Advanced Synthesis & Catalysis

Accepted Article

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To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.202000186

Link to VoR: https://doi.org/10.1002/adsc.202000186

10.1002/adsc.202000186

FULL PAPER

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

In Situ Ring-Closing Strategy for Direct Synthesis of N-Heterocyclic Carbene Nickel Complexes and Their Application in Coupling of Allylic Alcohols with Aryl Boronic Acids

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Received:

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.

Abstract. A in situ ring-closing strategy was developed for the synthesis of N-heterocyclic carbene nickel complexes. The process was carried out in air, and did not require solvent purification. The resulting nickel complexes were investigated as catalysts for the coupling of allylic alcohols with aryl boronic acids. A wide range of allylic substrates and aryl acids proved to be applicable to this catalytic system. Control experiments suggest that the Ni(0) may be the true active species in the coupling reactions.

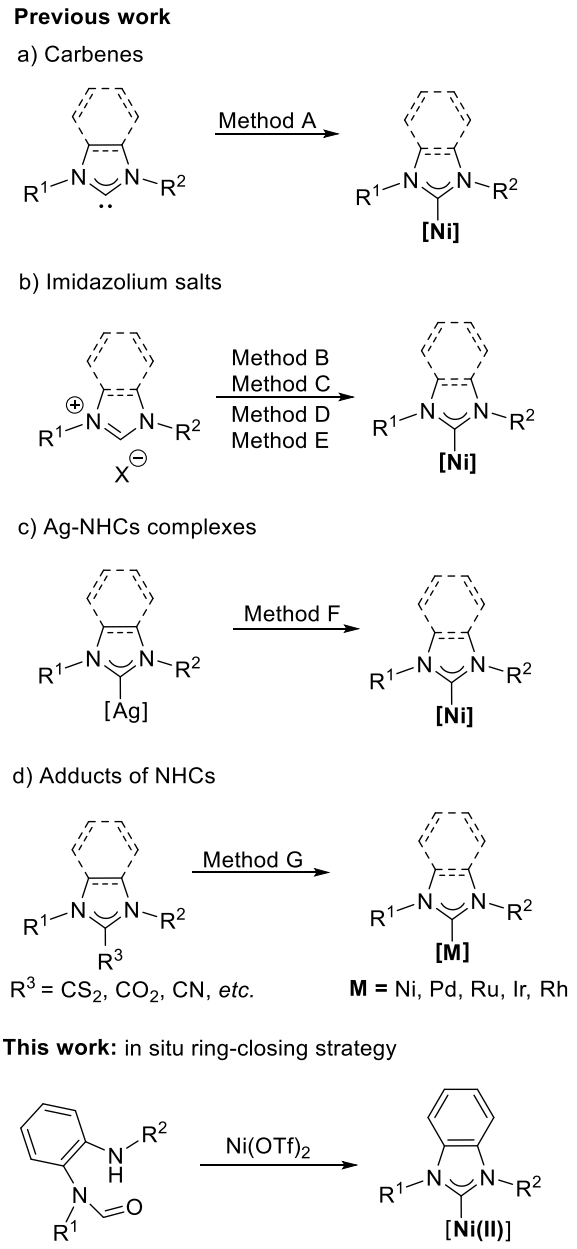
Keywords: nickel; N-heterocyclic carbene; allylic alcohol; catalyst synthesis; coupling reaction

Introduction

In 1964, Fischer synthesized the first stable metal carbene complex.[1] However, following the synthesis of the Cr-NHC (N-heterocyclic carbene) (Öfele[2]) and Hg-NHC complexes (Wanzlick[3]) in 1968, only a few chemists (such as Lappert) continued exploring NHC complexes over the next two decades. Since then, NHC were successfully obtained by Arduengo in 1991[4] and Herrmann, in 1995, reported the first application of Pd-NHC complexes as homogeneous catalysts in Heck coupling.[5] NHC, as a powerful class of ligands, have attracted considerable attention in catalysis,[6] organometallic chemistry[7], and materials science[8] owing to their unique electron-donor properties and steric-tuning superiority[9]. Nickel is an ideal choice as a catalyst because of its relatively high abundance and low cost, thus several strategies were developed for the synthesis of nickel-NHC complexes. Nickel-NHC are most frequently prepared from already prepared air- and moisture-sensitive free carbenes, which limits the tolerance for other functionalities (method A).[10, 11, 12, 13, 14] The reactions of imidazolium salts with basic metal precursors provide an alternative route for the synthesis of nickel-NHC complexes (method B).[15, 16, 17, 18, 19, 20] The direct deprotonation reaction of an imidazolium salt with a base is also widely applied for obtaining the corresponding nickel-NHC complexes (method C).[21, 22, 23, 24, 25] These complexes may also be attained by electrochemical methods using imidazolium salts as carbene sources and nickel plates as the anodes (method D).[26] A practical route toward nickel-NHC complexes has also been developed using imidazolium salts or silver NHC complexes with nickel powder (method E).[27, 28] Readily available Ag(I)-NHC complexes have also been employed as NHC transfer agents for the preparation the nickel-NHC complexes (method F).[29, 30, 31, 32] Yet another successful method for the synthesis of NHC complexes relies on the thermal decomposition of the carbene adducts of CS_2,[33] CO_2,[34] cyanide,[35] phosphenium,[36] and pentafluorobenzene (method G).[37] Simplifying the experimental conditions for the synthsis of nickel NHC catalysts is crucial for industrial applications; thus, the development of a facile synthetic route is an important challenge in organometallic chemistry.

Our group has made long-standing efforts to design of unsymmetrical pyridine-bridged pincer-type NHC and using them as ligands for synthesis of their transition metal complexes such as Fe-, Pd- and Ru-NHC complexes.[38, 39, 40, 41, 42] Herein, we report an alternative approach for the synthesis of nickel-NHCs complexes via in situ ring-closing. The nickel complexes were structurally characterized using single-crystal X-ray diffraction (Scheme 2). These synthetic procedures are carried out in air and do not require solvent purification, which is a priority for simplification of the experimental process. Further, the nickel complexes **C1-C5** act as efficient catalysts for the coupling of allylic alcohols with aryl

boronic acids, resulting in desired products with good yields under mild reaction conditions.

