Meta-Selective C–H Functionalization of Aryl Boronic Acids Directed by a MIDA-Derived Boronate Ester

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Supporting Information

Contents

General Synthetic Information

All reactions were performed under nitrogen using oven-dried glassware unless stated otherwise. Yields refer to chromatographically and spectroscopically (^{1}H-NMR) homogenous materials, unless otherwise indicated. MeCN, CH_2Cl_2, THF, Et_2O, DMF, and toluene were dried and deoxygenated with a Grubbs PureSolv 400 solvent purification system. Hexafluorisopropanol (HFIP) was supplied by Fluorochem and used in without further purification. The moisture content of the solvents was monitored by Karl Fischer coulometric titration (Mettler-Toledo DL39). **Reagents**: used as purchased from commercial sources, unless otherwise stated, and used according to COSHH regulations. **Chromatography**: Flash column chromatography (FCC) was performed on silica gel (Merck Kieselgel 60 F254 230-400 mesh) unless otherwise stated. **Melting Points**: determined on a Stanford Research System OptiMelt. Boronic acid MIDA-DG esters were observed to degrade before melting, characterized by discolouration. **Thin Layer Chromatography (TLC)**: performed on Merck aluminium-backed plates pre-coated with silica (0.2 mm, 60 F254) which were visualized either by quenching of ultraviolet fluorescence (λmax = 254 and 366 nm) or staining with; potassium permanganate/Δ, bromocresol green/Δ or phosphomolybdic acid/Δ TLC dips prepared according to general procedures. **^{1}H NMR spectra**: recorded on a 400 or 500 MHz Bruker AMX-400/500 instrument. Chemical shifts (δH) are quoted in parts per million (ppm), referenced to the appropriate residual solvent peak. **^{13}C NMR spectra**: recorded at 101 MHz or 125 MHz on a Bruker AMX-400/500 instrument Chemical shifts (δC) are quoted in parts per million (ppm), referenced to the appropriate residual solvent peak. **^{11}B NMR spectra**: recorded at 128 MHz on a Bruker AMX-400 instrument. Chemical shifts (δB) are quoted in parts per million (ppm), referenced to $BF_3.Et_2O$ in $CHCl_3$. ^{11}B NMR were recorded using quartz NMR tubes for representative samples of MIDA-DG and pinacol boronate esters in an attempt to exclude the broad borosilicate peak from the spectra, however, due to the presence of borosilicate in the NMR probes, this was unsuccessful. Consequently, ^{11}B NMR were recorded in borosilicate NMR tubes, with samples sufficiently concentrated to make sure the characteristic peaks were clearly visible against the broad background peak. Product mixtures that are fully characterized were analyzed and characterized using 2D COSY, HSQC and HMBC techniques (mostly pinacol boronate ester products). **High Resolution Mass Spectra**: recorded on either a VG platform II or VG AutoSpec spectrometer, with only molecular ions ([MH]+, [MNa]+, [MK]+, [MH_2O]+, [MH]-) and major peaks being reported. ES TOF (Electro-spray ionization, time-of-flight) and APCI (atmospheric pressure chemical ionization) ionization methods were used.

Notes on the Handling of MIDA-DG Boronate Esters

Similar to *N*-methyliminodiacetic acid (MIDA) boronate esters, MIDA-DG (*N*-methyliminodiacetic acid tethered directing groups) have unique properties derived from the MIDA functional group. All MIDA-DG esters synthesised thus far have been free-flowing solids, stable for extended periods on the bench top and to silica gel purifications. MIDA-DG esters are insoluble in Et_2O, sparingly soluble in chlorinated solvents and EtOAc, and soluble in THF, MeCN and other polar solvents.

MIDA-DG boronates can be synthesised simply by refluxing in MeCN with an equal amount of boronic acid overnight. They can also be condensed in the microwave by heating to 130 °C for 10 minutes, however this method is less effective with *ortho*-substituted boronic acids, which can require longer reaction times. To purify the MIDA-DG boronate esters, they can be precipitated with Et_2O or simply dry loaded directly onto a silica plug. The silica can subsequently be washed with Et_2O to remove organic by-products, before the MIDA-DG boronates are selectively eluted using EtOAc or 1:1 MeCN:Et_2O, termed a 'catch and release' purification.

Regioisomeric mixtures of MIDA-DG boronates that form during C–H functionalisations are often inseparable using normal phase chromatography. To circumvent this issue, the mixtures were purified using the 'catch and release' procedure, deprotected using K_3PO_4 or NaOH and then separated and fully characterised after subsequent functionalisations.

Design of Experiment (DOE) Optimisation of C–H Alkenylations

Due to the observed behaviour of phenyl MIDA-DG boronates, namely degradation of the PhB(MIDA-DG) over time, a DOE approach to optimisation was chosen. It was believed a balance would be required between temperature, time, oxidant equivalents and HFIP:DCE solvent ratio to maximise the yield obtained while minimising the amount of degradation.

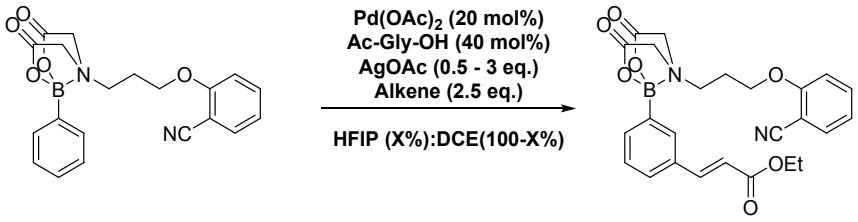
The software used for the DOE optimisation was JMP Pro 14. Definitive screening design experiments were performed in all cases, using the factors and ranges given below. The design generates a number of experiments where each factor investigated is at either a minimum, maximum or midpoint value. The data obtained from these experiments is combined and evaluated to allow predictions of the ideal values for the desired outcome (in this case highest yield). The minimum and maximum values are chosen to include the anticipated ideal values within their range. If the ideal value falls outside the range chosen, the model can prove ineffective.

