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ARTICLE

Ruthenium-Catalyzed C–H Allylation of Arenes with Allylic Amines

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The Ru-catalyzed pyridyl-directed C–H allylation of arenes with allylic amines has been developed. The reaction was carried out in the presence of 5 mol % of $[Ru(p\text{-cymene})Cl_2]_2$ and 0.5 equiv. of AgOAc in CF_3CH_2OH at 75 °C, affording allylated products of arenes in moderate to excellent yields. The method exhibits a wide scope of allylic amines and arenes and shows good compatibility of functional groups. Pyrazolyl- and pyrimidyl-directed C–H allylation of arenes were also performed under the same conditions.

Introduction

The allyl group is a prominent structural motif found in many natural products and bioactive molecules. The compounds containing allyl moiety are also versatile building blocks in organic synthesis.[1] Therefore, allylation reactions have attracted much attention and a number of allylation methods have been developed.[1,2] Allylic surrogates used in various allylation reactions include allylic halides,[3] allylic alcohol[4] or its derivatives,[5] allenes,[6] 1,3-dienes,[7] and so on. Compared with above the allylation agents, allylic amines have rarely been employed due to the stability of the C–N bond.[2g] However, it would be worthwhile to explore the reactions with allylic amines from the perspective of understanding their reactivity and finding novel allylation agents. Some successful trials have been carried out.[8,9] For example, Trost and Spagnol developed a Ni-catalyzed cross-coupling of organoboronic acids with allylamines with high regioselectivity in 1995.[9a] In 2007, List's group reported a highly enantioselective α-allylation of aldehydes catalyzed by palladium-based catalysts.[9b] In 2011 Zhang et al. performed a Pd-catalyzed α-allylation of carbonyl compounds by reaction of allylic amines with ketones and aldehydes.[9c] Recently Huang and co-workers reported a new method for the formation of β,γ-unsaturated amides by Pd-catalyzed carbonylation of allylamines via C–N bond activation.[9d] On the other hand, C–H activation and functionalization represent an atom-economic transformation. A series of C–H allylation reactions of unreactive systems by using allylic halides, allylic alcohols and their derivatives have been carried out.[2-5] Inspired by previous work, we initiated a study of transition-metal-catalyzed allylation of arenes with allylic amines via C–H and C–N bond activation. Herein, we report the results.

Results and discussion

We commenced screening of reaction conditions by employing reaction of 2-phenylpyridine (**1a**) with N-allyl-N-methylaniline (**2a**) as the model reaction. The catalyst systems for Ni- or Pd-catalyzed allylic alkylation of carbonyl compounds were demonstrated to be ineffective to our reaction.[9c,9e] Ruthenium was reported to catalyze the C–H functionalization of arenes[5a,10] and the C–N bond cleavage of allylic amines.[11] Hence we tried to use ruthenium complex $[Ru(p\text{-cymene})Cl_2]_2$ as the catalyst. The reaction of **1a** with 2 equiv. of **2a** in MeOH at 75 °C in the presence of $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %) and AgOAc (1.0 equiv.) resulted in a mixture of **3aa** (26%) and **3aa'** (16%) after 12 h (Table 1, entry 1). The positive result encouraged us to further examine the reaction in different solvents. The use of both EtOH and *i*-PrOH as solvents also led to positive results and the latter exhibited better selectivity (entries 2 and 3 in Table 1). However, use of aprotic solvents involving toluene, THF and DMF gave negative results (entries 4-6 in Table 1). This experimental fact might imply that the reaction was promoted via a hydrogen bond-assisted activation as that in Pd-catalyzed allylic alkylation of carbonyl compounds.[9c] CF_3CH_2OH was found to be a better solvent than the alcohols mentioned above and the reaction in CF_3CH_2OH gave **3aa** in 52% yield (entry 7 in Table 1). $(CF_3)_2CHOH$ exhibited poorer efficiency compared with CF_3CH_2OH. The reaction in $(CF_3)_2CHOH$ led to a mixture of **3aa** (40%) and **3aa'** (10%) (entry 8 in Table 1). Hence the further condition screenings were performed in CF_3CH_2OH. Increasing loading of allylic amine markedly enhanced the product yield. Employing 4 equiv. of allylic amine gave excellent reaction result and

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† Electronic Supplementary Information (ESI) available: Details of the mechanistic study and copies of NMR spectra of the cross-coupling products. This material is available free of charge via the Internet at http://pubs.acs.org. See DOI: 10.1039/x0xx00000x

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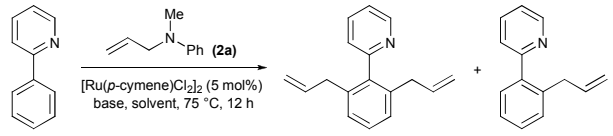
Table 1 Optimization of reaction conditions[a]



Entry	Base (equiv.)	**2a** (equiv.)	solvent	yield (%)[b] **3aa** (**3aa'**)
1	AgOAc (1)	2	MeOH	26 (16)
2	AgOAc (1)	2	EtOH	16 (26)
3	AgOAc (1)	2	*i*-PrOH	29 (0)
4	AgOAc (1)	2	Toluene	–
5	AgOAc (1)	2	THF	–
6	AgOAc (1)	2	DMF	–
7	AgOAc (1)	2	CF_3CH_2OH	52 (0)
8	AgOAc (1)	2	$(CF_3)_2CHOH$	40 (10)
9	AgOAc (1)	3	CF_3CH_2OH	80 (0)
10	AgOAc (1)	4	CF_3CH_2OH	86 (0)
11	AgOAc (1)	5	CF_3CH_2OH	88 (0)
12[c]	AgOAc (1)	4	CF_3CH_2OH	78 (14)
13[d]	AgOAc (1)	4	CF_3CH_2OH	74 (0)
14[e]	AgOAc (1)	4	CF_3CH_2OH	85 (0)
15	AgOAc (1.5)	4	CF_3CH_2OH	80 (0)
16	AgOAc (0.5)	4	CF_3CH_2OH	90 (0)
17	AgOAc (0.2)	4	CF_3CH_2OH	79 (0)
18[f]	AgOAc (0.5)	4	CF_3CH_2OH	91 (0)
19[g]	AgOAc (0.5)	4	CF_3CH_2OH	83 (0)
20	KOAc (1)	4	CF_3CH_2OH	81 (0)
21	AgOTf (0.5)	4	CF_3CH_2OH	8 (30)
22	Ag_2O (0.5)	4	CF_3CH_2OH	3 (41)
23	AgF (0.5)	4	CF_3CH_2OH	7 (29)
24	none	4	CF_3CH_2OH	5 (35)
25[h]	AgOAc (0.5)	4	CF_3CH_2OH	–
26[i]	AgOAc (0.5)	4	CF_3CH_2OH	88 (0)

[a] Unless otherwise specified, the reactions were carried out on a 0.2 mmol scale according to the conditions indicated by above equation. [b] Isolated yield. [c] 2.5 mol % $[Ru(p\text{-cymene})Cl_2]_2$ was employed. [d] Reaction time was 6 h. [e] Reaction time was 24 h. [f] Reaction was run at 100 °C. [g] Reaction was run at 50 °C. [h] No $[Ru(p\text{-cymene})Cl_2]_2$ was employed. [i] The reaction was on a 4 mmol scale.

