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Tandem Pd-Catalyzed Double C−C Bond Formation: Effect of Water

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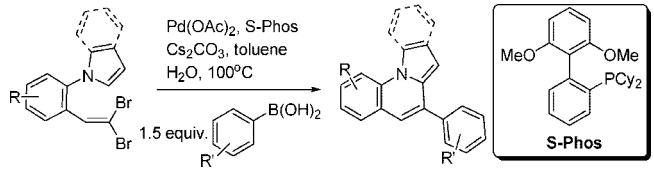

A highly efficient water-accelerated palladium-catalyzed reaction of *gem*-dibromoolefins with a boronic acid via a tandem Suzuki−Miyaura coupling and direct arylation is reported. A wide range of aryl, alkenyl, and alkyl boronic acids, as well as a variety of substitution patterns on the phenyl ring, are tolerated. Additionally, mechanistic studies were conducted to ascertain the order of the couplings as well as the role(s) of water. Results from this study indicate that the major pathway is a Suzuki−Miyaura coupling/direct arylation sequence and that water accelerates the Pd(0) formation and Suzuki−Miyaura coupling.

Introduction

The development of efficient strategies for the C−C bond-forming processes continues to be of major importance in synthetic organic chemistry[1] with many efficient C−C bond forming processes developed in the field of organopalladium-catalyzed reactions.[2] The most reliable class of C−C bond formation is via the use of the Pd-catalyzed coupling reaction of an aryl or vinyl halide with an organometallic reagent.[3] Examples include Suzuki−Miyaura coupling (organoboron),[3a−c] Stille coupling (organostannane),[3d,e] Negishi coupling (organozinc),[3f] or Hiyama coupling (organosilane).[3g] An attractive alternative to this method is the use of direct arylation, which does not require the creation of a reactive functionality prior to the coupling (i.e., metalation).[4] In the last two decades, this area has undergone tremendous growth and new types of direct arylation have been developed.[4]

It has been our aim to develop new tandem processes and now report a Suzuki−Miyaura coupling-direct arylation,[5] using catalytic palladium. To the best of our knowledge, this combination has not yet been explored, despite the fact that these two transformations have thoroughly been studied and expanded in recent times. This combination can increase the efficiency and modularity of the reactions by reducing the number of chemical transformations and chemical waste.

As a part of our research in Pd-catalyzed tandem reactions, we have reported on the utility of *gem*-dihalovinyl systems for syntheses of heterocycles (Scheme 1).[6] This system has important features:[7] (1) the *gem*-dihalovinyl system is more reactive toward Pd complexes compared to the corresponding mono halo-compound, thereby rendering cross-coupling more

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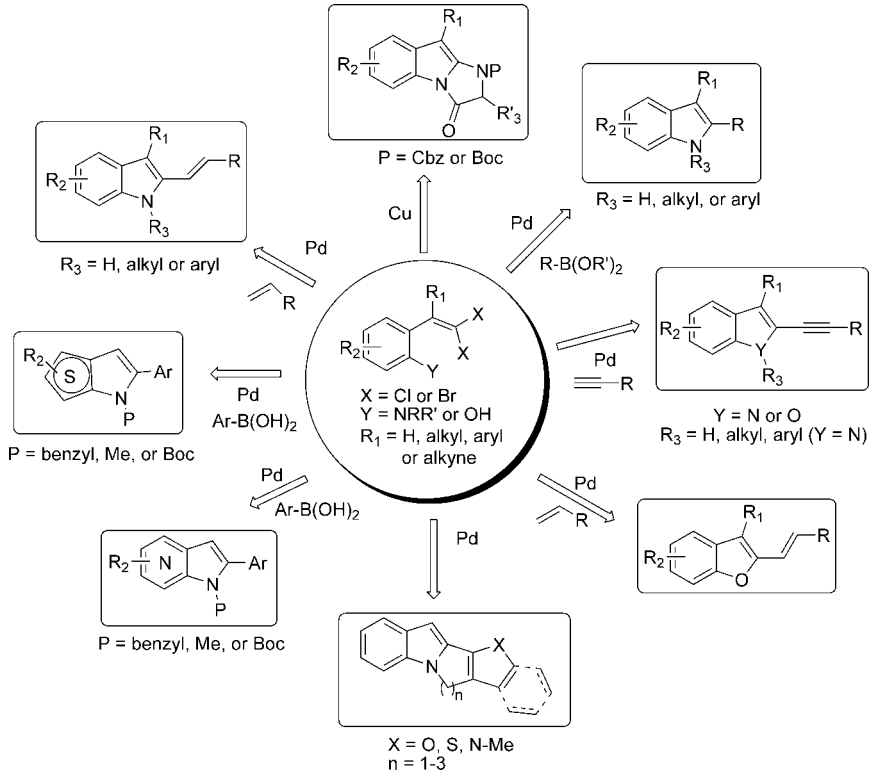
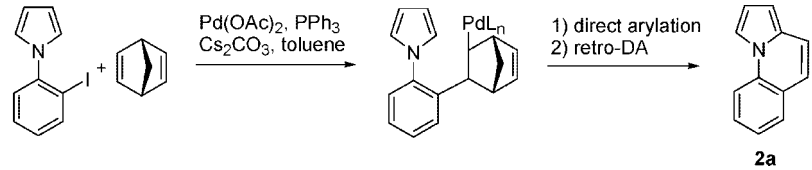
SCHEME 1. Transformations with the Dihalovinyl System



