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A calix[4]arene based boronic acid catalyst for amide bond formation: proof of principle study

Asslly Tafara Mafaune and Gareth E. Arnott*

Department of Chemistry and Polymer Science, Stellenbosch University, Private Bag X1, Matieland, South Africa
Email: arnott@sun.ac.za

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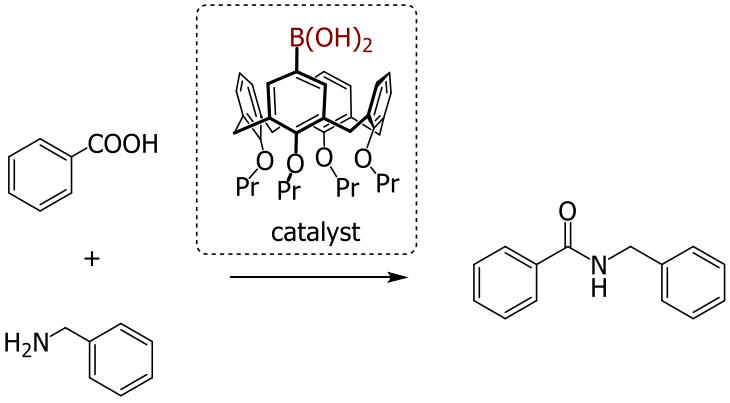
Abstract

A calix[4]arene boronic acid was synthesized and tested for catalysis in amide formation. The results were positive and paved the way for future designs, even though protodeboronation was observed under the conditions employed.

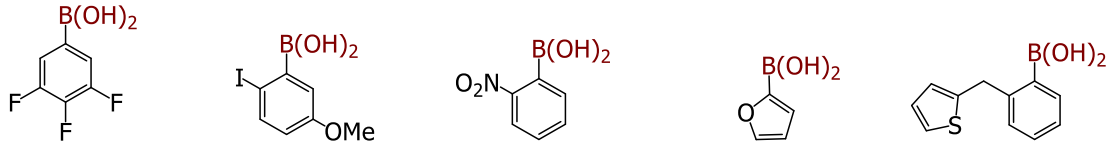


Keywords: Amide bond catalysis, calix[4]arene boronic acid, protodeboronation

Introduction

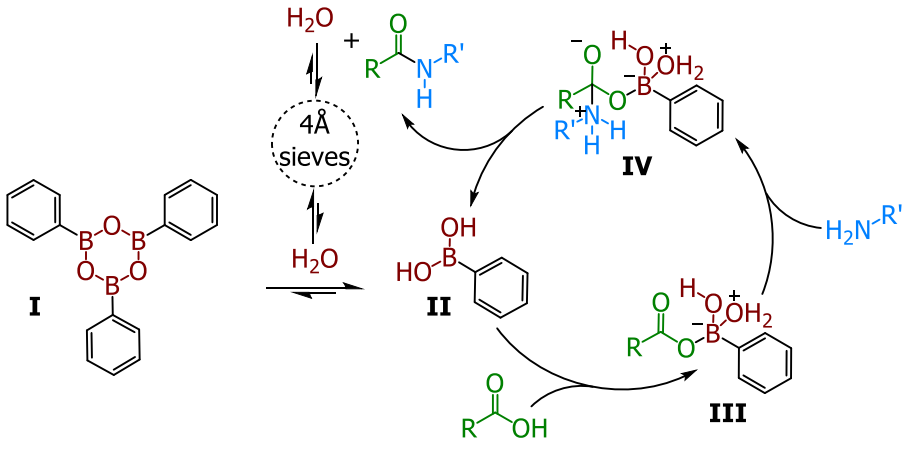
The importance of amide bonds to human kind cannot be overemphasized; they are ubiquitous in nature and indispensable in chemical applications. They can be found in compounds such as the polymers that make our lives easier; the insecticides and agrochemicals that ensure that we have food on our tables; and most notably in the pharmaceutical drugs that help us live longer. Amide bonds are also part of the building blocks of biological systems, linking together amino acid units forming peptides, proteins and enzymes. The amide is arguably the most important functional group in chemistry and it also happens to be the most frequently synthesized in medicinal chemistry.[1] Because of the versatility and importance of the amide bond, catalytic direct amide formation has been highlighted as a top priority reaction from a green chemistry viewpoint. This has led to its identification as one of the critical research areas by the *ACS Green Chemistry Institute Roundtable*.[2] There has therefore been an explosion of methods that explore amide bond formation, with particular emphasis on catalytic variants which have been recently reviewed by many groups.[3–8]