higher loading of allylic amine did not markedly increase the product yield (entries 9-11 in Table 1). Lowering the amount of $[Ru(p\text{-cymene})Cl_2]_2$ to 2.5 mol % resulted in decrease of **3aa** yield along with formation of **3aa'** in 14% yield (entry 12 in Table 1). If the reaction time was shortened to 6 h the yield of **3aa** decreased to 74%. However, extending reaction time to 24 h did not increase the product yield (entries 13 and 14 in Table 1). Next, we examined the effect of AgOAc dosage and found 0.5 equiv of AgOAc loading was optimal (entries 15-17 in Table 1). The effect of temperature was next tested. Higher temperature than 75 °C did not enhance the product yield and lower temperature than 75 °C led to decrease of the yield (entries 18 and 19 in Table 1). Other bases including KOAc, AgOTf, Ag_2O, and AgF were also tested (entries 20-23 in Table 1). KOAc was a good base but less effective than AgOAc. AgOTf, Ag_2O, and AgF led to a mixture of **3aa** and **3aa'** in relatively low yields. In the absence of a base the reaction still occurred and gave a mixture of **3aa** (5%) and **3aa'** (35%) in relatively low overall yield (entry 24 in Table 1). In the absence of a Ru catalyst the reaction cannot occur (entry 25 in Table 1). Other Ru complexes including $RuH_2(CO)(PPh_3)_3$, $Cp^*Ru(PPh_3)_2Cl$, $[Cp^*RuCl]_4$ and $RuCl_2(PPh_3)_3$ were also noneffective or less effective than $[Ru(p\text{-cymene})Cl_2]_2$ (Table S1 in the ESI). Finally, the optimized conditions were demonstrated to suit for the reaction with a larger scale of substrates. 0.4 Mmol of **1a** was treated with 4 equiv. of **2a** under the optimized conditions to afford **3aa** in 88% yield (entry 26 in Table 1).

Next, we examined reaction of 2-phenylpyridine (**1a**) or 2-(*o*-tolyl)pyridine (**1b**) with different allylic amines under the optimized conditions and the results are listed in Table 2. N-Allyl-N-phenylaniline and N-allyl-N-phenylhydroxylamine reacted with **1a** to afford 2-(2,6-diallylphenyl)pyridine (**3aa**) in 72% and 38% yield, respectively (entries 2 and 3 in Table 2). Reaction of 2-(*o*-tolyl)pyridine (**1b**) with various allylic amines resulted in *ortho*-monoallylation species. In this case 2 equiv. of allylic amine was enough to complete the reaction. N-Allyl-N-methylaniline still exhibited good reactivity. Its reaction with **1b** gave 2-(2-allyl-6-methylphenyl)pyridine (**3ba**) in 88% yield (entry 4 in Table 2). Other phenyl allylamines including N-allyl-N-phenylaniline, N-allyl-N-phenylhydroxylamine, N,O-diallyl-N-phenylhydroxylamine, N-allylaniline, and N,N-diallylaniline reacted smoothly with **1b** to form **3ba** in 63%-92% yields (entries 5-9 in Table 2). It is noteworthy that N-allylaniline showed excellent reactivity in this transformation. Aliphatic allylic amines can also be used in this transformation. Reaction of 4-allylmorpholine with **1b** at 50 °C afforded **3ba** in 73% yield, which was higher than that obtained from the reaction at 75 °C (entry 10 in Table 2). Reaction of **1b** with either N-(but-3-en-2-yl)-N-methylaniline or (*E*)-N-(but-2-en-1-yl)-N-methyl-aniline gave high overall yields. But in each case a mixture of regio- and geo-isomers was obtained (entries 11 and 12 in Table 2).

To further examine the versatility of the reaction, we evaluated the scope of 2-arylpyridines using N-allyl-N-methylaniline (**2a**) as the allylation reagent. The results are summarized in Schemes 1 and 2, respectively. Compound **2a** reacted smoothly with electron-poor 2-arylpyridines including $2\text{-}(2\text{-}FC_6H_4)C_5H_4N$, $2\text{-}(2,4\text{-}F_2C_6H_3)C_5H_4N$, $2\text{-}(2\text{-}ClC_6H_4)C_5H_4N$, $2\text{-}(2\text{-}BrC_6H_4)C_5H_4N$, and $2\text{-}(2\text{-}CF_3C_6H_4)C_5H_4N$ to give the corresponding monoallylation products (**3ca**–**3ga**, Scheme 1) in moderate to good yields. Among the substrates $2\text{-}(2\text{-}ClC_6H_4)C_5H_4N$ showed higher reactivity. Both $2\text{-}(2\text{-}FC_6H_4)C_5H_4N$ and $2\text{-}(2,4\text{-}F_2C_6H_3)C_5H_4N$ displayed relatively low reactivity.

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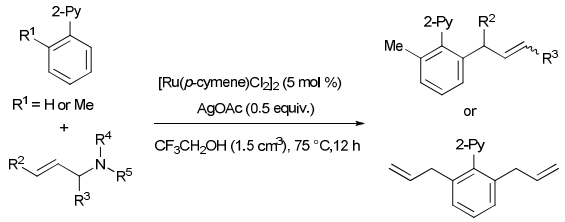
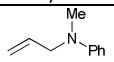
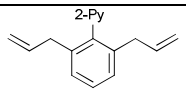
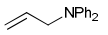
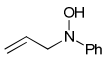
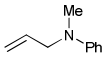
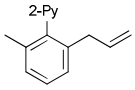
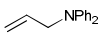
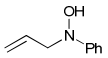
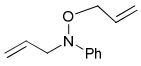
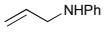
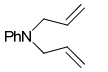
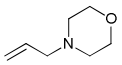
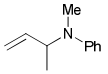
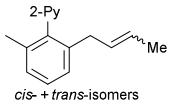
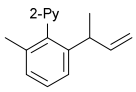
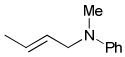
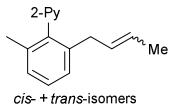
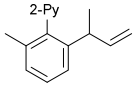
Part of the substrates remained unchanged. Under stronger conditions, reaction of 2-(2,4-$F_2C_6H_3$)C_5H_4N got improved to some extent. 2-*m*-Tolylpyridine, 2-(3,4-dimethylphenyl) pyridine, and 2-(biphenyl-3-yl)pyridine occurred *ortho*-C-H monoallylation at the less hindered sites even in the presence of excess allylic amine, affording the corresponding products in moderate yields (**3ha**-**3ja**, Scheme 1). Some starting materials remained unchanged. Both 2-(naphthalen-2-yl)pyridine and 2-(naphthalen-1-yl)pyridine also respectively reacted with **2a** under the standard conditions. The former gave monoallylation product 2-(3-allylnaphthalen-2-yl)pyridine (**3ka**, Scheme 1) in 51% yield, and the latter led to 2-(2-allylnaphthalen-1-yl)pyridine (**3la**, Scheme 1) in 85% yield.