General procedure for DOE reaction screening

PhB(MIDA-DG) (0.05 mmol, 19 mg), $Pd(OAc)_2$ (X eq.), Ac-gly-OH (X eq.) and AgOAc (X eq.) were added to a one dram (4 mL) vial. Ethyl acrylate (2.5 eq., 14 μL), HFIP(:DCE) (1 mL) and CH_2Br_2 (internal standard, 1 eq., 3.5 mL) were then added and the vial sealed. The reaction mixture was added to a hot plate at the desired temperature and stirred for the desired time. On completion, a 0.1 mL aliquot was taken, diluted with MeCN-d_3, filtered and a ^{1}H NMR taken. The yield was calculated by comparison of integrals between the product and the CH_2Br_2 internal standard.

Initial DOE Study

The initial DOE study focused on time, temperature, the HFIP:DCE ratio and oxidant equivalents (**Table S1**).



Factor	Minimum	Maximum
Time (hours)	10	48
Temperature (°C)	30	70
% HFIP	0	100
Oxidant equivalents	0.5	3

Table S1: Variable value ranges used during the initial DOE study. % HFIP corresponds to the HFIP:DCE ratio for instance 50% HFIP is equivalent to 1:1 DCE:HFIP

Percentage yield was chosen as the main response, with the *meta*:*para* selectivity also measured, but not included in the model initially. The experiments generated by the definitive screening model and the obtained yields are shown in **Table S2**.

Entry	Time (hours)	Temperature (°C)	% HFIP	Oxidant equivalents	Yield	*Meta*:*Para*
1	48	30	100	3	36	6.5:1.0
2	48	70	0	1.75	18	7.5:1.0
3	10	70	0	0.5	4	n.d.
4	29	70	100	3	45	2.3:1.0
5	48	50	0	3	8	n.d.
6	29	50	50	1.75	58	3.9:1.0
7	10	50	100	0.5	35	5.7:1.0
8	48	70	100	0.5	29	4.1:1.0
9	10	70	50	3	40	1.3:1.0
10	10	30	0	3	0	n.d.
11	48	30	50	0.5	44	4.0:1.0
12	29	30	0	0.5	0	n.d.
13	10	30	100	1.75	72	6.7:1.0

Legend:	Minima	Midpoint	Maxima	Yield:	>45%	>5.3:1.0

Table S2: Experiments performed and the results obtained during initial DOE study

With the experiments performed, the model was fit using the fit definitive screening tool. The model indicated that the most important continuous variable analysed was the percentage of HFIP used, with minimal effect from the other continuous variables. This was clear from the main effect residual plot graphs generated (**Figure S1**).

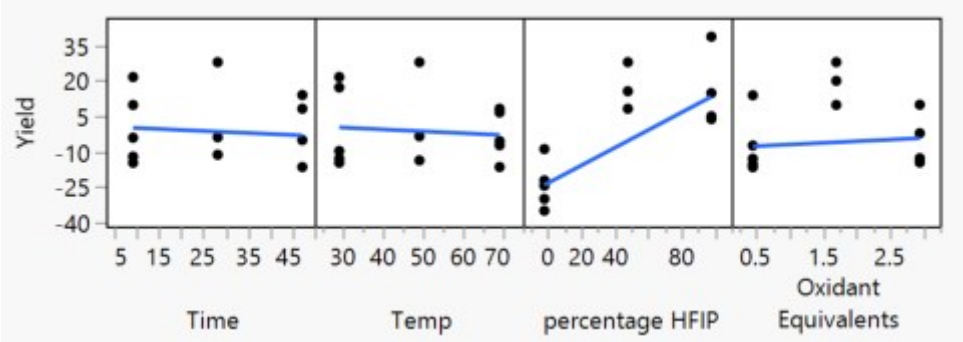


Figure S1: Main effect residual plot graphs displaying the trends in effect of each variable

Fitting the model solely on percentage HFIP and (percentage HFIP)*(percentage HFIP) gave a positive correlation between predicted and actual yield (**Figure S2**). The model had two outliers (entries 8 and 13) but an R^2 value of 0.75, which was considered indicative of a valid model.

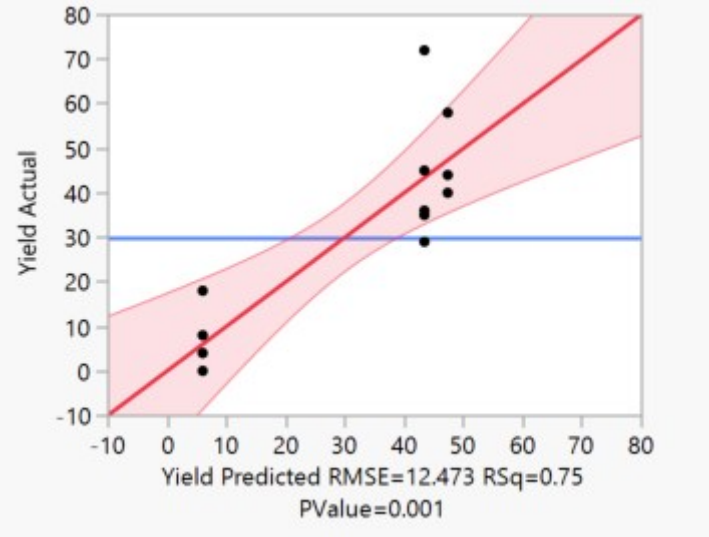


*Figure S2: Actual vs predicted yield based solely on % HFIP and %HFIP * %HFIP*

Unfortunately, due to the overwhelming influence of the percentage HFIP on the model, it was only useful for predicting the highest yielding value for this variable. This was predicted to be 70%, resulting in a yield of 52% (**Figure S3**).