Within the area of catalytic amide bond formation, arylboronic acids have emerged as organocatalysts that exhibit promising results. These were first highlighted by Yamamoto over 20 years ago, but have been more recently studied and updated by groups led by Whiting,[9–15] Hall,[16–18] Tam[19] and Blanchet[20,21] amongst others (Figure 1). The mechanism of the reaction has been investigated[22] (Scheme 1) and involves the fast formation of an acylboronate (**III**) species followed by reaction of the amine to give the tetrahedral intermediate (**IV**). The collapse of this intermediate has been found to be the rate determining step in this reaction, which is aided by Lewis basic groups near the boronic acid. The role of the 4Å molecular sieves is also crucial, as they are not only needed to remove the water formed but have also been implicated in the hydrolysis of the boroxine (**I**) intermediate which is catalytically inactive.[16]



Yamamoto (1996) | Hall (2012) | Liu & Whiting (2013) | Tam (2015) | Blanchet (2015)

Figure 1. Selected examples of arylboronic acids reported in the literature.

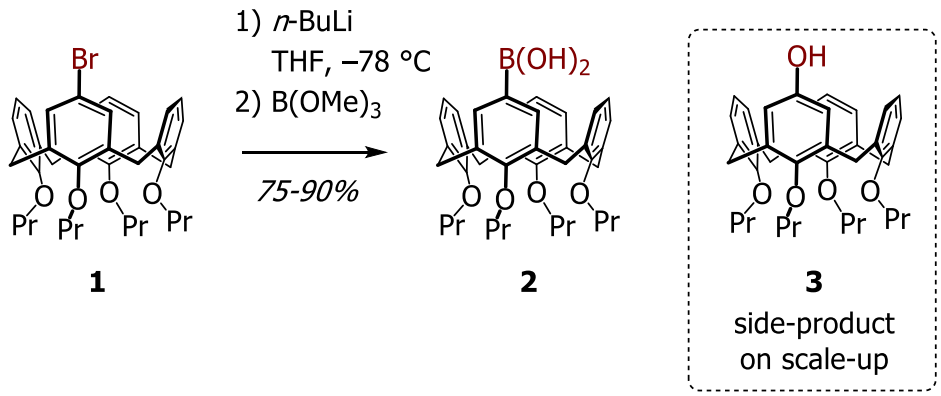


Scheme 1. Simplified catalytic cycle for arylboronic acid mediated amide bond formation.

Our group's interest in calix[4]arenes,[23] led us to the question of whether this would be an interesting scaffold to investigate in the context of boronic acid catalysis. Our reasoning was that the calix[4]arene can be easily modified and decorated with complementary functional groups, that may be designed to mimic an enzyme catalytic center. For example, non-covalent interactions, such as hydrogen bonding might draw the substrates to the active site for efficient catalysis, the same way the so-called enzymatic catalytic triad in some proteases works.[24] In order to lay the ground work for this idea, we embarked on a simple model study of a monofunctionalized calix[4]arene boronic acid (**2** in Scheme 2) to establish how the boronic acid fared in isolation. There was however one significant potential design flaw in this compound, namely the unavoidable propoxy group *para* to the boronic acid functional group. This was because electron-donating substituents have been shown to promote protodeboronation[25] (loss of boron) which results in the catalyst being destroyed *in situ*. Nevertheless, we have observed that the electron donating effect of the propoxy groups in tetra-propoxy-calix[4]arenes is not as pronounced as it is in planar aromatic systems, since the propoxy conformations limit the overlap of the lone pair orbitals with those of the calix[4]arene.[26] We therefore decided to conduct a simple study on calix[4]arene boronic acid **2** as a model for future functionalized derivatives. Herein we report our results.