Reaction of the 2-(4-substituted phenyl)pyridines with **2a** under the standard conditions resulted in bisallylation products (**3ma**-**3wa**, Scheme 2). The para-substituents included electron-donor groups such as Me, Ph, OMe, and OH and electron-withdrawing groups such as F, Cl, Br, COOEt, COOH, CF_3 and NO_2. Reaction of the substrates except 2-(4-nitrophenyl)pyridine gave good yields. It seems that the reactivity of the substrates is uncorrelated with the electron effect of the substituents at the para position of the phenyl rings. However, reaction of 2-(4-nitrophenyl)pyridine gave relatively low product yield (45%) for unclear reasons. Surprisingly, respective reaction of 2-(3-methoxyphenyl)-pyridine, 2-(3-fluorophenyl)pyridine and 2-(3-chlorophenyl)-pyridine with **2a** afforded bis-allylation products (**3xa**-**3za**, Scheme 2) in moderate to good yields. This is probably due to relatively small hindrance of these groups on the phenyl rings.

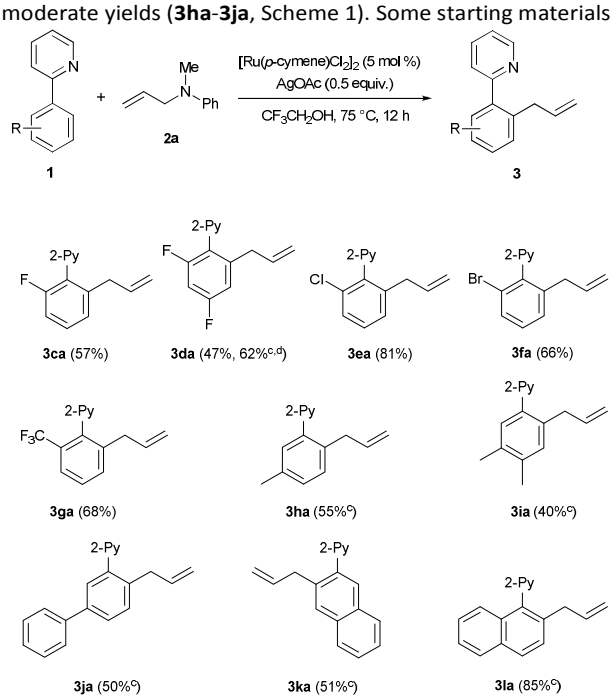
In addition, the catalyst system also suited for the bisallylation of arenes with other directing groups such as pyrazolyl group and pyrimidyl group. For example, reaction of 1-phenyl-1H-pyrazole with **2a** under the standard conditions

Table 2 Scope of allylic amines[a]



Entry	Allylic amine	Product	Yield (%)[b]
1[c]		 **3aa**	90
2[c]		**3aa**	72
3[c]		**3aa**	38
4		 **3ba**	88
5		**3ba**	68
6		**3ba**	63
7		**3ba**	38
8		**3ba**	92
9		**3ba**	65
10[d]		**3ba**	73
11		 *cis*- + *trans*-isomers  1:2.14:1.56	88[e]
12		 *cis*- + *trans*-isomers  1:2.24:1.60	82[e]

[a] Unless otherwise specified, the reactions were carried out on a 0.2 mmol scale according to the conditions indicated by above equation, 2 equiv. of allylic amines were employed. [b] Isolated yield. [c] 4 equiv. of allylic amines were employed. [d] The reaction was run at 50 °C. [e] Yield of the mixture.



Scheme 1 Monoallylation of of 2-arylpyridines.[a] Unless otherwise specified, the reactions were carried out on a 0.2 mmol scale according to the conditions indicated by the above equation, 2 equiv. of allylic amines were employed. [b] Yields of isolated products are reported. [c] 4 Equiv. of allylic amines were employed. [d] The reaction was run at 100 °C for 18 h in the presence of 7.5 mol % [Ru(*p*-cymene)Cl_2]$_2$.

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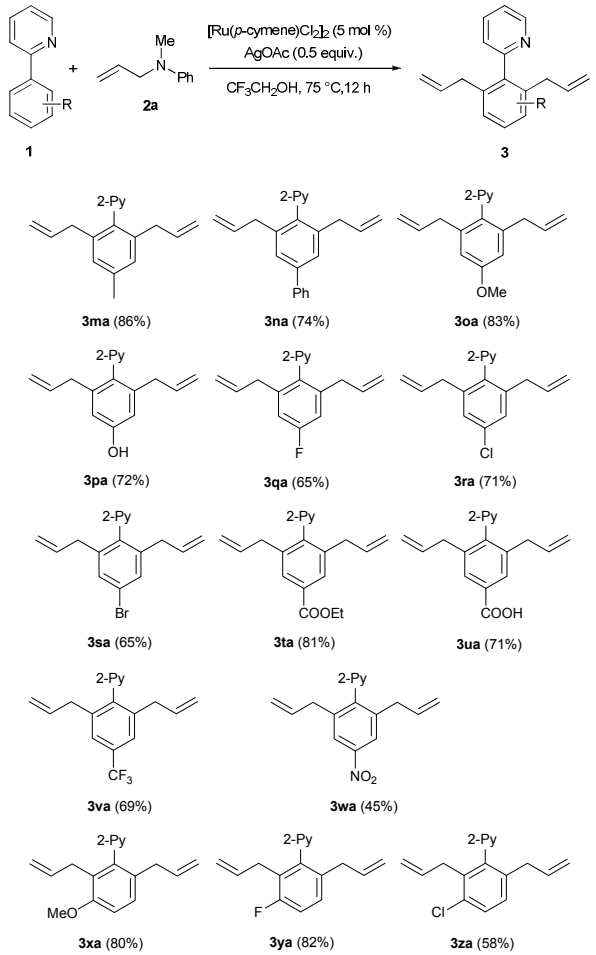
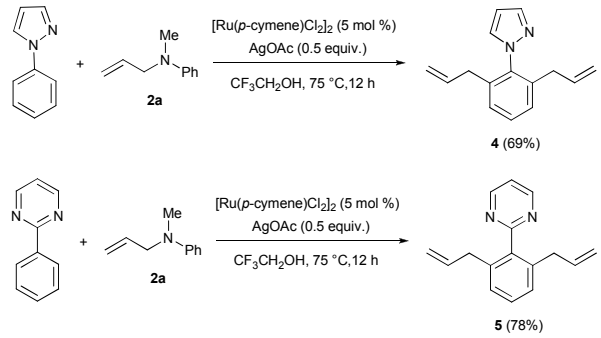
gave 1-(2,6-diallylphenyl)-1H-pyrazole (**4**) in 69% yield. Reaction of 2-phenylpyrimidine with **2a** under the standard conditions afforded 2-(2,6-diallylphenyl)pyrimidine (**5**) in 78% yield (Scheme 3).

