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CuI-catalyzed Suzuki coupling reaction of organoboronic acids with alkynyl bromides

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ABSTRACT

A CuI-catalyzed Suzuki cross-coupling reaction of organoboron derivatives with alkynyl bromides has been developed. In the presence of CuI (10 mol %) and 8-hydroxyquinoline (20 mol %), organoboron derivatives including aromatic and alkenyl boronic acids, potassium aryltrifluoroborates, and sodium tetraphenylborate reacted smoothly with 1-bromo-2-substituted acetylene to generate the corresponding cross-coupling products in good to excellent yields in C_2H_5OH. It is important to note that aromatic *N,O*-ligand 8-hydroxyquinoline is the most effective ligand for the reaction.

1. Introduction

The palladium catalyzed carbon–carbon cross-coupling of organometallic nucleophiles with organoelectrophiles is an important synthetic reaction in modern organic synthesis.[1] However, most organometallic compounds are sensitive to air and moisture, or toxic, and often will not tolerate functional groups, which may be important in complex syntheses. Constituting one of the few organometallic reagents that tolerate a wide range of functional groups, boronic acids are available and generally environmentally benign. In addition, they are inert to air and moisture, resistant to heat.

The Suzuki cross-coupling reaction of organoboronic acid with C_{sp2}–X has become a mainstay of modern synthetic organic chemistry for the preparation of biaryl compounds,[2] and has been broadly applied to the syntheses of natural products, agrochemicals, pharmaceuticals, polymers, and other materials.[3] Since its invention, the development of efficient and selective catalytic systems for the Suzuki cross-coupling reaction has attracted much attention. Traditional Suzuki coupling reactions generally employ palladium catalysts along with phosphine ligands in the presence of a base.[4] However, most of the phosphine ligands are toxic and sensitive to air and moisture, and the expensive palladium complexes tend to be difficult to manipulate and recover. Furthermore, the cross-coupling products are frequently contaminated by residual palladium black and ligands, which can be difficult to separate from the final products. Thus, development of phosphine-free and less expensive transition-metal non-palladium catalytic system instead of palladium is still a promising area for organic chemists. The copper-catalyzed Suzuki cross-coupling of vinyl halides and aryl halides with arylboronic acids was described in 2007.[5] Moreover, very recently, copper-catalyzed Sonogashira coupling reaction of terminal alkynes with aryl halides or arylboronic acids was developed.[6] As one of the substrates, organoelectrophiles, which contains C_{sp2}–X bonds (such as aryl- and alkenyl halides), C_{sp2}–OTf and C_{sp3}–OTf (aryl and alkyl triflates) bonds, and even C_{sp3}–X bonds (alkyl halides) were employed to couple with organoboron derivatives in the Suzuki reactions.[7] In contrast, organic halides, which contains C_{sp}–X bonds are quite rare to be used as organoelectrophiles due to the mixture of cross-coupling and home-coupling products obtained.[8] As part of our ongoing efforts devoted to copper-catalyzed organic reactions,[9] we were pleased to find that CuI-catalyzed Suzuki cross-coupling reaction of organoboron compounds, such as aryl and alkenyl boronic acids, potassium aryltrifluoroborates, and sodium tetraphenylborate reacted smoothly with alkynyl bromides, which contains C_{sp}–Br bonds to generate the corresponding cross-coupling products in good to excellent yields in C_2H_5OH in the presence of an effective *N,O*-ligand 8-hydroxyquinoline (Scheme 1).

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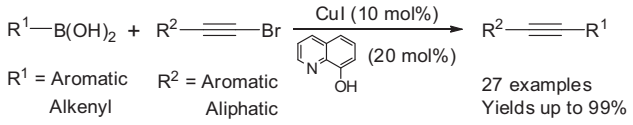
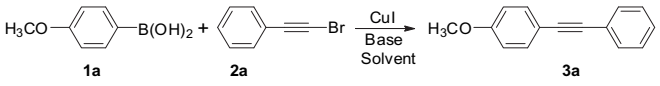


Scheme 1.