SCHEME 2. Initial Synthesis of Pyrrolo[1,2-*a*]quinoline



SCHEME 3. Our Strategy for the Synthesis of Substitued Pyrrolo[1,2-*a*]quinoline

facile, and (2) the oxidative addition to Pd is usually transselective due to steric effects of substituents in the β-position.

The direct arylation/Suzuki−Miyaura coupling sequence provides an interesting heterocyclic system via consecutive C−C bond formation. We chose the dihalovinyl pyrrole system **1** as a model substrate to synthesize pyrrole[1,2-*a*]quinoline **2b**, since we have shown[8a] that direct arylation on a pyrrole ring is a facile process to construct the pyrrolo[1,2-*a*]quinoline skeleton **2a**[8b−f] (Schemes 2 and 3). This product and its derivatives are known to exhibit biological activities including activation of caspases and inducing apoptosis[9a−d] in addition to electron transport properties.[9e]

Results and Discussion

Optimization of the Tandem Suzuki/Direct Arylation Reaction. Our first attempt to effect the reaction of dibromovinyl

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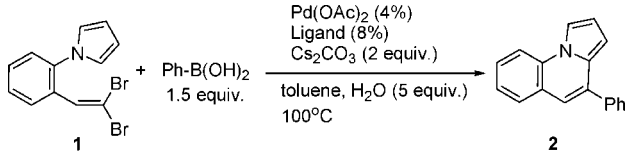
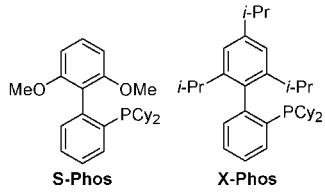
TABLE 1. Ligand Screening for the Tandem Reaction between 1 and $PhB(OH)_2$





entry	ligand	yield (%)[a]
1	PPh_3	55
2	P(*p*-tol)$_3$	65
3	S-Phos	90
4	X-Phos	85
5	dppf	68

[a] Isolated yield.

system **1** with phenyl boronic acid was promising in that the desired product **2** was obtained in 50% yield with $Pd(OAc)_2$ and PPh_3 in toluene at reflux. Among several parameters modified, the combination of $Pd(OAc)_2$, P(*o*-tolyl)$_3$, and Cs_2CO_3 at 100 °C in toluene was more effective. More significant improvement in reaction yields could be achieved by using Buchwald-type biphenyl ligands[10] such as S-Phos, leading to the desired product **2** in 75% yield. S-Phos was somewhat more effective than the hindered X-Phos ligand (Table 1). Furthermore, it was found that bidentate phosphine ligands such as dppf were slightly less reactive. The addition of water had a dramatic effect not only on the reactivity of diboromovinyl system **1**, but also on minimizing the formation of side products. Further improvement in reaction yield was realized by decreasing the reaction concentration. Further optimization showed that the desired product **2** was obtained in 90% yield with phenylboronic acid (1.5 equiv), toluene (0.04 M), $Pd(OAc)_2$ (4 mol %), S-Phos (8 mol %), Cs_2CO_3 (2 equiv), and water (5 equiv).

Scope of the Tandem Reaction. To establish the scope of this reaction, the effects of changing the boronic acid and the substituents at the aromatic ring were tested (Tables 2 and 3). Well-tolerated functional groups at different positions of the boronic acid include methyl, methoxy, Boc-protected amine, trifluoromethyl, fluoro, chloro, and TMS groups, which are useful for postmodifications[11,12] (Table 2, entries 1−19). In particular, the reaction was found to afford good to excellent yield for the desired product for electron-rich and electron-poor boronic acids (Table 2, entries 2−9) though very electron-poor (Table 2, entry 10) or electron-rich boronic acids (Table 2, entry 4) resulted in no reaction or reduced yield under the optimized conditions. In some substances, a significant improvement was realized by using 3 equiv of aryl boronic acid, presumably due to a competitive deboronation or homocoupling of aryl boronic acids (Table 2). In fact, the homocoupled biaryl product was sometimes observed when electron-rich or neutral boronic acids were used.

This methodology could also be extended to alkenyl and alkyl boronic acids affording the desired product in good yield though the addition of water was not necessary (Table 2, entries 13 and 16). The product of the reaction with alkenyl boronic acids was isolated as a single (*E*)-isomer under the optimized conditions. Coupling of sterically hindered boronic acids has historically proven to be a difficult task; however, with the dibromovinyl system **1**, the coupling proceeded in moderate to excellent yields with ortho-substituted boronic acids as hindered as 2-phenylboronic acid (Table 2, entries 12, 17, and 18). Heterocycles such as thiophene were compatible with this reaction (Table 2, entry 11). Usually, systems employing pinacol boranes in Pd-catalyzed reactions result in borylation products from aryl halides.[13] However, the use of **1** provided the reduced product **2v**, presumably via a transmetalation with the borane (Table 2, entry 21).