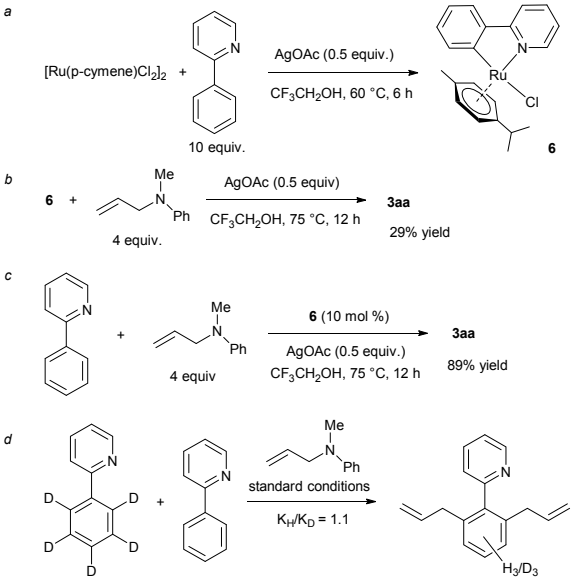


Scheme 2 Bisallylation of 2-arylpyridines. [a] The reactions were carried out on a 0.2 mmol scale according to the conditions indicated by above equation, 4 equiv. of allylic amines were employed. [b] Yields of isolated products are reported.



Scheme 3 pyrazolyl- and pyrimidyl-directed bisallylation reaction.

To probe the reaction mechanism, we made the following experiments. Reaction of $[Ru(p\text{-cymene})Cl_2]_2$ with 10 equiv. of 2-phenylpyridine in the presense of AgOAc (0.5 equiv.) in CF_3CH_2OH at 60 °C for 6 hours yielded ruthenium(II) complex **6** (*a* in Scheme 4). Structure of the complex was confirmed by comparing its spectroscopic data with those reported in literature.[12] No reaction occurred between $[Ru(p\text{-cymene})Cl_2]_2$ and N-allyl-N-methylaniline under the same conditions. Complex **6** was demonstrated to react with 4 equiv. of N-allyl-N-methylaniline in the presence of AgOAc (0.5 equiv.) to afford **3aa** in 29% yield (*b* in Scheme 4). Complex **6** was also demonstrated to catalyze reaction of **1a** or **1b** with **2a** under the optimized conditions to give the corresponding products in similar yields to those employing $[Ru(p\text{-cymene})Cl_2]_2$ as the catalyst (*c* in Scheme 4 and section 3.3 in the ESI). These experimental facts suggest that the cyclometalated complex could be an intermediate in the catalytic cycle. Furthermore, we measured the kinetic isotopic effect via reaction of **1a** and **1a**-D5 with **2a** under the standard conditions. A k_H/k_D value of 1.1 was obtained by analyzing ^1H NMR spectrum of the product (*d* in Scheme 4). This result suggests that the C–H bond cleavage may not be the rate-limiting step. As mentioned earlier, reaction of 2-(*o*-tolyl)pyridine with either N-(but-3-en-2-yl)-N-methylaniline or (E)-N-(but-2-en-1-yl)-N-methylaniline resulted in a mixture of regio- and geo-isomers (entries 11 and 12 in Table 2). This experimental fact implies that an η^3-allylruthenium intermediate is present in the catalytic cycle. The almost same distribution ratios of the products in the two reactions further proved that the same η^3-allylruthenium intermediates were formed. In addition, the catalytic reaction cannot occur in the aprotic solvents such as toluene, THF and DMF but proceeded in alcohols including MeOH, EtOH, *i*PrOH, $(CF_3)_2CHOH$ and CF_3CH_2OH (Table 1). We surmised that the protic solvents promote the C–N bond cleavage of allylic amines via a hydrogen-bond-activation.[9c]



Scheme 4 Preliminary mechanistic study.

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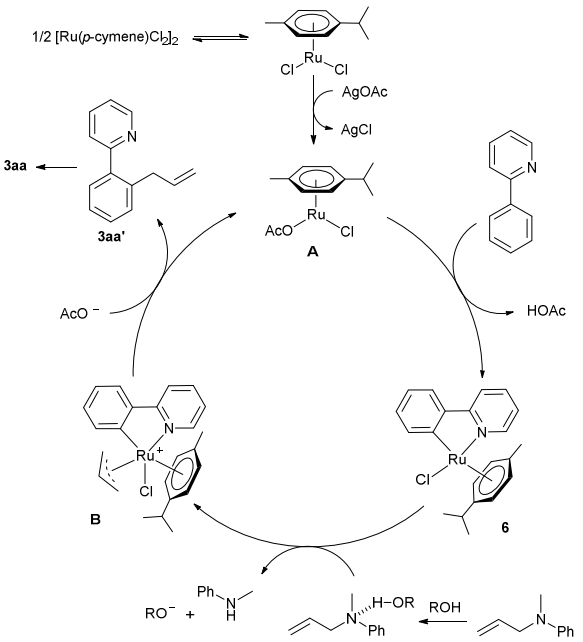
On the basis of above experimental results and literature report,[11a,13] we propose a plausible mechanism for the C–H allylation (Scheme 5). The formation of active catalyst **A** by action of $[Ru(p\text{-cymene})Cl_2]_2$ with AgOAc. Coordination of the pyridine group of compound **1a** to **A** and then *ortho*-phenyl C–H bond activation form five-membered ring ruthenium intermediate **6**. Reaction of complex **6** with the hydrogen-bond-activated **2a** affords an η^3-allyl complex **B**. Reductive elimination of **B** results in **3aa'** and regenerates active catalyst **A** in the presence of OAc^-. **3aa** is formed from **3aa'** via the same pathway as for **3aa'**.



Scheme 5 Proposed catalytic cycle.

Conclusions

In summary, a Ru-catalyzed method for allylation of arenes via cleavage of the C–N bond of allylic amines and pyridyl-directed aryl C–H activation has been developed. The reaction proceeded under mild conditions and afforded the allylation products in moderate to high yields. For 2-phenylpyridine and 2-(4-substituted phenyl)pyridines the reaction resulted in *ortho*-position bisallylation products of the phenyl groups. For the 2-(3-substituted phenyl)pyridines the reaction gave either monoallylation or bisallylation products depending on the steric hindrance of the 3-substituents. A range of functional groups including electron-withdrawing and electron-donor groups on the phenyl rings can be tolerated. Various allylamines including aromatic amines, aliphatic amines, and hydroxylamines were demonstrated to suit for this transformation. The reaction is proposed to proceed via a hydrogen-bond-promoted C–N bond cleavage of the allyl amines and a Ru(II)/Ru(IV) catalytic cycle.

Experimental

All reactions were performed under nitrogen atmosphere using standard Schlenk and vacuum line techniques. Toluene and THF were purified by JC Meyer Phoenix Solvent Systems. DCE was dried over CaH_2 and distilled under nitrogen. DMSO and DMF were dried over 4 Å molecular sieve, fractionally distilled under reduced pressure and stored under nitrogen. CF_3CH_2OH was dried over 4 Å molecular sieve and distilled under nitrogen. MeOH and EtOH were treated with Mg and then distilled under nitrogen. $[Ru(p\text{-cymene})Cl_2]_2$ was purchased from TCI (Shanghai) Development Co., Ltd. 2-Arylpyridines[13] and allylic amines[9c,14] were synthesized according to the reported methods. All other chemicals were obtained from commercial vendors and used as received. NMR spectra were recorded on a Bruker Avance III 400 spectrometer at ambient temperature. The chemical shifts of the ^1H NMR spectra were referenced to TMS or internal solvent resonances and the chemical shifts of the ^{13}C NMR spectra were referenced to internal solvent resonances. The chemical shifts of the ^{19}F NMR spectra were referenced to external CF_3COOH. High-resolution mass spectra (HR-MS) were acquired in the ESI mode using an Orbitrap mass analyzer.