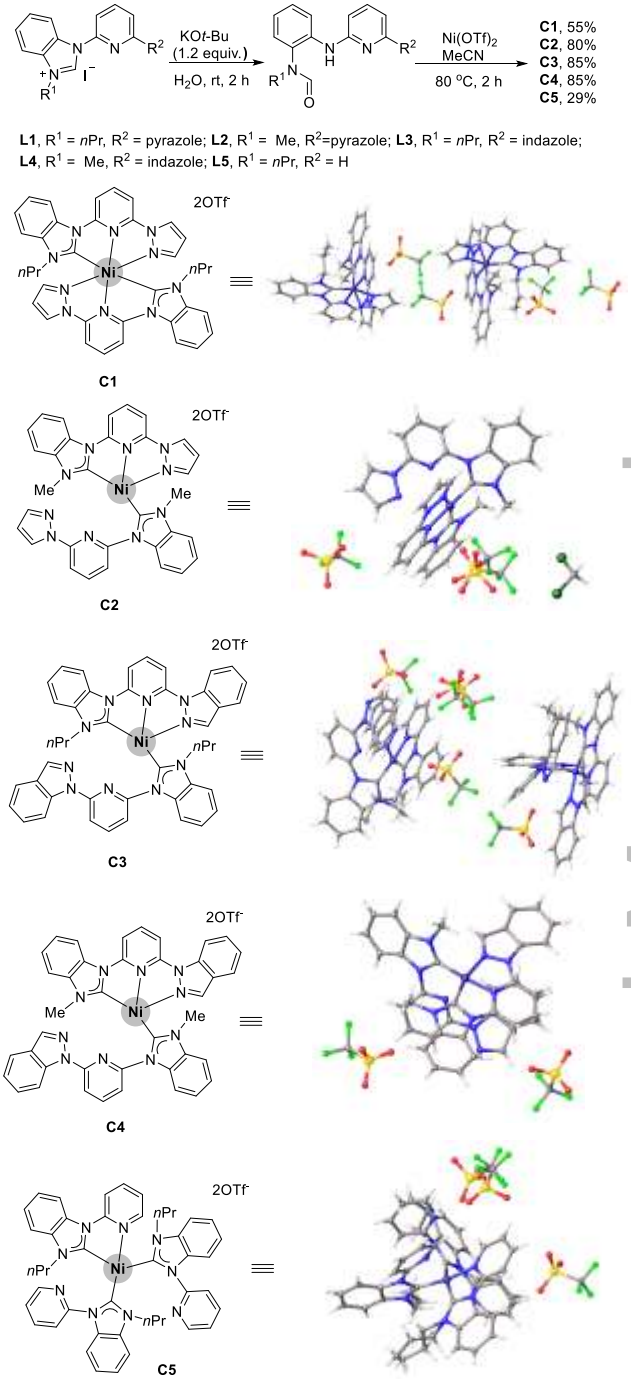


Scheme 1. Nickel-NHC complexes studied in this work.

Results and Discussion

Pyridine-bridged NHC precursors containing one substituted amino group and another substituted amide in the benzene ring (For the synthetic procedure for these ligands, see Scheme S1 in the Supporting Information for details), which can be easily hydrolyzed to ring-opening compounds via our previously reported benzimidazole salts [38-42] in the presence of base and water (Scheme 2),[43, 44] reacted with nickel(II) trifluoromethanesulfonate ($Ni(OTf)_2$) to produce multidentate nickel complexes **C1**-**C5** (Scheme 2) in 29-85% yield in air and without the need to purify the solvent.

The structures of the nickel complexes **C1**-**C5**, determined by single crystal X-ray diffraction, revealed significant differences in their coordination environments (Scheme 2).[45]



Scheme 2. Synthesis and X-ray structure Ni−NHC complexes of in this work.

Complex **C1** is six-coordinated, and contained two tridentate pyridine-bridged pincer-type ligands. Complex **C2**, Where the *N*-substituted alkyl group bearing benzimidazole salts changed from the *n*-propyl group to the methyl group, was also composed of two pyridine-bridged pincer-type ligands; however, complex **C2** is four-coordinated, wherein one ligand is tridentate and the NHC alone from the second ligand coordinated to the nickel atom.

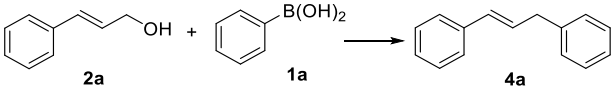
When the substituents with a pyridine core changed from pyrazole to indazole, the coordination environment of complexes **C3** and **C4**, containing either a *N*-methyl or a *N*-propyl group, was similar to that of complex **C2**. Complexes **C1-C4** involved tridentate CNN ligands; thus, a bidentate CN ligand was also investigated under the same reaction conditions. From X-ray crystallography data, complex **C5** consisted of three bidentate CN ligands. One ligand binds to the nickel atom in a bidentate manner, while only the NHC in the other two ligands are bound to the nickel atom. These results confirm that the NHCs preferentially bind to the nickel atom, even in the presence of ligands bearing nitrogen donors.[46, 47, 48]

The cross-coupling of unprotected allylic alcohols represents a powerful and atom economic method, which has attracted much attention.[49, 50] For example, the cross-coupling of allylic alcohols with aryl boronic acids has been developed, where palladium[51, 52, 53] and rhodium[54] are the catalysts. Although noble-metal catalysts are effective for the coupling between allylic alcohols and aryl boronic acids, their high costs hamper industrial applications. Recently, non-noble metal catalysts have been investigated for the cross-coupling of allylic alcohols with aryl boronic acids[55, 56] have shown promise. Therefore, we tested the performance of our developed nickel complexes **C1**-**C5** as catalysts for the cross-coupling of allylic alcohols with aryl boronic acids.

The coupling of cinnamic alcohol with phenyl boronic acid was chosen to optimize the reaction conditions using nickel complex **C5** as the catalyst (Table 1). The influence of the nature of bases was explored first and the best result was obtained with K_3PO_4 (Table 1, entries 1-3) in the presence of 4 mol% of **C5** in MeCN at 80 °C. The coupling of cinnamic alcohol with phenyl boronic acid was also investigated in the presence of different solvents (MeCN, THF, 1,4-dioxane, and toluene; Table 1, entries 3, 5-7). At 100 °C, a good yield (72%) was observed in MeCN (Table 1, entry 4) and excellent yield (90%) in toluene at 16 h (Table 1, entry 8). Overall, the most satisfactory result was obtained when benzene was used as the solvent (Table 1, entry 9).

Next, the coordination environment of each complex catalyst on their catalytic efficiency for the coupling of cinnamic alcohol with phenyl boronic acid was studied. Screening revealed that the best product yield (80%) was obtained with complex **C5** as the catalyst (Table 1, entries 9 and 10). This result indicated that the strong electron-donating tendency of the NHC governed the efficiencies of the catalysts. Next, the amount of complex **C5** was optimized. When the **C5** loading was lowered to 2.5 mol% or increased to 6 mol%, the yield dropped to 68% or slightly improved to 82%, respectively (Table 1, entries 11 and 12); however, a loading of 4 mol% resulted in better conversion (Table 1, entry 9). The amount of base was also examined. The results indicated that K_3PO_4 was crucial for a high yield of **4a**; decreasing the amount of K_3PO_4 to 0.2 mmol, resulted in a significant decline in the conversion (Table 1, entry 13). The yield of **4a** (81%) did not increase significantly when the amount of K_3PO_4 was increased to 0.4 mmol (Table 1, entry 14). Lowering the reaction temperature decreased the yield (46%) of **4a** (Table 1, entry 15). A higher yield (90%) could be obtained by a prolonging the reaction time from 12 to 16 h (Table 1, entry 16); however, further increasing the reaction time to 24 h did not significantly improve the product yield (Table 1, entry 17).

