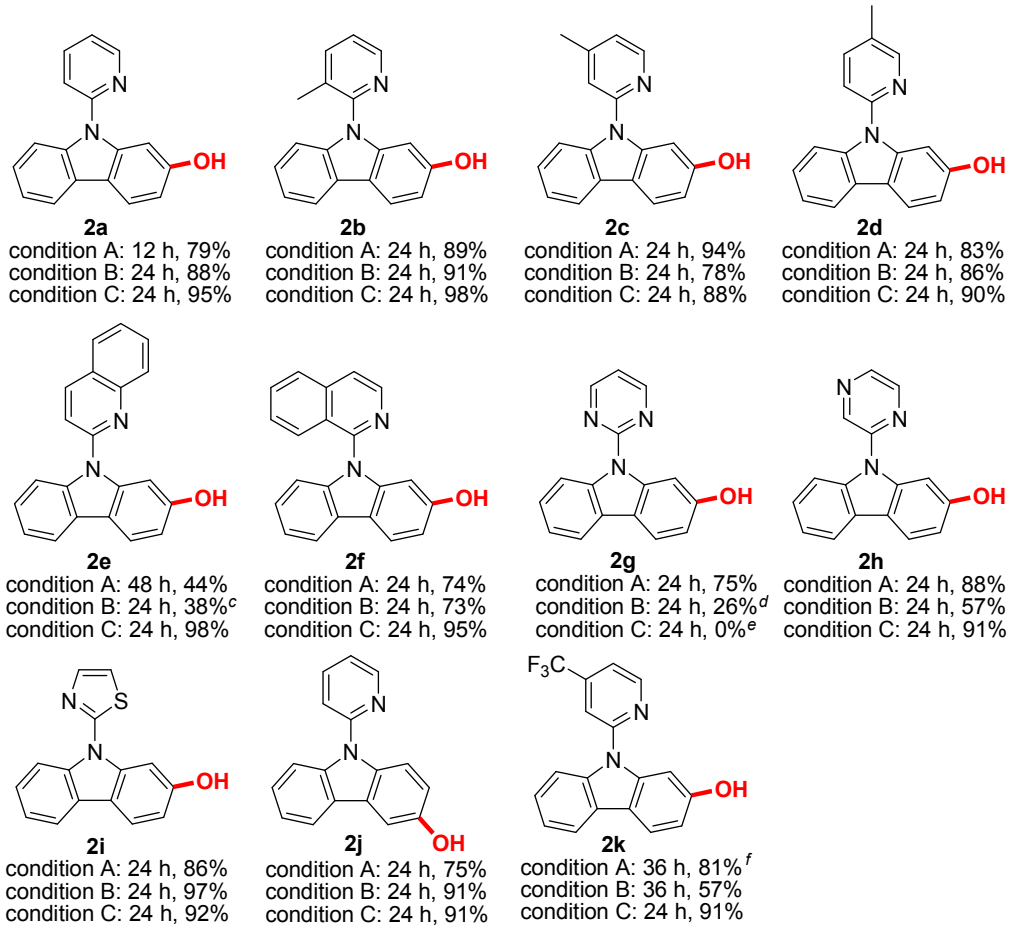
[a]All reactions wre conducted on a scale of 0.5-1.0 mmol unless otherwise noted. [b]Isolated yields after chromatography. [c] NR = no reaction. [d]Reaction was conducted on a scale of 5.0 mmol. [e]



Based on this idea, our initial investigations focused on the substrate of 2-bromo-9-(pyridin-2-yl)-9*H*-carbazole **1a** and catalyst CuCl in a mixture of DMSO and H_2O, where **1a** could be prepared in large-scale without purification through column chromatography according our previous reported method.[51] No reaction was observed employing **L1**, (±)-*trans*-cyclohexane-1,2-diamine **L2**, amino acid **L3** and **L4** as ligands (Table 1, entries 1-4), all of which could effectively promote C-N bond cross-coupling[51-55]. It has been well demonstrated that picolinic acid **L5**[30], *L*-proline **L6**[43], 2,2'-bipyridine **L7**, 1,10-phenanthroline **L8**[27,30], *D*-isoascorbic acid **L9**[41] and its salt **L10**[34,41], 1,3-dione **L11**[46] and **L12**[46] could serve as ligands to promote hydroxylation of aryl halide, to our disappointment, all of them did not work for this transformation (Table 1, entries 5-12), which was owing to the strong coordination ability or the pyridiyl group of the substrate **1a** to lead to deactivation of catalysts. It was encouraging to find that desired product 2-hydroxyl-9-(pyridin-2-yl)-9*H*-carbazole **2a** could be obtained in 79% yield with trace of byproduct Bis[2-(*N*-(2-pyridinyl)carbazolyl)] ether **3** in the presence of 2.1 equiv of $LiOH{\cdot}H_2O$ employing *N*,*N*'-bis(4-hydroxy-2,6-dimethylphenyl)-oxalamide **L14** as ligand, which was developed by Ma's group[28] (Table 1, entry 14). Then, the effects of various copper salts, bases and solvents on the reaction were also investigated. Both CuBr and CuI displayed efficient catalytic activities similar with that of CuCl, while $Cu(OAc)_2$ and $CuSO_4{\cdot}5H_2O$ gave lower yields (Table 1, entries 15-18). **2a** could be obtained in moderate yield if the reaction was carried out in DMF/H_2O, however, nearly no product was obtained using dioxane/H_2O as solvent, due to the poor solubility of **1a** and ligand **L14** in dioxane/H_2O (Table 1, entries 19, 20). Importantly, we found that base also played critical roles in the transformation. Thus, strong bases KOH and MeONa showed similar efficiency with $LiOH{\cdot}H_2O$, however, inexpensive NaOH was superior to $LiOH{\cdot}H_2O$ (Table 1, entries 21, 22 and 29). Notably, exclusive product **2a** could be obtained with high yields of 88-95% employing *t*-BuOLi, *t*-BuONa or *t*-BuOK as base (Table 1, entries 26-28, 30). This is probably due to their stronger ability for the deprotonation of the ligand and the *t*-BuOH in suit to inhibit the coupling of resultant **2a** with **1a**. However, weak bases would induce lower yields with significant byproduct **3** (Table 1, entries 23-25).

Table 2. Substrate Scope of CuCl-Catalyzed Hydroxylation





[a]Condition A: $LiOH{\cdot}H_2O$ as base at 100 °C; condition B: NaOH as base at 110 °C; condition C: *t*-BuONa as base at 110 °C. [b]Isolated yield. [c]20% **1e** was recycled. [d]74% 2-bromocarbazole was obtained. [e]99% 2-bromocarbazole was obtained. [f]At 110 °C.

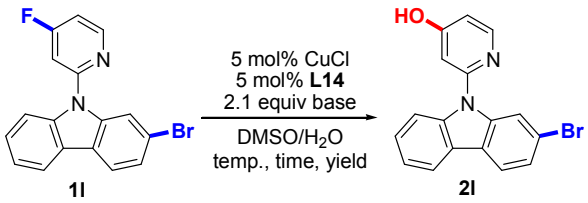
Having the optimized conditions in hand, we next turned our attention to examine the substrate scope of the *N*-heteroarylcarbazole bromide derivatives. The cheaper CuCl catalyst and the bis-oxalamide ligand **L14** were used with three different bases, $LiOH{\cdot}H_2O$, NaOH, and *t*-BuONa (Table 2). To our delight, electron-donating group -Me could be well tolerated, whether it was on 3-, 4- or 5-position of pyridyl ring, and desired products **2b-2d** could be achieved in high yields of 78-98%. For the substrate of

2-bromo-9-(quinolin-2-yl)-9*H*-carbazole **1e**, only 44% and 38% yields were obtained using $LiOH{\cdot}H_2O$ and NaOH as base respectively, however, *t*-BuONa enabled the hydroxylation to undergo smoothly to give **2e** with 98% yield. Similar result was also observed for substrate containing 1-isoquinolinyl group **1f**, and *t*-BuONa was proved to be a better base to give **2f** in 95% yield. For pyrimidine-based substrate **1g**, to our surprise, strong base *t*-BuONa would induce it to decompose completely, which involved nucleophilic substitution on 1-position of pyrimidine, and 2-bromocarbazole was separated in quantitative yield. However, desired product **2g** could be obtained in 75% employing $LiOH{\cdot}H_2O$ as base. Gratifyingly, incorporating other heteroaryl group, such as 2-pyrazinyl or 2-thiazolyl, into substrates also generated desired product **2h** and **2i** in excellent yields except adopting NaOH as base for **1h**. Furthermore, substrate bearing a bromide on 3-position of carbazole ring or a strong electron-withdrawing group $-CF_3$ on 4-position of pyridyl ring could also be hydroxylated efficiently to give **2j** or **2k** in high yields within expectations. Importantly, these obtained *N*-heteroarylcarbazol-2-ol derivatives can be as key intermediates for synthesis of platinum- and palladium-based phosphorescent materials, and provide various modified tetradentate ligands, which enable the materials to have tunable photophysical properties.[8-13,15,17]