Results and Discussion

Catalyst Synthesis



Scheme 2. Synthesis of calix[4]arene boronic acid and side-product obtained on scale-up.

The synthesis of the desired calix[4]arene boronic acid was relatively simple, and has been mentioned in the literature.[27] Starting from monobromocalix[4]arene **1**, which was also readily obtained via literature procedures,[28] we performed a lithium-halogen exchange followed by quenching with trimethyl borate to give calix[4]arene boronic acid **2** (Scheme 2). Whilst the calix[4]arene boronic acid **2** has been mentioned in the literature, it has not been isolated, but rather used as a crude mixture in a subsequent Suzuki coupling.[27] Unsurprisingly we therefore had some difficulty in isolating the product in reasonable yields, since large amounts of the protonated by-product formed and complicated purification. Isolation as the pinacol or propandiol boronic esters was possible, but did not address the poor yield. The solution involved meticulous drying of all reagents and using an excess (30 equivalents) of freshly distilled trimethyl borate. In this way, yields between 75-90% were routinely obtained on 1 g-scale reactions, and calix[4]arene boronic acid **2** could be fully characterized (see experimental section and electronic supplementary information).

Curiously, scaling up the reaction as little as two-fold resulted in the formation of known mono-hydroxy calix[4]arene **3** in yields greater than 40%. Recent reports using photoredox catalysis have demonstrated the potential for this sort of aerobic oxidation,[29,30] but in our case we do not knowingly have such catalysts present. This suggested that reactive oxygen species formed in some other way during the larger scale reaction, which is of interest but will only be investigated in future studies.

For comparison in the catalytic reactions, we also synthesized three known aryl-boronic acids as reference compounds (Figure 2). Phenyl boronic acid **4** was chosen as a known poor catalyst, whilst *o*-nitrophenylboronic acid **5** served as a known positive control. *p*-Propoxyphenylboronic acid **6** had not been investigated before and was chosen as a model to compare with the calix[4]arene boronic acid **2**.

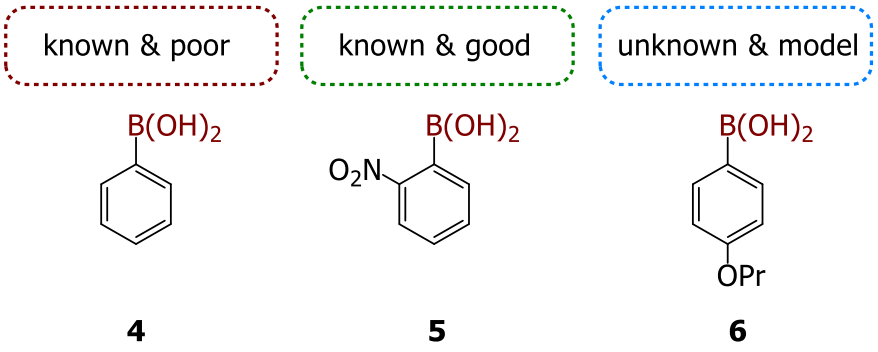


Figure 2. Arylboronic acids used as models to compare with our calix[4]arene boronic acid **2**.

