Supporting Information

**Employing Water as the Hydride Source in Synthesis: A Case Study
of Diboron Mediated Alkyne Hydroarylation**

Santhosh Rao, M. Nibin Joy and Kandikere Ramaiah Prabhu*

Department of Organic Chemistry,
Indian Institute of Science,
Bangalore 560 012,
Karnataka, India

*To whom correspondence should be addressed. E-mail: prabhu@iisc.ac.in

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1. Experimental section

A. Development of the reaction

Table S1. Screening of solvents and temperature

entry	solvent (2 mL)	temp (°C)	NMR yield (isolated yield) (%)		1a (%)
			3aw	4a	
1	Toluene	100	(36)	(51)	NIL
2	DME	100	70	25	NIL
3	THF	100	80	Trace	NIL
4	Dioxane	100	40	25	20
5	DCE	100	45	30	20
6	THF	80	82	Trace	NIL
7	THF	120	77	Trace	NIL

NMR yield was calculated using 0.125 mmol terephthalaldehyde as internal standard.

Table S2. Screening of stoichiometric equivalence of water

entry	H_2O equiv	NMR yield (isolated yield) (%)		1a (%)
		3aw	4a	
1	5	82	Trace	NIL
2	3	82	Trace	NIL
3	2	84	Trace	NIL
4	1	60	15	20

NMR yield was calculated using 0.125 mmol terephthalaldehyde as internal standard

Table S3. Screening of stoichiometric equivalence of Boronic acid and B₂Pin₂

entry	B ₂ pin ₂ (equiv)	2w (equiv)	NMR yield (isolated yield) (%)		1a (%)
			3aw	4a	
1	1.1	1.1	84	Trace	NIL
2	1.1	1.5	84	Trace	NIL
3	1.1	1	83	Trace	NIL
4	1.1	2	84	Trace	NIL
5	1	1	88	Trace	NIL

NMR yield was calculated using 0.125 mmol terephthalaldehyde as internal standard.

Even though the yield of the reaction was found to be 88% at this stage, a trace amount (<5%) of the starting material diphenylacetylene was being over-reduced to the corresponding alkane. Further optimization studies were focused to reduce the over reduction so as to improve the yield of the required hydroarylated product.

Table S4. Screening of time and stoichiometric equivalence of catalyst/ligand

entry	Pd(OAc) ₂	PCy ₃	time (h)	NMR yield (isolated yield) (%)	
				3aw	5a
1	5 mol %	10 mol %	16	88	<5
2	2.5 mol %	5 mol %	16	87	<3
3	2 mol %	4 mol %	16	87	<3
4	1 mol %	2 mol %	16	92	<2
5	1 mol %	2 mol %	8	95	<2
6	1 mol %	2 mol %	4	97 (87)	< 1

NMR yield was calculated using 0.125 mmol terephthalaldehyde as internal standard.

Table S5. Control experiments for understanding the role of B₂Pin₂

entry	B ₂ Pin ₂ (equiv)	NMR yield (Isolated yield) (%)		
		3aw	4a	1a recovered
1	----	(80)	Nil	(11)
2	0.1	(77)	2	(15)
3	0.2	(44)	3	(44)
4	0.5	(64)	4	(27)
5	1	(87)	<5	nil
6	2.1	(82)	<5	nil

NMR yield was calculated using 0.125 mmol terephthalaldehyde as internal standard.

Table S6. Control experiments with different equivalents of B₂Pin₂ with phenylacetylene and phenylboronic acid

We also performed a similar set of reactions with a completely different set of substrates i.e. using phenylacetylene and phenylboronic acid. A similar trend was observed (see Table 1, manuscript) even in this case and results are presented below:

B ₂ pin ₂ (equiv)	3ca (NMR yield)
0	61%
0.1	61%
0.2	64%
0.5	52%
0.9	57%
1	75%

Controls to understand the role of water in the system

Arylboronic acids do comprise water. Hence, a control excluding water also resulted in the product formation, wherein the hydrogen was derived from the boronic acid functionality. Hence, even arylboronic acid can act as water donor in the system. Employing pinacolato group containing boron functionality did not result in the product formation. However, when 2 equiv of water was included in the system, 66% of the product was observed.

B. General Experimental procedure**Synthetic method example**

To a pre-dried 10 mL screw cap equipped reaction vial, water (1 mmol, 18 mg), diphenylacetylene (**1a**, 0.5 mmol, 89.1 mg), B_2Pin_2 (0.5 mmol, 127 mg), 4-acetylphenylboronic acid (**2w**, 0.5 mmol, 82 mg), PCy_3 (2 mol %, 2.8 mg) and $\text{Pd}(\text{OAc})_2$ (1 mol %, 1.1 mg) were added, dissolved in dry THF (2 mL) and the reaction mixture was heated in a pre-heated metal block for 4h with continuous stirring. After the completion of the reaction, the reaction mixture

was filtered using a short column using diethyl ether. The filtrate was distilled under reduced pressure and the crude mixture was dissolved in sufficient amount of CDCl_3 . To this, 0.125 mmol terephthalaldehyde as internal standard was added, dissolved and submitted for NMR analysis. The crude mixture was then purified by column chromatography to afford the title compound in 87% isolated yield.

