Supplementary Material

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

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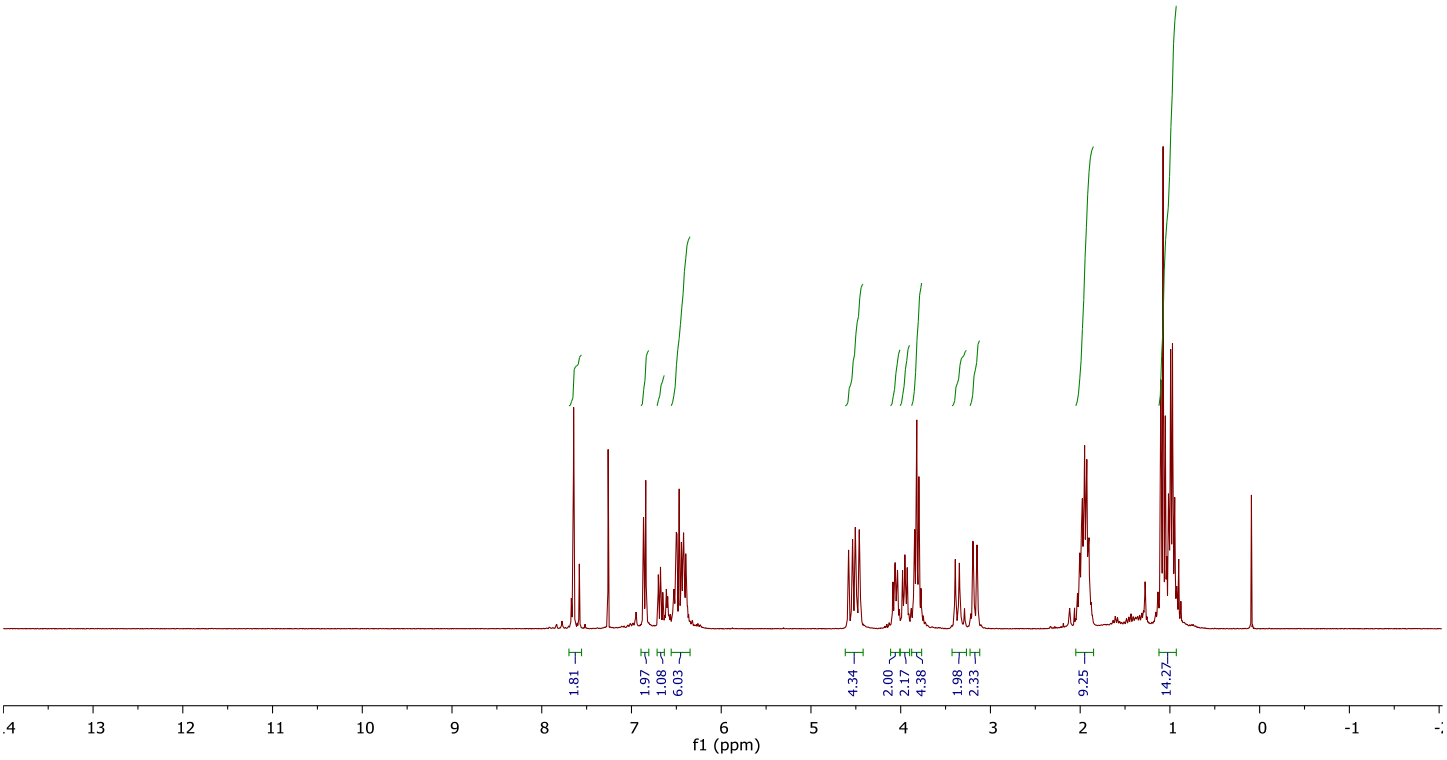
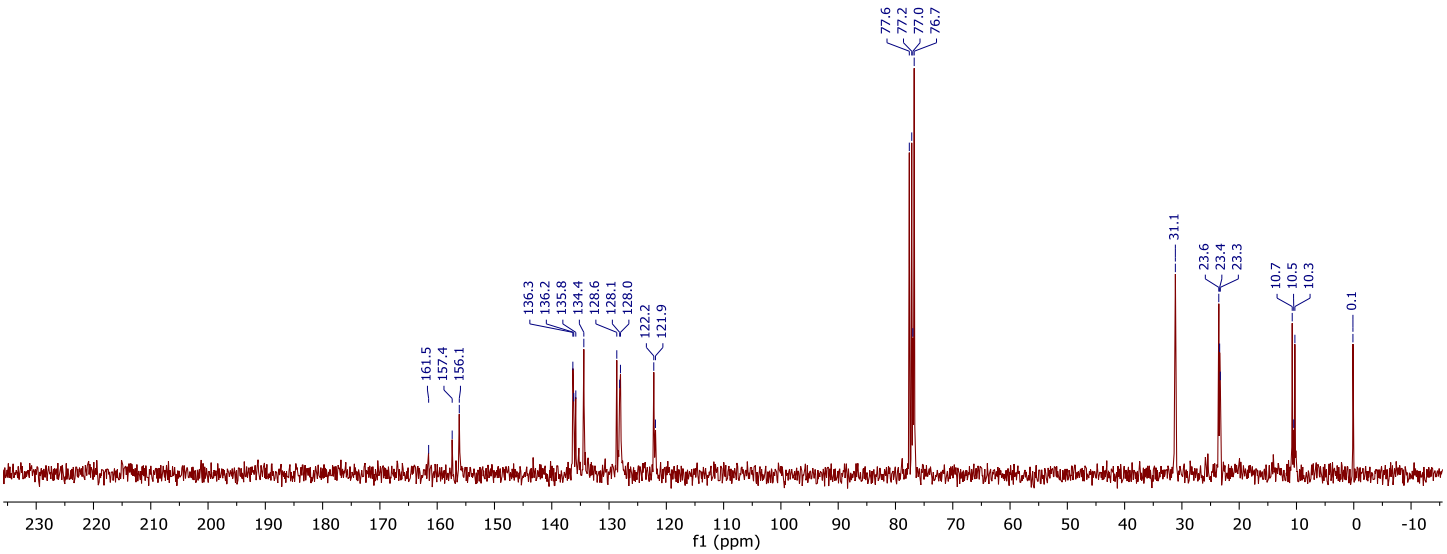
25,26,27,28-tetrapropoxycalix[4]arene-5-boronic acid