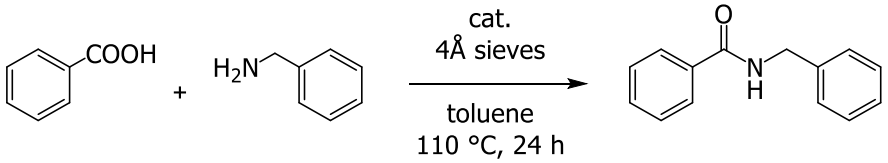
Catalytic study

Since the literature is replete with examples of catalysis using aryl-boronic acids, it was easy enough to select a method that had already been fine-tuned to compare with. In this regard, a number of important decisions were made with respect to substrate, solvent, and additive. The choice of substrate was important since many simple carboxylic acids will readily undergo amide bond formation under thermal conditions.[31] Benzoic acid is however extremely resistant to this, so was therefore selected as a challenging substrate. The amine chosen was benzylamine, primarily for its chromophore, but the product, *N*-benzylbenzamide, is also a useful reagent for butyllithium titrations.[32] The solvent for these reactions has also been extensively studied; recently dichloromethane has emerged as a preferred solvent for room temperature variants of this reaction,[16,19,20] but none of these highly active catalysts are particularly good at using benzoic acid as a substrate. Nevertheless, we did try one reaction in dichloromethane, but as expected, it did not give any discernible product. This left refluxing toluene (110 °C) or fluorobenzene (85 °C), which were known as good solvents, however in our hands, reactions performed in fluorobenzene always resulted in lower yields than the corresponding ones in toluene (see electronic supporting information (ESI) for more details). Then concerning additives, 4Å molecular sieves have been identified as essential, since they trap the water given off in the reaction, as well as potentially release a small amount of water, which is important for hydrolysis of boroxine intermediates.[16] The reactions themselves were monitored by HPLC in order to determine conversions (see ESI for details); the overall results can be seen in Table 1.

As expected, the thermal reaction was essentially non-existent (entry 1) with only a 2% conversion being detected after 24 hours. The reaction with boric acid was also an important control experiment, since it has been shown to be an effective catalyst in some cases of amide bond formation.[33,34] This was important as protodeboronation would lead to boric acid which would complicate the results. Under our conditions this

was shown to be a minor component of the reaction conversion (entry 5, boric acid), meaning boric acid formed via protodeboronation, could be discounted as significantly affecting the results. Looking at the individual catalysts, unsurprisingly phenylboronic acid (PBA) **4** performed poorly and *o*-nitrophenylboronic acid (*o*NPBA) **5** performed well, giving us the benchmarks to evaluate our two catalysts. *p*-Propoxyphenyl boronic acid (*p*PPBA) **6** gave rather unusual results in that its performance did not logically scale with increased catalyst loading. At low catalyst loading it was surprisingly effective, but dropped off as its concentration increased. We wondered whether this might be due to increased boroxine formation at higher concentrations. Our calix[4]arene boronic acid **2** gave promising results in that it could catalyze the reaction on a par with *o*NPBA **5** at higher catalyst loadings. Whilst these results are promising, they are not ideal since 20 mol % is an extremely inefficient amount when considering any form of catalysis. Nevertheless, for us the good news was that calix[4]arene boronic acid **2** could act as a catalyst and thus the potential for further elaboration was established.

Table 1. Results from the model catalytic study



		Catalyst conversion (%)[a]				
Entry	Loading (%)	boric acid[b]	PBA (**4**)	*o*NPBA (**5**)	*p*PPBA (**6**)	CalixBA (**2**)
1	0[c]	-	-	-	-	-
2	5	-	25	38	63	13
3	10	-	44	69	72	29
4	15	-	45	72	49	66
5	20	9	48	90	69	83

[a] measured by HPLC; [b] only determined at 20 mol% loading; [c] the uncatalyzed thermal reaction resulted in only a 2% conversion.