Table 1. Optimization of conditions.[a]



Entry	Cat. (mol%)	Base (mmol)	Solvent	Yield (%)
1	**C5** (4)	K_2CO_3 (0.3)	MeCN	35
2	**C5** (4)	KO*t*Bu (0.3)	MeCN	20
3	**C5** (4)	K_3PO_4 (0.3)	MeCN	48
4	**C5** (4)	K_3PO_4 (0.3)	MeCN	65[b](72[c])
5	**C5** (4)	K_3PO_4 (0.3)	THF	45
6	**C5** (4)	K_3PO_4 (0.3)	1,4-dioxane	55
7	**C5** (4)	K_3PO_4 (0.3)	toluene	68
8	**C5** (4)	K_3PO_4 (0.3)	toluene	85[b](90[c])
9	**C5** (4)	K_3PO_4 (0.3)	benzene	80
10	**C1**-**4** (4)	K_3PO_4 (0.3)	benzene	29-46[d]
11	**C5** (2.5)	K_3PO_4 (0.3)	benzene	68
12	**C5** (6)	K_3PO_4 (0.3)	benzene	82
13	**C5** (4)	K_3PO_4 (0.2)	benzene	63
14	**C5** (4)	K_3PO_4 (0.4)	benzene	81
15	**C5** (4)	K_3PO_4 (0.3)	benzene	46[e]
16	**C5** (4)	K_3PO_4 (0.3)	benzene	90[f]
17	**C5** (4)	K_3PO_4 (0.3)	benzene	91[g]

[a] Conditions: cinnamic alcohol (0.2 mmol), phenyl boronic acid (0.3 mmol), catalyst (loading amount as indicated in Table 1), base (loading amount as indicated in Table 1), solvent (1.5 mL), 80 °C, 12 h, under nitrogen atmosphere, determined by isolated yield. [b] 100 °C. [c] 100 °C, 16 h. [d] **C1**: 38%; **C2**: 46%; **C3**: 41%; **C4**: 29%. [e] 50 °C. [f] 16 h. [g] 24 h.

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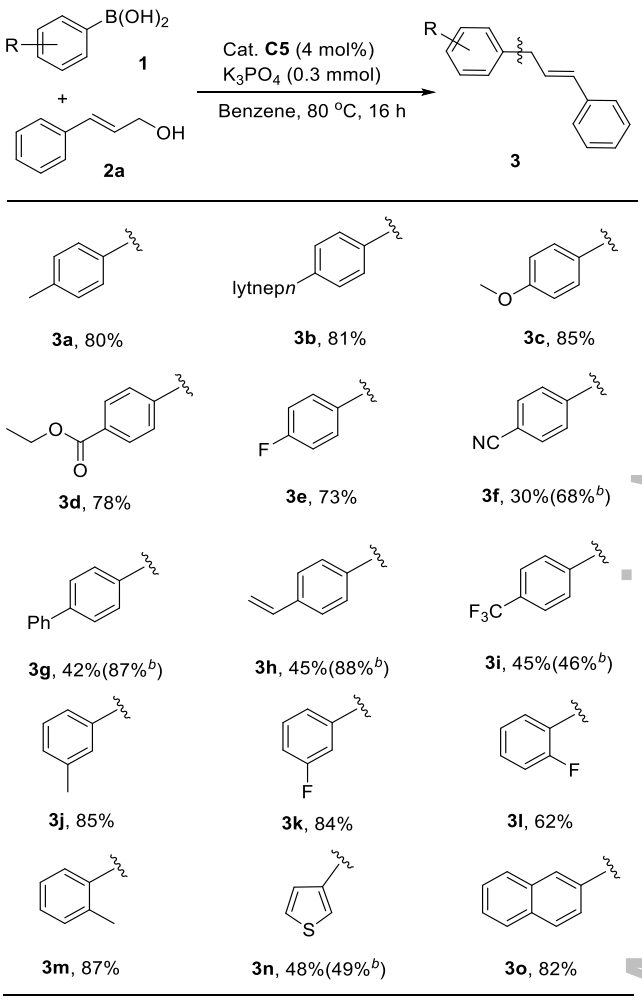
Having optimized the reaction conditions, we proceeded to explore the substrate scope of aryl boronic acids for the coupling with cinnamic alcohol (Table 2). Table 2 shows that electron-donating aryl boronic acids (**1a**-**c**) were effective substrates and afforded the desired products with good yields. However, the modification of aryl substituents on boronic acids have a significant impact on the reaction efficiency, and lower to good yields were obtained for aryl boronic acids bearing electron-withdrawing groups as well (**3d-i**). To our delight, the use of Zn powder as a reductant dramatically improved the reactivity of aryl boronic acids bearing electron-withdrawing groups such as cyano-, phenyl-, and vinyl-groups (**3f-h**, the yield in parentheses). The Zn powder likely functioned as a reductant and promoted the formation of Ni0) active species from the Ni(II) precursor. The rapid generation of Ni(0) active species maintained the relatively high concentration in the reaction process, which promoted the overall reaction rate.

Investigation of the reactivity of *meta*-substituted aryl boronic acids revealed that the corresponding products were obtained in 85% and 84% yields, respectively (**3j** and **3k**). The steric influence on aryl boronic acids were also studied, *ortho*-fluorophenyl and *ortho*-methylphenyl boronic acid afforded products **3l** and **3m** in good yields of 62% and 87%, respectively.

Table 2. Substrate scope for aryl boronic acids.[a]



[a] Conditions: cinnamic alcohol (0.2 mmol), aryl boronic acid (0.3 mmol), catalyst **C5** (4 mol%), K_3PO_4 (0.3 mmol), benzene (1.5 mL), 80 °C, 16 h, under nitrogen atmosphere, determined by isolated yield. [b] 0.2 mmol Zn powder as the reductant.

Encouraged by the outstanding catalytic performance of **C5** in the coupling of cinnamic alcohol with aryl boronic acids, thiophen-3-ylboronic acid and naphthalen-2-ylboronic acid were investigated for cross-coupling with cinnamic alcohol. Naphthalen-2-ylboronic acid was found to be compatible under the standardized conditions, achieving the desired product 82% yield (**3o**). However, heteroaryl boronic acids, such as thiophen-3-ylboronic acid, offered the desired product **3n** in a moderate yield of 48% under the current standard conditions. Even when Zn powder was added to the reaction system, only 49% of the desired coupling product was obtained (yield in parentheses).

To further demonstrate the application of this protocol, we investigated the substrate tolerance of the allylic alcohols for the cross-coupling of phenyl boronic acid (Table 3). Primary alcohol **2a** provided the desired product **4a** in 90% yield. We were pleased to observe that the secondary alcohol **2b** also reacted

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with phenyl boronic acid, giving the desired product **4b** in 78% yield. When isomeric allyl alcohols **2c** or **2d** were used instead of allyl alcohols **2a** or **2b**, the same cross-coupling product **4a** or **4b**, respectively, were obtained as the only observed product. The results indicated that substrates **2a** and **2c** (**2b** and **2d**) formed a common π-allylnickel intermediate and underwent a similar reaction. Heterocycles such as thiophenes (**2e**) are also suitable for this catalytic system.