2. Results and discussion

For optimization of the reaction conditions and identification of the best solvent, base, Cu source, ligand, reaction temperature and time, a reaction of 4-methoxyphenylboronic acid (**1a**) with 1-bromo-2-phenylacetylene (**2a**) was chosen as model one for the exploration. The results were summarized in Tables 1 and 2. Initially, our investigation was focused on the effect of solvent on the model reaction. As shown in Table 1, among the solvents tested, C_2H_5OH, CH_3NO_2, and $ClCH_2CH_2Cl$ were the most suitable reaction media for the model reaction carried out in the presence of CuI (10 mol %) and Na_3PO_4 (2.0 mmol) at 100 °C for 24 h (Table 1, entries 1–3). DMF, CH_3CN, DMSO, dioxane, THF, $C_6H_5CH_3$, and CH_3OH were inferior and generated the desired cross-coupling product **3a** in 67, 65, 63, 62, 55, 51, and 45% yields, respectively (Table 1, entries 4–10). Unfortunately, no cross-coupling product was isolated when the reaction was carried out in H_2O (Table 1, entry 11). Next, the effect of base on the model reaction was examined at 100 °C using 10 mol % of CuI as catalyst in C_2H_5OH. Na_3PO_4 was found to be the most effective base. Other bases, such as K_2CO_3, Na_2CO_3, KF, $(C_2H_5)_3N$, NaOAc, and Na_2HPO_4 were substantially less effective, and *t*-BuOK, Cs_2CO_3 and NaOH were no longer the effective bases in the model reaction due to their strong basicity (Table 1, entries 12–20). It should be noted that the cross-coupling of the model substrates could not occur in the absence of a suitable base (Table 1, entry 21).

Table 1
Effect of solvent and base on the model reaction[a]

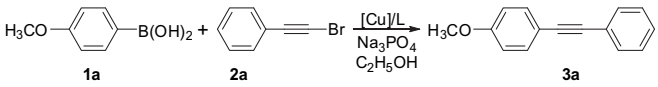


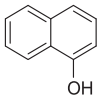
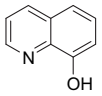
Entry	Solvent	Base	Yield (%)[b]
1	C_2H_5OH	Na_3PO_4	81
2	CH_3NO_2	Na_3PO_4	76
3	$ClCH_2CH_2Cl$	Na_3PO_4	73
4	DMF	Na_3PO_4	67
5	CH_3CN	Na_3PO_4	65
6	DMSO	Na_3PO_4	63
7	Dioxane	Na_3PO_4	62
8	THF	Na_3PO_4	55
9	$C_6H_5CH_3$	Na_3PO_4	51
10	CH_3OH	Na_3PO_4	45
11	H_2O	Na_3PO_4	0
12	C_2H_5OH	K_2CO_3	79
13	C_2H_5OH	Na_2CO_3	78
14	C_2H_5OH	KF	75
15	C_2H_5OH	$(C_2H_5)_3N$	65
16	C_2H_5OH	NaOAc	56
17	C_2H_5OH	Na_2HPO_4	43
18	C_2H_5OH	*t*-BuOK	Trace
19	C_2H_5OH	Cs_2CO_3	Trace
20	C_2H_5OH	NaOH	Trace
21	C_2H_5OH	—	0

[a] 4-Methoxyphenylboronic acid (1.0 mmol), (bromoethynyl)benzene (1.0 mmol), CuI (0.10 mmol), base (2.0 mmol), solvent (2.0 mL) at 80 °C for 24 h.
[b] Isolated yields.

Several copper sources were screened in the model reaction and the results were summarized in Table 2. The cross-coupling of the model reaction could be catalyzed by Cu^{I} salts, Cu^{I} oxide, Cu^{II} salts as well as Cu^{II} oxide, such as CuI, CuCl, CuBr, $CuCl_2$, Cu_2O, CuO, $Cu(NO_3)_2$, $Cu(OAc)_2$, $Cu(OTf)_2$, $CuSO_4$, and $Cu(acac)_2$ in the absence of any ligand and generated **3a** in 52–81% yields (Table 2, entries 1–11). It is evident that CuI was the most effective catalyst for the reaction. With respect to the catalyst loading, when less than 10 mol % of CuI was used, the reaction did not go to completion, but that a higher loading (up to 10 mol %) of CuI gave a good result. However, with an increased loading of CuI up to 15 mol %, there was no increase in the isolated yield of the product (Table 1, entry 1). In general, Cu(I)-catalyzed carbon–carbon and carbon–heteroatom bond formation reactions could be enhanced by a suitable ligand containing nitrogen or oxygen atoms.[10] When P-ligand, such as $(C_6H_5)_3P$, or 1,1′-bis(diphenylphosphino)ferrocene (DPPF) was added to the reaction systems, we found that $(C_6H_5)_3P$ accelerates the reaction to give **3a** in 85% yield, but DPPF decelerates the reaction to give **3a** in 71% yield (Table 2, entries 12 and 13). Monodentate aromatic *N*-ligand, such as pyridine and quinoline generated **3a** in 82% and 63% yields, respectively (Table 2, entries 14 and 15). But, bidentate aromatic *N*,*N*-ligand, such as 1,10-phenanthroline and 2,2′-dipyridine inhibited the reaction completely and only trace amount of **3a** was obtained (Table 2, entries 16 and 17).

