

## PAPER

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## A swift and efficient approach to boron-functionalized scaffolds: borylation of alkenes and alkynes using a carbon nanotube–copper ferrite catalyst†

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Boron-based molecules are ubiquitous in chemistry, where they are often used as synthetic intermediates and reagents, but also in biomedical applications.<sup>1</sup> Herbert C. Brown's research on boranes and borohydrides in the 1940s and 1950s<sup>2</sup> has sparked renewed interest in organoboron compounds, which boomed with the discovery of the Suzuki–Miyaura coupling reaction in 1979.<sup>3</sup> The latter transformation prompted research groups not only to further develop palladium-based coupling chemistry,<sup>4</sup> but also to explore better ways of accessing boronic acids and boronic esters.<sup>5</sup> On the other hand, compounds containing a C(sp<sup>2</sup>)-B bond are important motifs in medicinal chemistry, as they are versatile building blocks in drug discovery.<sup>6</sup> Accordingly, the pharmaceutical industry is actively searching for robust methodologies applied to the synthesis of C(sp<sup>2</sup>)-B substrates, prioritizing economic viability and sustainability.<sup>7</sup>

Over the last decade, some of us have been working on the design of carbon nanotube (CNT)-based nanohybrid catalysts to activate chemical processes in a robust and sustainable way.<sup>8</sup> CNTs were decorated with various transition metal nanoparticles,

We introduce herein a carbon nanotube–CuFe<sub>2</sub>O<sub>4</sub>-catalyzed borylation reaction of alkenes and alkynes as a practical and sustainable approach. Our system operates with low catalytic loading (0.05 mol%), under air, and the heterogeneous catalyst can be recycled *via* simple centrifugation. The methodology is of broad scope with a variety of substituted alkenes and alkynes.

such as ruthenium,<sup>9</sup> gold,<sup>10</sup> platinum,<sup>11</sup> or rhodium.<sup>12</sup> More recently, we showed that CNTs bearing bimetallic rhodium/ruthenium nanoparticles have unique characteristics in promoting reactions such as hydrophosphinylations,<sup>13</sup> hydrothiolations,<sup>14</sup> and also hydroborations<sup>15</sup> in excellent yields, with low catalyst loading (Scheme 1a). However, the above hydroboration reaction involved air- and moisture-sensitive pinacolborane, which necessitated an experimental set-up under inert atmosphere. Similarly, the use of noble metals (Ru and Rh) as catalytic materials was not fully satisfactory. With these features in mind, we hypothesized that the use cheaper and more accessible metals (*e.g.* copper)<sup>16</sup> on CNTs, combined with bench-stable boron sources (*e.g.* bis(pinacolato)diboron – B<sub>2</sub>pin<sub>2</sub>), could

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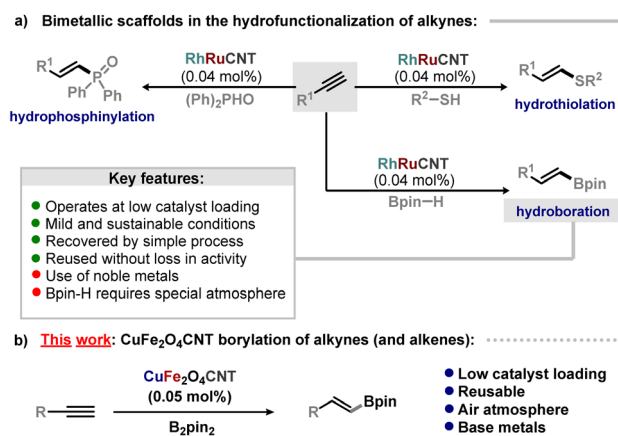
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**Scheme 1** Overview of previous works (a) and current approach for the borylation reaction (b).

