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FULL PAPER

Ru(II)-$^{PBT}NN^{X}N$ complex bearing functional 2-(pyridin-2-yl) benzo[*d*]thiazole ligand catalyzed α-alkylation of nitriles with alcohols

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Six tridentate NNN ligand precursors derived from 2-(pyridin-2-yl)benzo[d] thiazole(PBT) with different linkers, $^{PBT}NN^{X}N$ (X = NH, NMe, O, S) (**1a**–**1f**), have been successfully prepared. The electronic properties of $^{PBT}NN^{X}N$ ligands are well tunable by differing linkers between PBT skeleton and the pyridine ring, and/or by introducing electron-donating/withdrawing groups on the pyridine ring (R = OMe or F). The ligand precursors and representative complexes Ru ($^{PBT}NN^{NH}N$)$Cl_2(PPh_3)$ (**2a**), Ru ($^{PBT}NN^{NMe}N$)$Cl_2(PPh_3)$ (**2b**), and Ru ($^{PBT}NN^{S}N$)$Cl_2(PPh_3)$ (**2f**) have been characterized by NMR spectroscopy, high-resolution mass spectroscopy, and Fourier transform infrared (FT-IR). The molecular structures of **1f**, **2a**, and **2f** have been determined by X-ray diffraction study. The results indicate that $^{PBT}NN^{NH}N$ ligand in the complex presented coplanar with two five-membered chelating rings. It should be noted that **2a** featuring a NH group exhibits superior performance compared to those with other linkers (such as NMe, O, or S). A variety of heterocyclic and aromatic nitriles with aromatic and aliphatic alcohols have been explored in α-alkylation for good to excellent yields. Based on kinetic experiments and mechanistic studies, a proposed mechanism was put forward. Ru-H species and benzaldehyde, which was oxidized from benzyl alcohol, were detected in the catalytic cycle.

KEYWORDS

2-(pyridin-2-yl)benzo[*d*]thiazole (PBT), α-alkylation, alcoholsnitrilesRu (II) complex

1 | INTRODUCTION

α-Alkylated nitriles represent important structural scaffold applied in versatile biomacromolecules, fine chemicals, and carboxylic acid derivatives.[1–3] Conventional synthesis of α-alkylated nitriles with hazardous alkyl halides and strong bases often suffers from generating environmentally unfriendly byproducts.[4] Later, alkylation of nitriles via borrowing hydrogen strategy with alcohol as alkylation agent, has been developed as one of the most attractive and atom-economic transformation, with only water as a byproduct.[5,6]

Since 1981, when Grigg and co-workers first used $RuH_2(PPh_3)_4$ as a catalyst in the alkylation of nitriles with alcohol,[7] a lot of effort has been devoted to exploring various catalysts, including Ru,[8–15] Rh,[16,17] Ir,[18–22] Pd,[23] Os,[24] Fe,[25] and Mn[26]. Of these, Ru complexes are the most reported, for example Gunanathan's group reported that Ru(PNP) (PNP = bis(2-(diphenylphosphino)-ethyl)amine) pincer complex showed

good activity for α-alkylated reaction of arylmethyl nitriles.[13] Kundu and co-workers demonstrated that Ru complexes bearing *N6,N6′*-dimethyl-2,2'-bipyridine-6,6'-diamine ligand efficiently catalyzed α-alkylation of arylacetonitriles with alcohols.[14] Recently, Ru catalyst based on tridentate bipyridyl imidazoline catalyzed analogous reaction was reported by Song et al.[15]

Metal–ligand cooperation (MLC)[27–32] plays an important role in catalysis. It can dramatically promote the catalytic activity applied in borrowing hydrogen catalysis using ligands containing functional groups such as NH[33–37] and OH[38–40]. Among them, NNN ligands[41–43] bearing NH[44,45] coordinated with Ru metal could be potential chelating ligands due to their synthetic accessibility and excellent air- and moisture-stability compared to phosphine ligands.

Recently, our group explored the use of benzothiazole/benzoxazole and/or benzimidazole derivatives.[46–49] Based on our research, we predicted that 2-(pyridin-2-yl)benzo[*d*]thiazole (PBT)-pyridine ($^{PBT}NN^{X}N$) ligands would be good candidates for the α-alkylation of nitriles with alcohols. They possess planar geometry and an aromatic configuration with a large conjugated system. This has potential benefits for electronic transfer, which is important for metal–ligand cooperation.[27,28] The color-tuning of iridium complexes bearing 2-phenylbenzothiazole ligands has been achieved by changing the chromophore and/or groups on the benzothiazole moiety and/or phenyl ring, implying their prior properties for easy structural modification and tuneable electronic effect.[50–53] The catalytic activity for Suzuki cross-coupling of Pd (SCN) pincer complexes supported by thiophosphoryl-benzothiazole ligand is deeply influenced by the attached substituent group, suggesting that they could adjust catalytic reactivity.[54] Importantly, we have developed cyclometalated $^{ABO}N,P$ and $^{ABO}N,C_{(carbene)}$ chelated iridium-based complexes (ABO = 2-arylbenzo[*d*]oxazole), which exhibit superior catalytic performance in the α-alkylation of ketones, alcohols, and amines with primary alcohols[55] and the *N*-methylation of aromatic amines with methanol,[56] respectively.

From this work, we became interested in developing a new type of Ru catalyst based on 2-(pyridin-2-yl)benzo[*d*]thiazole (PBT)-pyridine ligands ($^{PBT}NN^{X}N$). The tuneable electronic properties of $^{PBT}NN^{X}N$ ligands can be achieved by the different linkers (such as NH, NMe, O, and S) between the 2-(pyridin-2-yl)benzo[*d*]thiazole skeleton and the pyridine ring, and/or by introducing electron-donating/withdrawing groups on pyridine ring (R = OMe or F). This new kind of catalyst was applied in the α-alkylation of nitriles and alcohols. It indicated that the Ru ($^{PBT}NN^{NH}N$)$Cl_2(PPh_3)$ complex featuring NH linker exhibited excellent catalytic activity.

2 | RESULTS AND DISCUSSION

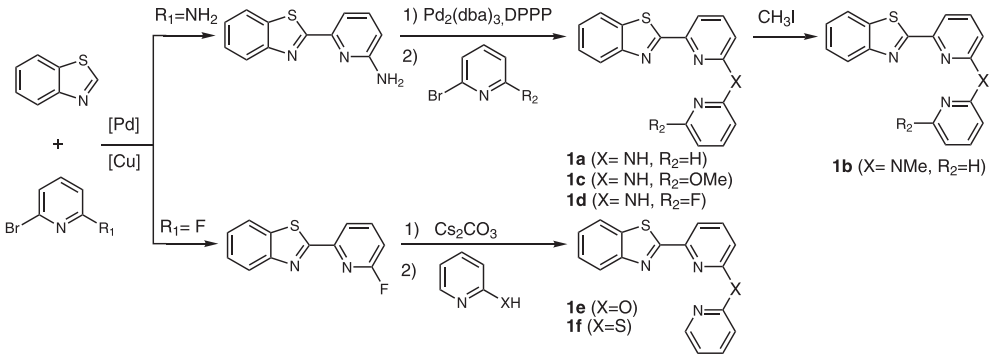
2.1 | Synthesis of $^{PBT}NN^{X}N$ (X = NH, NMe, O, S) ligands

Our study started with the synthesis of ligands. First, 6-(benzo[*d*]thiazol-2-yl)pyridin-2-amine and 2-(6-fluoropyridin-2-yl)benzo[*d*]thiazole were prepared as previously described[57] by the direct arylation of benzothiazole with 2-amino-6-bromopyridine and 2-bromo-6-fluoropyridine, respectively, as shown in Scheme 1. Then the ligands **1a**, **1c**, and **1d** were obtained by the Buchwald method of Pd-catalyzed C-N bond formation.[58] 6-(Benzo[*d*]thiazol-2-yl)pyridin-2-amine was treated with 2-bromopyridine, 2-bromo-6-methoxypyridine, and 2-bromo-6-fluoropyridine, respectively, in the presence of Pd (II) and 1,3-bis (diphenylphosphino)propane (DPPP) as catalyst to deliver the corresponding targeted products **1a**, **1c**, and **1d** in good yield.