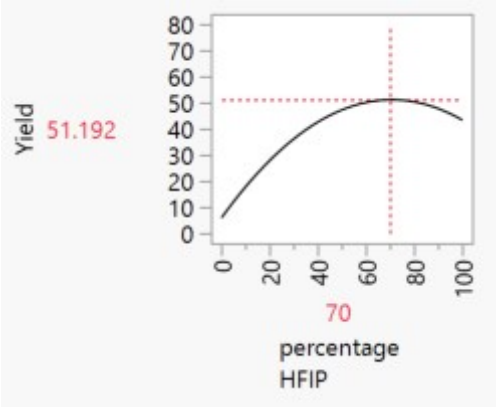


Figure S3: Prediction profile generated from the results of the initial DOE study.

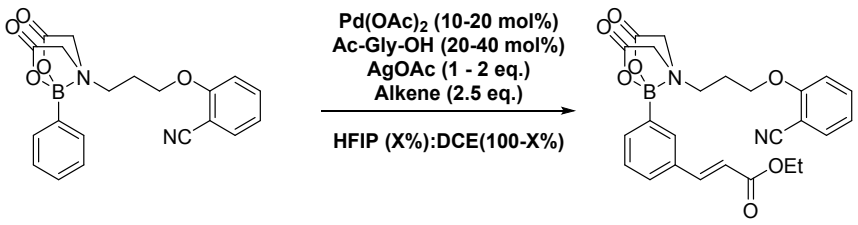
Interestingly, the model suggested that temperature had very little baring on the yield of the reaction, with yield actually slightly diminishing at higher temperatures [as expected due to degradation of the PhB(MIDA-DG)]. Consequently, room temperature (23 °C) was chosen as the temperature for future DOE studies. Time showed a similar trend, with slight degradation over time observed. Consequently, longer times were concluded to be detrimental to achieving high yields.

It was expected that the reaction time and number of equivalents of oxidant would have important effects on the reaction, however these were not picked up by the model due to the overwhelming effects from changing the percentage of HFIP. By narrowing the range used for the percentage HFIP from 0-100% to 50-100% (which includes the predicted ideal value of 70%) it was anticipated a more accurate model could be built and that this would allow the effects of reaction time and oxidant equivalents, as well as percentage HFIP to be evaluated. A second DOE study was therefore performed.

Second DOE study

The factors investigated were catalyst loading, time, percentage HFIP and equivalents of oxidant. In response to the results from the first study, temperature was kept constant at 23 °C and the percentage HFIP range made narrower. Catalyst loading was investigated, with the ratio of catalyst to ligand kept constant (cat:lig, 1:2). The

range of times investigated were also narrowed, from 10-48 hours to 1-18 hours and range of oxidant equivalents from 0.5-3 equivalents to 1-2 equivalents (**Table S3**).



Factor	Minimum	Maximum
Catalyst Loading (mol%)	10	20
Time (hours)	1	18
% HFIP	50	100
Oxidant equivalents	1	2

Table S3: Variable value ranges used during the initial DOE study. % HFIP corresponds to the HFIP:DCE ratio for instance 50% HFIP is equivalent to 1:1 DCE:HFIP

Percentage yield was again chosen as the response. The experiments generated by the definitive screening model and the obtained yields are shown in **Table S4**.

Entry	Catalyst Loading (mol%)	Time (hours)	% HFIP	Oxidant equivalents	Yield	*Meta*:*para*
1	20	18	50	1.5	51	4.5:1.0
2	15	1	50	1	4	n.d.
3	10	1	50	2	3	n.d.
4	10	1	100	1.5	7	n.d.
5	20	9.5	50	2	39	3.2:1.0
6	10	18	50	1	36	5.7:1.0
7	10	9.5	100	1	28	2.3:1.0
8	20	18	100	1	50	6.1:1.0
9	20	1	100	2	13	3.0:1.0
10	15	9.5	75	1.5	32	1.9:1.0
11	10	18	75	2	42	4.5:1.0
12	15	18	100	2	60	5.6:1.0
13	20	1	75	1	8	4.0:1.0

Legend:	Minima	Midpoint	Maxima	Yield:	>45%	>5.3:1.0

Table S4: Experiments performed and the results obtained during the second DOE study

The model was again fit using the fit definitive screening tool. The model predicted that between 50 and 100% the percentage of HFIP as solvent actually had very little effect and could be omitted from the model.

A positive correlation between predicted and actual yield was found, with an R^2 value of 0.95, again indicative of a valid model (**Figure S4**).