We could extend this method to include a variety of substituents on the dibromo alkene partner (Table 3). Both electronic and steric variation on the aromatic substituents afforded moderate to excellent yields. Interestingly, a substituent on the vinyl position did not affect the yield (Table 3, entry 2).

Given the success of direct arylation on pyrroles, we wished to extend this methodology to include other heteroaromatic ring systems. We found that the indole derivative **4** gave the desired product **5** in good yield (Scheme 4), while attempts to incorporate other aromatic ring systems such as furans, thiophenes, pyrazoles, and tetrazoles failed. Fortunately, we were pleased to see pyridine derivative **6** reacted under the optimized condition (Scheme 5) since a variety of substituted pyridine derivatives exhibit interesting biological activities.[14]

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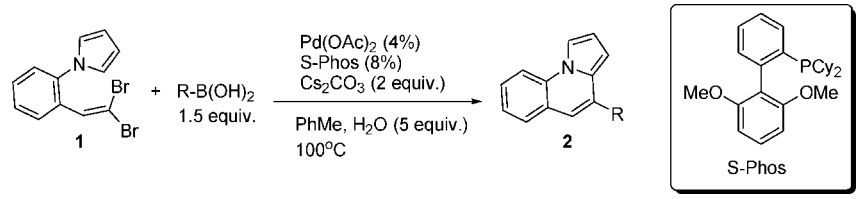
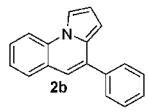
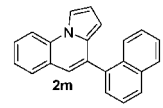
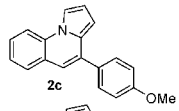
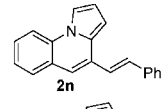
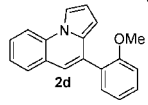
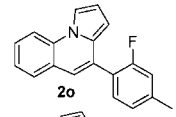
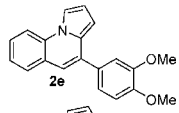
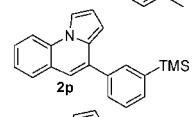
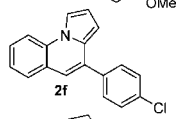
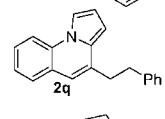
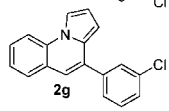
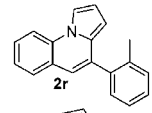
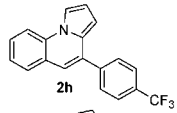
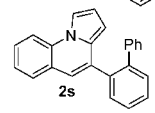
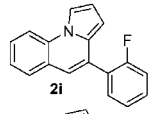
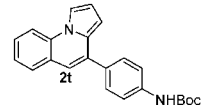
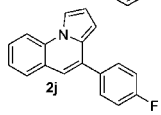
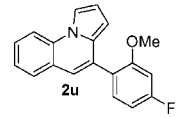
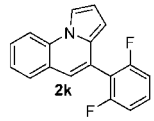
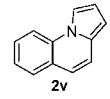
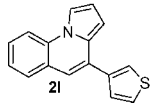
TABLE 2. Reaction Scope with Different Boronic Acids



entry	product	yield (%)[a]	entry	product	yield (%)[a]
1	 **2b**	90	12	 **2m**	64, 76[b]
2	 **2c**	76, 82[b]	13	 **2n**	62[c]
3	 **2d**	75, 95[b]	14	 **2o**	85, 99[b]
4	 **2e**	55, 67[b]	15	 **2p**	74, 89[b]
5	 **2f**	71	16	 **2q**	87[c]
6	 **2g**	62	17	 **2r**	87
7	 **2h**	62, 83[b]	18	 **2s**	45
8	 **2i**	46	19	 **2t**	74, 94[b]
9	 **2j**	86	20	 **2u**	56, 75[b]
10	 **2k**	-	21	 **2v**	73[d]
11	 **2l**	67			

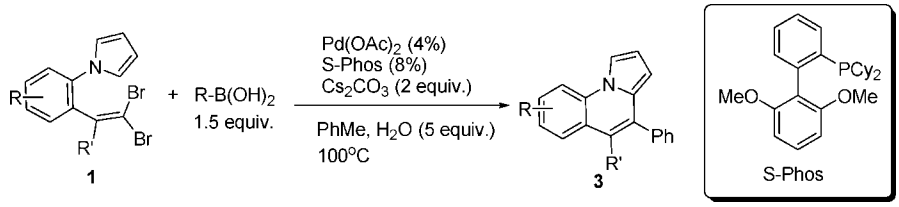
[a] Isolated yield. [b] 3 equiv of boronic acid was used. [c] Without water. [d] Reaction with HB_{pin}.