In the ^{1}H NMR spectra, the protons of N-*H* linker of ligands **1a**, **1c**, and **1d** display signals at δ = 10.00, 7.40, and 10.21 ppm, respectively (Supporting Information). It is worth noting that the H signal observed from the NH group in **1c** with methoxy substituted on the pyridine ring obviously occurred much further upfield, while the proton signal observed in the fluorine-substituted analogue of **1d** was slightly downfield shifted from that of **1a**. This illustrates that the electronic effect can be adjusted by changing the electron-donating/withdrawing groups on the pyridine ring of ligands. When the hydrogen atom on the NH moiety of **1a** was replaced with methyl by reacting with iodomethane (CH_3I), **1b** with NMe linker was obtained. In the ^{1}H NMR spectrum, **1b** shows one singlet for the methyl group at 3.74 ppm and the resonance signal of NH group obviously disappears. These results indicated the ligands **1a**–**1d** were formed.

The ligands **1e** and **1f**, containing O and S linkers, were synthesized by nucleophilic aromatic substitution (S_NAr) following our group's previous report.[47] 2-(6-Fluoropyridin-2-yl)benzo[*d*]thiazole reacted with 2-hydroxypyridine and 2-mercaptopyridine, respectively, gave **1e** and **1f** in ca. 75 and 86% yield. The ligands were characterized by ^{1}H and ^{13}C NMR spectra and high-resolution mass spectrometry (HRMS). Fortunately, single crystals of **1f** for X-ray diffraction analysis were obtained in *n*-hexane/dichloromethane. The molecular structure is shown in Figure 1 and selected bond lengths and angles are listed in Table 1. The benzothiazole and pyridine ring of PBT are almost coplanar with a small dihedral angle of 5.34°. Although the torsion angle of the two pyridine rings is 75.88°, the $^{PBT}NN^{S}N$ ligand is non-coplanar, which benefits for the chelating coordination of the ligand precursor with the metal centre.

SCHEME 1 Synthesis of $^{PBT}NN^{X}N$ (X = NH, NMe, O, S) ligands. [Pd] = Pd $(OAc)_2$, [Cu] = Cu $(OAc)_2 \cdot H_2O$, DPPP = 1,3-bis (diphenylphosphino)propane



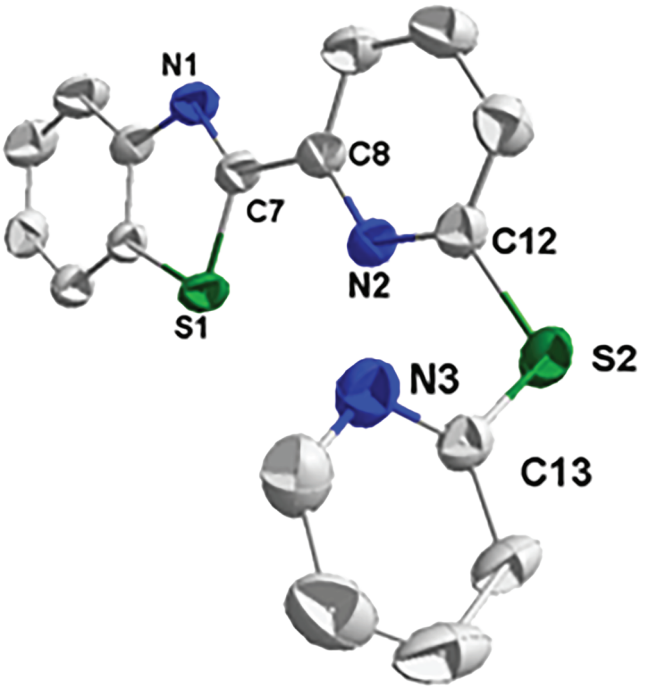


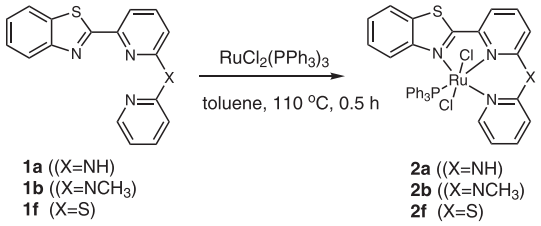
FIGURE 1 Molecular structure of **1f**. Thermal ellipsoids shown at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity

TABLE 1 Selected bond lengths and angles for ligand **1f**

Bond	Bond length (Å)	Bond	Bond angle (°)
N(1)-C(7)	1.294(2)	C(13)-S(2)-C(12)	102.77(7)
S(1)-C(7)	1.7426(15)	C(12)-N(2)-C(8)	116.84(14)
C(7)-C(8)	1.471(2)	C(8)-C(7)-S(1)	119.09(11)
S(2)-C(12)	1.7877(17)	N(2)-C(8)-C(7)	115.57(14)
N(3)-C(13)	1.365(2)	N(3)-C(13)-S(2)	121.84(12)

2.2 | Synthesis of Ru($^{PBT}NN^{X}N$)$Cl_2(PPh_3)$ (X = NH, NMe, S) complexes

To further explore the properties of Ru complexes, three representative compounds, **2a**, **2b**, and **2f**, were synthesized as shown in Scheme 2. Equivalent reaction of **1a**, **1b** and **1f** with $RuCl_2(PPh_3)_3$ in refluxing toluene for 0.5 hr yielded the corresponding complexes Ru($^{PBT}NN^{NH}N$)$Cl_2(PPh_3)$ (**2a**), Ru($^{PBT}NN^{NMe}N$)$Cl_2(PPh_3)$ (**2b**), and Ru($^{PBT}NN^{S}N$)$Cl_2(PPh_3)$ (**2f**). All these complexes are stable.



SCHEME 2 Synthesis of Ru ($^{PBT}NN^{X}N$)$Cl_2(PPh_3)$ (X = NH, NMe, S) complexes

The ^{31}P NMR signals of **2a** in dimethyl sulfoxide (DMSO)-d_6, and **2b** and **2f** in $CDCl_3$ appear at 31.40, 46.03, and 42.18 ppm, respectively, which is similar to the spectroscopic features of the Ru(II)-$NN^{X}N$ complexes reported previously.[15,59] The ^1H NMR chemical shifts of **2a** reveal a multiplet peak at 9.73 ppm for the NH moiety, which slightly shifts upfield 0.27 ppm from the ligand **1a** (δ_{NH} 10.00 ppm). The CH_3 resonance of the NMe linker in **2b** appears at 5.30 ppm, a downfield shift of 1.56 ppm in comparison to **1b**. Complex **2a** was further identified by X-ray crystallography. It was grown from DMSO layered with anhydrous ether. As can be seen from Figure 2 and Table 2, 2**a** is converted to cation **2a**·DMSO with a Cl^- as anion, which was coordinated with the Ru metal center through sulfur atom of DMSO, which occurs easily according to previous literature.[60] Cl^- was lost from the ruthenium atom. It formed a more stable cationic compound **2a**·DMSO with a weak coordinating anion Cl^-. It also adopts distorted-octahedral geometry surrounded by a $^{PBT}NN^{NH}N$ ligand, triphenyl phosphine (PPh_3), a Cl atom, and a DMSO molecule. $^{PBT}NN^{NH}N$ ligand coordinates with the Ru atom via benzothiazolyl and bipyridyl N atoms. The angles of N-Ru-P are close to right angles, showing that PPh_3 is situated *trans* to DMSO. The Ru-N bond length is in the range of 2.04–2.13 Å. The $^{PBT}NN^{NH}N$ ligand in the **2a**·DMSO is essentially coplanar