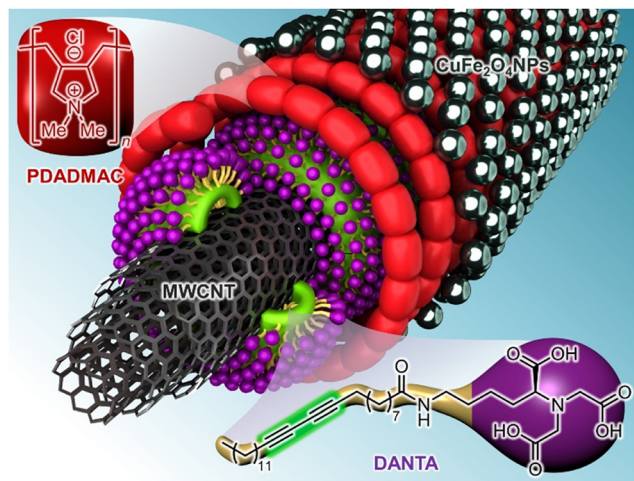


Fig. 1 Illustration of the CuFe<sub>2</sub>O<sub>4</sub>CNT nanohybrid with chemical structures of DANTA and PDADMAC.

provide a more sustainable route to borylated molecules (Scheme 1b).

The copper-based catalyst was assembled using our previously reported procedure.<sup>17</sup> Briefly, the grafting of copper ferrite (CuFe<sub>2</sub>O<sub>4</sub>) nanoparticles at the surface of carbon nanotubes involved a layer-by-layer approach in four steps: i) anionic DANTA amphiphiles were first adsorbed onto multiwalled carbon nanotubes (MWCNTs), forming a primary layer; ii) the diacetylene motifs within the amphiphile's lipophilic chains were photopolymerized to reinforce the supramolecular architecture; iii) a secondary cationic polymer (PDADMAC) layer was deposited; and finally iv) pre-synthesized CuFe<sub>2</sub>O<sub>4</sub> nanoparticles were added to provide access to the CuFe<sub>2</sub>O<sub>4</sub>CNT nanohybrid (Fig. 1). The polyammonium network in this structure created a 3D framework that secured and stabilized the nanoparticles. The heterogeneous CuFe<sub>2</sub>O<sub>4</sub>CNT catalyst was recovered as an aqueous suspension, and copper concentration was quantified using inductively coupled plasma mass spectrometry (ICP-MS, [Cu] = 1.2 mM).

With the nanotube-based catalyst in hands, we set a model reaction involving phenylacetylene (**1a**) as the alkyne

partner, B<sub>2</sub>pin<sub>2</sub> as the boron source, CuFe<sub>2</sub>O<sub>4</sub>CNT (0.05 mol% loading) as the catalyst, Cs<sub>2</sub>CO<sub>3</sub> as the base, and MeOH as the solvent (see ESI† for the solvent exchange procedure). Satisfactorily, after 20 h at 50 °C, the target compound **2a** was obtained in 61% yield (Table 1, entry 1). Yet, better yields could be obtained by changing the base for a stronger one such as NaOMe (72%, entry 2), KO<sup>t</sup>Bu (72%, entry 3), or NaO<sup>t</sup>Bu (80%, entry 4) that provided the best results. Working at room temperature with NaO<sup>t</sup>Bu led to a decrease in the recovered yield of **2a** (36%, entry 5), and increasing temperature to 70 °C (entry 6) did not improve the yield significantly (81%). Changing the solvent for EtOH (entry 7, traces) or THF (entry 8, 20% yield) had a detrimental effect on the overall conversion. The 0.05 mol% loading represents a good compromise between sustainability and efficacy. We also tested lower loadings and found that similar conversions could be obtained with values as low as 0.01 mol%, but with a much longer reaction time (72 h vs. 24 h).

The optimized reaction conditions were then applied to different alkene and alkyne substrates to investigate the scope of the transformation (Scheme 2). Variations in the aromatic ring of alkyne **1a** by insertion of electron-donating or withdrawing groups resulted in variable reaction yields. A methoxy group in *para* position of the aromatic ring led to a small decrease in yield (**2b**, 74% yield). The same comment applies to methoxy in the *ortho* position (**2c**, 50% yield). Replacing the *para* methoxy with less donating methyl group resulted in a slight decrease in yield (66% for **2d**). A more substantial drop was observed with bromine at the *para* position (33% yield for **2e**) and fluorine at the *para* (**2f**, 56% yield) or *meta* position (**2g**, 61% yield). While the presence of other *para* electron-withdrawing groups like –CF<sub>3</sub> and phenyl only slightly lowered the yield (67% yield for **2h** and 66% yield for **2i**), the reaction was severely hampered by the two –CF<sub>3</sub> groups of **1j**, yielding only trace amounts of **2j**.