Table 2
Effect of Cu source and ligand on the model reaction[a]



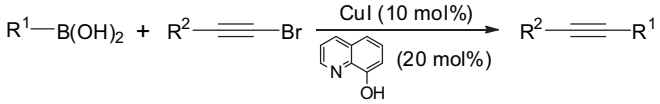
Entry	Cu source	Ligand	Yield (%)[b]
1	CuI	—	81
			71[c]
			56[d]
			81[e]
2	CuCl	—	77
3	CuBr	—	76
4	$CuCl_2$	—	73
5	Cu_2O	—	77
6	CuO	—	72
7	$Cu(NO_3)_2$	—	68
8	$Cu(OAc)_2$	—	61
9	$Cu(OTf)_2$	—	57
10	$CuSO_4$	—	53
11	$Cu(acac)_2$	—	52
12	CuI	PPh_3	85
13	CuI	DPPF	71
14	CuI	Pyridine	82
15	CuI	Quinoline	63
16	CuI	1,10-Phenanthroline	Trace
17	CuI	2,2′-Dipyridine	Trace
18	CuI	TMHD	74
19	CuI		57
20	CuI		99
21	CuI	$HOCH_2CH_2NH_2$	NR
22	CuI	$(HOCH_2CH_2)_2NH$	NR
23	CuI	TMEDA	NR
24	CuI	L-Prolinol	NR

DPPF=1,1′-bis(diphenylphosphino)ferrocene, TMHD=2,2,6,6-tetramethyl-3,5-heptanedione, TMEDA=*N*,*N*,*N*′,*N*′-tetramethylethylenediamine.
[a] 4-Methoxyphenylboronic acid (1.0 mmol), (bromoethynyl)benzene (1.0 mmol), Cu source (0.10 mmol), ligand (0.20 mmol) if added, Na_3PO_4 (2.0 mmol), C_2H_5OH (2.0 mL) at 80 °C for 24 h.
[b] Isolated yields.
[c] CuI (0.05 mmol).
[d] CuI (0.02 mmol).
[e] CuI (0.15 mmol).

Meanwhile, bidentate aliphatic *O*,*O*-ligand, such as 2,2,6,6-tetramethyl-3,5-heptadione (TMHD), as well as monodentate aromatic *O*-ligand, such as 1-naphthol added to the reaction system also could not assist the CuI-catalyzed cross-coupling reaction, and conversely, restrain the reactivity of catalyst (Table 2, entries 18 and 19). To our delight, isolated yield of **3a** was increased up to 99% when bidentate aromatic *N*,*O*-ligand, such as 8-hydroxyquinoline was added to the reaction (Table 2, entry 20). However, bidentate aliphatic *N*,*N*-ligand, such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), and bidentate aliphatic *N*,*O*-ligand, such as $HOCH_2CH_2NH_2$, $(HOCH_2CH_2)_2NH$, and L-prolinol inhibited the reaction completely, and no corresponding product was obtained and starting materials were recovered (Table 2, entries 21–24). During the course of our further optimization of the reaction conditions, the reaction was generally completed within 24 h when it was performed at 100 °C by using 10 mol % of CuI in the presence of 8-hydroxyquinoline (20 mol %) in C_2H_5OH.

Under the optimized reaction conditions, which involve the use of 10 mol % of CuI as catalyst in the presence of 8-hydroxyquinoline (20 mol %) in C_2H_5OH, the reactions of a variety of organoboron derivatives with different substituted ethynyl bromides were investigated to examine the scope of this cross-coupling reaction, and the results were summarized in Table 3. At the beginning of the search for the organoboron substrate scope, (bromoethynyl)

Table 3
CuI-catalyzed Suzuki coupling reactions of organoboronic acids with alkynyl bromides[a]