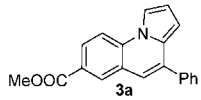
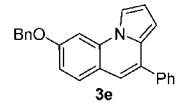
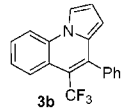
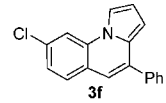
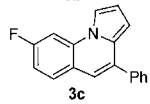
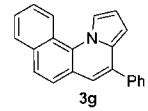
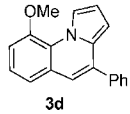
We next examined other organoboron reagents including aryl pinacol borane, alkenyl boronate ester, and trialkyl boron reagents (Table 4). Coupling under the optimized conditions gave the desired products **8** in moderate yields. In particular, the pinacol borane species showed no reactivity in the absence of water, indicating that the boron species involved in the transmetalation step should contain one or more hydroxyl groups, in accord with the observation made by Batey and co-workers in coupling between organotrifluoroborate salts and aryl halides.[15]

We also explored the reactivity of the products to undergo subsequent transformations. For instance, treatment of **2b** with BuLi, followed by quenching with ethyl chloroformate afforded 2-ethyl ester **9** in 60% yield, indicating that the proton next to the pyrrole nitrogen is the most acidic (Scheme 6). This result led us to examine the Pd-catalyzed direct arylation to compare the regioselectivity. Under conditions described by Seregin et

(15) Batey, R. A.; Quach, T. D. *Tetrahedron Lett.* **2001**, *42*, 9099.

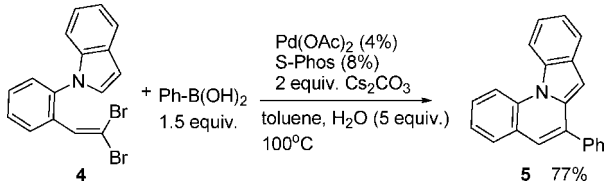
TABLE 3. Reaction Scope of the Tandem Reaction Varying Phenyl Substituents



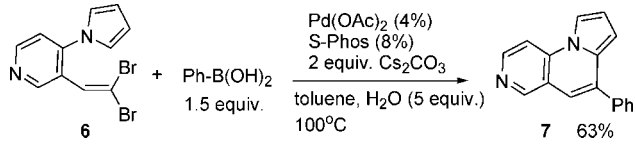
entry	product	yield[a] (%)	entry	product	yield[a] (%)
1	 3a	70	5	 3e	52
2	 3b	85	6	 3f	83
3	 3c	88	7	 3g	72
4	 3d	93			

[a] Isolated yield.

SCHEME 4. Tandem Reaction of the Dibormovinyl Indole System



SCHEME 5. Tandem Reaction of the Dibormovinyl Pyridine System



al.,[16] the pyrroloquinoline **2b** was regioselectively coupled with trimethylsilyl acetyl bromide to give **10** in 67% yield (Scheme 6).

Mechanistic Considerations. Furstner reported the formation of pyrrole[1,2-*a*]quinolines using an alkyne precursor,[17] which suggested products **2b** were formed via an intermediate alkyne (Scheme 7). This process could happen through base-induced elimination[17] or through an initial oxidative addition of Pd into the C−Br bond trans to the aryl group, followed by β-hydride elimination.[18] To test this possibility, alkynes **11a**,**b** were subjected to the reaction conditions with phenyl boronic acid in the presence of palladium. The desired product was not observed and further experiments with deuterated starting material **14** gave **15** with 100% deuterium remaining (Scheme 8).

Eliminating alkynes such as **11** from the reaction pathway indicated that the reaction must proceed via a sequential replacement of the halogens. Accordingly, there are two possible pathways (Scheme 9). The first is one that proceeds with direct arylation, followed by Suzuki−Miyaura coupling. The second pathway reverses the order of events such that Suzuki−Miyaura coupling precedes the direct arylation. Further experiments were performed to elucidate the order of coupling by subjecting possible intermediates to the reaction conditions. Intermediate **12** quantitatively led to production of **2b** (Scheme 10), in accord with path A. However, the formation of intermediate **12** is unfavored due to steric effects that disfavor the oxidative addition to the C−Br bond cis to the aryl group.[7] On the other hand, the direct arylation of **13** in the presence of 0.5 equiv of $PhB(OH)_2$ gave a mixture of the desired product **2b** and bis-Suzuki coupling product **16** (Scheme 11). The double Suzuki coupling product **16** has been observed as a side product when more than 1.5 equiv of boronic acids was used with **1**, suggesting that **13** is a possible intermediate under the reaction conditions (Scheme 9, path B). Unfortunately, intermediate **13** could not be detected during the reaction probably because the second step is too fast.