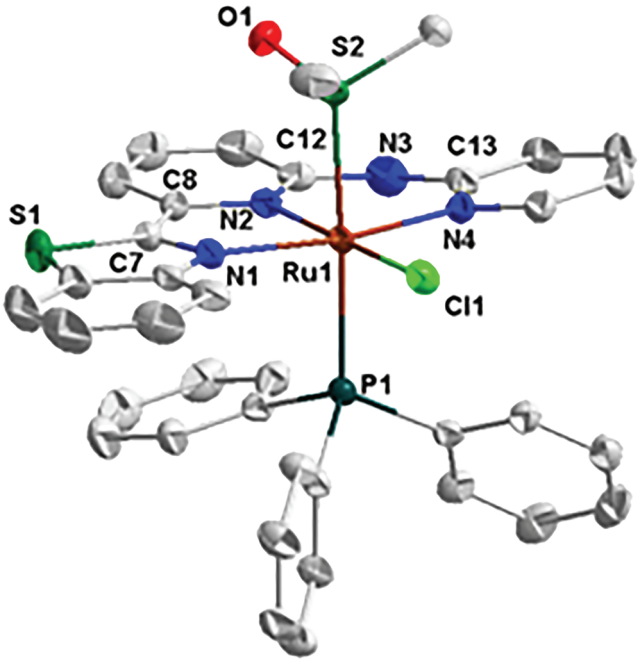


FIGURE 2 Molecular structure of **2a**·DMSO. Thermal ellipsoids shown at the 50% probability level. Hydrogen atoms, Cl-counterion ion and solvent molecules are omitted for clarity

TABLE 2 Selected bond lengths and angles for complex **2a**·DMSO

Bond	Bond length (Å)	Bond	Bond angle (°)
Ru(1)-N(2)	2.041(3)	N(2)-Ru(1)-N(4)	91.77(11)
Ru(1)-N(4)	2.109(3)	N(2)-Ru(1)-N(1)	79.12(12)
Ru(1)-N(1)	2.127(3)	N(4)-Ru(1)-N(1)	169.75(11)
Ru(1)-S(2)	2.3255(9)	N(2)-Ru(1)-S(2)	87.47(8)
Ru(1)-P(1)	2.3887(9)	N(2)-Ru(1)-P(1)	90.48(8)
Ru(1)-Cl(1)	2.4339(9)	N(4)-Ru(1)-P(1)	92.99(8)

with the two adjacent five-membered Ru-N-C-C-N chelate rings.[61] This coplanar structure could be essential for efficient π conjugation between a lone pair of the NH linker and the PBT backbone. The resulting conjugated system could confer fast electronic transfer, which helps the reaction rate.[62]

Good-quality single crystals of **2f** were recrystallized from *n*-hexane/dichloromethane and characterized by X-ray crystallography (Figure 3 and Table 3). The complex shows typical distorted-octahedral geometry with the ruthenium center coordinated by $^{PBT}NN^{S}N$ and PPh_3 as well as two chloride ligands. There is little change of N-C, S-C bonds lengths in the benzothiazole and pyridine rings compared to **1f**. Due to coordination with the Ru metal center, the dihedral angle of the two pyridine rings decreases to 51.86° compared to **1f**.

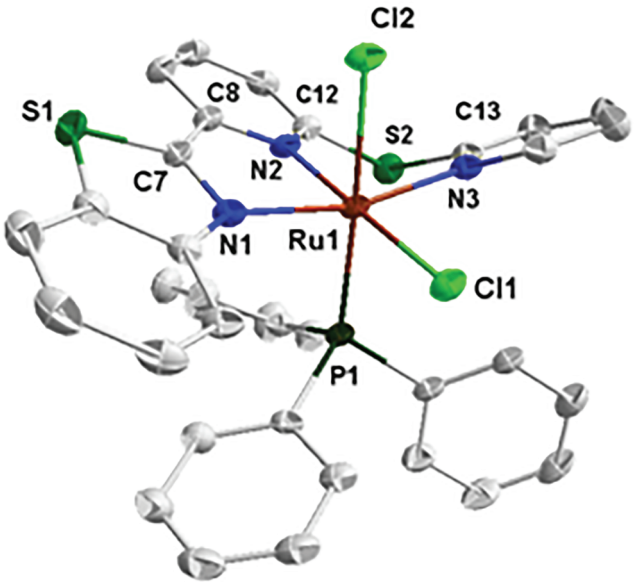


FIGURE 3 Molecular structure of **2f**. Thermal ellipsoids shown at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity

TABLE 3 Selected bond lengths and angles for complex **2f**

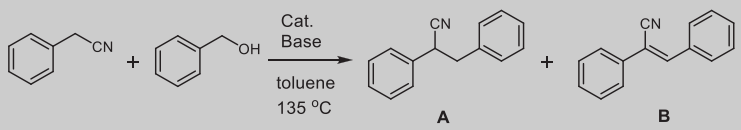
Bond	Bond length (Å)	Bond	Bond angle (°)
N(1)-C(7)	1.323(2)	N(2)-Ru(1)-N(1)	79.44(6)
S(1)-C(7)	1.7243(18)	N(2)-Ru(1)-N(3)	92.58(6)
S(2)-C(12)	1.7692(19)	N(2)-Ru(1)-Cl(2)	85.89(4)
Ru(1)-N(1)	2.0880(15)	N(2)-Ru(1)-P(1)	95.10(4)
Ru(1)-N(2)	2.0175(15)	P(1)-Ru(1)-Cl(1)	88.242(16)
Ru(1)-N(3)	2.1033(15)		

2.3 | Catalytic activity for α-alkylation of nitriles

Next we investigated the catalytic activity of the Ru complexes for α-alkylation of nitriles with alcohols. First, the reaction of benzyl cyanide with benzyl alcohol was taken as a benchmark reaction in the presence of KO^{t}Bu in toluene at 135 °C under nitrogen atmosphere (N_2) for 0.5 hr (Table 4).

Initially, 1 mol% of $RuCl_2(PPh_3)_3$ with $^{PBT}NN^{X}N$ (X = NH, NMe, O, S) ligands **1a–1f** as precatalyst in the presence of 10 mol% KO^{t}Bu as base was used, providing the desired product 2,3-diphenylpropanenitrile (**A**) together with 2,3- diphenylacrylonitrile (**B**) as byproduct. The result shows that using $RuCl_2(PPh_3)_3$ with **1a** (X = NH) as catalyst affords **A** in 80% yield and **B** in 15% yield (Table 4, entry 1). The catalytic activity of **1b** (X = NMe) was much lower than that of **1a**, which clearly emphasizes the performance of the acidic NH moiety in

TABLE 4 Optimization of Ru-catalyzed α-alkylation of nitrile[a]



Entry	Cat.	Base	Yield of A (%)[b]	Yield of B (%)[b]
1	**1a** + $RuCl_2(PPh_3)_3$	KO^{t}Bu	80	17
2	**2a**	KO^{t}Bu	82	16
3	**1b** + $RuCl_2(PPh_3)_3$	KO^{t}Bu	49	33
4	**2b**	KO^{t}Bu	51	34
5	**1c** + $RuCl_2(PPh_3)_3$	KO^{t}Bu	65	21
6	**1d** + $RuCl_2(PPh_3)_3$	KO^{t}Bu	59	24
7	**1e** + $RuCl_2(PPh_3)_3$	KO^{t}Bu	43	29
8	**1f** + $RuCl_2(PPh_3)_3$	KO^{t}Bu	45	33
9	**2f**	KO^{t}Bu	35	32
10	**2a**	NaO^{t}Bu	14	77
11	**2a**	Cs_2CO_3	37	53
12	**2a**	$NaHCO_3$	26	69
13	**2a**	KOH	54	36
14	**2a**	K_3PO_3	0	0
15[c]	**2a**	KO^{t}Bu	10	78
16[d]	**2a**	KO^{t}Bu	5	82
17[e]	**2a**	KO^{t}Bu	53	22
18[f]	**2a**	KO^{t}Bu	>99	0