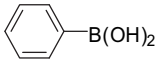
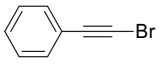
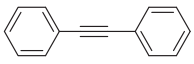
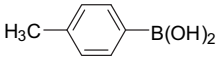
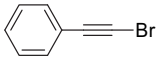
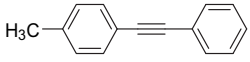
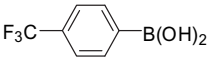
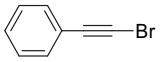
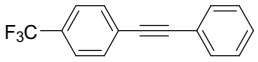
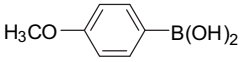
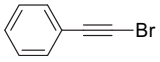
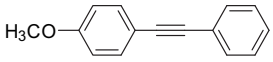
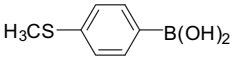
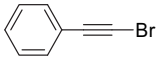
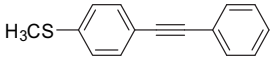
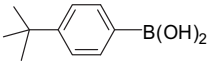
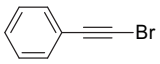
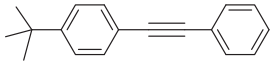
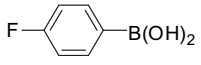
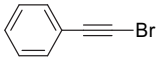
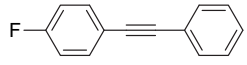
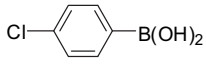
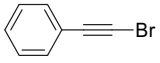
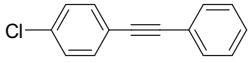
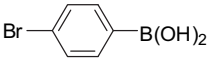
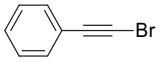
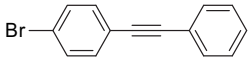
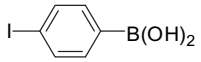
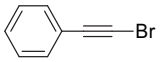
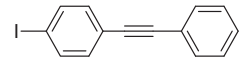
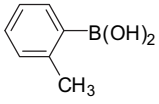
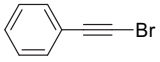
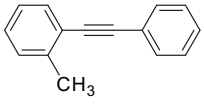
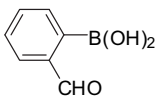
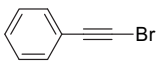
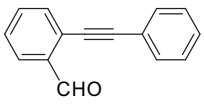
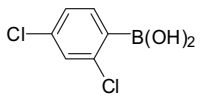
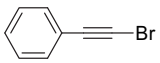
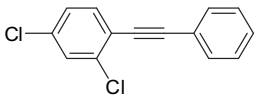
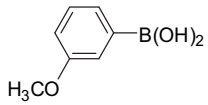
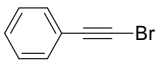
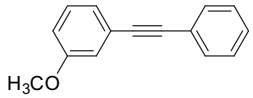
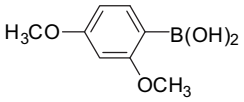
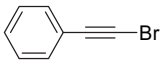
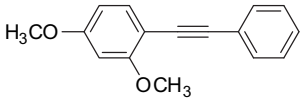
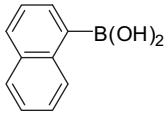
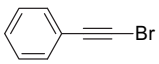
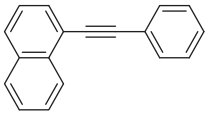
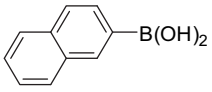
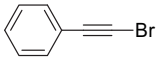
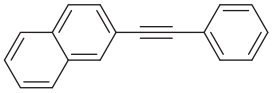
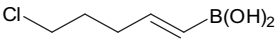
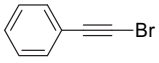
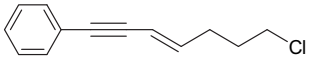
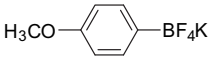
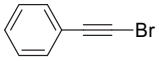
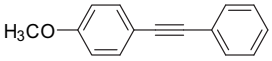
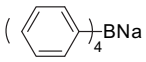
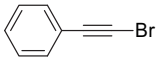
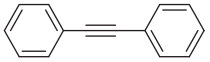
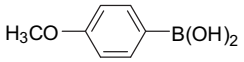
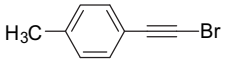
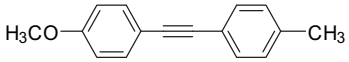
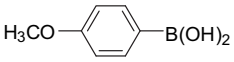
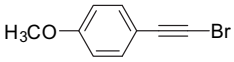
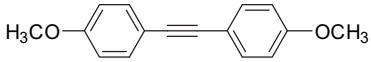
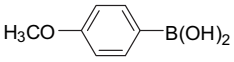
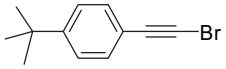
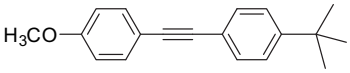
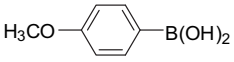
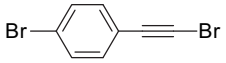
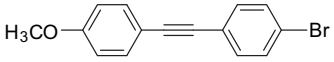
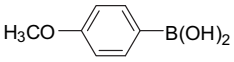
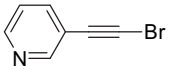
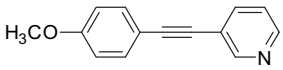
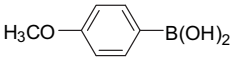
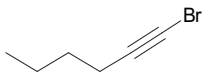
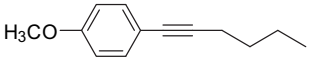
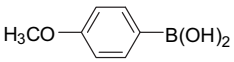
Entry	R^1—$B(OH)_2$	R^2—≡—Br	R^2—≡—R^1	Yield (%)[b]
1				99
2				99
3				93
4				99
5				98
6				96
7				89
8				94
9				93
10				90
11				99
12				86
13				90

Table 3 (*continued*)

Entry	R^1—$B(OH)_2$	R^2—≡—Br	R^2—≡—R^1	Yield (%)[b]
14				97
15				99
16				99
17				98
18				77
19				97
20				96
21				96
22				99
23				93
24				93
25				92
26				64
27				70

[a] Organoboron compound (1.0 mmol), alkynyl bromide (1.0 mmol), CuI (0.10 mmol), 8-hydroxyquinoline (0.20 mmol), Na_3PO_4 (2.0 mmol), C_2H_5OH (2.0 mL) at 80 °C for 24 h.