//Drafts/2018/Asslly/Data/Calix B Acid/

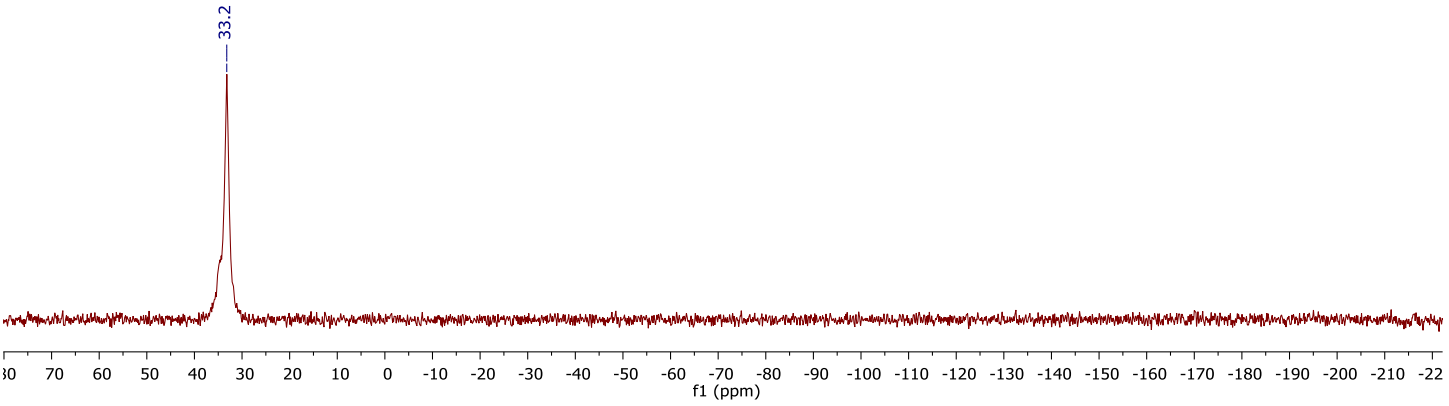
^{1}H NMR Spectrum



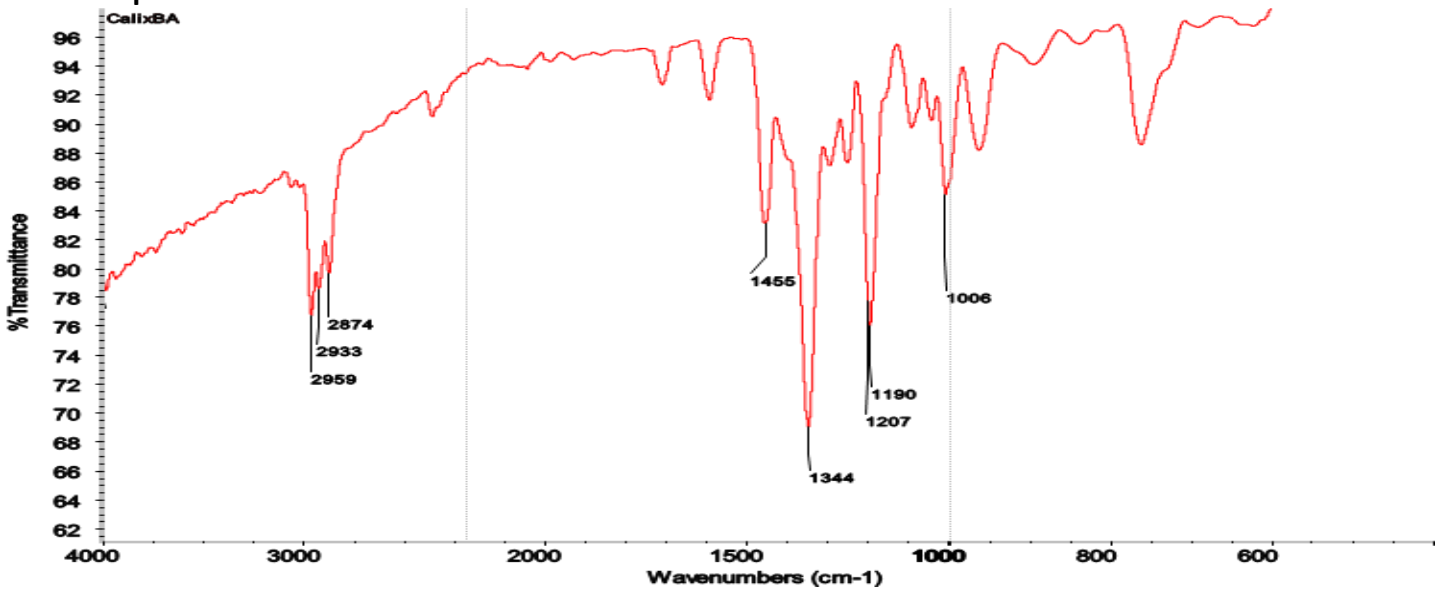
^{13}C NMR Spectrum



^{11}B NMR Spectrum

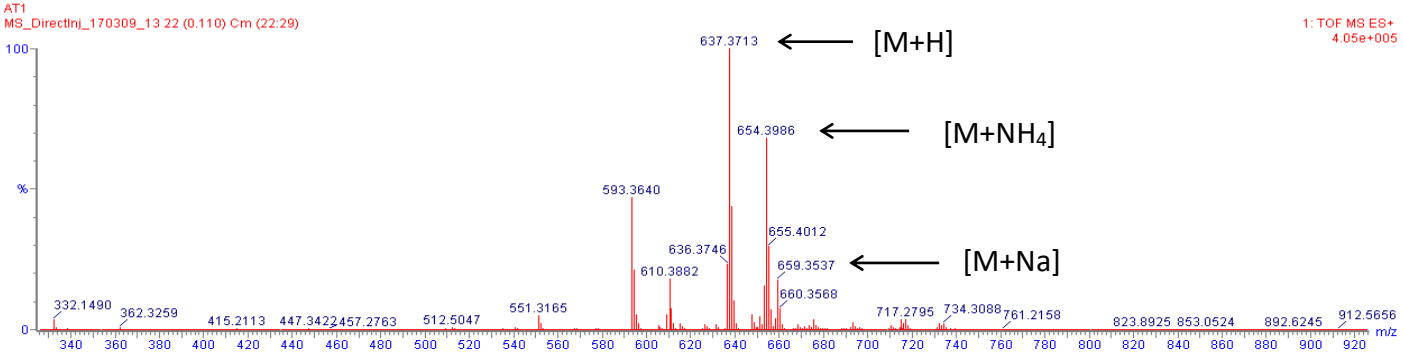


Infrared Spectrum



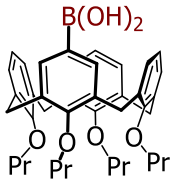
Mass Spectrum

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	O	S	B
637.3713	637.3713	0.0	0.0	10.5	C34 H52 O7 S B3	459.8	64.313	0.00	34	52	7	1	3
	637.3714	-0.1	-0.2	-0.5	C19 H49 O17 B8	459.9	64.339	0.00	19	49	17		8
	637.3715	-0.2	-0.3	16.5	C42 H53 O3 S	408.3	12.770	0.00	42	53	3	1	
	637.3710	0.3	0.5	4.5	C26 H51 O11 S B6	459.9	64.356	0.00	26	51	11	1	6
	637.3717	-0.4	-0.6	5.5	C27 H50 O13 B5	460.0	64.418	0.00	27	50	13		5
	637.3719	-0.6	-0.9	11.5	C35 H51 O9 B2	430.0	34.422	0.00	35	51	9		2
	637.3700	1.3	2.0	16.5	C40 H50 O6 B	413.6	18.034	0.00	40	50	6		1
	637.3698	1.5	2.4	10.5	C32 H49 O10 B4	459.9	64.381	0.00	32	49	10		4
	637.3729	-1.6	-2.5	-0.5	C21 H52 O14 S B7	459.9	64.390	0.00	21	52	14	1	7



Catalytic Results Raw Data

Toluene, reflux, 24 h