Synthesis of 2-(3-fluorophenyl)pyridine and 2-(3-chlorophenyl)-pyridine

2-(3-Fluorophenyl)pyridine and 2-(3-chlorophenyl)pyridine were synthesized according to the reported method.[13a]

2-(3-Fluorophenyl)pyridine. ^1H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, *J* = 4.7 Hz, 1H), 7.81–7.64 (m, 4H), 7.47–7.36 (m, 1H), 7.28–7.19 (m, 1H), 7.09 (dt, *J* = 8.4, 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.38 (d, *J* = 246.3 Hz), 156.08 (d, *J* = 2.7 Hz), 149.82 , 141.77 (d, *J* = 7.6 Hz), 136.95 , 130.29 (d, *J* = 8.2 Hz), 122.73, 122.47 (d, *J* = 2.8 Hz), 120.63 , 115.85 (d, *J* = 21.3 Hz), 113.93 (d, *J* = 22.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ –112.91. HR-MS: m/z 174.0705 $[M+H]^+$, calcd for $C_{11}H_9NF$ 174.0714.

2-(3-Chlorophenyl)pyridine. ^1H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, *J* = 4.7 Hz, 1H), 8.01 (s, 1H), 7.89–7.82 (m, 1H), 7.75 (dt, *J* = 7.7, 1.6 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.43–7.35 (m, 2H), 7.28–7.21 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.03, 149.88, 141.25, 137.01, 134.95, 130.07, 129.03, 127.20, 125.04, 122.77, 120.68. HR-MS: m/z 190.0408 $[M+H]^+$, calcd for $C_{11}H_9NCl$ 190.0418.

General procedure for the allylation of arenes with allylic amines

2-Arylpyridines (0.2 mmol), allylic amines (2 or 4 equiv.), AgOAc (0.5 equiv.), $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %), and CF_3CH_2OH (1.5 cm^3) were successively added into a Schlenk tube. The mixture was stirred at 75 °C for 12 hours. Upon cooling to room temperature, the resulting mixture was diluted with EtOAc and filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography to afford the desired product.

2-(2,6-Diallylphenyl)pyridine (3aa). Elution with EtOAc/ petroleum ether 1/20 (v/v), colorless oil, yield 42.4 mg (90%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, *J* = 4.1 Hz, 1H), 7.70 (t, *J* =

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7.6 Hz, 1H), 7.33–7.21 (m, 3H), 7.16 (d, *J* = 7.6 Hz, 2H), 5.88-5.70 (m, 2H), 4.91 (d, *J* = 10.0 Hz, 2H), 4.80 (d, *J* = 17.0 Hz, 2H), 3.23–3.00 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.03, 149.49, 140.09, 138.06, 137.36, 135.91, 128.35, 127.40, 125.24, 121.96, 115.57, 37.98. HR-MS: m/z 236.1422 $[M+H]^+$, calcd for $C_{17}H_{18}N$ 236.1434.

2-(2-Allyl-6-methylphenyl)pyridine (3ba). Elution with EtOAc/petroleum ether 1/20 (v/v), colorless oil, yield 36.9 mg (88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 4.7 Hz, 1H), 7.73 (dt, *J* = 7.7, 1.8 Hz, 1H), 7.30–7.20(m, 3H), 7.13 (d, *J* = 7.6 Hz, 2H), 5.87-5.72 (m, 1H), 4.94–4.87 (m, 1H), 4.84–4.76 (m, 1H), 3.12 (s, 2H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.52, 149.64, 140.31, 137.80, 137.43, 136.18, 136.12, 128.15, 128.08, 126.93, 124.88, 121.86, 115.50, 37.95, 20.40. HR-MS: m/z 210.1279 $[M+H]^+$, calcd for $C_{15}H_{16}N$ 210.1277.

2-(2-Allyl-6-fluorophenyl)pyridine (3ca). Elution with EtOAc/petroleum ether 1/20 (v/v), colorless oil, yield 24.2mg (57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 4.7 Hz, 1H), 7.74 (t, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.34–7.23 (m, 2H), 7.10 (d, *J* = 7.7 Hz, 1H), 7.02 (t, *J* = 8.9 Hz, 1H), 5.86-5.70 (m, 1H), 4.92 (d, *J* = 10.1 Hz, 1H), 4.83 (d, *J* = 17.0 Hz, 1H), 3.33 (d, *J* = 6.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.21 (d, *J* = 246.5 Hz), 154.01, 149.56, 140.98 (d, *J* = 2.4 Hz), 136.73, 136.15, 129.61 (d, *J* = 9.0 Hz), 128.30 (d, *J* = 15.5 Hz), 125.86 (d, *J* = 1.7 Hz), 125.33 (d, *J* = 3.1 Hz), 122.48 , 115.98 , 113.53 (d, *J* = 22.7 Hz), 37.25 (d, *J* = 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ –116.53. HR-MS: m/z 214.1030 $[M+H]^+$, calcd for $C_{14}H_{13}FN$ 214.1027.

2-(2-Allyl-4,6-difluorophenyl)pyridine (3da). Elution with EtOAc/petroleum ether 1/20 (v/v), colorless oil, yield 21.1 mg (47%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 4.4 Hz, 1H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.31–7.25 (m, 1H), 6.86 (d, *J* = 9.4 Hz, 1H), 6.77 (t, *J* = 9.1 Hz, 1H), 5.83–5.69 (m, 1H), 4.98 (d, *J* = 10.0 Hz, 1H), 4.87 (d, *J* = 17.0 Hz, 1H), 3.31 (d, *J* = 6.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.51 (dd, *J* = 249.6, 13.2 Hz), 160.43 (dd, *J* = 248.8, 12.7 Hz), 153.24 , 149.69 , 142.82 (dd, *J* = 8.9, 3.6 Hz), 136.31 , 135.83 , 125.99 (d, *J* = 1.6 Hz) , 124.55 (dd, J = 15.7, 3.8 Hz), 122.65 , 116.81 , 112.32 (dd, *J* = 21.4, 3.4 Hz), 101.91 (dd, *J* = 26.9, 25.6 Hz), 37.26 (dd, *J* = 2.6, 1.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ –110.27 (d, *J* = 7.6 Hz), –112.38 (d, *J* = 7.6 Hz). HR-MS: m/z 232.0933 $[M+H]^+$, calcd for $C_{14}H_{12}F_2N$ 232.0932.