We also explored the electronic effect of allylic alcohol substituents on the reaction. Allylic alcohol bearing electron-donating groups, such as methyl and methoxy groups (Table 3, **2f** and **2i**), showed higher reactivity than those with electron-withdrawing groups, including chloro, fluoro, trifluoromethyl, and ester groups (Table 3, **2j** and **2n**-**p**). All *meta*-substituted substrates were tolerated in the transformation (Table 3, **2g** and **2k**). The electronic effect of *ortho*-substitution on the aryl ring of the allylic alcohol was also investigated. The allylic alcohol bearing an electron-donating group, such as 2-methyl or methoxy group at the *ortho*-position reacted with phenyl boronic acid to give good yields (**4h** and **4m**). However, an allylic alcohol bearing an electron-withdrawing group at the *ortho*-position, such as the 2-chloro group, did not yield the desired product **4l**.

Table 3. Substrate scope for allylic alcohols.[a]

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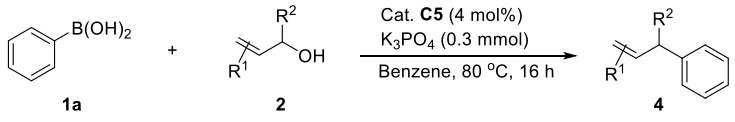
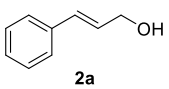
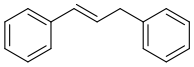
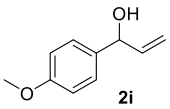
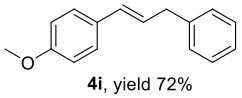
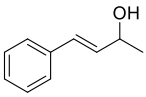
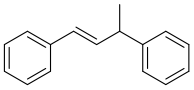
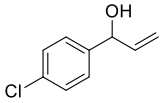
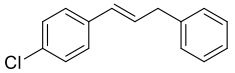
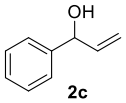
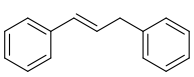
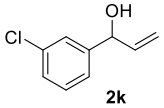
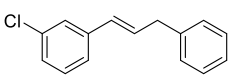
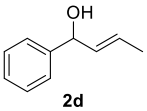
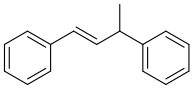
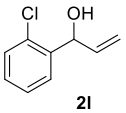
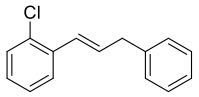
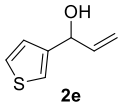
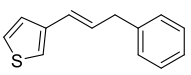
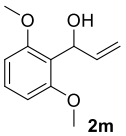
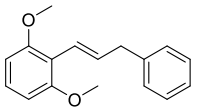
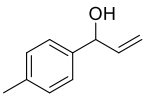
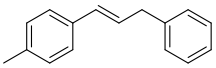
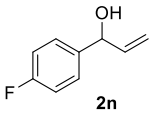
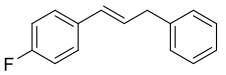
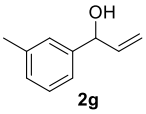
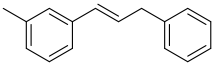
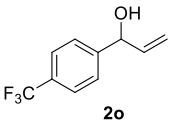
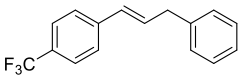
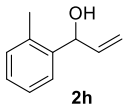
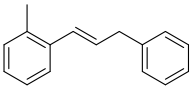
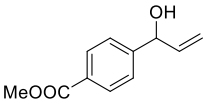
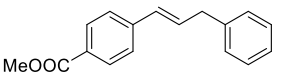


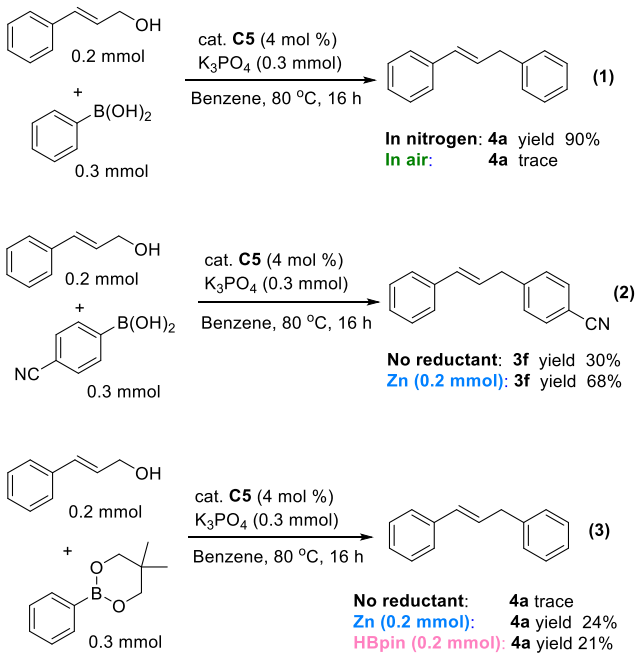
1a 2 4

Entry	Allylic alcohol	Product	Entry	Allylic alcohol	Product
1	 **2a**	 **4a**, yield 90%	9	 **2i**	 **4i**, yield 72%
2	 **2b**	 **4b**, yield 78%	10	 **2j**	 **4j**, yield 68%
3	 **2c**	 **4a**, yield 88%	11	 **2k**	 **4k**, yield 65%
4	 **2d**	 **4b**, yield 75%	12	 **2l**	 **4l**, trace
5	 **2e**	 **4e**, yield 61%	13	 **2m**	 **4m**, yield 85%
6	 **2f**	 **4f**, yield 83%	14	 **2n**	 **4n**, yield 64%
7	 **2g**	 **4g**, yield 69%	15	 **2o**	 **4o**, yield 39%
8	 **2h**	 **4h**, yield 77%	16	 **2p**	 **4p**, yield 71%

[a] Conditions: allylic alcohol (0.2 mmol), phenylboronic acid (0.3 mmol), catalyst **C5** (4 mol%), K_3PO_4 (0.3 mmol), benzene (1.5 mL), 80 °C, 16 h, under nitrogen atmosphere, determined by isolated yield.

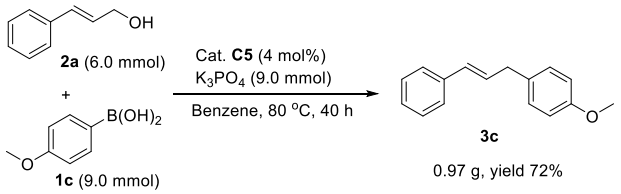
To identify the active species of nickel in the catalytic reaction process, several control experiments were performed (Scheme 3). Notably, inert atmosphere protection was necessary for a high yield of **4a** because the reaction was terminated in air (Scheme 3, eq. 1). It was likely that the oxygen in air significantly inhibited formation of the active species; this implies that Ni(0), obtained via the reduction of Ni(II) complex **C5** by the aryl boronic acid, may be the true active species. As further proof for this assumption, using Zn powder as a reductant in the coupling reaction results in a remarkable increase in the yield of **3f** from 30% to 68% (Scheme 3, eq. 2). The coupling reaction between cinnamic alcohol and organoboronic esters did not occur under nitrogen atmosphere. When Zn powder or pinacolborane was used as a reductant in the reaction system, the catalytic activity improved significantly (Scheme 3, eq. 3). This suggests that reductants such as Zn powder and pinacolborane played a crucial role, possibly reducing the Ni(II) complex **C5** to form a Ni(0) active intermediate, thus promoting the catalytic performance. In addition, the stability of Ni(II) complex of **C5** was evaluated under 80 °C in benzene or under 100 °C in toluene for 16 h in the absence of substrates. The results show that 0.1 mmol of Ni(II) complex **C5** can be recovered quantitatively by column chromatography, which indicates that Ni(II) complex **C5** is stable at high temperature for a long time.