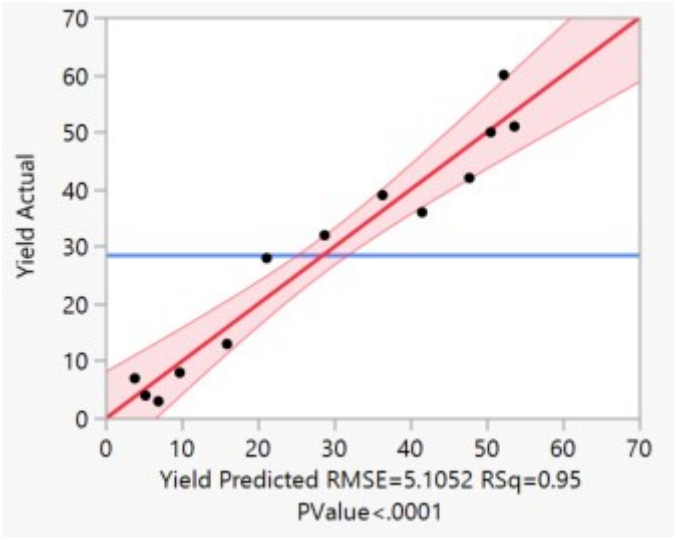


Figure S4:Predicted vs actual yield plot, showing the increased accuracy of the second model

Unfortunately, it appeared the ranges for catalyst loading, time and equivalents of oxidant may have been too narrow, as shown by the predictive graphs below (**Figure S5**). If the optimum value was within the investigated range, a curved prediction with a clear peak would be expected (*see* prediction graph from initial DOE study).

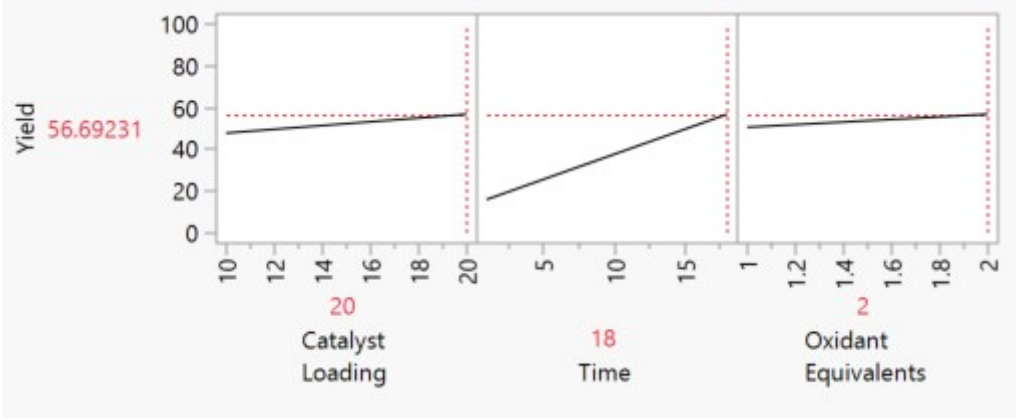


Figure S5: Predictive graphs generated during the second DOE study.

The information was used to predict the highest yielding reaction conditions. Using the prediction profiler (**Figure S6**) the optimum conditions are shown in **Scheme S1**:

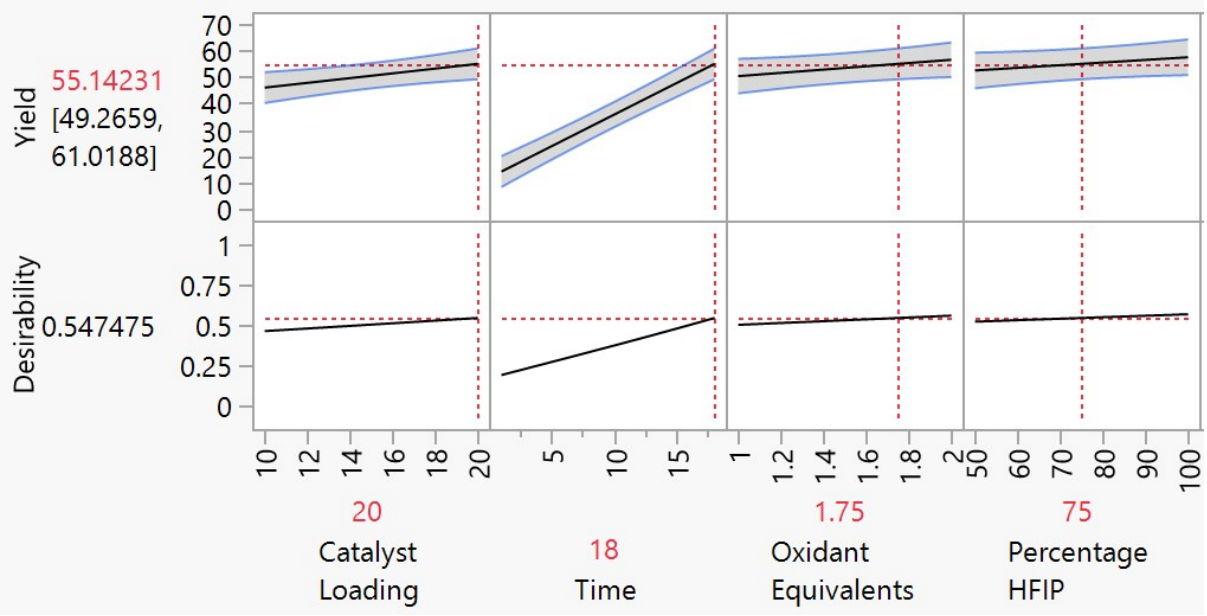
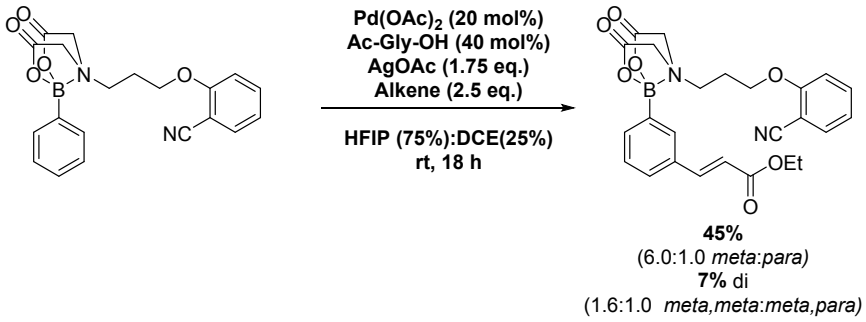
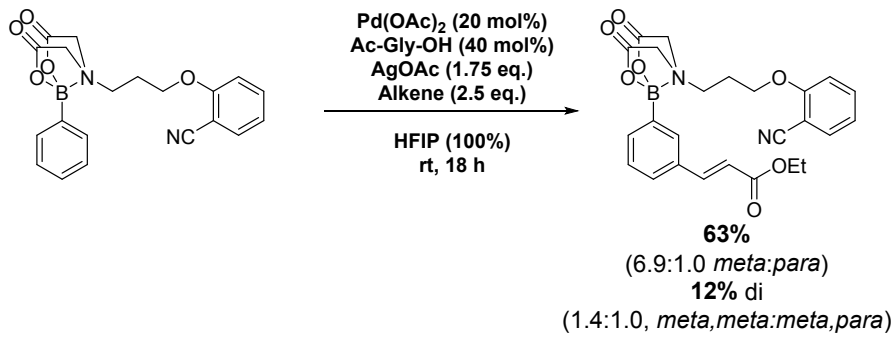