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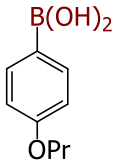
catalyst loading	Run 1	Run 2	Run 3	Run 4	Run 5	Average	Standard deviation
5%	14	10	11	16	15	13.2	2.3
10%	19	34	21	38	35	29.4	7.8
15%	64	56	67	70	74	66.2	6.1
20%	84	83	81	82	*	82.5	1.1

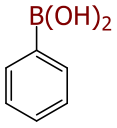
* reaction spill



6

Catalyst loading	Run 1	Run 2	Run 3	Average	Standard deviation
5%	63	63	*11**	63.0	0.0
10%	64	73	79	72.0	6.2
15%	55	55	37	49.0	8.5
20%	67	71	70	69.3	1.7

* 11% conversion measured, thus determined to be an outlier



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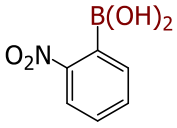

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catalyst loading	PBA 4	*o*NPBA 5
5%	25	38
10%	44	69
15%	45	72
20%	48	90

Known catalysts only determined once since they followed the expected literature trends

Fluorobenzene, reflux, 24 h

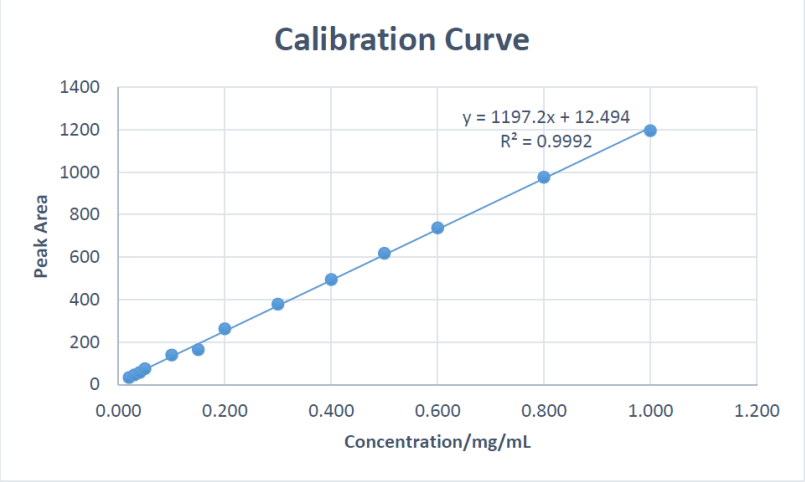
Catalyst loading	*o*NPBA (5)	*p*PPBA (6)	CalixBA (2)
5%	30	-	1
10%	50	-	2
15%	62	-	2
20%	68	2	3

HPLC Calibration method

The conversions were calculated using an HPLC (High Performance Liquid Chromatography) method, using an external standard method due to its simplicity considering that only one test reaction was used.

External Standard Method

A calibration curve was drawn from the data collected from the response of the method of analysis to known quantities of *N*-benzylbenzamide, the reaction product. Different concentrations of the analyte were used to make standard solutions. The peak area of each standard solution was plotted against its concentration, which were selected to be of a concentration range that covered the concentrations of *N*-benzylbenzamide in the crude to be analyzed.



Graph 1: Calibration curve for the *N*-benzylbenzamide external standard.

CHROMATOGRAPHIC CONDITIONS	
CHROMATOGRAPHIC COLUMN	Agilent, Eclipse Plus C18 150 mm x 4.6 mm x 5 µm
MOBILE PHASE A	80% acetonitrile
MOBILE PHASE B	20% water
FLOW RATE	2.0 mL/min
OVEN TEMPERATURE	40 °C
INJECTION VOLUME	5 µl (automated)
WAVELENGTH	260 nm (bandwidth = 4 nm)