10.1002/adsc.202000186



Scheme 3. Control experiments of coupling.

In addition, gram-scale experiment was carried out under the optimized conditions. The reaction of **2a** with **1c** was easily scaled up to the gram scale to give **3c** in 72% of yield at 80 °C for 40 h (Scheme 4).



Scheme 4. Gram-scale synthesis.

In order to gain insight into the active Ni species in the reaction, we performed a control experiment using high-resolution ESI-MS (positive ion mode). We mixed the solution of **C5** (4 mol%) with phenyl boronic acid (0.3 mmol) and K_3PO_4 (0.3 mmol) in 1.5 mL of acetonitrile (because the substrates have better solubility in acetonitrile than benzene), a new cluster peak at m/z 314.1657 was observed which was attributed to bidentate nickel(0) aquo complex **C5-H$_2$O** generated from the reduction of **C5** (For the ESI-MS spectra of nickel(0) aquo complex **C5-H$_2$O**, see Scheme S3 in the Supporting Information for details). The previous reports[55, 56, 57] have also indicated that the bidentate nickel(0) complexes are more beneficial to oxidative addition than multi-dentate nickel(0) complexes. The above results indicated that a bidentate nickel(0) intermediates, generated from the reduction of **C5**, considered as the real active species. Based on these experimental results, a plausible reaction mechanism was proposed (Figure 1). At the beginning of the reaction, the nickel complex **C5** was reduced by aryl boronic acid and K_3PO_4 to form bidentate Ni(0) active species **C5a**. Next, **C5a** reacted with allylic alcohol to generate a π-allylnickel(II) intermediate **C5b** via oxidative addition. **C5b** could then interact with the aryl boronic acid to form intermediate **C5c**, which subsequently underwent transmetalation with the aryl boronic acid, resulting in the formation of **C5d**. The coupling product was obtained by reductive elimination from intermediate **C5d**.

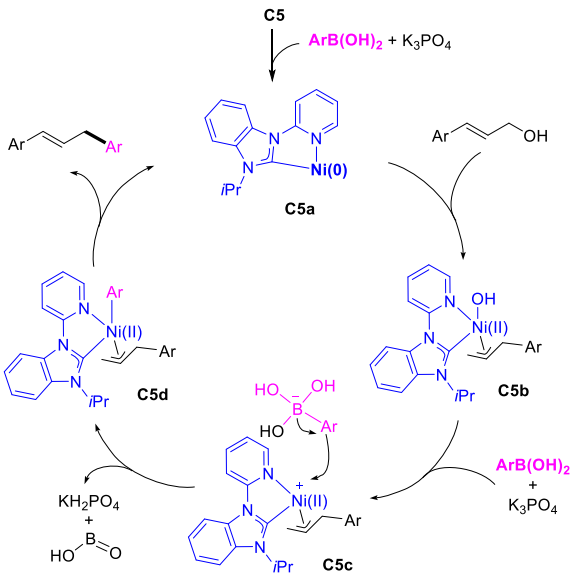


Figure 1. Reaction mechanism.

Conclusion

In conclusion, we developed a practical and efficient system for the nickel-catalyzed coupling of allylic alcohols with aryl boronic acids. This catalytic system accommodates a wide range of allylic alcohols and aryl boronic acids, yielding a series of allylic arene products. The key to achieving good yields in the transformation is the use of NHC nickel complexes, which are synthesized by a convenient and facile in situ ring-closing strategy. The control experiments suggested that Ni(0) was formed via reduction of the nickel complexes, and is real active species in the nickel-catalyzed cross-coupling of allylic alcohols with aryl boronic acids.

Experimental Section

General procedure for the synthesis of nickel complexes C1-C5

Nickel complex C1. *N*-(2-((6-(1*H*-pyrazol-1-yl)pyridin-2-yl)amino)phenyl)-*N*-propylformamide (193 mg, 0.6 mmol) and Ni(OTf)$_2$ (107 mg, 0.3 mmol) were added to a 25 mL Schlenk tube and dissolved in acetonitrile (5 mL) under air. The mixtures were heated to 80 °C for 2 h. After the reaction, the mixture was concentrated under vacuum and the red solid complex **C1** was obtained by flash chromatography (dichloromethane/methanol (DCM/MeOH) = 30:1). Yield:

158 mg, 55%. M.P.=140.6-142.5 °C. Anal. Calcd for $C_{38}H_{34}F_6N_{10}NiO_6S_2$: C, 47.37; H, 3.56; N, 14.54; S, 6.65. Found: C, 47.31; H, 3.95; N, 14.62; S, 7.61. HRMS (positive ESI): $[M\text{-}OTf]^+$ calcd for $C_{37}H_{34}F_3N_{10}NiO_3S^+$ 813.1847, Found 813.1819.

Nickel Complex C2. *N*-(2-((6-(1*H*-pyrazol-1-yl)pyridin-2-yl)amino)phenyl)-*N*-methylformamide (176 mg, 0.6 mmol) and $Ni(OTf)_2$ (107 mg, 0.3 mmol) were added to a 25 mL Schlenk tube and dissolved in acetonitrile (5 mL) under air. The mixtures were heated to 80 °C for 2 h. After the reaction, addition of ethyl acetate gave a yellow-green solid complex **C2**, which was filtered and dried under vacuum. Yield: 217 mg, 80%. M.P.=157.3-158.6 °C. Anal. Calcd for $C_{34}H_{26}F_6N_{10}NiO_6S_2$: C, 45.00; H, 2.89; N, 15.44; S, 7.07. Found: C, 44.95; H, 3.28; N, 15.89; S, 7.90. HRMS (positive ESI): $[M+H]^+$ calcd for $C_{34}H_{27}F_6N_{10}NiO_6S_2^+$ 907.0825, Found 907.0807.

Nickel Complex C3. *N*-(2-((6-(1*H*-indazol-1-yl)pyridin-2-yl)amino)phenyl)-*N*-propylformamide (223 mg, 0.6 mmol) and $Ni(OTf)_2$ (107 mg, 0.3 mmol) were added to a 25 mL Schlenk tube and dissolved in acetonitrile (5 mL) under air. the mixture was heated to 80 °C for 2 h. After the reaction, addition of ethyl acetate gave an orange solid complex **C3**, which was filtered and dried under vacuum. Yield: 270 mg, 85%. M.P.=271.4-272.3 °C. Anal. Calcd for $C_{46}H_{38}F_6N_{10}NiO_6S_2$: C, 51.94; H, 3.60; N, 13.17; S, 6.03. Found: C, 51.75; H, 3.49; N, 13.29; S, 6.26. HRMS (positive ESI): $[M\text{-}OTf]^+$ calcd for $C_{45}H_{38}F_3N_{10}NiO_3S^+$ 913.2160, Found 913.2166.