Unfortunately, this finding was to be further tempered by the fact that we could show complete protodeboronation of the calix[4]arene catalyst after 24 hours reaction time. The reasons for this are almost certainly promoted by the *para*-propoxy substituent. We could show that the protodeboronation was not only due to high temperatures since the catalyst remained intact when heated in toluene with molecular sieves for 24 hours. However, when either the benzoic acid or benzylamine were added, protodeboronation occurred, suggesting that the substrates themselves were catalyzing this. At room temperature, no protodeboronation was observed under the reaction conditions, so this still bodes well for further development. Indeed the stage has been set for the next generation of calix[4]arene boronic acid catalysts to be investigated. Ideally, this will be by introducing an *ortho*-functional group like those reported by Hall or Blanchet (Figure 1), which has the added interesting feature of being inherently chiral which we are also interested in.[23]

Conclusions

At the outset this was not meant to be a quintessential catalyst but a test of the concept of a calix[4]arene boronic acid to catalyze amidation. This study has shown that this can be applied to calix[4]arenes, although protodeboronation is a significant issue at high temperatures. Unexpectedly, we also identified a rather active *para*-propoxyphenyl boronic acid not yet employed for this purpose in the literature. Whilst at this stage no benefit of the supramolecular calixarene cavity was observed, in future work we would like to functionalize the upper rim in such a way as to either, 1) allow for development along the lines of enzyme mimicry, or 2) develop an inherently chiral version capable of kinetic resolution.

Experimental Section

General. The chemicals used in this research project were purchased from Sigma Aldrich or Merck. THF and toluene were distilled over sodium metal in an inert atmosphere of nitrogen. Benzophenone indicator was used for THF distillation. Appropriate purification methods were used for other reagents requiring prior purification.[35] *N*-benzylbenzamide was used for titrating alkyllithiums in THF solvent at –41 °C as per the reported procedure.[32] Low temperature reactions were carried out in a Dewar flask: acetone/dry ice (–78 °C) and acetonitrile/dry ice (–41 °C) were used for the low temperature reactions. High temperature reactions were carried out using a Heidolph magnetic stirrer plate with a temperature-regulating probe in either a paraffin or a silicon oil bath. Reactions requiring inert conditions were carried out in an argon atmosphere. The argon was dried over activated 4 Å molecular sieves in the Schlenk line. For the lithiation reactions glassware was dried overnight and cooled in an inert atmosphere (filled with dry argon). Flash column chromatography was carried out using Merck silica gel 60 (0.040 – 0.063 mm particle size). Thin layer chromatography (TLC) was carried out with pre-coated TLC sheets ALUGRAM Xtra SIL G/UV layer consisting of 0.20 mm silica gel 60 with florescent indicator UV254. A UV lamp was used to monitor the TLC. ^{1}H, ^{11}B and ^{13}C NMR spectroscopic experiments were carried out at 25 °C on a 300 MHz Varian VNMS instrument (96 MHz for ^{11}B; 75 MHz for ^{13}C). The solvent used for NMR spectroscopy was chloroform-*d*. Infrared spectroscopy was carried out on a Nexus Thermo-Nicolet FT-IR instrument with a diamond tip. All samples were analyzed in the solid state. Mass spectrometry was performed at the Stellenbosch University Central Analytical Facility (CAF). Electrospray ionization (ESI) was used in a Waters API Q-TOF Ultima spectrometer. Melting point determination was done in a Gallenkamp Melting Point Apparatus. HPLC was performed on a Agilent Eclipse Plus C18 column (150 mm x 4.6 mm x 5µm) at 40 °C using a mobile phase of 80:20:0.05 acetonitrile:water:trifluoroacetic acid at 2.0 mL/min flow rate.

Synthesis of 25,26,27,28-tetrapropoxycalix[4]arene-5-boronic acid. 5-Bromo-25,26,27,28-tetrapropoxycalix[4]-arene **1** (1.00 g, 1.49 mmol) was transferred into an oven dried Schlenk tube and dried under high vacuum at 80 °C for 2 hours. The Schlenk tube was then gently reheated under vacuum with a heat gun to ensure that any residual moisture was flushed from the tube. The tap of the Schlenk tube was then closed and it was removed from the vacuum and backfilled with argon. An oven dried stir bar, further dried by heating with a heat gun, was then added to the Schlenk followed by dry THF (20 mL). The solution was then cooled to –78 °C in an acetone-dry ice bath in a Dewar vessel. *n*-BuLi (2.1 mmol, 2.2 M, 0.95 mL, 1.4 equiv) was added slowly running it along the walls of the vessel making sure the temperature did not rise above –78 °C. The reaction was allowed to stir for 15 minutes at –78 °C. Freshly distilled $B(OMe)_3$ (45 mmol, 5.0 mL, 30 equiv) was added