[a]Reaction conditions: benzyl cyanide (1 mmol), benzyl alcohol (2 mmol), cat. (1 mol%), base (10 mol%), toluene (1 ml), N_2, 135 °C, 0.5 hr.
[b]With 1,3,5 trimethoxybenzene as the internal standard.
[c]KO^{t}Bu (5 mol%).
[d]KO^{t}Bu (1.0 equiv).
[d]Heated at 125 °C.
[e]1 hr.

catalytic activity enhancement[63] (Table 4, entry 3). It should be noted that the activity of $^{PBT}NN^{NH}N$ ligand with electron-donating methoxy on the pyridine ring was better than that of the electron-withdrawing fluoro substituent (Table 4, entries 5 and 6). When the reactions with **1e** (X = O) and **1f** (X = S) were performed, **1e** was formed selectively in 34% yield (Table 4, entry 7) and **1f** produced a mixture of **A** and **B** in 45% and 33% yields, respectively (Table 4, entry 8). The result further proves the better reactivity of **1a** containing NH linker than O or S linkers. Similar product distribution could be achieved under the catalysis of complexes **2a**, **2b**, and **2f** to that of the reactions catalyzed by $RuCl_2(PPh_3)_3$ with **1a**, **1b**, and **1f** as precatalyst (Table 4, entries 2, 4, and 9), indicating that Ru($^{PBT}NN^{X}N$) $Cl_2(PPh_3)$ complex generated in situ could be applied in the reaction of α-alkylation of nitrile with alcohol. Other different bases, such as NaO^{t}Bu, Cs_2CO_3, $NaHCO_3$, KOH, and K_3PO_3, were then examined (Table 4, entries 10–14). They rendered the reaction less active than with KO^{t}Bu. Decreasing or increasing the amount of KO^{t}Bu lowered the yields of desired product to 10% and 5%, respectively (Table 4, entries 15 and 16). When the temperature was reduced 125 °C, products of **A** and B were obtained in 53% and 22% yields, respectively (Table 4, entry 17). Finally, when the reaction time with **2a** was lengthened to 1 h, nearly quantitative yield (99%) was obtained (Table 4, entry 18).

With the optimal reaction conditions known, we explored the scope of substrates using 1 mol% of **2a** as catalyst and 10 mol% of KO^{t}Bu in toluene (1 ml) at 135 °C under N_2 atmosphere for 1 hr (Table 5).

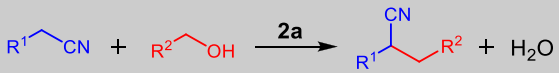
In general, methyl (-Me) and methoxy (-OMe) substituted nitriles reacted well with benzyl alcohol and provided the corresponding alkylated products **a1**–**a3** in

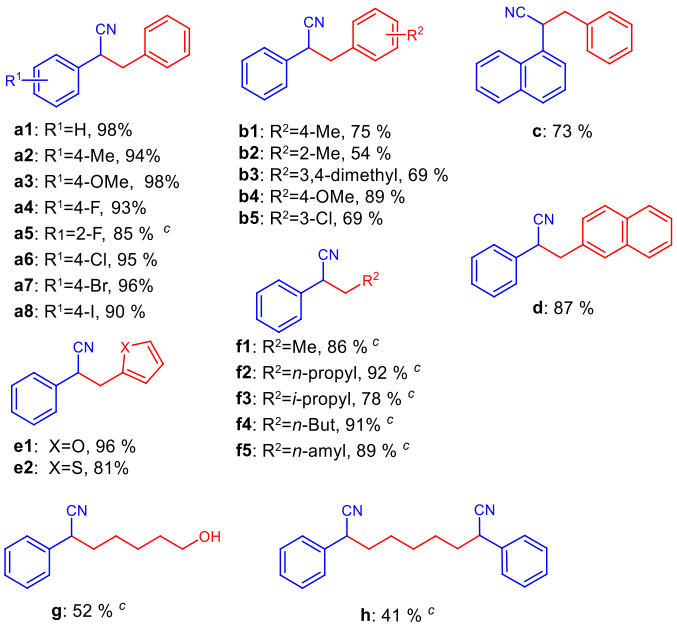
excellent yields. Almost no effect on the reactivity was observed by introducing an electron-withdrawing group such as fluorine, chlorine, bromine, or iodine in the *para*- or *ortho*- position of aromatic acetonitriles, and excellent yields were obtained (**a4**–**a8**). Of these, interestingly, 2-fluorophenylacetonitrile was also well tolerated in 85% yield by extending the reaction time (**a5**). A range of aromatic alcohols was further investigated. Moderate to high yields for the reaction with benzyl cyanide were also obtained for the 4-Me, 2-Me, 3,4-dimethyl, 4-OMe, and 3-Cl substituted alcohols derivatives (**b1–b5**). Gratifyingly, 2-naphthalenemethanol with benzyl cyanide and 1-naphthylacetonitrile with benzyl alcohol reacted smoothly and the corresponding products **c** and **d** were isolated in 73% and 87% yields, respectively. Heterocyclic alcohols such as furfuryl alcohol and 2-(hydroxymethyl) thiophene were efficiently transformed into desired products **e1** and **e2**. Surprisingly, the highly challenging nonactivated aliphatic alcohols were subjected to catalysis. A variety of linear and nonlinear alcohols such as ethyl alcohol, *n*-butanol, *i*-butanol, 1-pentanol, and 1-hexanol were also successfully converted in a prolonged reaction time, providing moderate to high yields (**f1**–**f5**). When 1,5-pentanediol smoothly reacted with benzyl alcohol, the mono-substituted product **g** was generated in moderate yield (52%) under optimal conditions, while the dialkylated product 2,8-diphenylnonanedinitrile (**h**) was isolated in 41% yield. The raw materials were almost completely converted. However, attempts to react acetonitrile and *n*-butyronitrile with benzyl alcohol were unsuccessful. Overall, Ru($^{PBT}NN^{NH}N$)Cl_2(PPh_3) showed excellent catalytic performance in catalysis of α-alkylation of nitriles with alcohols.

2.4 | Kinetic experiments

To understand the reaction mechanism for α-alkylation of nitriles catalyzed by **2a**, kinetic profiles were recorded under the optimal reaction conditions by ^{1}H NMR. As shown in Figure 4, both **A** and **B** were formed at the beginning of the reaction in 10 min. **A** exhibited a significantly increased initial reaction rate (initial turnover frequency (TOF) = 222 hr^{-1}) compared to **B** (initial

TABLE 5 Scope of α-alkylation of nitriles with alcohols catalyzed by **2a**[a,b]





[a]Reaction conditions: nitriles (1 mmol), alcohols (2 mmol), **2a** (1 mol%), KO^{t}Bu (10 mol%), toluene (1 ml), 135 °C, N_2, 1 hr.
[b]Isolated yield.
[c]2 hr.

TOF = 69 hr^{-1}) in 20 min. **A** continued gradually producing and **B** began to decline after 1 hr. This result indicates that generation of **A** and reduction of **B** occur simultaneously. Desired product **A** for nearly 99% yield were almost completely formed within 1 hr, while **B** completely disappeared in solution. We speculate that the superior performance of **2a** can be attributed to the coplanar $^{PBT}NN^{NH}N$ ligand with a large conjugated system in comparison with other reported Ru complexes.[13–15]

2.5 | Mechanistic investigation

These results show that precursors containing the NH moiety have much better catalytic activity than NMe, O or S linkers (Table 4, entry 1–8) for the α-alkylation reaction. To further explore the reaction mechanism, controlled experiments were carried out with **2a**.