Figure S6: Prediction profiles generated during the second DOE study.



Scheme S1: Testing the conditions predicted to be highest yielding.

Pleasingly, the yield obtained (52%) was within the range predicted by the model (55 ± 3%) and the selectivity (6.0:1.0 *meta*:*para*) was in line with the highest values obtained during DOE optimisation. However, it was noticed that during the initial DOE study, conditions very similar to these achieved a higher yield and selectivity (**Table S2,** entry 13, 72%, 6.7:1.0 *meta:para*). The key difference being the percentage of HFIP used. On repeating the reaction with 100% HFIP, a significant increase in yield was observed (**Scheme S2**) along with a concurrent increase in *meta:para* selectivity, in agreement with that achieved using similar conditions and higher than any previously obtained during the DOE optimisation.

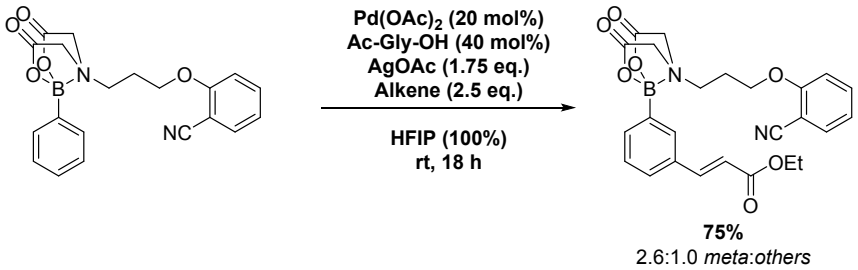


Scheme S2: Use of 100% HFIP resulted in a large jump in yield, which was missed by the DOE model generated.

Consequently, these conditions were chosen as the optimum ones for subsequent investigations into the scope of the reaction.

Control Reactions

A number of changes to the reaction conditions were also made to ensure that the optimum conditions had been used (**Table S5**).



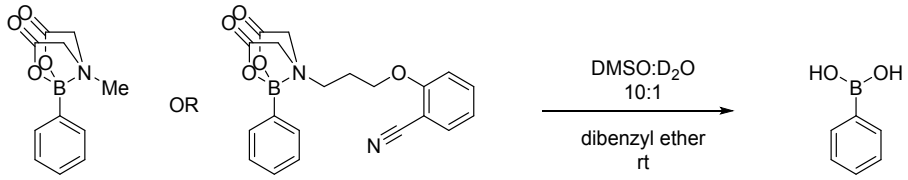
Entry	Variation from Standard Conditions	meta	para	meta, meta	meta, para	Total
1	No variation	55%	8%	7%	5%	75%
2	No $Pd(OAc)_2$	-	-	-	-	-
3	No AgOAc	13%	4%	-	-	17%
4	No Ac-Gly-OH	9%	4%	-	-	13%
5	PhenylB(MIDA) (no DG)	-	-	-	-	-
6	Inert (nitrogen) atmosphere used	56%	8%	5%	2%	71%
7	Ag_2SO_4 (1.75 eq.) as oxidant	13%	-	-	-	13%
8	Ag_2CO_3 (1.75 eq.) as oxidant	13%	2%	-	-	15%
9	Boc-Gly-OH (40 mol%) as ligand	4%	-	-	-	4%
10	Z-Gly-OH (40 mol%) as ligand	7%	-	-	-	7%
11	Ac-Ile-OH (40 mol%) as ligand	28%	5%	-	-	33%
12	Ac-Val-OH (40 mol%) as ligand	31%	6%	-	-	37%
13	2.0 eq. ethyl acrylate	42%	8%	6%	2%	58%
14	1.5 eq. ethyl acrylate	38%	6%	4%	1%	49%

Table S5: Variations to standard conditions and their effects on yield and selectivity.

These confirmed that all the components of the reaction were required.

PhB(MIDA-DG) Stability Test

The stability of phenylboronic acid MIDA-DG ester to hydrolysis compared to phenylboronic acid MIDA ester and other boronate esters was performed using the same method as Suginome et al. (*Org. Lett.* 2011, **13**, 2662-2665) to allow for comparison of results (**Scheme S3**).