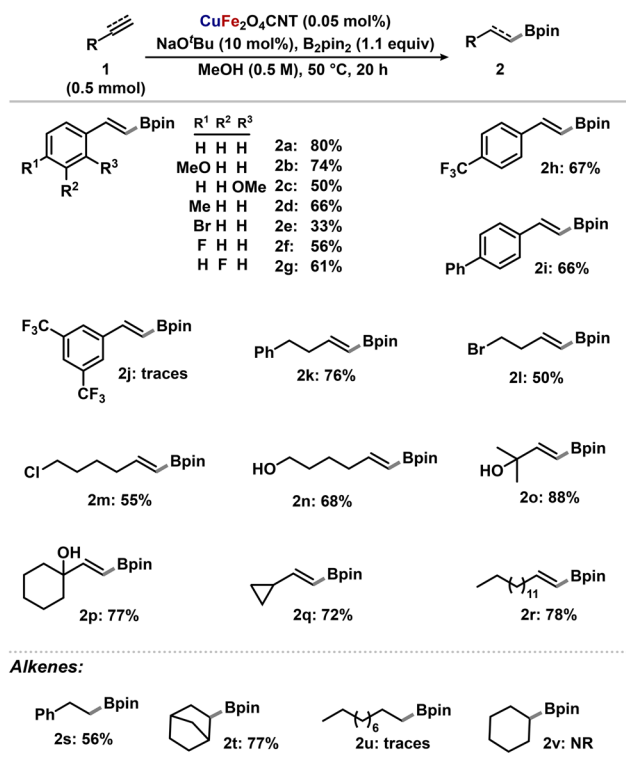
The reactivity of alkyl-substituted alkynes was next studied. We observed that the CuFe<sub>2</sub>O<sub>4</sub>CNT borylation reaction was compatible with a wide variety of functional groups borne by the alkyl chain, including phenyl (**2k**, 76% yield), halogens such as bromine (**2l**, 50% yield) or chlorine **2m** (55% yield), primary

Table 1 Optimization of the reaction conditions

Entry	Solvent	Base (mol%)	T (°C)	Yield <sup>a</sup> %
1	MeOH	Cs <sub>2</sub> Cl <sub>3</sub> (10)	50	61
2	MeOH	NaOMe (10)	50	72
3	MeOH	KO <sup>t</sup> Bu (10)	50	72
4	MeOH	NaO <sup>t</sup> Bu (10)	50	80
5	MeOH	NaO <sup>t</sup> Bu (10)	r.t.	36
6	MeOH	NaO <sup>t</sup> Bu (10)	70	81
7	EtOH	NaO <sup>t</sup> Bu (10)	50	Trace
8	THF	NaO <sup>t</sup> Bu (10)	50	20

General reaction conditions: solvent (1 mL); **1a** (0.5 mmol); B<sub>2</sub>pin<sub>2</sub> (1.1 equiv). <sup>a</sup> Isolated yields; r.t. = room temperature.