When the reaction occurred under an oxygen (O_2) atmosphere, no targeted product **A** was detected (Scheme 3a). The olefin product **B** was obtained in 99% yield, indicating that the presence of O_2 inhibits the formation of alkylated product. On replacing benzyl alcohol with benzaldehyde, benzyl cyanide reacted with benzaldehyde under optimal conditions to form **B** (97%), whereas less than 3% yield of **A** was detected (Scheme 3b). When **B** and benzyl alcohol were reacted, 95% yield of **A** was generated (Scheme 3c), illustrating that **B** is reduced to **A** when using benzyl alcohol as the hydrogen source. These results suggest that the olefin product **B** is the unsaturated intermediate for the α-alkylated product **A** under N_2.

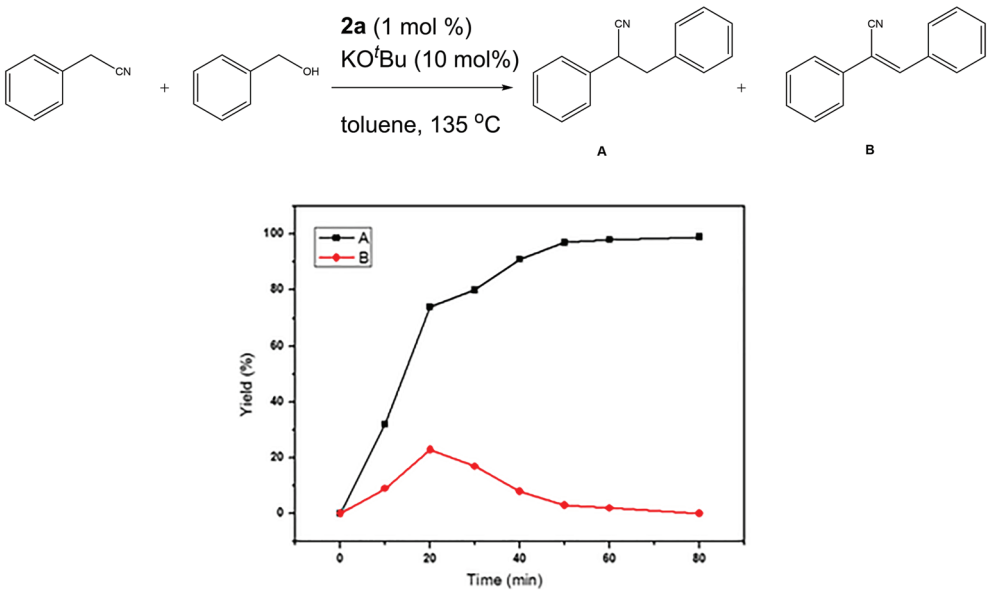
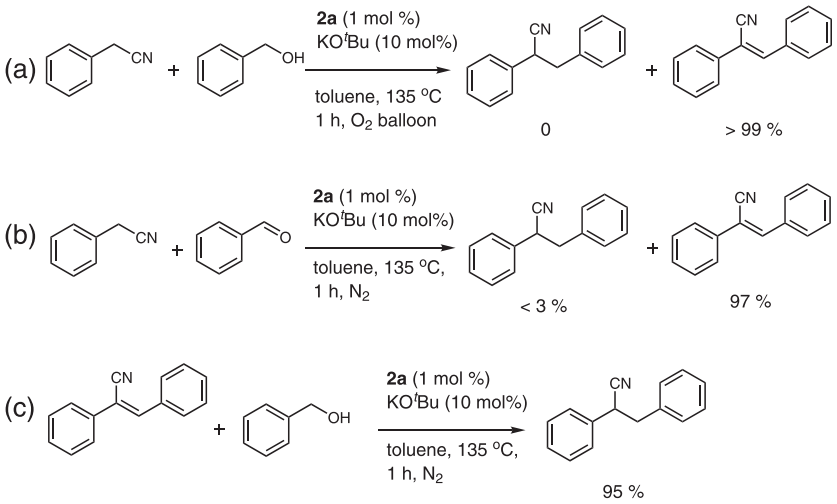


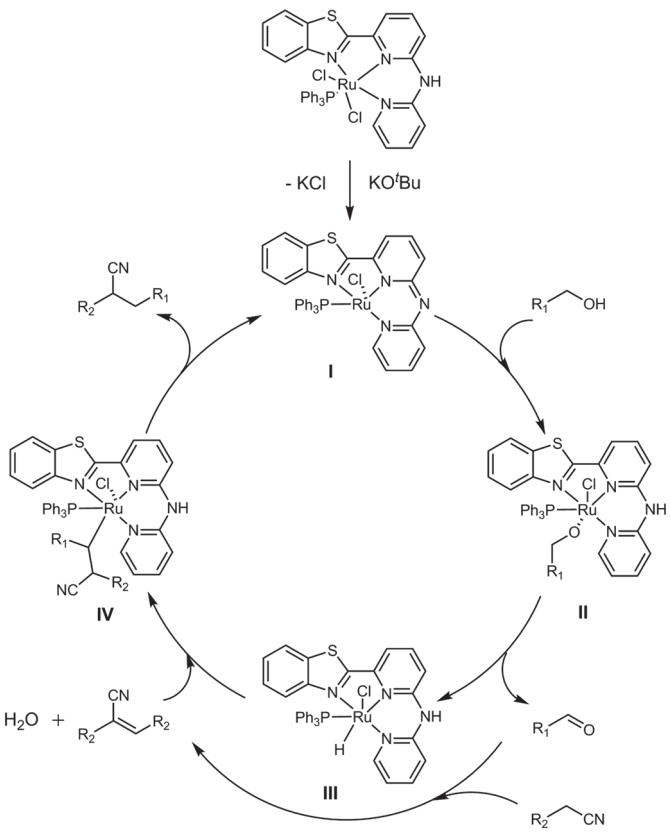
FIGURE 4 Kinetic profiles



SCHEME 3 Mechanistic experiments

2.6 | Proposed mechanism

On the basis of the above experimental results and previous reports,[13,15,26] a possible mechanism has been proposed, as shown in Scheme 4. Through metal–ligand cooperation,[27–32] the dearomatization/rearomatization process can be achieved via deprotonation/reprotonation of the NH linker. Since **2a** containing the NH linker is acidic, deprotonation occurs in the presence of base, which leads to dearomatization of the pyridine ring. We therefore speculated that the catalytic cycle is initiated by the formation of intermediate **I**, from dechlorination and deprotonation on reaction with KO^{t}Bu. This may explain why **2a** bearing an NH moiety dramatically improves the catalytic performance compared to NMe, O or S linkers. Regrettably, although we tried to obtain the intermediate **I**, we failed. An active Ru-methoxy complex **II** was generated in the presence of benzyl alcohol. Complex **II** on β-hydride abstraction generates the Ru-H species **III**, releasing the transient benzaldehyde intermediate. To detect the formation of any Ru-H species, the reaction of **2a** with benzyl alcohol in the presence of KO^{t}Bu was carried out under optimal reaction conditions. After removing solvent, the mixture was characterized by ^{1}H NMR. A triplet was observed at δ −10.05 ppm, indicating the formation of an Ru-H species.[64–66] Unfortunately, we failed to isolate the Ru-H species from the system. A signal for benzaldehyde was detected at δ 10.03 ppm. When **2a** was reacted with benzyl cyanide under the same conditions as above, the Ru-H signal was not observed. This shows that **2a** reacts with the benzyl alcohol rather than benzyl cyanide in the mixture. The benzaldehyde released and Ru-H active species were formed. Vinyl nitrile intermediate was formed from benzaldehyde and benzyl cyanide, which can undergo insertion into Ru-H on reaction with Ru dihydride intermediate **III** to generate the intermediate **IV**. Further elimination of Ru-alkyl ligand and a ligand backbone N-H proton can provide the α-alkylated nitrile product and regenerate the intermediate **I**. Further research into this mechanism is under way in our laboratory.