Given the above encouraging results, substrates with two halides were also explored. We were pleased to see that this CuCl-based catalytic system also worked well for various *N*-heteroarylcarbazole derivatives bearing two halides on heteroaryl or carbazolyl rings (Scheme 1). For example, 2-bromo-9-(4-fluoropyridin-2-yl)-9*H*-carbazole **1l** could be selectively hydroxylated from fluorine to form **2l** remaining bromide unchanged with $LiOH{\cdot}H_2O$ or *t*-BuONa as base in 27% and 55% yields respectively (eqs 1,2). Similar chemoselectivity was also observed for the chlorine substrate **1m** and 72% of **2l** was obtained using NaOH as base. It is worth mentioning that **2l** could be also separated in 50% yield without CuCl and **L14**, indicating that this reaction was involvement of nucleophilic substitution mechanism, owing to high activity of the chlorine on the 4-position of the pyridyl ring (eq 3). Interestingly, the remaining bromide of **2l** could be further hydroxylated to give **4a** in 69% in the presence of 4.2 equiv *t*-BuONa (eq 3). These reactions demonstrated that the

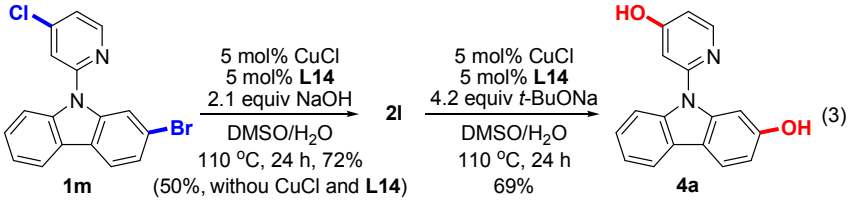
halides on the substrates could be hydroxylated separately through reaction condition control, making the functional group transformations to be more useful in organic synthesis. Furthermore, both bromides could be hydroxylated for **1n** in the presence of 10 mol% CuCl, 10 mol% **L14** and 4.2 equiv *t*-BuONa to give 63% of **4b** (eq 5). Interestingly, symmetric substrate **1o** could be also selectively hydroxylated through controlling the strength of the base to afford 2-hydroxyl product **2m** with $LiOH{\cdot}H_2O$ and 2,7-dihydroxyl product **4c** was not observed even reaction time was prolonged to 48 h (eq 6). However, **4c** could be formed using *t*-BuONa as base in 81% yield (eq 8). It is worth pointing out that the conversion of 2,7-dibromo-9-(pyrimidin-2-yl)-9*H*-carbazole **1p** could undergo smoothly with $LiOH{\cdot}H_2O$ as base to form 62% of 2,7-dihydroxyl product **4d** (eq 9), whose chemoselectivity was much different with **1o**. These results revealed that the reaction was influenced significantly by the nature of the substrates, and the choice of base was also critical to the successful transformation.

Scheme 1. CuCl-Catalyzed Selective Hydroxylation



Condition A: LiOH·H_2O, 100 °C, 24 h; **2l**, 27% (1)

Condition C: *t*-BuONa, 110 °C, 24 h; **2l**, 55% (2)



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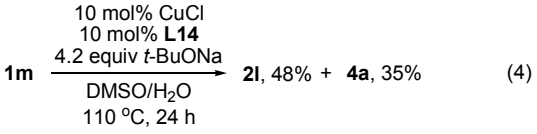

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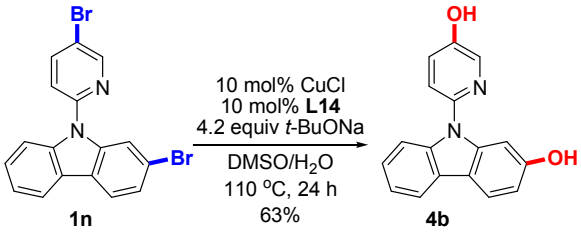
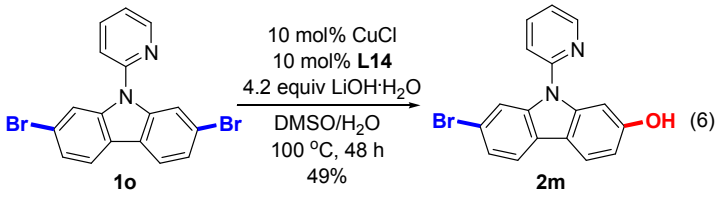
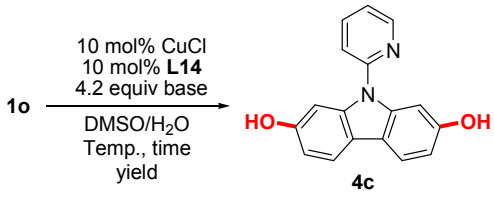


(5)

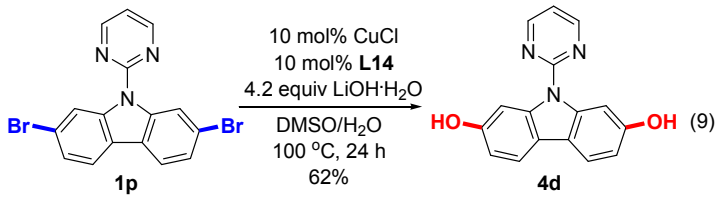


(6)



Condition B, NaOH, 110 °C, 24 h; **4c**, 24% (7)

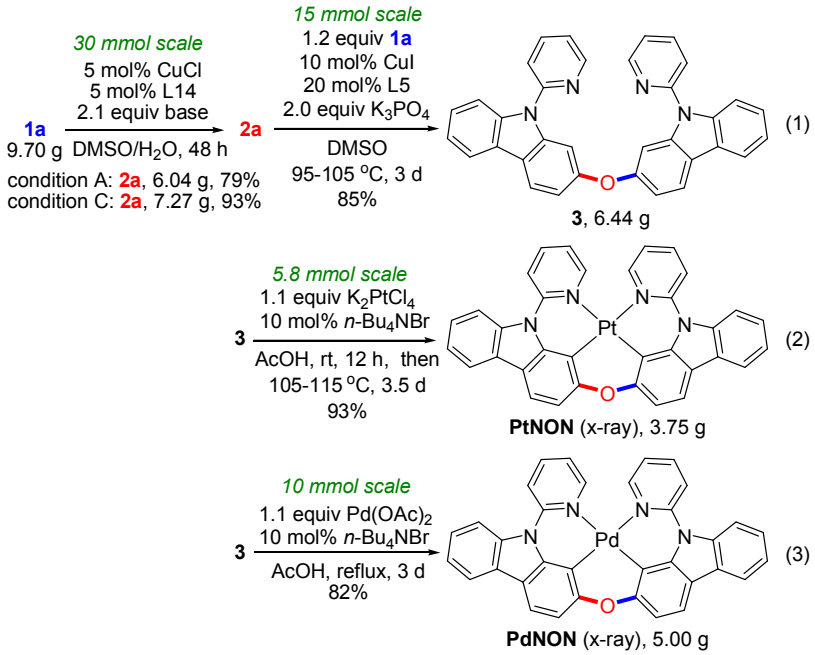
Condition C, *t*-BuONa, 110 °C, 24 h; **4c**, 81% (8)



(9)

To further demonstrate the practical utility of this protocol, gram-scale experiment was carried out under the optimized conditions to give **2a** in good to excellent yields (Scheme 2, eq 1), which was greatly superior to the previously reported route[50] (see Figure S2). Moreover, **PtNON**, a highly stable and efficient platinum-based phosphorescent emitter with sky blue emission[9], was effectively prepared via metallization with K_2PtCl_4 in gram-scale (3.75 g, eq 2) with a total yield of 64% for four steps from inexpensive 2-bromocarbazole (see Figure S2). which could provide a practical method for the synthesis of **PtNON** and benefit its application in OLED field. More importantly, a new palladium-based phosphorescent emitter **PdNON** was also synthesized concisely in gram-scale (5.00 g, eq 3), indicating the CuCl-catalyzed hydroxylation reaction would be useful in material science.

Scheme 2. Large-Scale Synthesis and Its Application



The molecular structures of both **PtNON** and **PdNON** were confirmed through single-crystal X-ray diffraction analysis (Figures 2). And B3LYP density functional theory (DFT) calculations were also performed using the Titan software package[56] (wave function, Inc.) at the LACVP**[56,57,] level to gain insightful understanding of the nature of transitions of the complexes. A similar theoretical approach had been utilized to investigate the optimized molecular geometry, ground and excited states properties for Pt(II) complexes.[56,57] And the bond lengths and angles from

DFT calculations matched well with these of the X-ray data (Table 3). It should be noted that the change of the central metal ion did not affect their bond lengths and angles significantly except the bond angle of **PtNON** (163.99°) was larger than that of **PdNON** (160.6°). Importantly, both complexes exhibited significant distortion from planarity on the carbazole section of the ligand, to accommodate square planar coordination to the metal, which can be prove by the bond angles of N1-Pt1(Pd1)-C1 and C1-Pt1(Pd1)-N4. These nonplanar structures of molecules could prevent the formation of excimers, which would benefit to their applications as blue phosphorescent emitters in display and lighting fields. In addition, the HOMO and LUMO orbitals for **PtNON** and **PdNON** were also shown in Figure 3. Their HOMO consisted of a mixture of localized carbazolyl-π and Pt-d orbitals, while their LUMO predominantly occupied on the pyridyl-π orbitals with very little metal orbital character. These indicated that the transitions could be assigned as a mixed state involving metal to ligand charge transfer (MLCT) and ligand centered charge transfer (LC).