Nickel Complex C4. *N*-(2-((6-(1*H*-indazol-1-yl)pyridin-2-yl)amino)phenyl)-*N*-methylformamide (206 mg, 0.6 mmol) and $Ni(OTf)_2$ (107 mg, 0.3 mmol) were added to a 25 mL Schlenk tube and dissolved in acetonitrile (5 mL) under air. the mixtures were heated to 80 °C for 2 h. After the reaction, addition of ethyl acetate gave a yellow solid complex **C4**, which was filtered and dried under vacuum. Yield: 256 mg, 85%. M.P.=186.5-187.7 °C. Anal. Calcd for $C_{42}H_{30}F_6N_{10}NiO_6S_2$: C, 50.07; H, 3.00; N, 13.90; S, 6.36. Found: C, 49.97; H, 2.98; N, 14.03; S, 7.10. HRMS (positive ESI): $[M\text{-}OTf]^+$ calcd for $C_{41}H_{30}F_3N_{10}NiO_3S^+$ 857.1534, Found 857.1531.

Nickel Complex C5. *N*-propyl-*N*-(2-(pyridin-2-ylamino)phenyl)formamide (153 mg, 0.6 mmol) and $Ni(OTf)_2$ (71 mg, 0.2 mmol) were added to a 25 mL Schlenk tube and dissolved in acetonitrile (5 mL) under air. The mixtures were heated to 80 °C for 2 h. After the reaction, the mixtures were concentrated under vocuum and the red solid complex **C5** was obtained by flash chromatography (dichloromethane/methanol (DCM/MeOH) = 30:1). Yield: 61.9 mg, 29%. M.P.=108.6-110.2 °C. Anal. Calcd for $C_{47}H_{45}F_6N_9NiO_6S_2$: C, 52.82; H, 4.24; N, 11.80; S, 6.00. Found: C, 52.81; H, 4.06; N, 11.30; S, 6.29. HRMS (positive ESI): $[M+H]^+$ calcd for $C_{47}H_{46}F_6N_9NiO_6S_2^+$ 1068.2281, Found 1068.2245.

Preparation of single crystals

Single crystals were obtained by the layer-to-layer diffusion method. The nickel complexes **C1-C5** were added to the MeCN solution (1 mL), and layered with diethyl ether. After 3 days, crystals suitable for single-crystal X-ray diffraction were obtained.

General procedure for the allylation of phenylboronic acid with allylic alcohols

In a 25 mL reaction tube with a stir bar, Cat. **C5** (8.5 mg, 0.008 mmol), K_3PO_4 (63.6 mg, 0.3 mmol), allyl alcohol (0.2 mmol) and phenylboronic acid (0.3 mmol) were taken. The reaction tube was vacuumed and then filled with nitrogen three times. Subsequently, benzene (1 mL) was added to the reaction tube. The mixture was stirred at 80 °C for 16 h. Then the mixture was concentrated under vacuum and allylated products were obtained by column chromatography (petroleum ether/ethyl acetate).

1-cinnamyl-4-methylbenzene (3a)[58]**:** colorless oil, 33 mg, 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.34 (m, 2H), 7.30-7.26 (m, 2H), 7.21-7.17 (m, 1H), 7.15-7.10 (m, 4H), 6.44 (d, J = 15.6 Hz, 1H), 6.37-6.30 (m, 1H), 3.50 (d, J = 6.4 Hz, 2H), 2.33 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.57, 137.09, 135.70, 130.86, 129.55, 129.20, 128.58, 128.51, 127.06, 126.13, 38.95, 21.05.

1-cinnamyl-4-pentylbenzene (3b)[58]**:** colorless oil, 42 mg, 81%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.35 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.12 (m, 5H), 6.48 (d, J = 15.6 Hz, 1H), 6.41-6.34 (m, 1H), 3.54 (d, J = 6.4 Hz, 2H), 2.60 (t, J = 7.8 Hz, 2H), 1.66-1.59 (m, 2H), 1.41-1.28 (m, 4H), 0.91 (t, J = 6.8 Hz, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.85, 137.59, 137.32, 130.89, 129.56, 128.55, 128.52, 127.07, 126.15, 39.01, 35.58, 31.58, 31.32, 22.60, 14.08.

1-cinnamyl-4-methoxybenzene (3c)[58]**:** colorless oil, 38 mg, 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.36 (m, 2H), 7.32-7.29 (m, 2H), 7.24-7.16 (m, 3H), 6.89-6.86 (m, 2H), 6.45 (d, J = 16 Hz, 1H), 6.39-6.32 (m, 1H), 3.81 (s, 3H), 3.51 (d, J = 6.8 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.04, 136.50, 131.15, 129.70, 128.64, 128.57, 127.45, 126.01, 125.07, 112.88, 54.25, 37.42.

ethyl 4-cinnamylbenzoate (3d)[51]**:** colorless oil, 36 mg, 78%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93-7.89 (m, 2H), 7.29-7.27 (m, 2H), 7.24-7.19 (m, 4H), 7.16-7.08 (m, 1H), 6.39 (d, J = 15.6 Hz, 1H), 6.29-6.21 (m, 1H), 4.29 (dd, J = 14.4 Hz, 7.2 Hz, 2H), 3.52 (d, J = 6.4 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.58, 144.45, 136.18, 130.74, 128.78, 127.62, 127.52, 127.08, 126.28, 125.13, 59.81, 38.25, 13.33.

1-cinnamyl-4-fluorobenzene (3e) [58]**:** pale yellow oil, 31 mg, 73%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.34 (m, 2H), 7.31-7.27 (m, 2H), 7.22-7.16 (m, 3H), 7.01-6.95 (m, 2H), 6.43 (d, J = 15.6 Hz, 1H), 6.35-6.28 (m, 1H), 3.50 (d, J = 6.8 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.54 (d, J = 242.3 Hz), 137.36, 135.77 (d, J = 3.2 Hz), 131.26, 130.07 (d, J = 7.8 Hz), 129.02, 128.57, 127.25, 126.17, 115.26 (d, J = 21.1 Hz), 38.52. ^{19}F NMR (376 MHz, $CDCl_3$): δ -117.23.

4-cinnamylbenzonitrile (3f) [51]**:** colorless oil, 13 mg, 30%; in the presence of 0.2 mmol Zn powder: 29 mg, 68%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.50 (m, 2H), 7.29-7.21 (m, 6H), 7.17-7.13 (m, 1H), 6.40 (d, J = 16 Hz, 1H), 6.25-6.18 (m, 1H), 3.52 (d, J = 6.8 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.79, 135.88, 131.39, 131.29, 128.42, 127.58, 126.50, 126.11, 125.16, 117.99, 109.11, 38.28.