SCHEME 4 Proposed mechanism

3 | CONCLUSIONS

In summary, we have developed six $^{PBT}NN^XN$ ligands, including four kinds of linkers (X = NH, NCH_3, O, S), and have introduced electron-donating/withdrawing groups on the pyridine ring (R = OMe or F) to adjust electronic effect. Three Ru($^{PBT}NN^XN$)$Cl_2(PPh_3)$ complexes, Ru($^{PBT}NN^{NH}N$)$Cl_2(PPh_3)$, Ru($^{PBT}NN^{NMe}N$)$Cl_2(PPh_3)$, and Ru($^{PBT}NN^SN$)$Cl_2(PPh_3)$, bearing PBT - pyridine ligands, were successfully prepared. The benzothiazole and adjacent pyridine ring of PBT in the ligand were determined to be coplanar by X-ray crystallography. Importantly, the $^{PBT}NN^{NH}N$ ligand in the complex also presented as coplanar with two five-membered chelate rings. In the α-alkylation of nitrile with alcohol, Ru($^{PBT}NN^XN$)$Cl_2(PPh_3)$ complexes could be generated in situ by the $^{PBT}NN^XN$ ligands and $RuCl_2(PPh_3)_3$. It was found that Ru($^{PBT}NN^{NH}N$)$Cl_2(PPh_3)$ containing NH functionality exhibited excellent catalytic activity in the α-alkylation of nitriles and alcohols with yields of up to 98%. A large variety of nitriles with aromatic and aliphatic alcohols were converted into α- alkylated products with high efficiency. Kinetic experiments and mechanistic studies suggested the presence of O_2 would inhibit the formation of alkylated product **A**. Olefin byproduct **B** as an unsaturated intermediate is reduced by benzyl alcohol. And benzyl alcohol is as hydrogen source. The mechanism of Ru($^{PBT}NN^{NH}N$)$Cl_2(PPh_3)$-catalyzed α-alkylation of nitriles with alcohols has been proposed. Benzyl alcohol is oxidized to benzaldehyde. The Ru-H species formed in the catalytic cycle was confirmed by NMR. Further mechanistic research and applications of this newly developed type of Ru catalyst are ongoing in our laboratory.

4 | EXPERIMENTAL SECTION

4.1 | General procedures

All commercially available compounds (Acros, Aldrich, Fluka, Merck, etc.) (from China or other countries) were used without purification. Dry solvents (such as dichloromethane) were collected from the solvent dispenser system. All reaction vials were purchased from Beijing Synthware Glass (Changping district, Beijing, China). Analytical thin layer chromatography was performed on GF 254 plates. Flash chromatography was performed on silica gel (200–300 mesh) by standard technical eluting with solvents as indicated. Reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. All starting materials for substrates synthesis were purchased from Energy Chemical, Macklin, Aladdin (Shanghai city, China) and used as received unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz NMR spectrometer (Germany) at 295 K in $CDCl_3$ or DMSO-d_6. HRMS (electron spray ionization ESI) analyses were performed at the EPSRC UK National Mass Spectrometry Facility, Swansea, UK. GC-MS analysis was conducted on an HP 5973 GCD system using a HP5MS column (30 m × 0.25 mm). Compounds described in the literature were characterized by comparison of their ^{1}H and/or ^{13}C NMR spectra to the previously reported data. Fourier transform infrared (FT-IR) spectra were performed on a Nicolet AVATAR-360 IR using KBr discs in the range of 4000–400 cm^{-1}.

Single crystal X-ray diffraction data for compounds **1f**, **2a**·DMSO, and **2f** were collected on a Bruker D8 VENTURE-MetalJet diffractometer equipped with a PHOTON II area detector and HELIOS multilayer optics monochromated Ga-K alpha radiation (lambda = 1.34138 Å). The data reduction was performed using APEX III software. Structures were solved by direct methods and refined by full-matrix least-squares methods based on F2 using SHELXL-2014 software. If not noted otherwise hydrogen atoms were positioned geometrically in idealized positions and refined with isotropic displacement parameters as riding atoms. If not noted otherwise all non-hydrogen atoms were refined anisotropically. Geometrical calculations were performed using SHELXL-2014 programs.[67] A summary of the crystal data and parameters of **1f**, **2a**·DMSO, and **2f** is given in Table 6.

CCDC 1934841 (**1f**), 1934842 (**2a**·DMSO), and 1934843 (**2f**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.2 | Synthesis of 1a–1f

The preparation of $^{PBT}NN^{X}N$ (X = NH, NMe, O, S) ligands **1a**–**1f** started with synthesis of 6-(benzo[*d*]thiazol-2-yl)pyridin-2-amine and 2-(6-fluoropyridin-2-yl)benzo[*d*]thiazole, according to the reference.[57] The reaction mixture of benzothiazole (2.0 mmol, 270.38 mg), 6-bromopyridin-2-amine or 2-bromo-6-fluoropyridine (2.2 mmol), Pd $(OAc)_2$ (1.0 mol%, 13.47 mg), Cu $(OAc)_2{\cdot}H_2O$ (20 mol%, 79.84 mg), PPh_3 (0.5 equiv, 262.2 mg), and K_2CO_3 (2.0 equiv, 552.8 mg) in toluene (5 ml) was refluxed for 10 hr in air. The mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was purified by silica gel column chromatography to obtain the corresponding product.

4.2.1 | 6-(benzo[d]thiazol-2-yl)pyridin-2-amine

79% isolated yield (white solid): ^{1}H NMR (400 MHz, DMSO): δ 8.12 (d, J = 7.9 Hz, 1H), 8.04 (d, J = 8.1 Hz, 1H), 7.55 (dt, J = 19.2, 7.6 Hz, 2H), 7.46 (dd, J = 13.9, 7.2 Hz, 2H), 6.62 (d, J = 8.2 Hz, 1H), 6.34 (s, 2H) ppm; ^{13}C NMR (101 MHz, DMSO): δ 170.53 (s), 160.07 (s), 154.21 (s), 148.80 (s), 138.54 (s), 135.73 (s), 126.77 (s), 125.85 (s), 123.39 (s), 122.79 (s), 111.36 (s), 108.91 (s) ppm. HRMS (ESI) calcd for $C_{12}H_9N_3S$ $[M + H^+]$ 228.0595, found 228.0573.

4.2.2 | 2-(6-fluoropyridin-2-yl)benzo[*d*]thiazole

81% isolated yield (light yellow solid): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 7.4 Hz, 1H), 8.10 (d, J = 8.2 Hz, 1H), 7.95 (dd, J = 14.5, 7.6 Hz, 2H), 7.53 (t, J = 7.7 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.04 (d, J = 8.1 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.18 (s), 154.12 (s), 142.02 (s), 136.22 (s), 126.46 (s), 125.92 (s), 123.70 (s), 122.05 (s), 117.97 (d, J = 3.9 Hz), 111.45 (s), 111.08 (s) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −66.55 (s) ppm. HRMS (ESI) calcd for $C_{12}H_7FN_2S$ $[M + H^+]$ 231.0392, found 231.0387.