It was found that the addition of water has a dramatic effect on the reaction rate. A recent report[19] by Buchwald suggested that water could serve as a promoter of Pd(0) formation by removing the phosphonium salt formed during reduction of Pd(II), thus resulting in increased rates of reactions. In our case, performing the reaction in the absence of water resulted in 95% conversion and moderate yields after 6 h (Table 5, entry 1), while water preactivated catalytic reactions (Table 5, entry 2) experienced 100% conversion and somewhat higher yields in

(16) Seregin, I. V.; Ryabova, V.; Gevorgyan, V. *J. Am. Chem. Soc.* **2007**, *129*, 7742.
(17) Mamane, V.; Hannen, P.; Furstner, A. *Chem. Eur. J.* **2004**, *10*, 4556.
(18) Shen, W.; Wang, L. *J. Org. Chem.* **1999**, *64*, 8873.

SCHEME 6. Synthetic Utility of Substrate 2b

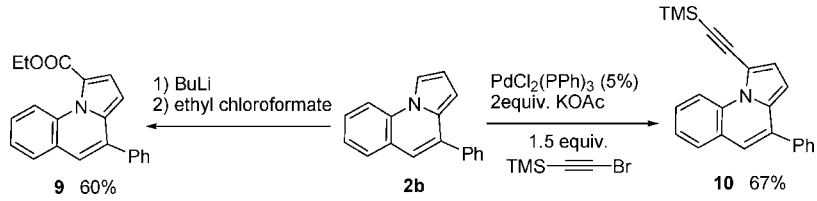
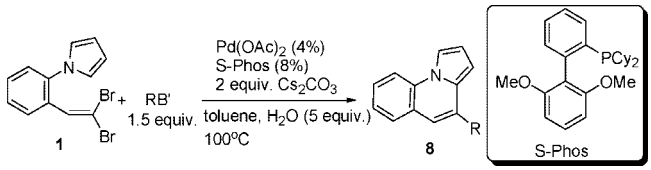
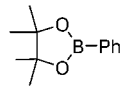
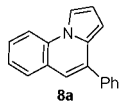
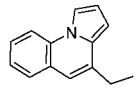
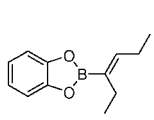
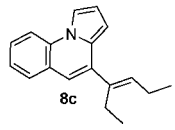


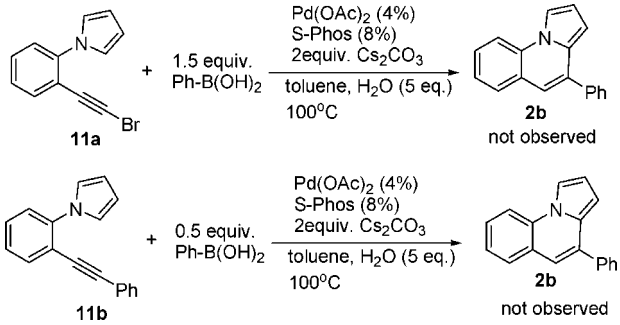
TABLE 4. Reaction Scope of the Tandem Reaction Varying Organoboron Reagents



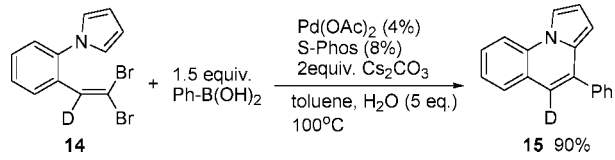
entry	RB'	Product	Yield (%)[a]
1		 8a	0[b]
			61
2		 8b	50
3		 8c	30

[a] Isolated yield. [b] Without water.

SCHEME 7. Possible Alkyne Intermediates Subjected to the Reaction Condition

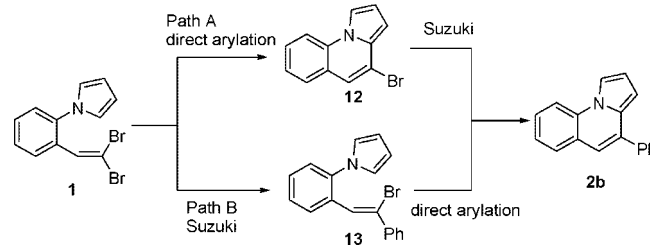


SCHEME 8. Deuterium Labeling Study

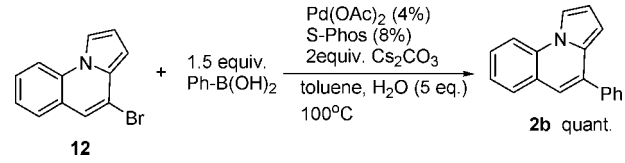


6 h. In addition, the formation of Pd(0) is easily monitored by a color change (yellow to dark green) in this system. Additional study showed that the direct arylation of **13** is not affected by water, suggesting the acceleration of the Suzuki coupling by water. Further studies demonstrated that water not only increased the reactivity (Table 5, entry 1 vs. entry 2), but also reduced the formation of byproduct perhaps via the acceleration of the