4-cinnamyl-1,1'-biphenyl (3g) [58]**:** white solid, 22 mg, 42%; in the presence of 0.2 mmol Zn powder: 47 mg, 87%, M.P.=59.7-61.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.54 (m, 2H), 7.57-7.54 (m, 2H), 7.46-7.42 (m, 2H), 7.40-7.29 (m, 7H), 7.24-7.19 (m, 1H), 6.51 (d, J = 15.6 Hz, 1H), 6.43-6.36 (m, 1H), 3.60 (d, J = 6.4 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.05, 139.30, 139.23, 137.47, 131.24, 129.11, 128.76, 128.54, 127.28, 127.17, 127.12, 127.06, 126.17, 39.01.

1-cinnamyl-4-vinylbenzene (3h) [58]**:** pale yellow oil, 19 mg, 45%; in the presence of 0.2 mmol Zn powder: 38 mg, 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.35 (m, 4H), 7.29 (t, J = 7.6 Hz, 2H), 7.21-7.18 (m, 3H), 6.70 (dd, J = 17.6 Hz, 10.8 Hz, 1H), 6.45 (d, J = 16 Hz, 1H), 6.38-6.30 (m, 1H), 5.72 (d, J = 17.6 Hz, 1H), 5.20 (d, J = 10.8 Hz, 1H), 3.53 (d, J = 6.4 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.85, 137.47, 136.63, 135.65, 131.16, 129.07, 128.87, 128.53, 127.15, 126.38, 126.15, 113.26, 39.07.

1-cinnamyl-4-(trifluoromethyl)benzene (3i) [58]**:** colorless oil, 23 mg, 45%; in the presence of 0.2 mmol Zn powder: 24 mg, 46%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8 Hz, 2H), 7.37-7.28 (m, 6H), 7.24-7.20 (m, 1H), 6.47 (d, J = 15.6 Hz, 1H), 6.35-6.28 (m, 1H), 3.59 (d, J = 6.8 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.32, 137.14, 131.96, 129.00, 128.49 (q, J=13.8 Hz), 127.93, 127.42, 126.20, 125.70, 125.43 (q, J=3.8 Hz), 39.10. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.31.

1-cinnamyl-3-methylbenzene (3j) [58]**:** colorless oil, 35 mg, 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 7.6 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.20 (t, J = 7.4 Hz, 2H), 7.05-6.98 (m, 3H), 6.45 (d, J = 15.6 Hz, 1H), 6.38-6.31 (m, 1H), 3.51 (d, J = 6.8 Hz, 2H) 2.33 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.13, 138.13, 137.55, 130.97,

129.46, 129.39, 128.52, 128.42, 127.10, 126.95, 126.15, 125.71, 39.34, 21.43.

1-cinnamyl-3-fluorobenzene (3k) [59]**:** pale yellow oil, 35 mg, 84%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.35 (m, 2H), 7.31-7.19 (m, 4H), 7.00 (d, J = 7.6 Hz, 1H), 6.96-6.88 (m, 2H), 6.46 (d, J = 16 Hz, 1H), 6.35-6.28 (m, 1H), 3.54 (d, J = 6.4 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.02 (d, J = 244.2 Hz), 142.77(d, J = 7.1 Hz), 137.26, 131.67, 129.89 (d, J = 8.3 Hz), 128.57, 128.28, 127.31, 126.19, 124.29 (d, J = 2.7 Hz), 115.53 (d, J = 21 Hz), 113.10 (d, J = 21 Hz), 39.02 (d, J = 1.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -113.49.

1-cinnamyl-2-fluorobenzene (3l) [60]**:** pale yellow oil, 26 mg, 62%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.34 (m, 2H), 7.30-7.26 (m, 2H), 7.25-7.17 (m, 3H), 7.10-7.01 (m, 2H), 6.46 (d, J = 16 Hz, 1H), 6.37-6.30 (m, 1H), 3.56 (d, J = 6.8 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.00 (d, J = 243.7 Hz), 137.35, 131.44, 130.67 (d, J = 4.7 Hz), 128.51, 127.90 (d, J = 8.0 Hz), 127.60, 127.19, 127.16, 127.00, 126.15, 124.09 (d, J = 3.6 Hz), 115.30 (d, J = 21.8 Hz), 32.24 (d, J = 3.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -118.41.

1-cinnamyl-2-methylbenzene (3m) [58]**:** colorless oil, 36 mg, 87%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.32 (m, 2H), 7.29-7.26 (m, 2H), 7.21-7.12 (m, 5H), 6.39-6.29 (m, 2H), 3.52 (d, J = 4.5 Hz, 2H), 2.33 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.26, 137.57, 136.45, 130.92, 130.25, 129.25, 128.58, 128.51, 127.07, 126.44, 126.13, 126.10, 36.90, 19.48.

3-cinnamylthiophene (3n) [51]**:** colorless oil, 19 mg, 48%; in the presence of 0.2 mmol Zn powder: 19 mg, 49%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.36 (m, 2H), 7.32-7.27 (m, 3H), 7.23-7.19 (m, 1H), 7.03-6.98 (m, 2H), 6.47 (d, J = 16 Hz, 1H), 6.40-6.33 (m, 1H), 3.56 (d, J = 6.8 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.55, 137.44, 131.07, 128.53, 128.36, 127.16, 126.14, 125.59, 120.88, 33.84.

2-cinnamylnaphthalene (3o) [51]**:** white solid, 40 mg, 82%, M.P.=39.5-40.2 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.77 (m, 3H), 7.67 (s, 1H), 7.47-7.40 (m, 2H), 7.39-7.36 (m, 3H), 7.31-7.27 (m, 2H), 7.22-7.18 (m, 1H), 6.49 (d, J = 15.6 Hz, 1H), 6.46-6.39 (m, 1H), 3.70 (d, J = 6 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.68, 137.48, 133.70, 132.20, 131.35, 129.09, 128.55, 128.07, 127.67, 127.53, 127.49, 127.18, 126.77, 126.19, 126.02, 125.36, 39.50.

(*E*)-prop-1-ene-1,3-diyldibenzene (4a) [51]**:** colorless oil, from **2a**: 35 mg, 90%; from **2c**: 34 mg, 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.18 (m, 10H), 6.46 (d, J = 16 Hz, 1H), 6.39-6.32 (m, 1H), 3.55 (d, J = 6.4 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.31, 137.62, 131.21, 129.37, 128.82, 128.64, 127.25, 126.32, 126.27, 39.50.

(*E*)-but-1-ene-1,3-diyldibenzene (4b) [61]**:** light yellow oil, from **2b**: 32 mg, 78%; from **2c**: 31 mg, 75%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.33 (m, 2H), 7.32-7.26 (m, 6H), 7.23-7.17 (m, 2H), 6.44-6.35 (m, 2H), 3.67-3.61 (m, 1H), 1.46 (d, J = 7.2 Hz, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.66, 137.60, 135.26, 128.51, 127.33, 127.07, 126.25, 126.17, 42.59, 21.25.