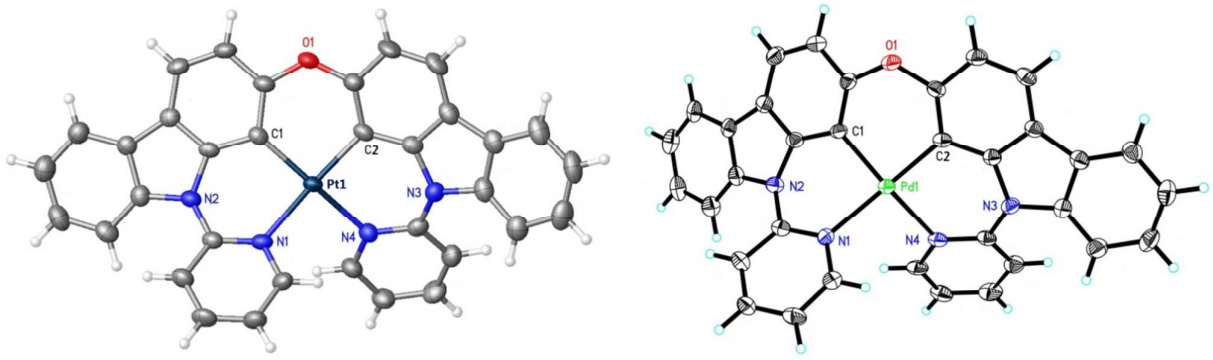


Figure 2. X-ray molecular structures of **PtNON** and **PdNON**. Ellipsoids are shown at the 50% probability level.

Table 3: Selected bond lengths and angles for **PtNON** and **PdNON** based on the DFT calculation and X-ray crystallographic analysis.

	PtNON		**PdNON**	
	calculation	X-ray	calculation	X-ray
Pt1(Pd1)-N1	2.19 Å	2.121 Å	2.20 Å	2.120 Å
Pt1(Pd1)-C1	1.99 Å	1.974 Å	1.99 Å	1.976 Å
Pt1(Pd1)-C2	1.99 Å	1.984 Å	1.99 Å	1.973 Å
Pt1(Pd1)-N4	2.19 Å	2.115 Å	2.19 Å	2.127 Å
N1-Pt1(Pd1)-C1	87.08°	90.50°	87.35°	89.7°
C1-Pt1(Pd1)-C2	94.61°	91.8°	92.51°	90.5°
C2-Pt1(Pd1)-N4	88.26°	90.29°	89.92°	91.4°
N1-Pt1(Pd1)-N4	93.83°	90.10°	94.50°	93.6°
N1-Pt1(Pd1)-C1	163.65°	163.20°	163.57°	164.4°
C1-Pt1(Pd1)-N4	166.68°	163.99°	164.84°	160.6°

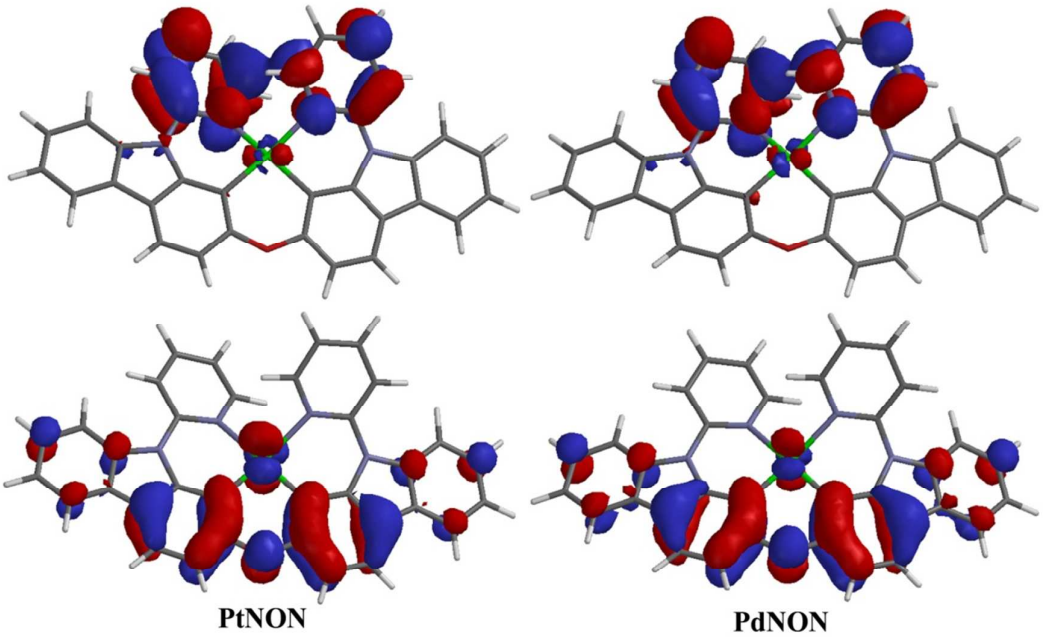


Figure 3. Calculated orbital density for the HOMO (down) and LUMO (up) of **PtNON** and **PdNON** at their optimized S_0 geometries.

The photophysical property of **PdNON** was also investigated and compared with that of **PtNON**[9] (Figure 4). **PdNON** exhibits a structured emission spectrum similar with that of

PtNON at 77K, but has a higher triplet state energy with dominant emission peak at 436 nm (438 nm for **PtNON**). However, **PdNON** has a Gaussian type emission spectrum peaking at 492 nm and a significant blue-shift of 16 nm comparing with that of **PtNON** peaking at 508 nm. This will provide an important approach to tune triplet energies and emission colours of phosphorescent complexes through central metal ion control, which is critical for the development of blue phosphorescent emitters.

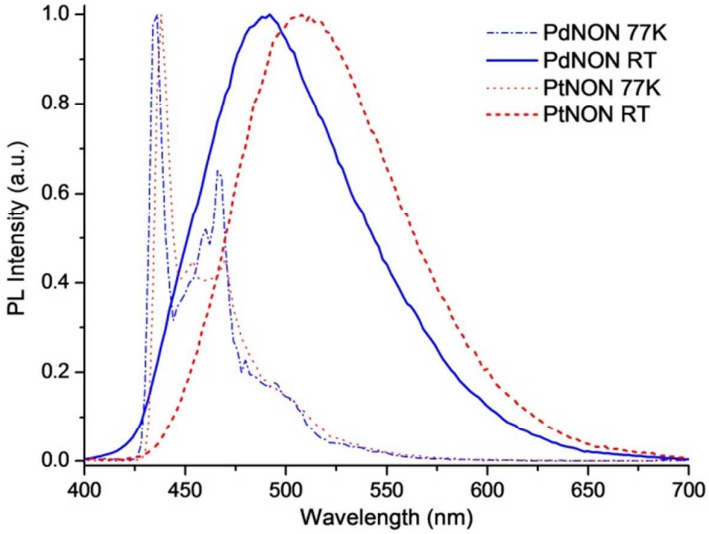


Figure 4. Photoluminescence spectra of **PdNON** and **PtNON** at 77K in 2-Me-THF and at room temperature in CH_2Cl_2.

■ CONCLUSION

In conclusion, we have realized an efficient and practical CuCl-catalyzed hydroxylation of *N*-heteroarylcarbazole bromides in up to 98% yield. It was found that both ligand and base were critical to this functional group transformation. t-BuONa was demonstrated to be a better base for the catalytic system to avoid the formation of the ether byproduct. Moreover, dihalide substrates could be hydroxylated separately or simultaneously through reaction condition control. Furthermore, this practical method was suitable for large-scale preparation, and was successfully applied in the gram-scale synthesis of phosphorescent emitters **PtNON** and **PdNON**, demonstrating its practicability in material science. Furthermore, the molecular structures of the metal complexes were confirmed by the X-ray crystal diffraction analysis, DFT calculation and photophysical properties were also investigated.

■ EXPERIMENTAL SECTION

General Information. ^{1}H NMR spectra were recorded at 400 or 500 MHz, and ^{13}C NMR spectra were recorded at 100 or 126 MHz NMR instruments in $CDCl_3$ or DMSO-d_6 solutions and chemical shifts were referenced to tetramethylsilane (TMS) or residual protiated solvent. If $CDCl_3$ was used as solvent, ^{1}H NMR spectra were recorded with TMS (δ = 0.00 ppm) as internal reference; ^{13}C NMR spectra were recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference. If DMSO-d_6 was used as solvent, ^{1}H NMR spectra were recorded with TMS (δ = 0.00 ppm) or residual H_2O (δ = 3.33 ppm) as internal reference; ^{13}C NMR spectra were recorded with DMSO-d_6 (δ = 39.52 ppm) as internal reference. All of the new compounds were analyzed for HRMS on an ESI-QTOF mass spectrometer using electrospray ionization in positive ion mode. Steady state emission experiments were performed on a Horiba Jobin Yvon FluoroLog-3 spectrometer. The following abbreviations (or combinations thereof) were used to explain ^{1}H NMR ultiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet, br = broad. Mass spectra were recorded on Voyager DE-STR MALDI-TOF mass spectrometer from Applied Biosystems. The Microanalysis Laboratory at Shanghai Institute of Organic Chemistry performed the elemental analysis. B3LYP density functional theory (DFT) calculations were performed using the Titan software package[56] (wave function, Inc.) at the LACVP**[56,57] level for DFT calculations.