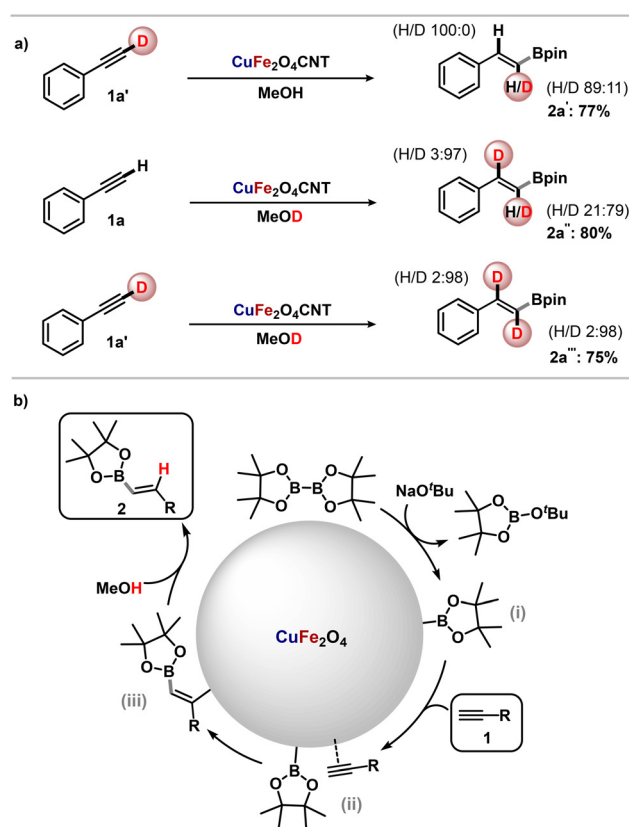


Scheme 2 Scope of the CuFe<sub>2</sub>O<sub>4</sub>CNT-catalyzed borylation reaction of alkenes and alkynes. NR: no reaction.

hydroxyl group (**2n**, 68% yield) and tertiary OH (**2o**, 88% yield). Interestingly, in the latter case the reaction was not affected by the bulkiness of the nearby tertiary alcohol. The same comment applies to cyclic alcohol **2p** (77% yield). The reaction also proceeded smoothly with cyclopropyl alkynes (**2q**, 72% yield) and unsubstituted aliphatic alkynes (**2r**, 78% yield). In all the above examples, the borylation reaction is taking place in an anti-Markovnikov fashion, leading exclusively to the C-terminal-borylated product and with *trans*-configuration. Although active on terminal alkynes, our system failed to promote the borylation of internal alkynes (e.g. diphenylacetylene).

As the borylation reaction was effective on alkynes, we next attempted performing the same transformation on alkenes. Borylations proceeded in average to good yields for styrene and norbornene, with derivatives **2s** and **2t** obtained in 56% and 77% yield, respectively. However, for linear 1-decene **1u**, only traces of the product **2u** were detected, and the reaction with cyclohexene **1v** did not proceed at all. It appears that only activated alkenes, i.e. those with aromatic conjugation or internal strain, are suitable for the CuFe<sub>2</sub>O<sub>4</sub>CNT-catalyzed borylation.

To better apprehend the reaction mechanism, experiments involving isotopic labelling with deuterium were carried out (Scheme 3a). The use of deuterated phenylacetylene **1a'** resulted in the formation of the deuterated product **2a'** in 77% yield, with however some loss of deuterium at the  $\alpha$  position to boron. In fact, while the starting phenylacetylene **1a'** was fully deuterated (ca. 96%), isotopic enrichment of **2a'**

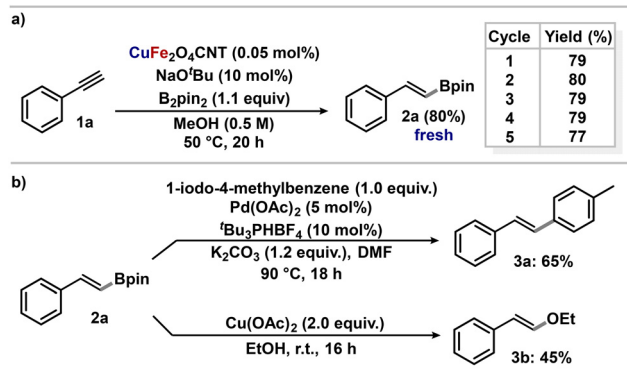


Scheme 3 a) Isotopic labelling experiments, and b) proposed mechanism.