(*E*)-3-(3-phenylprop-1-en-1-yl)thiophene (4e)[62]**:** pale yellow oil, 24 mg, 61%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.29 (m, 2H), 7.24-7.21 (m, 4H), 7.19-7.17 (m, 1H), 7.08 (d, J = 2.8 Hz, 1H), 6.45 (d, J = 15.6 Hz, 1H), 6.25-6.17 (m, 1H), 3.51 (d, J = 6.8 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.18, 140.09, 129.23, 128.70, 128.51, 126.20, 125.87, 125.35, 125.00, 121.06, 39.26.

(*E*)-1-methyl-4-(3-phenylprop-1-en-1-yl)benzene (4f)[63]**:** colorless oil, 34 mg, 83%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.28 (m, 2H), 7.26-7.19 (m, 5H), 7.09 (d, J = 8 Hz, 2H), 6.42 (d, J = 16 Hz, 1H), 6.33-6.26 (m, 1H), 3.53 (d, J = 6.8 Hz, 2H), 2.32 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.37, 136.86, 134.72, 130.94, 129.21, 128.68, 128.48, 128.19, 126.15, 126.04, 39.37, 21.17.

(*E*)-1-methyl-3-(3-phenylprop-1-en-1-yl)benzene (4g)[64]**:** colorless oil, 28 mg, 69%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.29 (m, 2H), 7.25-7.14 (m, 6H), 7.02-7.01 (m, 1H), 6.43 (d, J = 16 Hz, 1H), 6.37-6.30 (m, 1H), 3.54 (d, J = 6.4 Hz, 2H), 2.32 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.27, 138.05, 137.44, 131.15, 129.05, 128.70, 128.50, 128.43, 127.92, 126.87, 126.18, 123.31, 39.39, 21.41.

(*E*)-1-methyl-2-(3-phenylprop-1-en-1-yl)benzene (4h)[65]**:** colorless oil, 32 mg, 77%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.40 (m, 1H), 7.33-7.29 (m, 2H), 7.26-7.20 (m, 3H), 7.16-7.12 (m, 3H), 6.66 (d, J = 15.6 Hz, 1H), 6.26-6.19 (m, 1H), 3.57 (d, J = 6.8 Hz, 2H), 2.34 (s, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.34, 136.64, 135.12, 130.54, 130.21, 129.05, 128.65, 128.51, 127.08, 126.18, 126.06, 125.62, 39.68, 19.87.

(*E*)-1-methoxy-4-(3-phenylprop-1-en-1-yl)benzene (4i)[66]**:** colorless oil, 32 mg, 72%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.20 (m, 4H), 7.18-7.11 (m, 3H), 6.78-6.74 (m, 2H), 6.33 (d, J = 16 Hz, 1H), 6.18-6.10 (m, 1H), 3.72 (s, 3H), 3.45 (d, J = 6.8 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.81, 139.42, 129.40, 129.28, 127.61, 127.41, 126.19, 126.01, 125.07, 112.88, 54.22, 38.29.

(*E*)-1-chloro-4-(3-phenylprop-1-en-1-yl)benzene (4j) [67]**:** colorless oil, 31 mg, 68%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.20 (m, 9H), 6.39 (d, J = 16 Hz, 1H), 6.36-6.29 (m, 1H), 3.53 (d, J = 6 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.89, 136.00, 132.68, 130.05, 129.86, 128.69, 128.66, 128.58, 127.35, 126.31, 39.34.

(*E*)-1-chloro-3-(3-phenylprop-1-en-1-yl)benzene (4k)[68]**:** colorless oil, 29 mg, 65%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.30 (m, 3H), 7.25-7.19 (m, 5H), 7.18-7.15 (m, 1H), 6.39-6.37 (m, 2H), 3.54 (d, J = 4.8 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.73, 139.37, 134.47, 130.93, 129.77, 129.71, 128.68, 128.58, 127.05, 126.33, 126.08, 124.35, 39.29.

(*E*)-1,3-dimethoxy-2-(3-phenylprop-1-en-1-yl)benzene (4m) [69]**:** colorless oil, 43 mg, 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.19 (m, 4H), 7.13-7.09 (m, 1H), 7.03 (d, J = 8.4 Hz, 1H), 6.73-6.67 (m, 2H), 6.46 (d, J = 8.4 Hz, 2H), 3.74 (s, 6H), 3.51 (dd, J = 3.6 Hz, 2 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.27, 140.13, 132.30, 127.61, 127.28, 126.44, 124.80, 120.54, 113.75, 102.96, 54.69, 40.10.

(*E*)-1-fluoro-4-(3-phenylprop-1-en-1-yl)benzene (4n) [63]**:** colorless oil, 27 mg, 64%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.28 (m, 4H), 7.24-7.20 (m, 3H), 7.00-6.94 (m, 2H), 6.40 (d, J = 15.6 Hz, 1H), 6.30-6.23 (m, 1H), 3.53 (d, J = 6.8 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.07 (d, J = 244.5 Hz), 140.09, 133.66 (d, J = 3.3 Hz), 129.89, 129.05 (d, J = 2.2 Hz), 128.69, 128.56, 127.62, 127.55, 126.27,115.39 (d, J = 21.4 Hz), 39.32. ^{19}F NMR (376 MHz, $CDCl_3$): δ -115.30.

(*E*)-1-(3-phenylprop-1-en-1-yl)-4-(trifluoromethyl)benzene (4o) [66]**:** colorless oil, 20 mg, 39%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8 Hz, 2H), 7.35-7.31 (m, 2H), 7.25-7.22 (m, 3H), 6.47-6.46 (m, 2H), 3.56 (d, J = 4 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.94, 139.55, 132.14, 129.82, 128.77 (q, J = 13.4 Hz), 128.52, 128.43, 126.22, 126.07, 125.28 (q, J = 3.8 Hz), 122.73, 39.17; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.42.

methyl (*E*)-4-(3-phenylprop-1-en-1-yl)benzoate (4p) [64]**:** light yellow oil, 35 mg, 71%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.8 Hz, 2H), 7.33-7.30 (m, 2H), 7.24-7.20 (m, 3H), 6.49-6.47 (m, 2H), 3.89 (s, 3H), 3.56 (d, J = 5.2 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.96, 142.01, 139.61, 132.25, 130.25, 129.93, 128.74, 128.62, 126.40, 126.02, 52.04, 39.46.

Analytical methods

NMR spectra were recorded on a Bruker Avance III HD 400 spectrometer using TMS as an internal standard (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). Mass spectroscopy data were collected on a Shimadzu LCMS-IT-TOF mass spectrometer. Single crystal structures were determined on a Bruker D8 Venture X-ray diffractometer equipped with a PHOTON II CPAD detector.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21868033), Xinjiang Bingtuan Young and Middle-Aged Leading Scientists Program (2020CB027), Shihezi Young and Middle-Aged Leading Scientists Program (2019RC01), International Partnership Program of Shihezi University (GJHZ201908), Double First-Class Program of Shihezi University (SHYL-ZD201801). We thank Ji-Xing Zhao for his assistance with the single crystal X-ray diffraction, located at the Analysis and Testing Center, Shihezi University.

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10.1002/adsc.202000186

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