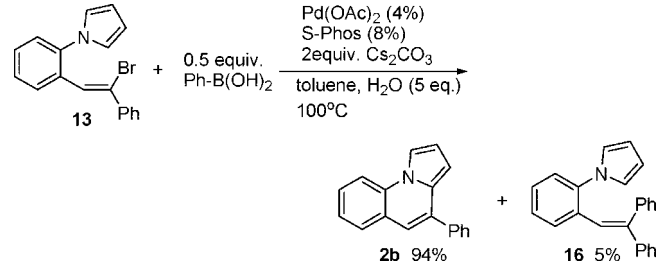
SCHEME 9. Possible Mechanistic Pathways for the Tandem Reaction



SCHEME 10. Possible Reaction Intermediate 12 Subjected to the Reaction Condition



SCHEME 11. Possible Reaction Intermediate 13 Subjected to the Reaction Condition



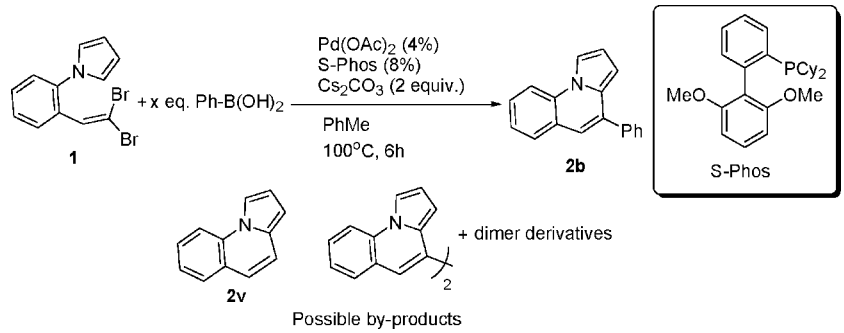
Suzuki coupling (Table 5, entry 2 vs. entry 3). Thus, we believe that water has dual roles: the preactivation of catalyst and the acceleration of the Suzuki coupling.

These results lead us to propose that the dominant process is the Suzuki coupling/direct arylation sequence (Scheme 12, path B) accompanied by a minor process involving the intermediate **12** (Scheme 12, path A). The Pd(II) source is first converted to Pd(0) in the presence of a ligand promoted by water. Pd(0) then undergoes oxidative addition into the *trans*-C−Br bond. The resulting intermediate **17** couples with a boronic acid to give the intermediate **13**, which subsequently undergoes coupling by direct arylation, presumably via an electrophilic substitution mechanism,[20] to give the desired product **2b**.

Conclusions

The synthetic utility of *gem*-dibromovinyl substrates **1** is illustrated by the sequential Suzuki−Miyaura coupling/direct arylation tandem reaction and represents an attractive method for the synthesis of N-fused heterocycles. This methodology is compatible with a variety of aryl, alkenyl, and alkyl boronic acids, as well as boronic esters, providing products that require multiple chemical transformations to match existing