Preparation of **1a**, **1c**, and **1d** was according to a previous report.[58] A 25-ml Schlenk flask was charged with 6-(benzo[d]thiazol-2-yl)pyridin-2-amine, and the corresponding 2-bromopyridine derivatives (1.2 equiv), $Pd_2(dba)_3$ (2 mol%), DPPP (4 mol%), sodium *tert*-butoxide (1.4 equiv), and dry toluene (5 ml). Under nitrogen atmosphere, the mixture was stirred at 110 °C for 12 hr. The mixture was cooled to room temperature then

TABLE 6 X-ray crystallographic data for **1f**, **2a**·DMSO, and **2f**

	1f	2a·DMSO	2f
Formula	$C_{17}H_{11}N_3S_2$	$C_{37}H_{33}Cl_2N_4OPRuS_2$	$C_{37}H_{30}Cl_6N_3PRuS_2$
Formula weight	321.41	816.73	925.50
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group	P-1	$P2_12_12_1$	$P2_1/c$
a (Å)	8.9410(3)	9.8758(5)	11.9590(6)
b (Å)	9.0739(4)	15.6264(9)	14.9888(8)
c (Å)	10.5558(4)	22.6357(13)	22.0606(11)
α (°)	86.9670(18)	90	90
β (°)	75.7466(19)	90	101.6710(10)
γ (°)	62.5396(19)	90	90
V (Å^3)	734.68(5)	3493.2(3)	3872.6(3)
Z	2	4	4
ρ_{calcd} (mg·mm^{-3})	734.68(5)	1.553	1.587
μ (mm^{-1})	2.149	0.805	5.851
F (000)	332	1664	1864
θ range (°)	4.790 to 59.375	1.799 to 26.999	4.168 to 57.999
Index ranges	−11 ≤h ≤10, −11 ≤k ≤11, −13 ≤l ≤13	−10 ≤h ≤12, −19≤k ≤19, −28≤l ≤28	−15≤h ≤15, −18 ≤k ≤18, −27≤l ≤27
Reflections collected	9308	24807	57907
Independent reflections	3230 (R [int] = 0.0279)	7610 (R [int] = 0.0388)	8183 (R [int] = 0.0342)
Completeness to theta = 53.594°	99.1%	99.5%	99.9%
Maximum and minimum transmission	0.752 and 0.647	0.802 and 0.758	0.805 and 0.627
Data/restraints/parameters	3230/0/199	7610/0/439	8183/27/470
Goodness-of-fit on F^2	1.028	1.020	1.057
Final *R* indices (I > 2sigma(I))	R1 = 0.0376, wR2 = 0.1145	R1 = 0.0275, wR2 = 0.0529	R1 = 0.0252, wR2 = 0.0620
R indices (all data)	R1 = 0.0410, wR2 = 0.1192	R1 = 0.0345, wR2 = 0.0551	R1 = 0.0262, wR2 = 0.0625
Largest diff. Peak and hole	0.406 and −0.322 e.Å^{-3}	0.455 and −0.349 e.Å-3	0.792 and −0.819 e.Å^{-3}

concentrated in vacuo and purified by flash column chromatography with petroleum ether/ethyl acetate to afford the corresponding ligands.

4.2.3 | 1a: 6-(benzo[*d*]thiazol-2-yl)-*N*-(pyridin-2-yl)pyridin-2-amine

83% isolated yield (white solid): ^{1}H NMR (400 MHz, DMSO): δ 10.00 (s, 1H), 8.29 (dd, J = 4.9, 1.1 Hz, 1H), 8.19 (d, J = 7.4 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 7.8 Hz, 1H), 7.91–7.76 (m, 3H), 7.67 (dd, J = 8.0, 0.8 Hz, 1H), 7.61–7.53 (m, 1H), 7.53–7.44 (m, 1H), 7.01–6.93 (m, 1H) ppm; ^{13}C NMR (101 MHz, DMSO): δ 169.80 (s), 154.70 (s), 154.26 (s), 148.33 (s), 148.11 (s), 139.24 (s), 138.23 (s), 135.70 (s), 127.00 (s), 126.20 (s), 123.61 (s), 122.95 (s), 119.11 (s), 117.09 (s), 114.83 (s), 112.56 (s), 112.24 (s) ppm. HRMS (ESI) calcd for $C_{17}H_{12}N_4S$ [M + H$^+$] 305.0861, found 305.0855.

4.2.4 | 1c:6-(benzo[*d*]thiazol-2-yl)-*N*-(6-methoxypyridin-2-yl)pyridin-2-amine

80% isolated yield (white solid): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, J = 8.1 Hz, 1H), 7.98 (d, J = 7.9 Hz,

1H), 7.93 (d, J = 7.4 Hz, 1H), 7.74 (t, J = 7.8 Hz, 1H), 7.68–7.56 (m, 2H), 7.52 (t, J = 7.7 Hz, 1H), 7.42 (dd, J = 14.5, 6.6 Hz, 2H), 7.35–7.25 (m, 1H), 6.40 (d, J = 7.9 Hz, 1H), 3.96 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.70 (s), 163.14 (s), 154.38 (s), 153.55 (s), 151.62 (s), 149.23 (s), 140.50 (s), 138.50 (s), 136.05 (s), 126.22 (s), 125.49 (s), 123.56 (s), 121.91 (s), 113.35 (s), 113.14 (s), 103.16 (s), 102.40 (s), 53.51 (s) ppm. HRMS (ESI) calcd for $C_{18}H_{14}N_4OS$ [M + H^+] 335.0967, found 335.0963.

4.2.5 | 1d: 6-(benzo[*d*]thiazol-2-yl)-*N*-(6-fluoropyridin-2-yl)pyridin-2-amine

85% isolated yield (white solid): ^{1}H NMR (400 MHz, DMSO) δ 10.25 (s, 1H), 8.18 (d, J = 7.8 Hz, 1H), 8.11 (dd, J = 10.9, 5.0 Hz, 2H), 7.98 (dd, J = 16.6, 8.2 Hz, 1H), 7.94–7.84 (m, 2H), 7.53 (dq, J = 15.9, 7.5 Hz, 3H), 6.67 (dd, J = 7.8, 2.2 Hz, 1H) ppm; ^{13}C NMR (101 MHz, DMSO) δ 169.60 (s), 163.17 (s), 160.83 (s), 154.24 (d, J = 11.8 Hz), 152.86 (d, J = 15.8 Hz), 148.43 (s), 143.70 (d, J = 7.8 Hz), 139.54 (s), 135.73 (s), 127.09 (s), 126.32 (s), 123.71 (s), 122.99 (s), 115.06 (s), 113.29 (s), 108.85 (s), 100.36 (s) ppm; ^{19}F NMR (376 MHz, DMSO): δ −69.51 (s) ppm. HRMS (ESI) calcd for $C_{17}H_{11}FN_4S$ [M + H^+] 323.0767, found 323.0789.

Preparation of **1b** was as follows. To a 25-ml Schlenk flask was added **1a** (1 mmol), excess iodomethane (CH_3I), and acetonitrile (2 ml). The mixture was stirred under 80 °C over an oil bath for 8 h. The reaction solution was then concentrated under vacuum and purified by flash column chromatography to afford the product.

4.2.6 | 1b:6-(benzo[*d*]thiazol-2-yl)-*N*-methyl-*N*-(pyridin-2-yl)pyridin-2-amine

75% isolated yield (light yellow solid): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, J = 3.7 Hz, 1H), 8.09 (d, J = 8.1 Hz, 1H), 7.90 (dd, J = 12.7, 7.7 Hz, 2H), 7.63 (dd, J = 13.6, 6.9 Hz, 2H), 7.49 (t, J = 7.6 Hz, 1H), 7.37 (dd, J = 18.5, 8.1 Hz, 2H), 7.25 (d, J = 8.3 Hz, 1H), 7.01–6.91 (m, 1H), 3.74 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.34 (s), 157.34 (s), 156.82 (s), 154.38 (s), 149.12 (s), 148.18 (s), 137.90 (s), 137.29 (s), 136.17 (s), 126.06 (s), 125.32 (s), 123.41 (s), 121.83 (s), 117.93 (s), 115.79 (s), 114.41 (s), 112.72 (s), 35.92 (s) ppm. HRMS (ESI) calcd for $C_{18}H_{14}N_4S$ [M + H^+] 319.1017, found 319.1012.

Preparation of **1e** and **1 f** was according to our published procedure.[47] To a 25-mL tube were added 2-(6-fluoropyridin-2-yl)benzo[*d*]thiazole (1 mmol), Cs_2CO_3 (652 mg, 2 mmol, 2.0 equiv), 2-hydroxypyridine or pyridine-2-thiol (2 mmol), and dimethyl formamide (DMF) (2 ml), and the tube was sealed with a glass stopper. The mixture was warmed over a 120 °C oil bath for 12 hr. When completed, the reaction solution was diluted with NH_4Cl solution (20 ml) and extracted with ethyl acetate (3 × 10 ml). The organic layer was separated, dried with anhydrous sodium sulfate, filtered, concentrated, and purified by flash chromatography with petroleum ether/ethyl acetate to afford the product.