*Scheme S3: Conditions used to measure the stability of PhB(MIDA-DG) **7** against PhB(MIDA)*

For the PhB(MIDA): A solution of PhB(MIDA) (5.0 mg, 0.02 mmol) and dibenzyl ether (3.8 µL, 0.02 mmol) in DMSO-d_6 (0.7 mL) and D_2O (0.07 mL) and ^1H NMR spectra taken at intervals of 24 hours starting at 0 hours.

For the PhB(MIDA-DG: A solution of PhB(MIDA-DG) (8.1 mg, 0.02 mmol) and dibenzyl ether (3.8 µL, 0.02 mmol) in DMSO-d_6 (0.7 mL) and D_2O (0.07 mL) and ^1H NMR spectra taken at intervals of 24 hours starting at 0 hours for 72 hours.

The obtained data is tabulated and plotted below (**Figure S7**).

Time (h)	MIDA ^1H integral	MIDA-DG ^1H integral	MIDA mmol	MIDA-DG mmol	MIDA %	MIDA-DG %
0	2.39	2.12	0.024	0.021	100	100
24	2.28	1.57	0.023	0.016	95	74
48	2.07	1.07	0.021	0.011	87	50
72	1.91	0.75	0.019	0.008	80	35

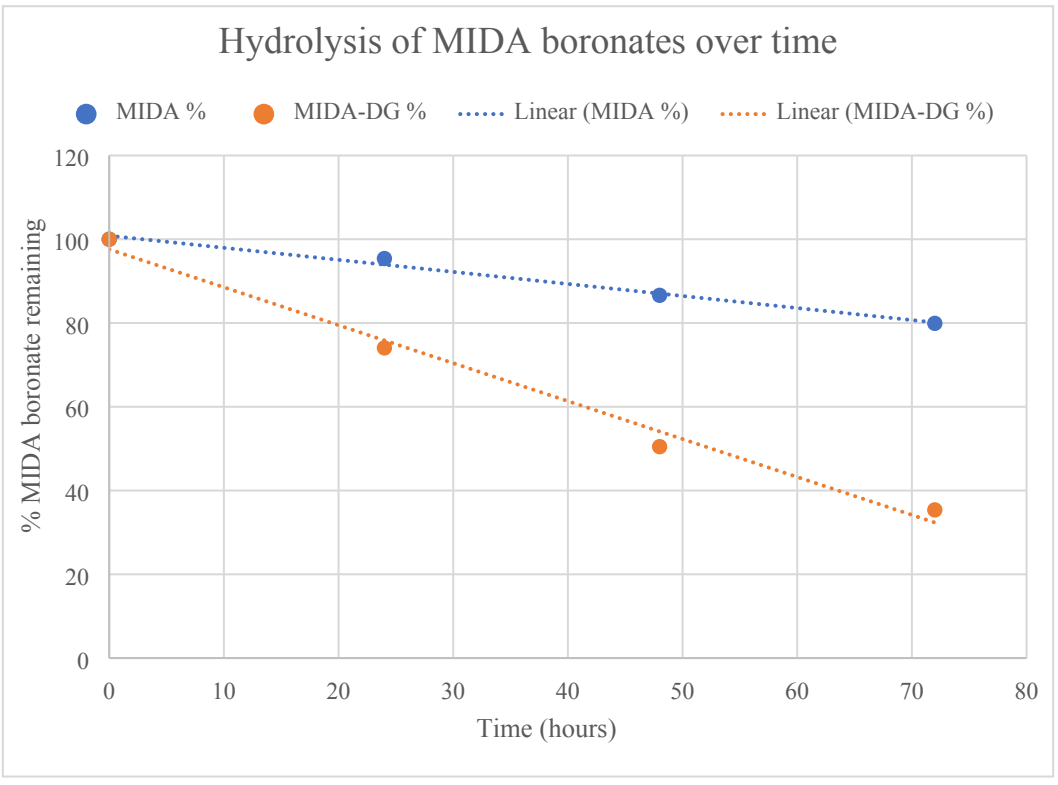


Figure S7: The measured half-lifes of the MIDA and MIDA-DG boronate esters

The half-life of PhB(MIDA-DG) is **53 hours**, the half-life of PhB(MIDA) is **177 hours**.

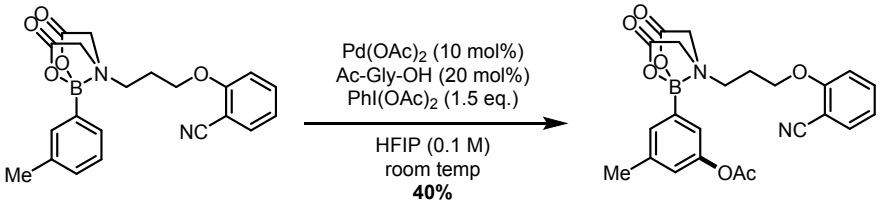
Comparison with other boronate esters. Our data can be compared with that published by Suginome et al. (**Table S6**).