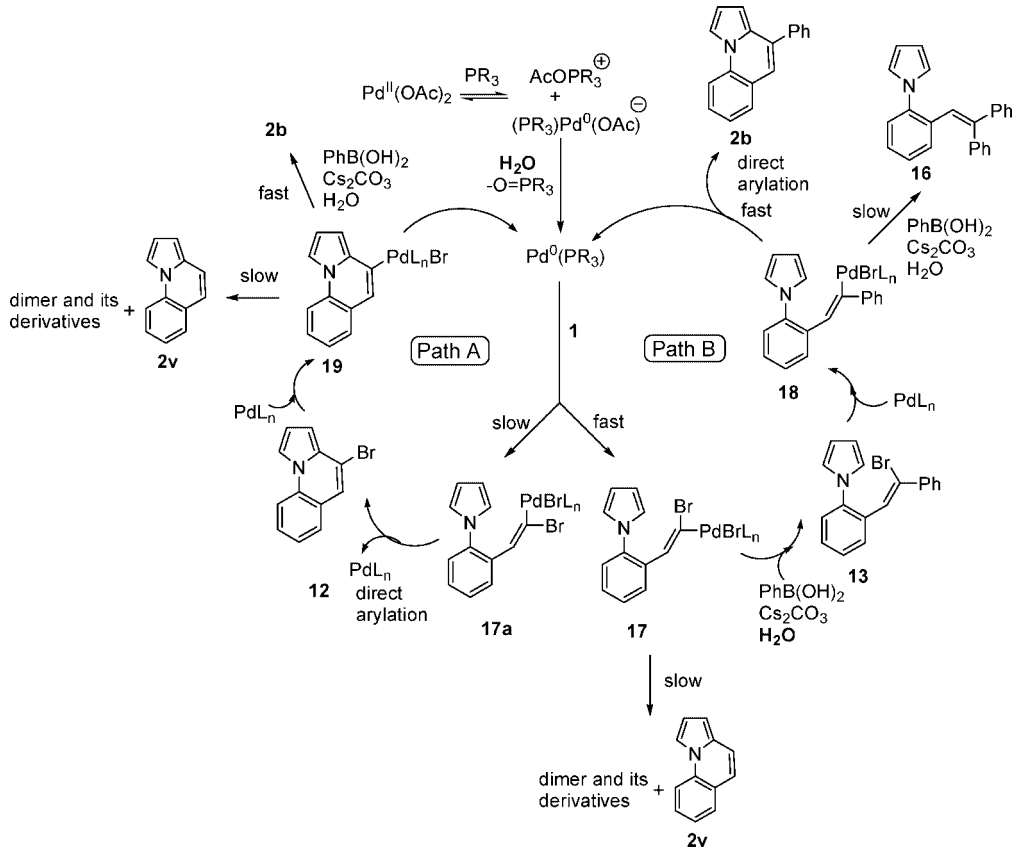
TABLE 5. Effect of Water



entry	water	*x*, equiv	yield (%)[a]
1	no	1.5	70−80[b,c,d]
2	0.1 equiv	1.5	75−82[c,e]
3	5 equiv	1.5	90[f]

[a] NMR yield. [b] 5% **1** remained. [c] Several byproducts found. [d] Slow color change within 3 h. [e] Preactivation of catalyst system by water. [f] Fast color change within 5 min.

SCHEME 12. Proposed Mechanism for the Tandem Reaction



methods. In general, yields for this reaction were good to excellent, allowing it a versatile approach. Mechanistic investigation indicates that Suzuki−Miyaura coupling occurs prior to direct arylation. In particular, water has a dramatic effect on both the reactivity of the substrate and the reduction of the byproduct.

Experimental Section

The following represents experimental procedures toward the synthesis of products **2i**, **3a**, **9**, and **10**, including experimental details and characterization data for the compounds. The information for all other compounds can be found in the Supporting Information.

General Procedure for the Tandem Reaction. In a sealable microwave tube with a PTFE faced silicone septum cap *gem*-dibromoolefin (0.3 mmol, 1.0 equiv), boronic acid (1.5 equiv), Cs_2CO_3 (2 equiv), $Pd(OAc)_2$ (4 mol %), and S-Phos (8 mol %) were added. After the flask was purged with argon for 10 min, toluene (7.5 mL) and water (5 equiv) were successfully added, and the sealed reaction tube (caution: build-up of pressure is possible; use a safety shield) was heated at 100 °C in a preheated oil bath. After 12 h, the mixture was diluted with Et_2O (5 mL) and filtered

through Celite. The crude material was purified by flash chromatography with EtOAc:hexanes system containing 5% Et_3N to afford a corresponding product.

4-(2-Fluorophenyl)pyrrolo[1,2-*a*]quinoline (2i). 2i was synthesized according to the general procedure with 1-[2-(2,2-dibromovinyl)phenyl]-1*H*-pyrrole and 2-fluoromethylphenyl boronic acid (1.5 equiv) by flash column chromatography (pentane:triethyl amine, 95:5) as a green solid (36.1 mg, 46%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (1H, m), 7.89 (1H, d, J = 5.6 Hz), 7.67 (1H, dd, J = 7.6 Hz, J = 1.2 Hz), 7.60 (1H, dt, J = 7.6 Hz, J = 2.0 Hz), 7.52 (1H, dt, J = 7.2 Hz, J = 1.6 Hz), 7.43−7.37 (1H, m), 7.33 (1H, dt, J = 8.4 Hz, J = 1.2 Hz), 7.26−7.19 (2H, m), 7.04 (1H, s), 6.79 (1H, dd, J = 4.0 Hz, J = 3.2 Hz), 6.39 (1H, dt, J = 4.0 Hz, J = 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 159.1, 133.1, 131.5, 131.4, 130.9, 130.0, 129.9, 129.0, 128.2, 126.8, 126.5, 124.3, 124.3, 124.2, 124.0, 123.9, 120.0, 116.9, 116.4, 116.1, 114.3, 113.0, 112.7, 103.4, 103.3; ν_{max}/cm^{-1} ($CHCl_3$) 3142, 3106, 3061, 1718, 1612, 1576, 1539, 1490, 1457, 1448, 1419, 1364, 1341, 1318, 1301, 1259, 1247, 1219, 1164, 1097, 1038, 993, 938, 925, 870, 841, 798, 756, 696; *m*/*z* (EI) calcd for $C_{18}H_{12}FN$ 261.0954, found 261.0961; mp 80−82 °C.

4-Phenylpyrrolo[1,2-*a*]quinoline-7-carboxylic Acid Methyl Ester (3a). 3a was synthesized according to the general procedure with 3-(2,2-dibromovinyl)-4-pyrrol-1-yl-benzoic acid methyl ester and phenyl boronic acid (1.5 equiv) by flash column chromatography (5% ethyl acetate in pentane:triethyl amine, 95:5) as a pale yellow solid (63.3 mg, 70%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (1H, d, J = 1.6 Hz), 8.15 (1H, dd, J = 8.8 Hz, J = 2.0 Hz), 7.95(1H, dd, J = 2.8 Hz, J = 1.2 Hz), 7.90 (1H, d, J = 8.8 Hz), 7.70 (2H, m), 7.50−7.40 (3H, m), 7.03 (1H, s), 6.84 (1H, dd, J = 4.0 Hz, J = 2.8 Hz), 6.65 (1H, dd, J = 3.6 Hz, J = 1.2 Hz), 3.97 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 138.7, 135.6, 133.8, 131.4, 131.1, 128.9, 128.7, 128.5, 125.6, 124.1, 118.1, 114.3, 114.0, 113.5, 104.6, 52.4; ν_{max}/cm^{-1} ($CHCl_3$) 3128.9, 2066.7, 3019.2, 2948.1, 1708.9, 1612.5, 1490.2, 1442.9, 1351.4, 1310.0, 1296.8, 1279.7, 1266.7, 1200.5, 1157.3, 1111.9, 783.6, 764.8, 737.2, 700.3; *m*/*z* (EI) calcd for $C_{20}H_{15}NO_2$ 301.1103, found 301.1107; mp 120−121 °C.