4.2.7 | 1e: 2-(6-(pyridin-2-yloxy)pyridin-2-yl)benzo[*d*]thiazole

75% isolated yield (white solid): ^{1}H NMR (400 MHz, DMSO): δ 8.39 (d, J = 7.7 Hz, 1H), 8.27–8.10 (m, 3H), 8.07–7.95 (m, 2H), 7.60 (t, J = 7.7 Hz, 2H), 7.53 (t, J = 7.5 Hz, 1H), 6.59 (d, J = 9.2 Hz, 1H), 6.48 (t, J = 6.7 Hz, 1H) ppm; ^{13}C NMR (101 MHz, DMSO) δ 168.08 (s), 161.61 (s), 154.17 (s), 152.18 (s), 150.432 (s), 141.79 (s), 140.39 (s), 137.27 (s), 135.89 (s), 127.01 (s), 126.70 (s), 124.14 (s), 123.94 (s), 123.13 (s), 121.49 (s), 120.39 (s), 106.71 (s) ppm. HRMS (ESI) calcd for $C_{17}H_{11}N_3OS$ [M + H^+] 306.0701, found 306.0796.

4.2.8 | 1f: 2-(6-(pyridin-2-ylthio)pyridin-2-yl)benzo[*d*]thiazole

86% isolated yield (white solid): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (d, J = 4.5 Hz, 1H), 8.16 (d, J = 7.7 Hz, 1H), 8.07 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.72 (d, J = 4.0 Hz, 3H), 7.44 (ddd, J = 23.4, 15.2, 7.5 Hz, 3H), 7.27 (d, J = 4.1 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.80 (s), 157.63 (s), 155.26 (s), 154.17 (s), 151.42 (s), 150.25 (s), 137.62 (s), 137.06 (s), 136.22 (s), 127.66 (s), 126.21 (s), 125.63 (s), 123.56 (s), 122.39 (s), 121.90 (s), 117.95 (s) ppm. HRMS (ESI) calcd for $C_{17}H_{11}N_3S_2$ [M + H^+] 322.0473, found 322.0467.

4.3 | Synthesis of 2a, 2b, and 2f

The general procedure for **2a**, **2b**, and **2f** was as follows. To a 25-mL Schlenk flask was added $RuCl_2(PPh_3)_3$ (0.194 g, 0.2 mmol) and **1a** (**1b** or **1 f**) (0.2 mmol) in 5 ml toluene and the mixture was refluxed for 0.5 hr. The mixture was cooled to room temperature and filtered. The precipitate was washed with Et_2O (3 × 10 ml) then dried in *vacuo* to afford the corresponding solid.

4.3.1 | 2a 71% isolated yield (red-purple solid): FT-IR (KBr):1637.47 (m), 1485.85 (s), 1460.21 (w), 1437.29 (w), 1172.57 (w), 1091.22 (w), 770.43 (w), 697.76 (w)

^{1}H NMR (400 MHz, DMSO): δ 9.73 (d, J = 8.4 Hz, 1H), 9.42 (d, J = 6.0 Hz, 1H), 8.26 (d, J = 8.0 Hz, 1H), 7.86 (t, J = 7.5 Hz, 2H), 7.71 (ddd, J = 17.6, 15.6, 7.5 Hz, 3H), 7.51 (s, 1H), 7.37 (d, J = 8.2 Hz, 1H), 7.22 (dd, J = 8.1, 4.1 Hz, 3H), 7.08–6.96 (m, 13H), 6.81 (t, J = 6.5 Hz, 1H) ppm; ^{13}C NMR (101 MHz, DMSO): δ 167.66 (s), 153.47 (s), 152.53 (s), 151.56 (d, J = 17.2 Hz), 150.30 (s), 138.10 (s), 136.79 (s), 133.33 (s), 132.91 (d, J = 9.7 Hz), 131.13 (s), 130.75 (s), 130.09 (s), 128.43 (d, J = 9.0 Hz), 127.91 (s), 125.44 (s), 124.12 (s), 120.19 (s), 117.80 (s), 117.03 (s), 115.24 (s) ppm; ^{31}P NMR (162 MHz, DMSO): δ 31.40 (s) ppm. HRMS (ESI) calcd for $C_{35}H_{27}Cl_2N_4PRuS$ [M-Cl$^-$] 703.0426 (100%), 705.0437 (59%), found 703.0428 (100%), 705.0435 (83%).

4.3.2 | 2b 69% isolated yield (red-brown solid): FT-IR (KBr):1635.42 (s), 1473.65 (m), 1432.12 (s), 1359.79 (m), 1091.48 (w), 750.99 (w), 698.12 (w), 528.19 (w)

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.34 (d, J = 5.0 Hz, 1H), 9.50 (d, J = 9.0 Hz, 1H), 7.78–7.71 (m, 1H), 7.65 (d, J = 7.5 Hz, 1H), 7.56 (t, J = 7.8 Hz, 2H), 7.43–7.31 (m, 2H), 7.09 (t, J = 6.6 Hz, 3H), 7.03 (t, J = 6.5 Hz, 1H), 6.99–6.85 (m, 12H), 6.71 (d, J = 8.2 Hz, 1H), 6.67 (d, J = 8.1 Hz, 1H), 5.30 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.36 (s), 136.44 (s), 133.04 (s), 128.61 (s), 127.91 (s), 127.34 (s), 126.78 (s), 121.25 (s), 118.74 (s), 113.71 (s), 41.34 (s) ppm; ^{31}P NMR (162 MHz, $CDCl_3$): δ 46.03 (s) ppm. HRMS (ESI) calcd for $C_{36}H_{29}Cl_2N_4PRuS$ [M-Cl$^-$] 717.0583 (100%), 719.0593 (59%), found 717.0588(100%), 719.0574 (77%).

4.3.3 | 2f 65% isolated yield (red-brown solid): FT-IR (KBr): 1651.88 (m), 1456.27 (m), 1431.98 (s), 1390.37 (w), 1090.05 (w), 768.23 (w), 694.00 (w), 527.97 (w)

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.62 (d, J = 4.7 Hz, 1H), 8.85 (d, J = 8.5 Hz, 1H), 7.99–7.92 (m, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.61–7.48 (m, 2H), 7.37 (d, J = 7.2 Hz, 1H), 7.30 (s, 2H), 7.27–7.19 (m, 2H), 7.11 (dd, J = 14.3, 7.0 Hz, 9H), 7.02–6.85 (m, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.70 (s), 159.74 (s), 155.50 (s), 153.21 (s), 135.37 (s), 134.80 (s), 134.38 (s), 133.66 (d, J = 9.0 Hz), 132.81 (s), 128.71 (s), 127.93 (s), 127.11 (d, J = 9.3 Hz), 125.11 (s), 124.71 (s), 123.02 (s), 122.82 (s), 121.29 (s) ppm; ^{31}P NMR (162 MHz, $CDCl_3$): δ 42.18 (s) ppm. HRMS (ESI) calcd for $C_{35}H_{26}Cl_2N_3PRuS_2$ [M-Cl$^-$] 720.0038 (100%), 722.0049 (59%), found 720.0012 (100%), 722.0010 (76%).

4.4 | General procedure for α-alkylation of nitriles with alcohols

Under nitrogen atmosphere, a mixture of nitriles (1 mmol), alcohols (2 mmol), **2a** (1 mol%), KO^{t}Bu (10 mol%), and dry toluene (1 ml) in a 15-ml Schlenk tube was stirred at 135 °C for the certain time. After the reaction was complete, the solvents were removed under vacuum and the residue was purified by silica gel column chromatography (petroleum ether / ethyl acetate (PE/EtOAc) 50:1–10:1) to afford the corresponding product.

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