C. Preliminary Mechanistic Studies

Determining the intermediate

A) Two-step process

An oven dried, screw cap equipped reaction vial with a magnetic stir bar was charged with diphenylacetylene (0.5 mmol, 89.1 mg), B_2pin_2 (0.5 mmol, 1 equiv, 127.0 mg), PPh_3 (10 mol %, 13.1 mg), H_2O (2.5 mmol, 5 equiv, 45.0 mg) and $\text{Pd}(\text{OAc})_2$ (5 mol %, 5.6 mg). The reaction mixture was then dissolved in toluene solvent (1.5 mL) and stirred at rt for 14 h. Crude mixture was then filtered through a short column with 230-400 mesh silica bed using Et_2O , concentrated and transferred to another oven dried, screw cap equipped reaction vial containing a magnetic stir bar. To this H_2O (1 mmol, 2 equiv, 18 mg), 4-acetylphenylboronic acid (**2w**, 0.5 mmol, 1 equiv, 82 mg), PCy_3 (2 mol %, 2.8 mg), and $\text{Pd}(\text{OAc})_2$ (1 mol %, 1.1 mg) were added. The reaction mixture was then dissolved in dry THF solvent (2 mL) and stirred at 80 °C for 4h. Crude mixture was then filtered through a short column with 230-400 mesh silica bed using Et_2O , concentrated and analyzed.

B) Probing the Possible Hydroborylated Intermediate

To a pre-dried 10 mL screw cap equipped reaction vial, water (1 mmol, 18 mg), **4a** (0.5 mmol, 153.1 mg), 4-acetylphenylboronic acid (**2w**, 0.5 mmol, 82 mg), PCy_3 (2 mol %, 2.8 mg) and

$\text{Pd}(\text{OAc})_2$ (1 mol %, 1.1 mg) were added, dissolved in dry THF (2 mL) and the reaction mixture was heated in a pre-heated metal block for 4h with continuous stirring. After the completion of the reaction, the reaction mixture was filtered using a short column using diethyl ether. The filtrate was distilled under reduced pressure and the crude mixture was dissolved in sufficient amount of CDCl_3 . To this, 0.125 mmol terephthalaldehyde as internal standard was added, dissolved and submitted for NMR analysis.

Determining the active catalyst³

A) Using catalytic amount of $\text{Pd}(\text{PCy}_3)_2$

To a pre-dried 10 mL screw cap equipped reaction vial, water (1 mmol, 18 mg), diphenylacetylene (**1a**, 0.5 mmol, 89.1 mg), B_2Pin_2 (0.5 mmol, 127 mg), 4-acetylphenylboronic acid (**2w**, 0.5 mmol, 82 mg) and $\text{Pd}(\text{PCy}_3)_2$ (1 mol %, 3.3 mg) were added, dissolved in dry THF (2 mL) and the reaction mixture was heated in a pre-heated metal block for 4h with continuous stirring. After the completion of the reaction, the reaction mixture was filtered using a short column using diethyl ether. The filtrate was distilled under reduced pressure and the crude mixture was dissolved in sufficient amount of CDCl_3 . To this, 0.125 mmol terephthalaldehyde as internal standard was added, dissolved and submitted for NMR analysis. The crude mixture was then purified by column chromatography to afford the compound **3aw** in 42% isolated yield.

B) Using a catalytic amount of $\text{Pd}(\text{PCy}_3)_2$ and AcOH

To a pre-dried 10 mL screw cap equipped reaction vial, acetic acid (20 mol %, 6 mg), water (1 mmol, 18 mg), diphenylacetylene (**1a**, 0.5 mmol, 89.1 mg), B_2Pin_2 (0.5 mmol, 127 mg), 4-acetylphenylboronic acid (**2w**, 0.5 mmol, 82 mg) and $\text{Pd}(\text{PCy}_3)_2$ (1 mol %, 3.3 mg) were added, dissolved in dry THF (2 mL) and the reaction mixture was heated in a pre-heated metal block for

4h with continuous stirring. After the completion of the reaction, the reaction mixture was filtered using a short column using diethyl ether. The filtrate was distilled under reduced pressure and the crude mixture was dissolved in sufficient amount of CDCl_3 . To this, 0.125 mmol terephthalaldehyde as internal standard was added, dissolved and submitted for NMR analysis. The crude mixture was then purified by column chromatography to afford the compound **3aw** in 62% isolated yield.

The same procedure was followed for the following control wherein 2 mol % of AcOH was used instead of 20 mol %.

Note: 2 mol % AcOH was added by preparing a stock solution of 6 mg of AcOH in 3 mL of THF (0.6 mg in 0.5 mL of THF).

An additional control was performed using the same procedure wherein 2 mol % of AcOH was used but with B_2pin_2 omitted from the reaction.

C) Probing Palladium's C-B Oxidative Addition Capability

To a pre-dried 10 mL screw cap equipped reaction vial, water (1 mmol, 18 mg), B_2Pin_2 (0.5 mmol, 127 mg), 4-acetylphenylboronic acid (**2w**, 0.5 mmol, 82 mg), PCy_3 (2 mol %, 2.8 mg) and $\text{Pd}(\text{OAc})_2$ (1 mol %, 1.1 mg) were added, dissolved in dry THF (2 mL) and the reaction mixture was heated in a pre-heated metal block for 4h with continuous stirring. After the completion of the reaction, the reaction mixture was filtered using a short column using diethyl ether. The

filtrate was distilled under reduced pressure and the crude mixture was dissolved in sufficient amount of CDCl_3 . To this, 0.125 mmol terephthalaldehyde as internal standard was added, dissolved and submitted for NMR analysis.

2. References

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3. NMR spectral data