2-(2-Allyl-6-chlorophenyl)pyridine (3ea). Elution with EtOAc/petroleum ether 1/20 (v/v), colorless oil, yield 37.2 mg (81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 4.4 Hz, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.31–7.23 (m, 3H), 7.20 (d, *J* = 7.6 Hz, 1H), 5.86-5.67 (m, 1H), 4.93 (d, *J* = 10.0 Hz, 1H), 4.81 (d, *J* = 17.0 Hz, 1H), 3.17 (d, *J* = 6.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.08, 149.48, 140.49, 139.07, 136.44, 136.11, 133.27, 129.25, 127.96, 127.39, 125.37, 122.45, 116.11, 37.93. HR-MS: m/z 230.0728 $[M+H]^+$, calcd for $C_{14}H_{13}ClN$ 230.0731.

2-(2-Allyl-6-bromophenyl)pyridine (3fa). Elution with EtOAc/petroleum ether 1/20 (v/v), colorless oil, yield 36.4 mg (66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76–8.67 (m, 1H), 7.75 (dt, *J* = 7.7, 1.8 Hz, 1H), 7.52 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.33–7.23 (m, 3H), 7.20 (t, *J* = 7.7 Hz, 1H), 5.84–5.69 (m, 1H), 4.97-4.89 (m, 1H), 4.86–4.76 (m, 1H), 3.23-3.07 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.63, 149.45, 140.93, 140.56, 136.47, 136.17, 130.60, 129.62, 128.57, 125.26, 123.36, 122.53, 116.19, 38.27. HR-MS: m/z 274.0213 $[M+H]^+$, calcd for $C_{14}H_{13}BrN$ 274.0226.

2-(2-Allyl-6-(trifluoromethyl)phenyl)pyridine (3ga). Elution with EtOAc/petroleum ether 1/20 (v/v), colorless oil, yield 35.6 mg (68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, *J* = 4.2 Hz, 1H), 7.73 (dt, *J* = 7.7, 1.8 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.55–7.40 (m, 2H), 7.35–7.23 (m, 2H), 5.85–5.68 (m, 1H), 5.01-4.90 (m, 1H), 4.88–4.77 (m, 1H), 3.20-2.99 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.51, 149.11, 140.30, 138.76, 136.34, 135.83, 133.06, 128.95 (q, *J* = 29.9 Hz), 128.37, 125.12, 125.11, 124.14 (q, *J* = 275.2 Hz), 124.03 (q, *J* = 5.3 Hz), 122.58, 116.41, 37.44. ^{19}F NMR (376 MHz, $CDCl_3$): δ –57.29. HR-MS: m/z 264.0993 $[M+H]^+$, calcd for $C_{15}H_{13}F_3N$ 264.0995.

2-(2-Allyl-5-methylphenyl)pyridine (3ha). Elution with EtOAc/petroleum ether 1/20 (v/v), colorless oil, yield 23.0 mg (55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, *J* = 4.4 Hz, 1H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.27-7.12 (m, 4H), 5.94-5.79 (m, 1H), 4.94 (d, *J* = 10.0 Hz, 1H), 4.88 (d, *J* = 17.1 Hz, 1H), 3.44 (d, *J* = 6.3 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.98, 149.27, 140.33, 137.95, 136.12, 135.91, 134.57, 130.60, 130.11, 129.27, 124.24, 121.76, 115.50, 37.10, 21.07. HR-MS: m/z 210.1274 $[M+H]^+$, calcd for $C_{15}H_{16}N$ 210.1277.

2-(2-Allyl-4,5-dimethylphenyl)pyridine (3ia). Elution with EtOAc/petroleum ether 1/20 (v/v), colorless oil, yield 17.9 mg (40%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, *J* = 4.2 Hz, 1H), 7.69 (dt, *J* = 7.7, 1.8 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.24–7.16 (m, 2H), 7.07 (s, 1H), 5.94–5.81 (m, 1H), 4.99–4.85 (m, 2H), 3.43 (d, *J* = 6.4 Hz, 2H), 2.29 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.98, 149.27, 138.15, 138.02, 136.93, 136.05, 134.87, 134.57, 131.45, 131.20, 124.25, 121.55, 115.38, 37.10, 19.63, 19.36. HR-MS: m/z 224.1423 $[M+H]^+$, calcd for $C_{16}H_{18}N$ 224.1434.

2-(4-Allyl-[1,1'-biphenyl]-3-yl)pyridine (3ja). Elution with EtOAc/petroleum ether 1/20 (v/v), colorless oil, yield 27.1 mg (50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, *J* = 4.8 Hz, 1H), 7.73 (dt, *J* = 7.7, 1.8 Hz, 1H), 7.66–7.55 (m, 4H), 7.48–7.36 (m, 4H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.28–7.22 (m, 1H), δ 5.97–5.84 (m, 1H), 5.02–4.88 (m, 2H), 3.52 (d, *J* = 6.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.87, 149.30, 140.89, 140.81, 139.33, 137.57, 136.90, 136.31, 130.65, 128.82, 128.75, 127.30, 124.28, 121.95, 115.82, 37.24. HR-MS: m/z 272.1421 $[M+H]^+$, calcd for $C_{20}H_{18}N$ 272.1434.

2-(3-Allylnaphthalen-2-yl)pyridine (3ka). Elution with EtOAc/petroleum ether 1/20 (v/v), colorless oil, yield 25.0 mg (51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76–8.67 (m, 1H), 7.90-7.80 (m, 3H), 7.79–7.72 (m, 2H), 7.53–7.40 (m, 3H), 7.31-7.25 (m, 1H), 5.97-5.83 (m, 1H), 5.01–4.94 (m, 1H), 4.93–4.85 (m, 1H), 3.68 (d, *J* = 6.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ160.04, 149.18, 139.25, 137.46, 136.40, 135.98, 133.49, 132.12, 129.32, 128.54, 127.97, 127.36, 126.46, 125.83, 124.50, 121.95, 115.95, 37.86. HR-MS: m/z 246.1264 $[M+H]^+$, calcd for $C_{18}H_{16}N$ 246.1277.

2-(2-Allylnaphthalen-1-yl)pyridine (3la). Elution with EtOAc/petroleum ether 1/20 (v/v), colorless oil, yield 41.7 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, *J* = 4.7 Hz, 1H), 7.89-7.81

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(m, 2H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.46–7.26 (m, 6H), 5.95–5.81 (m, 1H), 4.96 (d, *J* = 10.1 Hz, 1H), 4.89 (d, *J* = 17.1 Hz, 1H), 3.38–3.22 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.58, 149.81, 137.36, 136.88, 136.15, 135.27, 132.60, 132.34, 128.50, 127.95, 127.82, 126.24, 125.91, 125.78, 125.27, 122.20, 115.78, 38.09. HR-MS: m/z 246.1276 $[M+H]^+$, calcd for $C_{18}H_{16}N$ 246.1277.

2-(2,6-Diallyl-4-methylphenyl)pyridine (3ma). Elution with EtOAc/petroleum ether 1/20 (v/v), colorless oil, yield 42.7 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, *J* = 4.2 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.27-9.19 (m, 2H), 6.97 (s, 2H), 5.88–5.68 (m, 2H), 4.90 (d, *J* = 10.0 Hz, 2H), 4.81 (d, *J* = 17.0 Hz, 2H), 3.17–3.00 (m, 4H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.20, 149.48, 137.93, 137.92, 137.53, 137.37, 135.86, 128.10, 125.47, 121.83, 115.47, 38.00, 21.35. HR-MS: m/z 250.1592 $[M+H]^+$, calcd for $C_{18}H_{20}N$ 250.1590.