General Experimental Procedure for Hydroxylation of 2-Bromo-9-(pyridin-2-yl)-9*H*-carbazole and Its Analogues. 2-Bromo-9-(pyridin-2-yl)-9*H*-carbazole or its analogues, CuCl, ligand and base were added to a dry Schlenk tube equipped with a magnetic stir bar. The tube was then evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then DMSO and H_2O were added into the tube under nitrogen atmosphere. The tube was placed in oil bath (100 or 110 ^{0}C) and stirred for 12-48 h until the starting material was consumed completely monitoring by TLC. Then the mixture was cooled down, diluted with ethyl acetate. The organic layer was then separated, and aqueous layer was extracted with ethyl acetate three times. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford the desired product (Unless other notes, Condition A: $LiOH{\cdot}H_2O$ as base at 100 ^{o}C; Condition B: NaOH as base at 110 ^{o}C; Condition C: *t*-BuONa as base at 110 ^{o}C).

9-(Pyridin-2-yl)-9*H*-carbazol-2-ol (**2a**):

Condition A: Following the general procedure, the reaction of **1a** (323.2 mg, 1.00 mmol, 1.0 eq), CuCl (5.0 mg, 0.05 mmol, 0.05 eq), ligand **L14** (16.4 mg, 0.05 mmol, 0.05 eq) and $LiOH{\cdot}H_2O$ (88.1 mg, 2.1 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 100 ^oC for 12 hours afforded **2a** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 206.9 mg in 79% yield.

Condition B: Following the general procedure, the reaction of **1a** (161.1 mg, 0.5 mmol, 1.0 eq), CuCl (2.5 mg, 0.03 mmol, 0.05 eq), ligand **L14** (8.2 mg, 0.03 mmol, 0.05 eq) and NaOH (42.0 mg, 1.1 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 24 hours afforded **2a** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 114.5 mg in 88% yield.

Condition C: Following the general procedure, the reaction of **1a** (161.1 mg, 0.5 mmol, 1.0 eq), CuCl (2.5 mg, 0.03 mmol, 0.05 eq), ligand **L14** (8.2 mg, 0.03 mmol, 0.05 eq) and *t*-BuONa (100.9 mg, 1.1 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 24 hours afforded **2a** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 123.5 mg in 95% yield.

mp: 191.1-192.4 ^oC. ^1H NMR (500 MHz, DMSO-d_6): δ 6.79 (dd, J = 8.5, 2.0 Hz, 1H), 7.18 (d, J = 2.0 Hz, 1H), 7.23-7.26 (m, 1H), 7.32 (td, J = 8.5, 1.0 Hz, 1H), 7.47 (ddd, J = 7.5, 5.0, 1.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.99 (d, J = 8.5 Hz, 1H), 8.06 (d, J = 7.5 Hz, 1H), 8.11 (td, J = 8.0, 2.0 Hz, 1H), 8.72 (ddd, J = 5.0, 2.0, 0.5 Hz, 1H), 9.61 (s, 1H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 97.1, 110.3, 110.8, 115.9, 119.0, 119.1, 120.78, 121.1, 121.8, 124.0, 124.5, 138.8, 139.3, 140.5, 149.5, 150.9, 157.0. HRMS (ESI): calcd for $C_{17}H_{13}N_2O$ $[M + H]^+$ 261.1022, found 261.1028.

9-(3-Methypyridin-2-yl)-9*H*-carbazol-2-ol (**2b**):

Condition A: Following the general procedure, the reaction of **1b** (337.2 mg, 1.00 mmol, 1.0 eq), CuCl (5.0 mg, 0.05 mmol, 0.05 eq), ligand **L14** (16.4 mg, 0.05 mmol, 0.05 eq) and $LiOH{\cdot}H_2O$ (88.1 mg, 2.1 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 100 ^oC for 24 hours afforded **2b** (eluent: petroleum ether/ethyl acetate = 10:1-3:1) as a brown solid 245.2 mg in 89% yield.

Condition B: Following the general procedure, the reaction of **1b** (84.3 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.01 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.01 mmol, 0.05 eq) and NaOH (21.0 mg, 0.53 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 24 hours afforded **2b** (eluent:

petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 65.2 mg in 91% yield.

Condition C: Following the general procedure, the reaction of **1b** (212.9 mg, 0.63 mmol, 1.0 eq), CuCl (3.1 mg, 0.03 mmol, 0.05 eq), ligand **L14** (10.3 mg, 0.03 mmol, 0.05 eq) and *t*-BuONa (127.1 mg, 1.32 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 24 hours afforded **2b** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 168.9 mg in 98% yield.

mp: 242.8-244.4 ^oC. ^1H NMR (500 MHz, DMSO-d_6): δ 2.01 (s, 3H), 6.38 (d, J = 2.0 Hz, 1H), 6.74 (dd, J = 8.5, 2.5 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 7.21 (td, J = 7.5, 1.0 Hz, 1H), 7.27 (td, J = 7.0, 1.0 Hz, 1H), 7.57 (dd, J = 8.0, 5.0 Hz, 1H), 8.00 (d, J = 8.5 Hz, 1H), 8.04-8.07 (m, 2H), 8.57 (dd, J = 4.5, 1.0 Hz, 1H), 9.50 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 16.9, 95.8, 109.6, 109.8, 115.1, 119.4, 112.0, 121.4, 123.2, 124.2, 124.4, 131.0, 139.6, 141.0, 141.4, 147.8, 148.8, 157.0. HRMS (ESI): calcd for $C_{18}H_{15}N_2O$ $[M + H]^+$ 275.1179, found 275.1191.

9-(4-Methypyridin-2-yl)-9*H*-carbazol-2-ol (**2c**):

Condition A: Following the general procedure, the reaction of **1c** (337.2 mg, 1.00 mmol, 1.0 eq), CuCl (5.0 mg, 0.05 mmol, 0.05 eq), ligand **L14** (16.4 mg, 0.05 mmol, 0.05 eq) and LiOH·H_2O (88.1 mg, 2.1 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 100 ^oC for 24 hours afforded **2c** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 258.4 mg in 94% yield.

Condition B: Following the general procedure, the reaction of **1c** (84.3 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.01 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.01 mmol, 0.05 eq) and NaOH (21.0 mg, 0.53 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 24 hours afforded **2c** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 53.8 mg in 78% yield.

Condition C: Following the general procedure, the reaction of **1c** (210.0 mg, 0.62 mmol, 1.0 eq), CuCl (3.1 mg, 0.03 mmol, 0.05 eq), ligand **L14** (10.2 mg, 0.03 mmol, 0.05 eq) and *t*-BuONa (124.9 mg, 1.30 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 24 hours afforded **2c** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 150.1 mg in 88% yield.

mp: 178.4-179.2 ^oC. ^1H NMR (500 MHz, DMSO-d_6): δ 2.48 (s, 3H), 6.78 (dd, J = 8.5, 2.0 Hz, 1H), 7.16 (d, J = 2.0 Hz, 1H), 7.23-7.26 (m, 1H), 7.30-7.33 (m, 2H), 7.57 (s, 1H), 7.68 (d, J = 8.5 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 7.5 Hz, 1H), 8.57 (d, J = 5.0 Hz, 1H), 9.59 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 20.7, 97.2, 110.3, 110.9, 115.8, 119.2, 119.5, 120.7, 121.1, 122.9, 124.0,

124.5, 138.9, 140.6, 149.1, 150.5, 151.0, 157.0. HRMS (ESI): calcd for $C_{18}H_{15}N_2O$ $[M + H]^+$ 275.1179, found 275.1190.

9-(5-Methypyridin-2-yl)-9*H*-carbazol-2-ol (**2d**):

Condition A: Following the general procedure, the reaction of **1d** (337.2 mg, 1.00 mmol, 1.0 eq), CuCl (5.0 mg, 0.05 mmol, 0.05 eq), ligand **L14** (16.4 mg, 0.05 mmol, 0.05 eq) and $LiOH·H_2O$ (88.1 mg, 2.1 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 100 ^oC for 24 hours afforded **2d** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 226.6 mg in 83% yield.

Condition B: Following the general procedure, the reaction of **1d** (55.7 mg, 0.17 mmol, 1.0 eq), CuCl (0.8 mg, 0.01 mmol, 0.05 eq), ligand **L14** (2.6 mg, 0.01 mmol, 0.05 eq) and NaOH (13.9 mg, 0.35 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 24 hours afforded **2d** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 39.0 mg in 86% yield.