Entry	Boronate ester	Half-life (hours)
1	PhB(dan)*	> 1440
2	PhB(MIDA)**	159
3	PhB(pin)*	78
4	PhB(MIDA-DG)	53
5	PhB(aam)*	10
6	PhB(pza)*	0.07

*Table S6: Comparison of boronate ester stabilities *Values taken from Suginome et al. Org. Lett. 2011, **13**, 2662-2665 **Value averaged from Suginome et al. and experimental data shown above. dan = 1,8-diaminonapthalene, pin = pinacol, MIDA = N-methyliminodiacetic acid, MIDA-DG = N-methyliminodiacetic acid tethered directing group, aam = anthranilamide, pza = 2-(pyrazol-5-yl)-aniline.*

Design of Experiment (DOE) Optimisation of C–H Acetoxylations

Applying conditions based upon those in the literature (*Nature* **2014**, *507*, 215), with 3-methylphenylboronic acid MIDA-DG ester (chosen to simplify analysis), a yield of 40% of only the *meta*-acetoxylated isomer was obtained (**Scheme S4**).



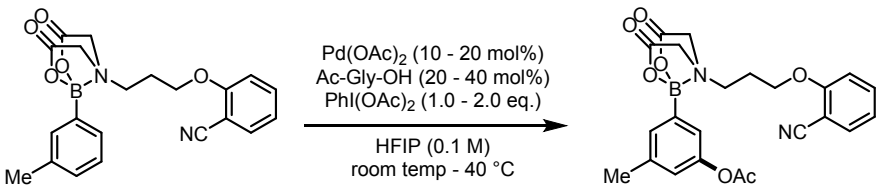
Scheme S4: Initial screening of conditions.

Once again, a DOE approach was taken to optimising the reaction conditions. The software used for the DOE optimisation was again JMP Pro 14, with the included definitive screening design tool used to generate the experiment designs. Four extra runs were included in the design in an attempt to improve the accuracy of the model.

General procedure for DOE reaction screening

PhB(MIDA-DG) (0.05 mmol, 19 mg), $Pd(OAc)_2$ (X eq.), Ac-gly-OH (X eq.) and $PhI(OAc)_2$ (X eq.) were added to a one dram (4 mL) vial. HFIP (1 mL) and CH_2Br_2 (internal standard, 1 eq., 3.5 mL) were then added and the vial sealed. The reaction mixture was added to a hot plate at the desired temperature and stirred for the desired time. On completion, a 0.1 mL aliquot was taken, diluted with MeCN-d_3, filtered and a ^{1}H NMR taken. The yield was calculated by comparison of integrals between the product and the CH_2Br_2 internal standard.

The initial DOE study focused on reaction time, temperature, the catalyst loading and the amount of $PhI(OAc)_2$ oxidant used. The ranges investigated are shown in **Table S7**.



Entry	Variable	Minimum Value	Maximum Value
1	Catalyst Loading (mol%)	10	20
2	Oxidant (equivalents)	23	40
3	Temperature (°C)	25	40
4	Time (hours)	6	24

Table S7: Variable value ranges used during the DOE study.

Percentage yield was chosen as the response. *Meta*:*para* selectivity was not included as the *meta* isomer was formed selectively. The experiments generated by the definitive screening model and the obtained yields are shown in **Table S8**.

Entry	Catalyst Loading (mol%)	Oxidant (equivalents)	Temperature (°C)	Time (hours)	Yield
1	10	2	33	6	33
2	10	1.5	25	6	37
3	20	1	40	6	43
4	20	2	25	24	42
5	10	1	25	24	45
6	10	1	40	6	46
7	20	1	33	24	43
8	20	2	40	6	43
9	15	1	25	6	43
10	10	2	25	24	38
11	15	1.5	33	15	33
12	20	1.5	40	24	56
13	15	2	40	24	45
14	10	1	40	24	48
15	20	2	25	6	42
16	10	2	40	15	33
17	20	1	25	15	37

Legend:	Minima	Midpoint	Maxima	Yield:	>40%

Table S8:Experiments performed and the results obtained during the DOE study.

With the experiments performed, the model was fit with personality set to 'Standard Least Squares' and emphasis on 'Effect Screening'. Unfortunately, the accuracy of the model was lower than those fit in previous studies, despite the inclusion of extra experiment. This can be seen from the predicted against actual yield plot (**Figure S8**) which has a number of outliers, a RMSE of 5.311 and a RSq value of just 0.41.

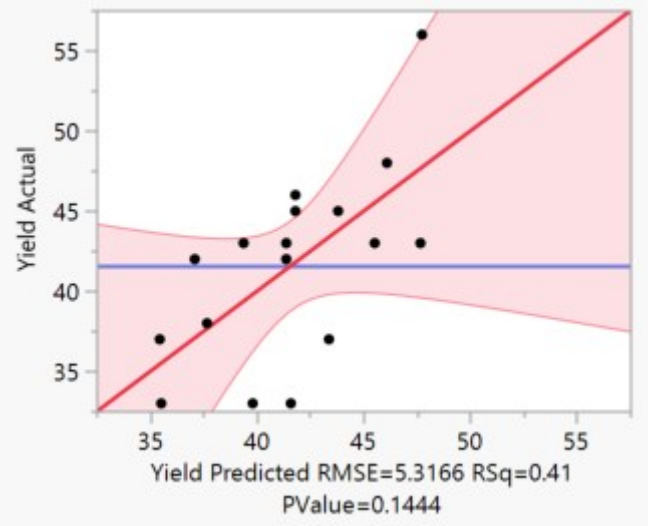


Figure S8: The fitted model had a low accuracy, as can be seen from the predicted vs actual yield plot.

Despite this, the prediction profiles generated by the model could be used to gain information about the reaction (**Figure S9**). A positive correlation was observed between all the variables and yield, except for the $PhI(OAc)_2$. This was indicative of a degradation pathway involving the oxidant.