and the reaction left to stir for 3.5 h in the bath whilst it slowly warmed up. HCl (4 M, 10 mL) was then added and the reaction removed from the bath and allowed to stir at room temperature for 1 h. Extraction was then carried out using DCM (2 x 100 mL). The organic phase was washed with water, dried over anhydrous $MgSO_4$ and filtered to obtain the crude. The compound was isolated via silica gel column chromatography using a gradient elution of ethyl acetate: petroleum ether (starting with 5, 10, 15 and finally 20% ethyl acetate mobile phase). About 0.5% acetic acid was added to the mobile phase to alleviate tailing of the acid. In this way, a 90% yield (0.850 g, 1.34 mmol) of the boronic acid was obtained as a fine white powder. mp 144-145 °C. IR (cm^{-1}) 1344 (s, B–O stretch). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (s, 2H, Ar***H***), 6.85 (d, *J* 7.5 Hz, 2H, Ar***H***), 6.68 (t, *J* 7.5 Hz, Ar***H***) 6.56 – 6.35 (m, 6H, Ar***H***), 4.56 (d, *J* 13.4 Hz, Ar***CH$_{2(ax)}$***Ar), 4.48 (d, *J* 13.4 Hz, Ar***CH$_{2(ax)}$***Ar), 4.06 (t, *J* 7.8 Hz, 2H, O***CH$_2$***CH_2CH_3), 3.95 (t, *J* 7.8 Hz, 2H, O***CH$_2$***CH_2CH_3), 3.82 (t, *J* 7.2 Hz, 4H, O***CH$_2$***CH_2CH_3), 3.37 (d, *J* 13.4 Hz, 2H, Ar***CH$_{2(eq)}$***Ar), 3.17 (d, *J* 13.4 Hz, 2H, Ar***CH$_{2(eq)}$***Ar), 2.05 – 1.85 (m, 8H, CH_2***CH$_2$***CH_3), 1.08 (t, *J* 7.3 Hz, 6H, CH_2***CH$_3$***), 0.99 (t, *J* 7.3 Hz, 3H, CH_2***CH$_3$***), 0.97 (t, *J* 7.3 Hz, 3H, CH_2***CH$_3$***) ppm. ^{11}B NMR (96 MHz, $CDCl_3$) δ 33.2 ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.5, 157.4, 156.1, 136.3, 136.2, 135.8, 134.4, 128.6, 128.1, 128.0, 122.2, 121.9, 77.0, 76.7, 31.1, 23.6, 23.4, 23.3, 10.7, 10.5, 10.03 ppm. $[M+H]^+$ calcd for $C_{40}H_{50}BO_6$: 637.3700; found: 637.3713.

Catalytic reactions. A round-bottomed flask was equipped with a stirrer bar and a condenser. Benzoic acid (0.819 mmol, 100 mg), followed by solvent (fluorobenzene or toluene) (5.0 mL) and benzylamine (0.819 mmol, 89 µL) were added, followed by catalyst (5, 10, 15 or 20 mol%) and powdered molecular sieves (>250 mg). The mixture was allowed to stir at reflux for 24 h in an inert atmosphere, before filtering off the molecular sieves and washing with ethyl acetate and dichloromethane. The solvent was removed under reduced pressure and dried. HPLC analysis samples were then prepared by dissolving the crude in acetonitrile and performing appropriate dilutions. (t_r = 0.90 min in 80:20 acetonitrile:water).

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Supplementary Materials

Copies of the IR, MS, ^{1}H, ^{13}C and ^{11}B NMR spectra for calixarene boronic acid **2** and tables of results from HPLC runs are included.

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