Condition C: Following the general procedure, the reaction of **1d** (183.2 mg, 0.54 mmol, 1.0 eq), CuCl (2.7 mg, 0.03 mmol, 0.05 eq), ligand **L14** (8.9 mg, 0.03 mmol, 0.05 eq) and *t*-BuONa (109.0 mg, 1.13 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 24 hours afforded **2d** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 133.9 mg in 90% yield.

mp: 201.3-202.6 ^oC. ^1H NMR (500 MHz, DMSO-d_6): δ 2.43 (s, 3H), 6.77 (dd, J = 8.0, 2.0 Hz, 1H), 7.10 (d, J = 2.0 Hz, 1H), 7.22-7.25 (m, 1H), 7.29-7.32 (m, 1H), 7.62-7.64 (m, 2H), 7.93 (ddd, J = 8.5, 2.5, 0.5 Hz, 1H), 7.98 (d, J = 8.5 Hz, 1H), 8.04-8.06 (m, 1H), 8.55 (dd, J = 2.0, 1.0 Hz, 1H), 9.59 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 17.5, 97.0, 110.2, 110.7, 115.8, 118.6, 119.2, 120.6, 121.1, 123.9, 124.5, 131.3, 139.0, 139.6, 140.7, 148.6, 149.5, 157.0. HRMS (ESI): calcd for $C_{18}H_{15}N_2O$ $[M + H]^+$ 275.1179, found 275.1180.

9- (Quinolin-2-yl)-9*H*-carbazol-2-ol (**2e**):

Condition A: Following the general procedure, the reaction of **1e** (93.3 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.013 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and $LiOH·H_2O$ (22.0 mg, 0.53 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 100 ^oC for 48 hours afforded **2e** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 33.8 mg in 44% yield.

Condition B: Following the general procedure, the reaction of **1e** (93.3 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.013 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and NaOH (21.0 mg, 0.53

mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 24 hours afforded **2e** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 29.4 mg in 38% yield and **1e** was recycled 18.5 mg in 20% yield.

Condition C: Following the general procedure, the reaction of **1e** (93.3 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.013 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and *t*-BuONa (50.5 mg, 0.53 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 24 hours afforded **2e** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 76.4 mg in 98% yield.

mp: 217.3- 218.7 ^oC. ^1H NMR (500 MHz, DMSO-d_6): δ 6.83 (dd, J = 8.5, 2.0 Hz, 1H), 7.28-7.31 (m, 1H), 7.37 (td, J = 8.0, 1.0 Hz, 1H), 7.40 (d, J = 2.0 Hz, 1H), 7.67-7.70 (m, 1H), 7.86-7.89 (m, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.5 Hz, 1H), 8.03 (d, J = 8.5 Hz, 1H), 8.09 (t, J = 8.5 Hz, 2H), 8.12-8.13 (m, 1H), 8.66 (d, J = 8.5 Hz, 1H), 9.67 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 97.7, 110.7, 111.3, 116.2, 117.7, 119.3, 121.2, 121.3, 124.4, 124.7, 126.3, 126.5, 128.1(2C), 130.6,138.8, 139.5, 140.5, 147.0, 150.4, 157.2. HRMS (ESI): calcd for $C_{21}H_{15}N_2O$ $[M + H]^+$ 311.1179, found 311.1170.

9- (Isoquinolin-2-yl)-9*H*-carbazol-2-ol (**2f**):

Condition A: Following the general procedure, the reaction of **1f** (186.6 mg, 0.50 mmol, 1.0 eq), CuCl (2.5 mg, 0.025 mmol, 0.05 eq), ligand **L14** (8.2 mg, 0.025 mmol, 0.05 eq) and $LiOH{\cdot}H_2O$ (44.1 mg, 1.05 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 100 ^oC for 24 hours afforded **2f** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 114.5 mg in 74% yield.

Condition B: Following the general procedure, the reaction of **1f** (93.3 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.013 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and NaOH (21.0 mg, 0.53 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 24 hours afforded **2f** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 56.3 mg in 73% yield.

Condition C: Following the general procedure, the reaction of **1f** (186.6 mg, 0.50 mmol, 1.0 eq), CuCl (2.5 mg, 0.025 mmol, 0.05 eq), ligand **L14** (8.2 mg, 0.025 mmol, 0.05 eq) and *t*-BuONa (100.9 mg, 1.05 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 24 hours afforded **2f** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 147.9 mg in 95% yield.

mp: 247.5-248.2 ^oC. ^1H NMR (500 MHz, DMSO-d_6): δ 6.37 (d, J = 2.0 Hz, 1H), 6.78 (dd, J = 8.5,

2.0 Hz, 1H), 6.96-6.98 (m, 1H), 7.21-7.26 (m, 2H), 7.48 (d, J = 7.5 Hz, 1H), 7.62-7.66 (m, 1H), 7.88-7.92 (m, 1H), 8.06 (d, J = 8.0 Hz, 1H), 8.12-8.13 (m, 2H), 8.23 (d, J = 8.0 Hz, 1H), 8.66 (d, J = 5.5 Hz, 1H), 9.49 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 96.4, 110.1, 110.4, 115.5, 119.4, 120.4, 121.5, 121.8, 123.6, 124.4, 124.4, 124.8, 127.6, 128.7, 131.4, 138.3, 140.8, 142.2, 142.4, 149.3, 157.0. HRMS (ESI): calcd for $C_{21}H_{15}N_2O$ $[M + H]^+$ 311.1179, found 311.1186.

9- (Pyrimidin-2-yl)-9*H*-carbazol-2-ol (**2g**):

Condition A: Following the general procedure, the reaction of **1g** (54.3 mg, 0.17 mmol, 1.0 eq), CuCl (0.8 mg, 0.008 mmol, 0.05 eq), ligand **L14** (2.8 mg, 0.008 mmol, 0.05 eq) and $LiOH{\cdot}H_2O$ (15.0 mg, 0.36 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 100 ^{o}C for 24 hours afforded **2g** (eluent: petroleum ether/ethyl acetate = 5:1-1:1) as a brown solid 33.2 mg in 75% yield.

Condition B: Following the general procedure, the reaction of **1g** (81.0 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.013 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and NaOH (21.0 mg, 0.53 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^{o}C for 24 hours using petroleum ether/ethyl acetate = 5:1-3:1 as eluent afforded 2-bromocarbazole 46.6 mg in 74% yield and **2g** as a brown solid 17.1 mg in 26% yield.

Condition C: Following the general procedure, the reaction of **1g** (81.0 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.013 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and *t*-BuONa (50.5 mg, 0.53 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^{o}C for 24 hours afforded 2-bromocarbazole (eluent: petroleum ether/ethyl acetate = 5:1-3:1) 61.7 mg in 99% yield.

2g: mp: 157.1-158.8 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 6.85 (dd, J = 8.0, 2.0 Hz, 1H), 7.32 (td, J = 7.5, 1.0 Hz, 1H), 7.37-7.40 (m, 1H), 7.41 (t, J = 4.5, 1H), 7.98 (d, J = 8.5 Hz, 1H), 8.05 (dd, J = 7.5, 0.5 Hz, 1H), 8.25 (d, J = 2.0 Hz, 1H), 8.72 (d, J = 8.0 Hz, 1H), 8.99 (d, J = 4.5 Hz, 2H), 9.69 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 102.5, 111.3, 115.9, 116.9, 117.2, 118.7, 120.5, 122.3, 124.9, 125.5, 138.3, 139.9, 157.2, 158.3, 158.6 (2C). HRMS (ESI): calcd for $C_{16}H_{12}N_3O$ $[M + H]^+$ 262.0975, found 262.0977. **2-Bromocarbazole**: ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.17-7.20 (m, 1H), 7.29 (dd, J = 8.5, 2.0 Hz, 1H), 7.40-7.43 (m, 1H), 7.51 (d, J = 8.5 Hz, 1H), 7.67 (d, J = 2.0 Hz, 1H), 8.07 (d, J = 8.5 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H), 11.40 (s, 1H). The structure was confirmed by comparison of ^{1}H NMR spectrum with that of purchased sample.

9- (Pyrazin-2-yl)-9*H*-carbazol-2-ol (**2h**):

Condition A: Following the general procedure, the reaction of **1h** (54.3 mg, 0.17 mmol, 1.0 eq), CuCl (0.8 mg, 0.008 mmol, 0.05 eq), ligand **L14** (2.8 mg, 0.008 mmol, 0.05 eq) and $LiOH{\cdot}H_2O$ (15.0 mg, 0.36 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 100 ^oC for 24 hours afforded **2h** (eluent: petroleum ether/ethyl acetate = 5:1-1:1) as a brown solid 39.2 mg in 88% yield.

Condition B: Following the general procedure, the reaction of **1h** (81.0 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.013 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and NaOH (21.0 mg, 0.53 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 24 hours afforded **2h** (eluent: petroleum ether/ethyl acetate = 5:1-1:1) as a brown solid 37.7 mg in 57% yield.