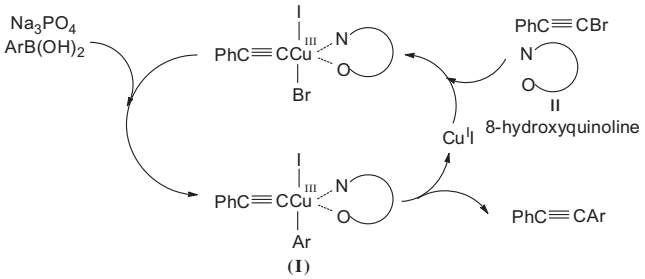
[b] Isolated yields.

benzene (**2a**) was used as one of the model substrate and a variety of organoboronic acids were examined for the coupling reactions (Table 3, entries 1–18). As can be seen from Table 3, the reactivity of both aromatic and alkenyl boronic acids was observed, in which aromatic boronic acids were much more reactive than alkenyl one (Table 3, entries 1–17 vs 18). Aromatic boronic acids with electron-donating groups (such as CH_3, CH_3O, *t*-C_4H_9, CH_3S) or electron-withdrawing groups (such as CF_3, CHO, F, Cl, Br, I) on the aromatic rings, as well as 1-naphthaleneboronic acid and 2-naphthaleneboronic acid, reacted with (bromoethynyl)benzene (**2a**) completely and generated the corresponding cross-coupling products in good to excellent yields (Table 3, entries 1–17). In most cases, almost quantitative yields were obtained. It is important to note that the location of the substituents on the aromatic rings in arylboronic acids had little effect on the reaction, or even on the *ortho*-position (Table 3, entries 11–13 and 15). It is noteworthy that the reactivity of C_{sp}—Br in 1-bromo-2-phenylacetylene is more than that of C_{sp2}—Br in 4-bromophenylboronic acid, and that of

C_{sp2}–I in 4-iodophenylboronic acid (Table 3, entries 9 and 10). Fortunately, the cross-coupling reaction involving alkenyl boronic acid also gave the desired product in 77% isolated yield (Table 3, entry 18). As an alternative to organoboronic acids and esters, organotrifluoroborate salts have emerged as a new class of air-stable boron derivatives, facile to prepare, easy to handle, and feasible to utilize in a number of organic transformations.[3a,11] When the reaction of potassium aryltrifluoroborates with (bromoethynyl) benzene (**2a**) was performed under the present reaction conditions, as expected, excellent yield of the desired product was obtained (Table 3, entry 19). In addition, as a stable and commercially available borate source, sodium tetraphenylborate[12] was also coupled with (bromoethynyl)benzene (**2a**) completely to generate the corresponding product in 96% yield (Table 3, entry 20).

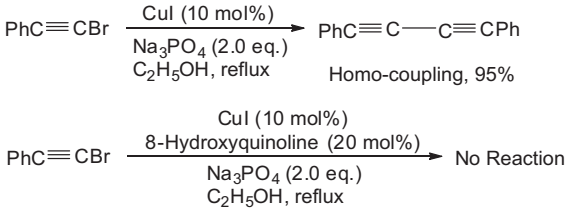
Subsequently, a variety of 1-bromo-2-substituted acetylene were surveyed for the scope of C_{sp}–Br substrates and the results listed in Table 3 indicated that 2-aryl and 2-alkyl ethynyl bromides, such as -bromo-2-(*p*-methylphenyl)acetylene, 1-bromo-2-(*p*-methoxyphenyl)acetylene, 1-bromo-2-(*tert*-butylphenyl)acetylene, 1-bromo-2-(*p*-bromophenyl)acetylene, 1-bromo-2-(*m*-pyridyl)acetylene, 1-bromo-2-butylacetylene, and 1-bromo-2-hexylacetylene displayed high reactivity to 4-methoxyphenylboronic acid under present reaction conditions and good to excellent yields of desired cross-coupling products were obtained (Table 3, entries 21–27). As it is evident from Table 3, the reactivity of 1-bromo-2-aryl acetylenes was more reactive than that of 1-bromo-2-alkyl acetylenes (Table 3, entries 21–25 vs 26–27). For 1-bromo-2-aryl acetylenes, it should also be noted that electron-donating groups (such as CH_3O, CH_3, t-C_4H_9), electron-withdrawing groups (such as Br) and their location on the aromatic rings also had little effect on the reactions (Table 3, entries 21–25).