2-(3,5-Diallyl-[1,1'-biphenyl]-4-yl)pyridine (3na). Elution with EtOAc/petroleum ether 1/20 (v/v), colorless oil, yield 46.3 mg (74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 4.8 Hz, 1H), 7.73 (dt, *J* = 7.7, 1.8 Hz, 1H), 7.66–7.59 (m, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.40 (s, 2H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.31–7.24 (m, 2H), 5.90–5.77 (m, 2H), 4.99–4.90 (m, 2H), 4.89–4.81 (m, 2H), 3.29–3.08 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.88, 149.60, 141.21, 139.16, 138.61, 137.27, 135.99, 128.80, 127.38, 127.32, 126.32, 125.36, 122.05, 115.84, 38.16. HR-MS: m/z 312.1749 $[M+H]^+$, calcd for $C_{23}H_{22}N$ 312.1747.

2-(2,6-Diallyl-4-methoxyphenyl)pyridine (3oa). Elution with EtOAc/petroleum ether 1/20 (v/v), colorless oil, yield 44 mg (83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, *J* = 4.4 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.20–7.10 (m, 2H), 6.83 (s, 2H), 5.78–5.62 (m, 2H), 4.84 (d, *J* = 10.0 Hz, 2H), 4.74 (d, *J* = 17.0 Hz, 2H), 3.73 (s, 3H), 3.11–2.92 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.30, 158.95, 149.46, 139.65, 137.12, 135.88, 133.02, 125.73, 121.80, 115.77, 112.68, 55.26, 38.16. HR-MS: m/z 266.1541 $[M+H]^+$, calcd for $C_{18}H_{20}NO$ 266.1539.

3,5-Diallyl-4-(pyridin-2-yl)phenol (3pa). Elution with EtOAc/petroleum ether 1/3 (v/v), white solid, yield 36.3 mg (72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.96-9.23 (b, 1H), 8.67 (d, *J* = 3.8 Hz, 1H), 7.75 (t, *J* = 7.3 Hz, 1H), 7.36–7.22 (m, 2H), 6.39 (s, 2H), 5.75–5.60 (m, 2H), 4.83 (d, *J* = 9.8 Hz, 2H), 4.71 (d, *J* = 17.0 Hz, 2H), 3.08–2.84 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.94, 156.93, 148.44, 139.27, 137.15, 136.77, 130.95, 126.59, 122.28, 115.55, 115.465, 38.01. HR-MS: m/z 252.1377 $[M+H]^+$, calcd for $C_{17}H_{18}NO$ 252.1383.

2-(2,6-Diallyl-4-fluorophenyl)pyridine (3qa). Elution with EtOAc/petroleum ether 1/20 (v/v), colorless oil, yield 33.1 mg (65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 4.4 Hz, 1H), 7.73 (dt, *J* = 7.7, 1.8 Hz, 1H), 7.31–7.25 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 9.6 Hz, 2H), 5.85–5.69 (m, 2H), 4.96 (dd, *J* = 10.4, 1.6 Hz, 2H), 4.84 (dd, *J* = 17.2, 1.6 Hz, 2H), 3.20–2.97 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.57 (d, *J* = 246.7 Hz), 158.30, 149.70, 140.74 (d, *J* = 7.7 Hz), 136.49, 136.15, 136.12, 125.49, 122.20, 116.38, 113.98 (d, *J* = 21.4 Hz), 37.92 (d, *J* = 1.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ –114.36. HR-MS: m/z 254.1341 $[M+H]^+$, calcd for $C_{17}H_{17}FN$ 254.1340.

2-(2,6-Diallyl-4-chlorophenyl)pyridine (3ra). Elution with EtOAc/petroleum ether 1/20 (v/v), colorless oil, yield 38.3 mg (71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 4.6 Hz, 1H), 7.72 (t, *J* = 7.9 Hz, 1H), 7.32–7.24 (m, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.16 (s, 2H), 5.87–5.66 (m, 2H), 4.96 (d, *J* = 10.1 Hz, 2H), 4.83 (d, *J* = 17.4 Hz, 2H), 3.18–2.96 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.02, 149.71, 140.17, 138.57, 136.42, 136.15, 133.95, 127.32, 125.28, 122.29, 116.43, 37.77. HR-MS: m/z 270.1047 $[M+H]^+$, calcd for $C_{17}H_{17}ClN$ 270.1044.

2-(2,6-Diallyl-4-bromophenyl)pyridine (3sa). Elution with EtOAc/petroleum ether 1/20 (v/v), colorless oil, yield 40.8 mg (65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, *J* = 4.8 Hz, 1H), 7.73 (dt, *J* = 7.7, 1.7 Hz, 1H), 7.31 (s, 2H), 7.30–7.24 (m, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 5.83-5.67 (m, 2H), 5.00–4.91 (m, 2H), 4.88–4.78 (m, 2H), 3.16–2.98 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.02, 149.71, 140.44, 139.06, 136.41, 136.15, 130.25, 125.22, 122.31, 116.46, 37.72. HR-MS: m/z 314.0541 $[M+H]^+$, calcd for $C_{17}H_{17}BrN$ 314.0539.

Ethyl 3,5-diallyl-4-(pyridin-2-yl)benzoate (3ta). Elution with EtOAc/petroleum ether 1/20 (v/v), white solid, yield 49.5 mg (81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77–8.67 (m, 1H), 7.85 (s, 2H), 7.75 (dt, *J* = 7.7, 1.8 Hz, 1H), 7.34–7.27 (m, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 5.86-5.72 (m, 2H), 5.02-4.88 (m, 2H), 4.86–4.76 (m, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.26–3.05 (m, 4H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.66, 158.11, 149.59, 144.39, 138.61, 136.65, 136.10, 130.30, 128.61, 124.94, 122.37, 116.15, 61.08, 37.87, 14.44. HR-MS: m/z 308.1639 $[M+H]^+$, calcd for $C_{20}H_{22}NO_2$ 308.1645.

3,5-Diallyl-4-(pyridin-2-yl)benzoic acid (3ua). Elution with EtOAc/petroleum ether 1/3 (v/v), white solid, yield 39.6 mg (71%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.04 (b, 1H), 8.69 (d, *J* = 4.3 Hz, 1H), 7.88 (dt, *J* = 7.7, 1.7 Hz, 1H), 7.75 (s, 2H), 7.45–7.38 (m, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 5.80–5.66 (m, 2H), 4.96-4.88 (m, 2H), 4.87–4.78 (m, 2H), 3.09 (s, 4H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 167.18, 157.24, 149.41, 144.22, 138.25, 136.66, 136.40, 130.37, 128.04, 124.74, 122.65, 116.20, 37.21. HR-MS: m/z 280.1328 $[M+H]^+$, calcd for $C_{18}H_{18}NO_2$ 280.1332.