Condition C: Following the general procedure, the reaction of **1h** (81.0 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.013 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and *t*-BuONa (50.5 mg, 0.53 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 24 hours afforded **2h** (eluent: petroleum ether/ethyl acetate = 5:1-1:1) as a brown solid 59.6 mg in 91% yield.

mp: 204.9-206.1 ^oC. ^1H NMR (500 MHz, DMSO-d_6): δ 6.83 (dd, J = 8.5, 2.0 Hz, 1H), 7.23 (d, J = 2.0 Hz, 1H), 7.29 (td, J = 7.5, 1.0 Hz, 1H), 7.33-7.37 (m, 1H), 7.77 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 8.5 Hz, 1H), 8.07-8.09 (m, 1H), 8.71 (d, J = 3.0 Hz, 1H), 8.81 (dd, J = 2.5, 1.5 Hz, 1H), 9.12 (d, J = 1.0 Hz, 1H), 9.70 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 97.2, 110.9, 111.0, 116.2, 119.3, 121.3, 121.6, 124.5, 124.8, 138.5, 140.3, 140.7, 142.0, 143.8, 147.8, 157.3. HRMS (ESI): calcd for $C_{16}H_{12}N_3O$ $[M + H]^+$ 262.0975, found 262.0981.

9- (Thiazol-2-yl)-9*H*-carbazol-2-ol (**2i**):

Condition A: Following the general procedure, the reaction of **1i** (164.6 mg, 0.50 mmol, 1.0 eq), CuCl (2.5 mg, 0.025 mmol, 0.05 eq), ligand **L14** (8.2 mg, 0.025 mmol, 0.05 eq) and $LiOH{\cdot}H_2O$ (44.1 mg, 1.05 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 100 ^oC for 24 hours afforded **2i** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 113.9 mg in 86% yield.

Condition B: Following the general procedure, the reaction of **1i** (82.3 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.013 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and NaOH (21.0 mg, 0.53 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 24 hours afforded **2i** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 64.7 mg in 97% yield.

Condition C: Following the general procedure, the reaction of **1i** (164.6 mg, 0.50 mmol, 1.0 eq), CuCl (2.5 mg, 0.025 mmol, 0.05 eq), ligand **L14** (8.2 mg, 0.025 mmol, 0.05 eq) and *t*-BuONa (100.9 mg, 1.05 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 24 hours afforded **2i** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 122.8 mg in 92% yield.

mp: 152.6- 154.5 ^oC. ^1H NMR (500 MHz, DMSO-d_6): δ 6.86 (dd, J = 8.5, 2.0 Hz, 1H), 7.35 (td, J = 7.5, 1.0 Hz, 1H), 7.42-7.45 (m, 1H), 7.66 (d, J = 2.0 Hz, 1H), 7.76 (d, J = 3.5 Hz, 1H), 7.88 (d, J = 3.5 Hz, 1H), 8.03 (d, J = 8.5 Hz, 1H), 8.08-8.10 (m, 1H), 8.15 (d, J = 8.0 Hz, 1H), 9.87 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 99.6, 111.5, 112.0, 116.2, 116.3, 119.4, 121.4, 122.3, 124.7, 125.3, 138.4, 139.7, 140.1, 157.7, 158.3. HRMS (ESI): calcd for $C_{15}H_{11}N_2OS$ $[M + H]^+$ 267.0587, found 267.0575.

9-(Pyridin-2-yl)-9*H*-carbazol-3-ol (**2j**):

Condition A: Following the general procedure, the reaction of **1j** (61.9 mg, 0.19 mmol, 1.0 eq), CuCl (1.0 mg, 0.010 mmol, 0.05 eq), ligand **L14** (3.1 mg, 0.010 mmol, 0.05 eq) and $LiOH{\cdot}H_2O$ (16.7 mg, 0.40 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 100 ^oC for 24 hours afforded **2j** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 37.1 mg in 75% yield.

Condition B: Following the general procedure, the reaction of **1j** (80.8 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.01 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and NaOH (21.0 mg, 0.53 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 24 hours afforded **2j** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 59.0 mg in 91% yield.

Condition C: Following the general procedure, the reaction of **1j** (80.8 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.01 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.01 mmol, 0.05 eq) and *t*-BuONa (50.5 mg, 0.53 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 24 hours afforded **2j** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a brown solid 59.1 mg in 91% yield.

mp: 163.9-164.8 ^oC. ^1H NMR (500 MHz, DMSO-d_6): δ 6.95 (dd, J = 9.0, 2.5 Hz, 1H), 7.25-7.29 (m, 1H), 7.40-7.44 (m, 2H), 7.53 (d, J = 2.5 Hz, 1H), 7.68 (d, J = 9.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.5 Hz, 1H), 8.06-8.09 (m, 1H), 8.12 (d, J = 8.0 Hz, 1H), 8.70 (ddd, J = 5.0, 2.0, 0.5 Hz, 1H), 9.26 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 105.1, 111.3, 112.1, 115.3, 118.4, 120.3, 120.4, 121.3, 123.5, 124.5, 126.2, 132.7, 139.2 (2 C), 149.3, 151.1, 152.2. HRMS (ESI): calcd for

$C_{17}H_{13}N_2O$ $[M + H]^+$ 261.1022, found 261.1033.

9-(4-Trifluoromethylpyridin-2-yl)-9*H*-carbazol-3-ol (**2k**):

Condition A: Following the general procedure, the reaction of **1k** (106.0 mg, 0.27 mmol, 1.0 eq), CuCl (1.4 mg, 0.014mmol, 0.05 eq), ligand **L14** (4.5 mg, 0.014 mmol, 0.05 eq) and $LiOH{\cdot}H_2O$ (23.8 mg, 0.57 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 100 ^oC for 36 hours afforded **2k** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 72.1 mg in 81% yield.

Condition B: Following the general procedure, the reaction of **1k** (99.5 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.01 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and NaOH (21.0 mg, 0.53 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 36 hours afforded **2k** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 47.2 mg in 57% yield.

Condition C: Following the general procedure, the reaction of **1k** (96.0 mg, 0.245 mmol, 1.0 eq), CuCl (1.2 mg, 0.012 mmol, 0.05 eq), ligand **L14** (4.0 mg, 0.012 mmol, 0.05 eq) and *t*-BuONa (73.0 mg, 0.22 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 24 hours afforded **2k** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 73.0 mg in 91% yield.

mp: 155.1-156.7 ^oC. ^1H NMR (500 MHz, DMSO-d_6): δ 6.83 (dd, J = 8.0, 2.0 Hz, 1H), 7.22 (d, J = 2.0 Hz, 1H), 7.28 (t, J = 2.5 Hz, 1H), 7.35 (t, J = 3.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 5.0 Hz, 1H), 8.01 (d, J = 8.5 Hz, 1H), 8.07 (d, J = 6.5 Hz, 2H), 9.00 (d, J = 5.0 Hz, 1H), 9.71 (s, 1H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 97.2, 110.9, 110.9, 114.4 (d, J= 3.8 Hz, 1C), 116.2, 117.0 (q, J= 3.2 Hz, 1C), 119.2, 121.2, 121.6, 122.6 (q, J= 274.1 Hz, 1C), 124.4, 124.7, 138.5, 139.4 (q, J= 31.2 Hz, 1C), 140.2, 151.3, 152.0, 157.2. HRMS (ESI): calcd for $C_{18}H_{12}F_3N_2O$ $[M + H]^+$ 329.0896, found 329.0906.

2-Bromo -9-(4-hydroxypyridin-2-yl)- 9*H*-carbazole (**2l**) (Scheme 1, eqs 1-3):

Condition A: Following the general procedure, the reaction of **1l** (343.2 mg, 1.0 mmol, 1.0 eq), CuCl (5.0 mg, 0.05 mmol, 0.05 eq), ligand **L14** (16.4 mg, 0.05 mmol, 0.05 eq) and $LiOH{\cdot}H_2O$ (88.1 mg, 2.10 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 100 ^oC for 24 hours afforded **2l** (eluent: petroleum ether/ethyl acetate = 5:1-1:1) as a white solid 93.0 mg in 27% yield.

Condition C: Following the general procedure, the reaction of **1l** (168.4 mg, 0.49 mmol, 1.0 eq), CuCl (2.4 mg, 0.03 mmol, 0.05 eq), ligand **L14** (8.2 mg, 0.03 mmol, 0.05 eq) and *t*-BuONa (98.9 mg,

1.03 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 24 hours afforded **2l** (eluent: petroleum ether/ethyl acetate = 5:1-1:1) as a brown solid 74.3 mg in 55% yield.

Condition B: Following the general procedure, the reaction of **1m**(89.4 mg, 0.25 mmol, 1.0 eq), CuCl (1.3 mg, 0.01 mmol, 0.05 eq), ligand **L14** (4.1 mg, 0.013 mmol, 0.05 eq) and NaOH (21.0 mg, 0.53 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 24 hours afforded **2l** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 52.9 mg in 72% yield.