The proposed mechanism for the copper-catalyzed Suzuki coupling reaction of organoboronic acid with 1-bromo-2-substituted acetylene was shown in Scheme 2. The catalyst CuI first reacted with 1-bromo-2-substituted acetylene to form a Cu^{III} alkynylate complex via an oxidative addition process with the assistance of an efficient *N*,*O*-ligand, 8-hydroxyquinoline. The resulting Cu^{III} alkynylate complex subsequently reacted with organoboronic acid in the presence of Na_3PO_4 to form an intermediate species (**I**) through transmetallation, which underwent reductive elimination to give the corresponding cross-coupling product and regenerate Cu^{I} catalyst and ligand to complete this catalytic cycle.



Scheme 2. Possible mechanism of the reaction.

When the reaction used alkynyl bromide, such as (bromoethynyl)benzene as sole substrate without organoboronic acid was performed in the absence of 8-hydroxyquinoline under the reaction conditions, 95% yield of a homo-coupling product, 1,4-diphenylbuta-1,3-diyne was obtained. On the other hand, when the reaction was performed in the presence of 8-hydroxyquinoline, no reaction was occurred and starting material, (bromoethynyl)benzene was recovered in almost quantitative yield (Scheme 3). It is obvious that *N*,*O*-ligand, 8-hydroxyquinoline not only can assist this cross-coupling, but also restrain the homo-coupling of alkynyl bromide caused by CuI. Presumably, an accelerating effect of 8-hydroxyquinoline as *N*,*O*-ligand in the Cu^{I}-catalyzed cross-coupling reaction through oxidative addition/reductive elimination sequence process[13] is more than that of Cu^{I}-catalyzed homo-coupling reaction of alkynyl bromide via a free radical mechanism.[14] More detail investigation on the reaction mechanism and the role of 8-hydroxyquinoline is underway in our laboratory.



Scheme 3. The reaction of (bromoethynyl)benzene.

3. Conclusions

In summary, we have developed a novel CuI-catalyzed Suzuki cross-coupling reaction of organoboron derivatives with alkynyl bromides to form 1,2-disubstituted acetylenes. In the presence of CuI (10 mol %) and 8-hydroxyquinoline (20 mol %), organoboron compounds, including aryl and alkenyl boronic acids, potassium aryltrifluoroborates and sodium tetraphenylborate reacted smoothly with 1-bromo-2-substituted acetylene to generate the corresponding cross-coupling products in good to excellent yields in C_2H_5OH. It was found that aromatic *N*,*O*-ligand 8-hydroxyquinoline is the most effective ligand for the reaction. This methodology provides an efficient, alternative, and environmentally friendly process for the synthesis of symmetric and nonsymmetric 1,2-disubstituted acetylenes through Suzuki coupling reaction of organoboron derivatives with ethynyl bromides. The notable advantages of this methodology are mild reaction conditions, higher yields of the desired products and wide applicability to various substrates. Further investigation on the application of ethynyl bromides as organoelectrophiles with organometallics in organic synthesis is still underway in our laboratory.

4. Experimental

4.1. General methods

All ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker-DMX-400 MHz FT-NMR spectroscopy. Chemical shifts were given as δ value with reference to tetramethylsilane (TMS) as internal standard. Products were purified by flash column chromatography on 230–400 mesh silica gel, SiO_2.

The chemicals were purchased from commercial suppliers (Aldrich, USA and Shanghai Chemical Company, China) and used without purification prior to use.

4.2. General procedure for CuI-catalyzed Suzuki coupling reaction of organoboronic acids with alkynyl bromides

A 5.0 mL of reaction tube was charged with organoboron compound (1.0 mmol), alkynyl bromide (1.0 mmol), CuI (0.10 mmol), 8-hydroxyquinoline (0.20 mmol), ethanol (2.0 mmol). The mixture was stirred at 80 °C for 24 h, and then washed with ethyl acetate (3.0 mL×3), the combined ethyl acetate was concentrated under reduced pressure. The obtained residue was purified by flash column chromatography on silica gel (petroleum ether as eluting agent) to give the corresponding pure cross-coupling product.

4.3. Analytical data for the Suzuki coupling products

4.3.1. Diphenylacetylene[15]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.50 (m, 4H), 7.32–7.28 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.59, 128.31, 128.22, 123.28, 89.43.

4.3.2. Phenyl-p-tolyacetylene[15]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.48 (m, 2H), 7.41 (d, J=7.8 Hz, 2H), 7.29–7.26 (m, 3H), 7.10 (d, J=7.8 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.32, 131.47, 129.01, 128.23, 128.03, 123.58, 120.21, 89.63, 88.72, 21.40.