2-(2,6-Diallyl-4-(trifluoromethyl)phenyl)pyridine (3va). Elution with EtOAc/petroleum ether 1/20 (v/v), colorless oil, yield 41.8 mg (69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 4.8 Hz, 1H), 7.76 (dt, *J* = 7.7, 1.7 Hz, 1H), 7.43 (s, 2H), 7.34–7.28 (m, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 5.85–5.70 (m, 2H), 4.98 (dd, *J* = 10.0, 1.1 Hz, 2H), 4.84 (dd, *J* = 17.0, 1.5 Hz, 2H), 3.25–3.05 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.77, 149.81, 143.47, 139.31, 136.24, 130.50 (q, *J* = 32.1 Hz), 124.92, 124.29 (q, *J* = 273.4 Hz), 124.18 (q, *J* = 3.7 Hz), 122.52, 116.63, 37.88. ^{19}F NMR (376 MHz, $CDCl_3$): δ –62.55. HR-MS: m/z 304.1289 $[M+H]^+$, calcd for $C_{18}H_{17}F_3N$ 304.1308.

2-(2,6-Diallyl-4-nitrophenyl)pyridine (3wa). Elution with EtOAc/petroleum ether 1/10 (v/v), colorless oil, yield 25.1 mg (45%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79–8.71 (m, 1H), 8.05 (s, 2H), 7.81 (dt, *J* = 7.7, 1.7 Hz, 1H), 7.43–7.33 (m, 1H), 7.26 (d, *J* = 7.8 Hz, 1H), 5.88-5.72 (m, 2H), 5.10–4.98 (m, 2H), 4.97–4.79 (m, 2H), 3.29–3.08 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.90, 149.90, 147.77, 146.18, 140.49, 136.45, 135.52, 124.65, 122.86, 122.21, 117.24, 37.77. HR-MS: m/z 281.1285 $[M+H]^+$, calcd for $C_{17}H_{17}N_2O_2$ 281.1285.

2-(2,6-Diallyl-3-methoxyphenyl)pyridine (3xa). Elution with EtOAc/petroleum ether 1/20 (v/v), colorless oil, yield 42.3 mg

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(80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72-8.66 (m, 1H), 7.69 (dt, *J* = 7.7, 1.8 Hz, 1H), 7.29–7.18 (m, 2H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 5.86–5.70 (m, 2H), 4.92–4.85 (m, 1H), 4.84–4.74 (m, 2H), 4.69–4.60 (m, 1H), 3.83 (s, 3H), 3.28–3.18 (m, 1H), 3.11–2.94 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.93, 156.10, 149.33, 141.41, 137.80, 136.95, 135.72, 130.15, 128.01, 126.55, 125.28, 121.97, 115.18, 114.40, 110.62, 55.83, 37.43, 31.81. HR-MS: m/z 266.1534 $[M+H]^+$, calcd for $C_{18}H_{20}NO$ 266.1539.

2-(2,6-Diallyl-3-fluorophenyl)pyridine (3ya). Elution with EtOAc/petroleum ether 1/20 (v/v), colorless oil, yield 41.5 mg (82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, *J* = 4.4 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.32–7.25 (m, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.16–7.09 (m, 1H), 7.04 (t, *J* = 8.9 Hz, 1H), 5.85–5.67 (m, 2H), 4.91 (d, *J* = 10.3 Hz, 1H), 4.87 (d, *J* = 10.1 Hz, 1H), 4.79 (d, *J* = 17.0 Hz, 1H), 4.72 (d, *J* = 17.1 Hz, 1H), 3.31–3.16 (m, 1H), 3.15-2.96 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.87 (d, *J* = 244.2 Hz), 157.80 (d, *J* = 2.8 Hz), 149.48, 141.90 (d, *J* = 4.2 Hz), 137.12 , 135.93 , 135.80 , 133.78 (d, *J* = 3.5 Hz), 128.66 (d, *J* = 8.6 Hz), 125.17 (d, *J*=16.2), 125.14 , 122.30 , 115.70 , 115.24 , 115.00 (d, *J* = 22.5 Hz), 37.40 , 30.88 (d, *J* = 3.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ –120.17. HR-MS: m/z 254.1332 $[M+H]^+$, calcd for $C_{17}H_{17}FN$ 254.1340.

2-(2,6-Diallyl-3-chlorophenyl)pyridine (3za). Elution with EtOAc/petroleum ether 1/20 (v/v), colorless oil, yield 31.3 mg (58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, *J* = 4.8 Hz, 1H), 7.72 (dt, *J* = 7.7, 1.8 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.31–7.25 (m, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 5.84–5.68 (m, 2H), 4.96–4.87 (m, 2H), 4.84-4.76 (m, 1H), 4.73–4.63 (m, 1H), 3.39–3.29 (m, 1H), 3.19-3.11 (m, 1H), 3.11–2.94 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ158.29, 149.53, 142.15, 137.08, 136.75, 135.98, 135.44, 135.11, 132.83, 129.41, 128.62, 125.14, 122.37, 116.03, 115.67, 37.66, 35.32. HR-MS: m/z 270.1031 $[M+H]^+$, calcd for $C_{17}H_{17}ClN$ 270.1044.

1-(2,6-Diallylphenyl)-1*H*-pyrazole (4). Elution with EtOAc/petroleum ether 1/20 (v/v), colorless oil, yield 31.0 mg (69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 1.5 Hz, 1H), 7.44 (d, *J* = 2.2 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.7 Hz, 2H), 6.42 (t, *J* = 2.0 Hz, 1H), 5.89–5.72 (m, 2H), 5.03–4.94 (m, 2H), 4.93–4.85 (m, 2H), 3.02 (d, *J* = 14.4 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.20, 138.57, 138.45, 136.76, 131.91, 129.45, 128.06, 116.24, 105.79, 35.53. HR-MS: m/z 225.1376 $[M+H]^+$, calcd for $C_{17}H_{17}ClN$ 225.1386.

2-(2,6-Diallylphenyl)pyrimidine (5). Elution with EtOAc/petroleum ether 1/20 (v/v), colorless oil, yield 36.8 mg (78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (d, *J* = 4.9 Hz, 2H), 7.34–7.28 (m, 1H), 7.26 (t, *J* = 5.0 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 5.83–5.71 (m, 2H), 4.85 (dq, *J* = 10.0, 2.0 Hz, 2H), 4.77 (dq, *J* = 16.8, 2.0 Hz, 2H), 3.21 (d, *J* = 6.8 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.92, 156.93, 138.65, 137.93, 137.00, 128.94, 127.63, 119.11, 115.51, 38.04. HR-MS: m/z 237.1389 $[M+H]^+$, calcd for $C_{16}H_{17}N_2$ 237.1386.

Conflicts of interest

There are no conflicts to declare.

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Graphical abstract

Ruthenium-Catalyzed C-H Allylation of Arenes with Allylic Amines

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The Ru-catalyzed pyridyl-directed C-H allylation of arenes with allylic amines was carried out in the presence of 5 mol % of [Ru(*p*-cymene)Cl_2]$_2$ and 0.5 equiv. of AgOAc in CF_3CH_2OH.