Condition B (without CuCl and **L14**): Following the general procedure, the reaction of **1m** (89.4 mg, 0.25 mmol, 1.0 eq) and NaOH (21.0 mg, 0.53 mmol, 2.1 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 24 hours afforded **2l** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 42.7 mg in 50% yield.

mp: 125.7-126.1 ^oC. ^1H NMR (500 MHz, DMSO-d_6): δ 6.90 (dd, J = 5.5, 2.0 Hz, 1H), 7.10 (d, J = 2.0 Hz, 1H), 7.33-7.36 (m, 1H), 7.48 (dd, J = 8.0, 2.0 Hz, 1H), 7.49-7.52 (m, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 1.5 Hz, 1H), 8.21 (d, J = 7.5 Hz, 1H), 8.27 (d, J = 2.5 Hz, 1H), 8.44 (d, J = 5.5 Hz, 1H), 11.89 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 106.1, 110.6, 111.4, 114.2, 118.9, 120.6, 121.2, 122.1, 122.5, 122.7, 123.5, 126.8, 139.0, 139.8, 150.5, 151.6, 166.2. HRMS (ESI): calcd for $C_{17}H_{12}BrN_2O$ $[M + H]^+$ 339.0128, found 339.0138.

9-(4-Hydroxypyridin-2-yl)- 9*H*- carbazol-2-ol (**4a**) (Scheme 1, eqs 3, 4):

Condition C: Following the general procedure, the reaction of **2l** (48.7 mg, 0.14 mmol, 1.0 eq), CuCl (0.7 mg, 0.007 mmol, 0.05 eq), ligand **L14** (2.3 mg, 0.007 mmol, 0.05 eq) and *t*-BuONa (56.5 mg, 0.59 mmol, 4.2 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 110 ^oC for 24 hours afforded **4a** (eluent: petroleum ether/ethyl acetate = 5:1-1:1) as a white solid 26.7 mg in 69% yield.

Condition C: Following the general procedure, the reaction of **1m** (89.4 mg, 0.25 mmol, 1.0 eq), CuCl (2.5 mg, 0.025 mmol, 0.10 eq), ligand **L14** (8.2 mg, 0.025 mmol, 0.10 eq) and *t*-BuONa (100.9 mg, 1.05 mmol, 4.2 eq) in DMSO/H_2O (2.0 mL/1.0 mL) at 110 ^oC for 24 hours afforded **2l** (eluent: petroleum ether/ethyl acetate = 3:1-1:1) as a white solid: 40.4 mg in 48% yield and **4a** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 23.9 mg in 35% yield.

mp: 298.3-299.7 ^oC. ^1H NMR (500 MHz, DMSO-d_6): δ 6.77 (dd, J = 8.5, 2.0 Hz, 1H), 6.86 (dd, J = 6.0, 2.0 Hz, 1H), 7.03 (d, J = 2.0 Hz, 1H), 7.18 (d, J = 2.0 Hz, 1H), 7.21-7.24 (m, 1H), 7.31 (td, J =

7.5, 1.5 Hz, 1H), 7.69 (d, J = 8.5 Hz, 1H), 7.97 (d, J = 8.5 Hz, 1H), 8.04 (d, J = 7.5 Hz, 1H), 8.40 (d, J = 6.0 Hz, 1H), 9.58 (s, 1H), 11.08 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 97.3, 105.8, 110.1, 110.2, 111.0, 115.8, 119.0, 120.6, 121.0, 123.9, 124.4, 138.9, 140.6, 150.3, 152.3, 156.9, 166.0. HRMS (ESI): calcd for $C_{17}H_{13}N_2O_2$ $[M + H]^+$ 277.0972, found 277.0973.

9-(5-Hydroxypyridin-2-yl)- 9H- carbazol-2-ol (**4b**) (Scheme 1, eq 5):

Condition C: Following the general procedure, the reaction of **1n** (100.5 mg, 0.25 mmol, 1.0 eq), CuCl (2.5 mg, 0.03 mmol, 0.10 eq), ligand **L14** (8.2 mg, 0.03 mmol, 0.10 eq) and *t*-BuONa (100.9 mg, 1.05 mmol, 4.2 eq) in DMSO/H_2O (2.0 mL/1.0 mL) at 110 ^{o}C for 24 hours afforded **4b** (eluent: petroleum ether/ethyl acetate = 5:1-1:1) as a white solid 43.8 mg in 63% yield.

mp: 257.0-258.3 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 6.75 (dd, J = 8.0, 2.0 Hz, 1H), 6.95 (d, J = 2.0 Hz, 1H), 7.19-7.22 (m, 1H), 7.29 (td, J = 7.0, 1.0 Hz, 1H), 7.47-7.49 (m, 2H), 7.53 (d, J = 8.5 Hz, 1H), 7.96 (d, J = 8.5 Hz, 1H), 8.03 (d, J = 7.5 Hz, 1H), 8.24-8.25 (m, 1H), 9.54 (s, 1H), 10.26 (s, 1H) . ^{13}C NMR (100 MHz, DMSO-d_6): δ 96.4, 109.8, 110.2, 115.4, 119.1, 120.1, 120.5, 121.0, 123.4, 124.3, 125.2, 137.0, 139.4, 141.2, 142.2, 152.6, 156.9. HRMS (ESI): calcd for $C_{17}H_{13}N_2O_2$ $[M + H]^+$ 277.0972, found 277.0983.

7- Bromo -9-(pyridin-2-yl)- 9H- carbazol-2-ol (**2m**) (Scheme 1, eq 6):

Condition A: Following the general procedure, the reaction of **1o** (61.3 mg, 0.15 mmol, 1.0 eq), CuCl (1.5 mg, 0.015 mmol, 0.10 eq), ligand **L14** (4.9 mg, 0.015 mmol, 0.10 eq) and $LiOH{\cdot}H_2O$ (26.4 mg, 0.63 mmol, 4.2 eq) in DMSO/H_2O (2.0 mL/0.5 mL) at 100 ^{o}C for 48 hours afforded **2m** (eluent: petroleum ether/ethyl acetate = 5:1-3:1) as a white solid 24.5 mg in 49% yield.

mp: 196.0-196.7 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 6.82 (dd, J = 8.5, 2.0 Hz, 1H), 7.12 (d, J = 2.0 Hz, 1H), 6.82 (dd, J = 8.5, 2.0 Hz, 1H), 7.41 (dd, J = 8.0, 2.0 Hz, 1H), 7.51 (ddd, J = 7.5, 5.0, 1.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 1.5 Hz, 1H), 8.04 (dd, J = 8.0, 2.5 Hz, 1H), 8.14 (td, J = 8.0, 2.0 Hz, 1H), 8.74-8.76 (m, 1H), 9.74 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 97.0, 110.9, 113.6, 115.2, 117.0, 119.2, 120.9, 121.6, 122.3, 123.3, 123.6, 139.7, 139.7, 140.8, 149.7, 150.4, 157.6. HRMS (ESI): calcd for $C_{17}H_{12}BrN_2O$ $[M + H]^+$ 339.0128, found 339.0128.

9-(Pyridin-2-yl)- 9H- carbazol-2,7-diol (**4c**) (Scheme 1, eqs 7, 8):

Condition B: Following the general procedure, the reaction of **1o** (80.4 mg, 0.20 mmol, 1.0 eq), CuCl (2.0 mg, 0.02 mmol, 0.10 eq), ligand **L14** (6.5 mg, 0.02 mmol, 0.10 eq) and NaOH (33.6 mg, 0.84 mmol, 4.2 eq) in DMSO/H_2O (2.0 mL/1.0 mL) at 110 ^oC for 24 hours afforded **4c** (eluent: petroleum ether/ethyl acetate = 5:1-1:1) as a white solid 16.5 mg in 24% yield.

Condition C: Following the general procedure, the reaction of **1o** (100.5 mg, 0.25 mmol, 1.0 eq), CuCl (2.5 mg, 0.03 mmol, 0.10 eq), ligand **L14** (8.2 mg, 0.03 mmol, 0.10 eq) and *t*-BuONa (100.9 mg, 1.05 mmol, 4.2 eq) in DMSO/H_2O (2.0 mL/1.0 mL) at 110 ^oC for 24 hours afforded **4c** (eluent: petroleum ether/ethyl acetate = 5:1-1:1) as a brown solid 55.8 mg in 81% yield.

mp: 266.1-267.6 ^oC. ^1H NMR (500 MHz, DMSO-d_6): δ 6.71 (dd, J = 8.5, 2.0 Hz, 2H), 7.09 (d, J = 2.0 Hz, 2H), 7.45 (ddd, J = 7.5, 5.0, 1.0 Hz, 1H), 7.70 (d, J = 8.5 Hz, 1H), 7.80 (d, J = 8.0 Hz, 2H), 8.10 (td, J = 8.0, 2.0 Hz, 1H), 8.72 (ddd, J = 5.0, 2.0, 0.5 Hz, 1H), 9.37 (s, 2H) . ^{13}C NMR (100 MHz, DMSO-d_6): δ 97.2, 109.9, 116.5, 118.9, 119.8, 121.8, 139.3, 140.3, 149.5, 151.1, 155.6. HRMS (ESI): calcd for $C_{17}H_{13}N_2O_2$ $[M + H]^+$ 277.0972, found 277.0961.