4.3.3. (4-Trifluoromethylphenyl)phenylacetylene[15]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.60 (m, 4H), 7.57–7.54 (m, 2H), 7.39–7.35 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.83, 131.70, 129.90 (J=32.8 Hz), 128.81, 128.37, 127.10 (J=1.2 Hz), 125.31 (J=3.7 Hz), 123.92 (J=270.7 Hz), 122.52, 91.69, 87.91.

4.3.4. (4-Methoxyphenyl)phenylacetylene[15]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.46 (m, 4H), 7.37–7.30 (m, 3H), 6.87 (dd, J=8.7, 2.1 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.52, 133.01, 131.43, 128.28, 127.91, 123.49, 115.31, 113.88, 89.31, 88.01, 55.32.

4.3.5. Methyl(4-(phenylethynyl)phenyl)sulfane[15]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.49 (m, 2H), 7.42 (d, J=8.8 Hz, 2H), 7.32–7.30 (m, 3H), 7.17 (d, J=8.4 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.29, 131.82, 131.48, 128.28, 128.11, 125.79, 123.28, 119.50, 89.43, 89.18, 15.27.

4.3.6. (4-tert-Butylphenyl)phenylacetylene[16]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.51 (m, 2H), 7.47 (d, J=8.0 Hz, 2H), 7.38–7.35 (m, 2H), 7.34–7.32 (m, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.50, 131.56, 131.32, 128.28, 128.04, 125.33, 123.51, 120.23, 89.52, 88.71, 34.77, 31.17.

4.3.7. (4-Fluorophenyl)phenylacetylene[17]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.47 (m, 4H), 7.35–7.31 (m, 3H), 7.06–7.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.51 (d, J=248.1 Hz), 133.50 (d, J=8.9 Hz), 131.47, 128.32, 123.11, 119.31 (d, J=5.6 Hz), 115.59 (d, J=22.4 Hz), 89.02, 88.31.

4.3.8. (4-Chlorophenyl)phenylacetylene[18]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.50 (m, 2H), 7.45 (d, J=8.8 Hz, 2H), 7.36–7.34 (m, 3H), 7.32 (d, J=8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.23, 132.79, 131.58, 128.67, 128.47, 128.38, 122.90, 121.76, 90.29, 88.22.

4.3.9. (4-Bromophenyl)phenylacetylene[18]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.44 (m, 4H), 7.38–7.31 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.02, 131.61, 128.48, 128.39, 122.92, 122.51, 122.20, 90.51, 88.30.

4.3.10. (4-Iodophenyl)phenylacetylene[19]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J=8.4 Hz, 2H), 7.52–7.50 (m, 2H), 7.35–7.33 (m, 3H), 7.24 (d, J=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.48, 133.05, 131.57, 128.48, 128.36, 122.87, 122.76, 94.09, 90.77, 88.43.

4.3.11. Phenyl-o-tolyacetylene[16]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.48 (m, 3H), 7.33–7.29 (m, 3H), 7.21–7.20 (m, 2H), 7.16–7.13 (m, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.11, 132.44, 131.79, 131.46, 129.42, 128.30, 128.11, 125.54, 123.51, 122.98, 93.33, 88.33, 20.69.

4.3.12. 2-(Phenylethynyl)benzaldehyde[20]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.66 (s, 1H), 7.96–7.94 (m, 1H), 7.66–7.64 (m, 1H), 7.60–7.56 (m, 3H), 7.48–7.43 (m, 1H), 7.40–7.38 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.73, 135.80, 133.78, 133.20, 131.66, 129.06, 128.60, 128.51, 127.24, 126.87, 122.30, 96.31, 84.86.

4.3.13. (2,4-Dichlorophenyl)phenylacetylene[15]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.55 (m, 2H), 7.49 (d, J=8.4 Hz, 1H), 7.46 (d, J=2.0 Hz, 1H), 7.39–7.36 (m, 3H), 7.23 (dd, J=2.0, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.63, 134.46, 133.71, 131.70, 129.28, 128.82, 128.39, 126.95, 122.56, 121.83, 95.44, 85.20.

4.3.14. (3-Methoxyphenyl)phenylacetylene[15]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.52 (m, 1H), 7.53–7.50 (m, 1H), 7.36–7.33 (m, 2H), 7.34–7.31 (m, 2H), 7.14–7.11 (m, 1H), 7.07–7.04 (m, 1H), 6.91–6.88 (m, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.34, 132.49, 131.62, 129.39, 128.33, 124.25, 124.17, 123.17, 116.32, 114.94, 89.28, 89.17, 55.29.

4.3.15. (2,4-Dimethoxyphenyl)phenylacetylene[21]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J=8.8 Hz, 2H), 7.41 (d, J=8.4 Hz, 1H), 7.32–7.30 (m, 3H), 6.48–6.45 (m, 2H), 3.88 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.18, 161.12, 134.28, 131.46, 128.16, 127.73, 123.84, 104.97, 104.83, 98.44, 92.00, 85.75, 55.81, 55.39.