Procedure for the Synthesis of 4-Phenylpyrrolo[1,2-*a*]quinoline-1-carboxylic Acid Ethyl Ester (9). To a solution of 4-Phenylpyrrolo[1,2-*a*]quinoline (**2b**) (1 equiv, 0.3 mmol) in hexane was added BuLi (1.1 equiv, 1.6 M in hexane) dropwise at −78 °C. After 1 h at this temperature, ethyl chloroformate (1 equiv) was added dropwise at −78 °C, then the mixture was warmed to ambient temperature. Next, the reaction was quenched by water and the layers were separated. The aqueous layer was then extracted with ether. The combined organic layers were next dried (MgSO4), filtered, and concentrated in vacuo. The crude product was purified by column chromatography (pentane:triethylamine, 95:5) to yield the desired product **9** as a green solid (56.8 mg, 60%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (1H, d, J = 8.8 Hz), 7.71 (1H, dd, J = 7.6 Hz, J = 1.6 Hz), 7.65−7.62 (2H, m), 7.56−7.38 (6H, m), 7.26 (1H, s), 6.59 (1H, d, J = 4.4 Hz), 4.43 (2H, q, J = 7.2 Hz), 1.44 (3H, t, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 138.5, 138.1, 133.3, 132.2, 128.9, 128.7, 128.5, 127.6, 125.5, 124.9, 124.9, 123.4, 121.0, 120.0, 104.3, 60.9, 14.7; ν_{max}/cm^{-1} ($CHCl_3$) 3103.6, 3057.3, 3032.2, 2980.1, 1699.3, 1608.7, 1537.3, 1537.3, 1489.1, 1456, 1438.9, 1398.4, 1363.7, 1329.0, 1317.4, 1292.4, 1261.5, 1244.1, 1170.8, 1145.8, 1116.8, 1035.8, 977.9, 879.6, 788.9, 756.1, 740.7, 702.1, 669.3; *m*/*z* (EI) calcd for $C_{21}H_{17}NO_2$ 315.1259, found 315.1259; mp 75−77 °C.

Procedure for the Synthesis of 4-Phenyl-1-trimethylsilanylethynyl Pyrrolo[1,2-*a*]quinoline (10). In a 5.0 mL microwave tube equipped with a PTFE faced silicone septum cap were added phenylpyrrolo[1,2-*a*]quinoline (**2b**) (1 equiv, 0.3 mmol), 5 mol % of $PdCl_2(PPh_3)_2$, and 2 equiv of KOAc. Then, bromoalkyne (1.5 equiv) and anhydrous toluene (0.01 M) were successively added and the mixture was stirred for 12 h at 60 °C. The mixture was concentrated under reduced pressure and the residue was purified by flash-column chromatography (pentane:triethylamine, 95:5) to afford pure alkynyl-heterocycles **10** as a yellow solid (68.2 mg, 67%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (1H, d, J = 8.4 Hz), 7.33−7.27 (3H, m), 7.14−7.05 (4H, m), 7.01 (1H, t, J = 8.4 Hz), 6.72 (1H, d, J = 4.4 Hz), 6.70 (1H, s), 6.17 (1H, d, J = 4.4 Hz), 0.00 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 135.1, 133.0, 132.6, 128.8, 128.7, 128.7, 128.3, 126.8, 125.3, 124.4, 122.5, 120.6, 116.5, 111.0, 103.9, 102.0, 100.4, 0.000; ν_{max}/cm^{-1} ($CHCl_3$) 3059.2, 2045.7, 3032.2, 2957.0, 2897.2, 2139.1, 1601.0, 1537.3, 1489.1, 1452.5, 1440.9, 1375.3, 1317.4, 1290.4, 1249.9, 1184.3, 1184.3, 1051.2, 1033.9, 997.2, 902.7, 856.4, 842.9, 779.3, 758.1, 740.7, 700.2, 669.3, 648.1; *m*/*z* (EI) calcd for $C_{23}H_{21}NSi$ 339.1443, found 339.1443; mp 85−86 °C.

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Supporting Information Available: Experimental details and characterization data for all compounds and their precursors. This material is available free of charge via the Internet at http://pubs.acs.org.

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