was only 11%. This suggests some rapid H-D exchange between deuterated phenylacetylene and the methanolic solvent, under our reaction conditions. This was confirmed by conducting the reaction with authentic phenylacetylene **1a** but in deuterated methanol. In this case we detected the incorporation of deuterium not only at the expected benzylic position (ca. 97% isotopic enrichment), but also  $\alpha$  to boron (ca. 79% isotopic enrichment), suggesting H-D exchange on phenylacetylene and leading to compound **2a''** in 80% yield. Incorporation of deuterium at the benzylic position suggests the occurrence of a vinyl-metal intermediate that is protonated by the solvent in the last step. Finally, the reaction of deuterated phenylacetylene **1a'** as the alkyne source in MeOD led to the formation of doubly labelled **2a'''** in 75% yield and with high isotopic enrichment (ca. 98%) at the two positions. Of note, in the above transformations we did not observe any kinetic isotope effect, suggesting the rate-determining step does not involve the dissociation of either X-H(D) bond.

Based on previous works<sup>18</sup> and our deuterium labelling experiments, a possible reaction mechanism is proposed in Scheme 3b. The initial reaction between B<sub>2</sub>pin<sub>2</sub> and sodium *tert*-butoxide generates BpinO<sup>t</sup>Bu and intermediate (i) by addition of the other Bpin to the catalyst. This step is followed by coordination of the alkyne at the surface of the catalyst, where interactions with Bpin takes place (ii).





**Scheme 4** a) Recycling experiments, and b) synthetic applications of the  $\text{CuFe}_2\text{O}_4\text{CNT}$  catalyst.

Migratory insertion of the alkyne into the catalyst-Bpin bond generates intermediate (iii) whose protonation by methanol releases the desired borylated product. The catalytically active species in this  $\text{CuFe}_2\text{O}_4\text{CNT}$ -mediated transformation is likely copper, with the contribution of iron acting as a mild coordinating unit that activates the alkyne (or the alkene) in a synergistic fashion.<sup>19</sup>

The use of carbon nanotubes as platforms for the anchoring of metal nanoparticles permitted heterogenization of copper-ferrite and its recycling. To demonstrate recyclability of  $\text{CuFe}_2\text{O}_4\text{CNT}$ , the reaction with **1a** was repeated 6 times using a simple recycling protocol consisting in a mild centrifugation. The solvent phase containing the product was collected and the catalyst could be reused by adding fresh solvent and reagents. Of note, the Cu content of the solvent phase was measured by ICP-MS and was found to be below quantification thresholds, confirming that no significant leaching occurred during the catalytic cycle. In each successive reaction, borylated compound **2a** was obtained with nearly the same yield and within the same reaction time (Scheme 4a). Synthetic applicability of vinyl boronate ester **2a** was illustrated by performing a Suzuki reaction<sup>20</sup> leading to compound **3a** in 65% yield, and conversion into vinyl-ether **3b** in 45% yield in the presence of copper acetate in ethanol<sup>21</sup> (Scheme 4b).

## Conclusions

We report a heterogeneous carbon nanotube-copper ferrite-catalyzed borylation of alkynes and alkenes, achieving good yields and excellent recyclability, as the heterogeneous catalyst maintains its efficiency even after six cycles. This approach offers a practical, economical and sustainable method for synthesizing boron-based building blocks. The system presents significant advantages over existing techniques (see Table S1†), including low catalytic loadings, use of cheap base metals that are acting in a synergistic fashion to activate the alkyne partner (Fe) and promote the coupling reaction (Cu), use of an air- and moisture-tolerant boron source, and recovery/reuse of the  $\text{CuFe}_2\text{O}_4\text{CNT}$ -catalyst.

## Data availability

The authors confirm that the data supporting the findings of this study are available within the manuscript and its ESI.†

## Author contributions

Investigation, methodology and validation: M. P. N., L. A. M., J. A. T. K., V. G. and Y. Y.; writing – original draft: G. A. M. J. and E. N. S. J.; data curation, visualization, conceptualization, funding acquisition, project administration, writing – reviewing and editing: H. D. R. C., G. A. M. J., E. D., E. N. S. J. and E. G.; all authors revised and agreed with the present form of the paper.

## Conflicts of interest

The authors declare no conflict of interest.

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