4.3.16. 1-(Phenylethynyl)naphthalene[16]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, J=8.4 Hz, 1H), 7.76–7.71 (m, 2H), 7.66 (d, J=7.2 Hz, 1H), 7.56–7.54 (m, 2H), 7.51–7.47 (m, 1H), 7.44–7.40 (m, 1H), 7.36–7.32 (m, 1H), 7.31–7.25 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.22, 133.16, 131.63, 130.33, 128.73, 128.40, 128.35, 128.28, 126.74, 126.39, 126.18, 125.25, 123.35, 120.84, 94.29, 87.50.

4.3.17. 2-(Phenylethynyl)naphthalene[22]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.77–7.74 (m, 3H), 7.58–7.55 (m, 3H), 7.46–7.43 (m, 2H), 7.35–7.29 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.96, 132.74, 131.62, 131.39, 128.36, 128.34, 128.25, 127.96, 127.72, 127.71, 126.60, 126.49, 123.26, 120.53, 89.82, 89.75.

4.3.18. 7-Chloro-1-phenyl-3-hepten-1-yne[23]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45–7.43 (m, 2H), 7.32–7.29 (m, 3H), 6.24–6.13 (m, 1H), 5.74 (d, J=16.8 Hz, 1H), 3.51 (t, J=6.8 Hz, 2H), 2.36–2.28 (m, 2H), 1.93–1.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.50, 131.51, 128.09, 128.01, 123.27, 111.02, 88.51, 87.83, 44.11, 31.50, 30.12.

4.3.19. 4-Methyl-4′-methoxyldiphenylacetylene[22]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J=9.2 Hz, 2H), 7.40 (d, J=8.0 Hz, 2H), 7.14 (d, J=8.0 Hz, 2H), 6.87 (d, J=8.8 Hz, 2H), 3.82 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.46, 138.00, 132.95, 131.32, 129.06, 120.48, 115.58, 113.95, 88.63, 88.17, 55.27, 21.47.

4.3.20. Di(4-methoxylphenyl)acetylene[15]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J=8.8 Hz, 4H), 6.85 (d, J=8.8 Hz, 4H), 3.78 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.31, 132.80, 115.63, 113.89, 87.91, 55.18.

4.3.21. 1-tert-Butyl-4-((4-methoxyphenyl)ethynyl)benzene[24]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.43 (m, 4H), 7.34 (d, J=8.4 Hz, 2H), 6.85 (d, J=8.4 Hz, 2H), 3.79 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.45, 151.12, 132.96, 131.14, 125.27, 120.54, 115.61, 113.93, 88.66, 88.15, 55.22, 34.71, 31.15.

4.3.22. 1-Bromo-4-((4-methoxyphenyl)ethynyl)benzene[25]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47–7.45 (m, 4H), 7.36 (d, J=8.4 Hz, 2H), 6.88 (d, J=8.4 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.77, 133.05, 132.83, 131.54, 122.56, 122.03, 114.96, 114.03, 90.53, 87.03, 55.29.

4.3.23. 3-((4-Methoxyphenyl)ethynyl)pyridine[22]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 1H), 8.51 (d, J=6.4 Hz, 1H), 7.77–7.74 (m, 1H), 7.47 (d, J=8.4 Hz, 2H) 7.25–7.22 (m, 1H), 6.87 (d, J=8.4 Hz, 2H), 3.80 (s,

3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.88, 151.95, 148.06, 138.04, 133.04, 122.84, 120.65, 114.42, 113.96, 92.65, 84.61, 55.13.

4.3.24. 1-(4-Methoxylphenyl)-1-hexyne[26]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, J=8.8 Hz, 2H), 6.80 (d, J=8.8 Hz, 2H), 3.78 (s, 3H), 2.38 (t, J=7.2 Hz, 2H), 1.59–1.54 (m, 2H), 1.50–1.44 (m, 2H), 0.94 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.92, 132.80, 116.22, 113.73, 88.69, 80.18, 55.17, 30.93, 21.99, 19.06, 13.62.

4.3.25. 1-(4-Methoxylphenyl)-1-octyne[15]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, J=8.8 Hz, 2H), 6.81 (d, J=8.8 Hz, 2H), 3.79 (s, 3H), 2.38 (t, J=7.6 Hz, 2H), 1.61–1.55 (m, 2H), 1.48–1.43 (m, 2H), 1.33–1.31 (m, 4H), 0.90 (t, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.95, 132.83, 116.28, 113.78, 88.80, 80.20, 55.23, 31.38, 28.84, 28.61, 22.56, 19.41, 14.05.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2011.05.031.

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