9- (pyrimidin-2-yl)-9H- carbazol-2,7-diol (**4d**) (Scheme 1, eq 9):

Condition A: Following the general procedure, the reaction of **1p** (100.8 mg, 0.25 mmol, 1.0 eq), CuCl (2.5 mg, 0.03 mmol, 0.10 eq), ligand **L14** (8.2 mg, 0.03 mmol, 0.10 eq) and LiOH·H_2O (44.1 mg, 1.05 mmol, 4.2 eq) in DMSO/H_2O (2.0 mL/1.0mL) at 100 ^oC for 24 hours afforded **4d** (eluent: petroleum ether/ethyl acetate = 5:1-1:1) as a white solid 42.8 mg in 62% yield.

mp: 267.3-268.9 ^oC. ^1H NMR (500 MHz, DMSO-d_6): δ 6.77 (dd, J = 8.5, 2.0 Hz, 2H), 7.38 (t, J = 5.0 Hz, 1H), 7.78 (d, J = 8.5 Hz, 2H), 8.19 (d, J = 2.0 Hz, 2H), 8.97 (d, J = 5.0 Hz, 2H), 9.46 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 102.8, 110.9, 116.7, 117.8, 119.0, 139.6, 115.7, 158.3, 158.4. HRMS (ESI): calcd for $C_{16}H_{12}N_3O_2$ $[M + H]^+$ 278.0924, found 278.0916.

Large-scale Synthesis and Its application:

Synthesis of 9-(pyridin-2-yl)-9*H*-carbazol-2-ol **2a** (Scheme 2, eq 1): Condition A: Following the general procedure, the reaction of **1a** (9.70 g, 30.00 mmol, 1.0 eq), CuCl (148.5 mg, 1.50 mmol, 0.05 eq), ligand **L14** (493.0 mg, 1.50 mmol, 0.05 eq) and LiOH·H_2O (2.64 g, 63.0 mmol, 2.1 eq) in DMSO/H_2O (37.5 mL/9.5 mL) at 100 ^oC for 48 hours. Then the mixture was cooled to room temperature, then H_2O (100 mL) and EtOAc (100 mL) were added, filtered through a pad of celite,

and washed with EtOAc three times. The organic layer was then separated, and the aqueous layer was extracted with EtOAc (100 mL × 5). The combined organic layer was washed with water (50 mL) and then dried over Na_2SO_4, filtered, and the filtrate was concentrated in vacuum. The residue was recrystallized in PE/EtOAc (20 mL/20 mL) to afford the desired product **2a** as a white solid 5.61 g. The mother liquor was concentrated, and the residue was purified through column chromatography on silica gel using PE/DCM = 5:1−3:1 as eluent to afford **3** 246.6 mg in 3% yield and the product **2a** as a white solid 425.5 mg. The total yield of **2a** was 79%. The structure of **3** was confirmed by ^{1}H NMR.

Condition C: Following the general procedure, the reaction of **1a** (9.70 g, 30.00 mmol, 1.0 eq), CuCl (148.5 mg, 1.50 mmol, 0.05 eq), ligand **L14** (493.0 mg, 1.50 mmol, 0.05 eq) and *t*-BuONa (6.05 g, 63.0 mmol, 2.1 eq) in DMSO/H_2O (37.5 mL/9.5 mL) at 110 ^{o}C for 48 hours. Then the mixture was cooled to room temperature, and H_2O (100 mL) and EtOAc (100 mL) were added, filtered through a pad of celite, and washed with EtOAc three times. The organic layer was then separated, and the aqueous layer was extracted with EtOAc (100 mL × 5). The combined organic layer was washed with water (50 mL) and then dried over Na_2SO_4 and filtered, and the filtrate was concentrated in vacuum. The residue was recrystallized in PE/EtOAc (10 mL/10 mL) to afford the desired product as a white solid 5.77 g. The mother liquor was concentrated, and the residue was purified through column chromatography on silica gel using PE/DCM = 5:1−3:1 as eluent to afford the product as a white solid 1.5 g. The total yield was 93%. The structure of **2a** was confirmed by ^{1}H NMR.

Synthesis of 2-(9-(pyridin-2-yl)-9*H*-carbazol-2-yloxy)-9-(pyridin-2-yl)-9*H*-carbazole **3** (Scheme 2, eq 1): To a dry three-necked flask equipped with a magnetic stir bar, added **2a** (3.90 g, 15.00 mmol, 1.0 eq), **1a** (5.82 g, 18.00 mmol, 1.2 eq), CuI (0.29 g, 1.50 mmol, 0.1 eq), picolinic acid **L5** (0.37 g, 3.00 mmol, 0.2 eq), K_3PO_4 (6.37 g, 30.00 mmol, 2.0 eq). The flask was then evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then DMSO (60 mL) was added under nitrogen and the mixture was stirred at 95-105^{o}C for 3 days. The mixture was then cooled down to ambient temperature and diluted with ethyl acetate, filtered and washed with a plenty of ethyl acetate. The filtrate was then washed with water for three time and then dried over sodium sulfate. Filtered and the solvent was removed under reduced pressure, the residue was

purified through column chromatography on silica gel using petroleum ether/ethyl acetate (10:1-3:1) as eluent to obtain the desired product as a brown solid 6.44 g in 85% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.06 (dd, J = 8.4, 2.4 Hz, 2H), 7.33 (t, J = 7.2 Hz, 2H), 7.41-7.45 (m, 4H), 7.51 (d, J = 2.4 Hz, 2H), 7.76 (d, J = 8.0 Hz, 4H), 8.06 (td, J = 7.6, 2.0 Hz, 2H), 8.20 (d, J = 7.6 Hz, 2H), 8.24 (d, J = 8.4 Hz, 2H), 8.64 (dd, J = 5.6, 2.4 Hz, 2H). The spectroscopic data is in agreement with that previously reported.[9]

Synthesis of **PtNON**: Ligand **3** (2.92 g, 5.81 mmol, 1.00 eq), K_2PtCl_4 (2.65 g, 6.39 mmol, 1.10 eq), ^{n}Bu$_4$NBr (0.19 g, 0.58 mmol, 0.10 eq) were added to a dry three-necked flask equipped with a magnetic stir bar and a condenser. The flask was then evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then AcOH (350 mL) was added under nitrogen. The mixture was stirred at room temperature for 12 hours , then at 105-115 ^{o}C for 3.5 days. The mixture was then cooled down to ambient temperature and the solvent was evaporated under reduced pressure, the residue was purified through column chromatography on silica gel using petroleum ether/dichloromethane (1:1) as eluent to obtain the desired product as a yellow solid 3.75 g in 93% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.20 (d, J = 10.0 Hz, 2H), 7.31 (td, J = 7.0, 3.5 Hz, 2H), 7.42 (t, J = 9.0 Hz, 2H), 7.48-7.52 (m, 2H), 7.93 (d, J = 10.0 Hz, 2H), 8.08 (d, J = 10.0 Hz, 2H), 8.17-8.20 (m, 6H), 9.03 (d, J = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 93.9, 111.7, 114.2, 115.2, 115.9, 116.4, 119.6, 120.3, 122.7, 124.2, 127.7, 137.4, 139.7, 142.2, 147.7, 151.3, 152.0. The spectroscopic data is in agreement with that previously reported.[9]

Synthesis of **PdNON**: Ligand **3** (5.03 g, 10.00 mmol, 1.00 eq), $Pd(OAc)_2$ (2.47 g, 11.00 mmol, 1.10 eq), ^{n}Bu$_4$NBr (0.32 g, 1.00 mmol, 0.10 eq) were added to a dry three-necked flask equipped with a magnetic stir bar and a condenser. The flask was then evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then AcOH (500 mL) was added under nitrogen and the mixture was refluxed for 3 days. The mixture was then cooled down to ambient temperature and the solvent was evaporated under reduced pressure, the residue was purified through column chromatography on silica gel using petroleum ether/dichloromethane (2:1-3:2-1:1) as eluent to obtain the desired product as a yellow solid 5.00 g in 82% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.21 (d, J = 8.4 Hz, 2H), 7.33-7.37 (m, 2H), 7.40 (td, J = 7.6 Hz, 2H), 7.46-7.51 (m, 2H), 7.80 (d,

J = 8.0 Hz, 2H), 8.06 (d, *J* = 8.0 Hz, 2H), 8.14 (d, *J* = 3.6 Hz, 4H), 8.19 (d, *J* = 7.2 Hz, 2H), 8.90 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 107.8, 111.7, 114.0, 116.1, 116.3, 117.0, 119.6, 120.2, 122.5, 124.3, 127.6, 137.5, 140.4, 142.9, 148.5, 150.9, 151.0. HRMS (MALDI-FT_DHB): for $C_{34}H_{21}N_4O^{102}Pd$ $[M+H]^+$: calcd 603.0766, found 603.0763.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Comparison of synthetic route for critical intermediate **2a** and **PtNON** (Figure S2); Synthesis of ligands **L13** and **L14**; Synthesis of starting materials of **1m**, **1k** and **1p**; Our previous synthetic route for **2a**; NMR and HRMS spectra; IR and UV spectra for **2a**-**2j**, **2l**, **2m**, **4a** and **4c**. Crystallographic data (PDF). Compounds **PtNON** and **PdNON** (CIF).

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Notes

The authors declare no competing financial interest.

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