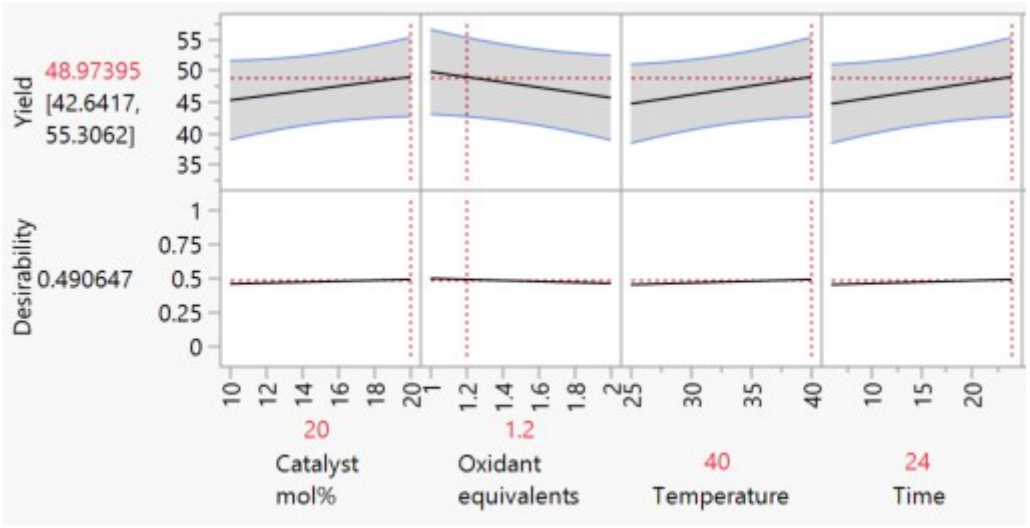


Figure S9: Prediction profiles generated during the DOE study, with the predicted optimal conditions

It was also observed that the model predicted a drop in just 3% yield on reducing the catalyst loading by 10% (**Figure S10**). Clearly, doubling the catalyst loading for such a small return in yield was not feasible and as such this variable was minimised.

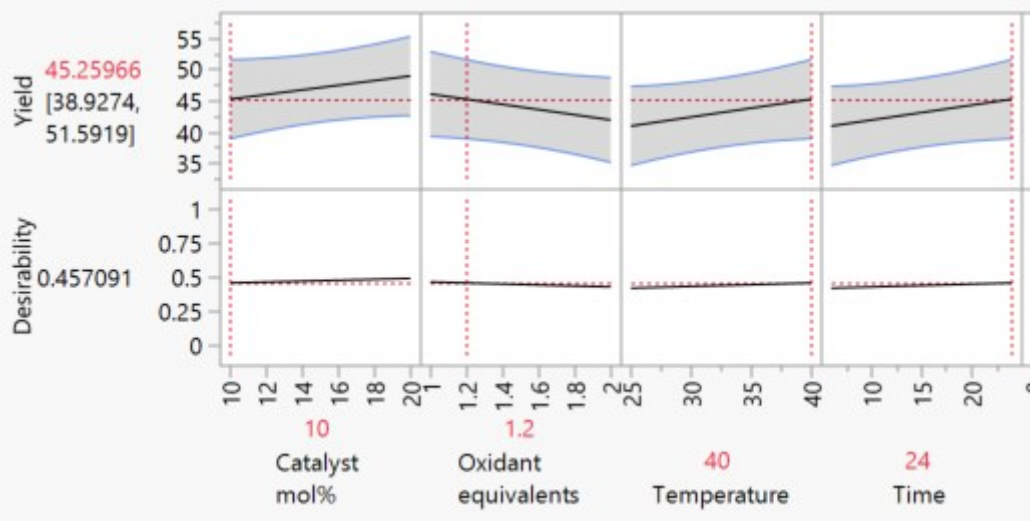
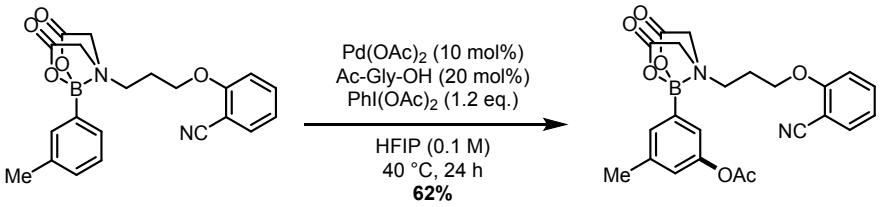


Figure S10: Lowering the catalyst loading was predicted to have little effect on yield.

Based on these above observations, the conditions expected to be optimal for the C–H acetoxylation are shown in **Scheme S5.**



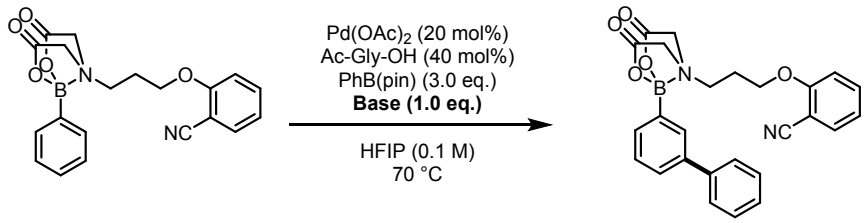
Scheme S5: Optimised C-H acetoxylation conditions.

Interestingly, a yield of 62% of only the desired *meta* isomer **14b** was achieved experimentally, an improvement of 17% on that predicted by the theoretical model (**Figure S10**).

Initial Investigations into C–H Arylations

Initial Hit Screen

An initial screen focusing only on the choice of base, with no oxidant present and identified CsF as a suitable base (**Table S9**).

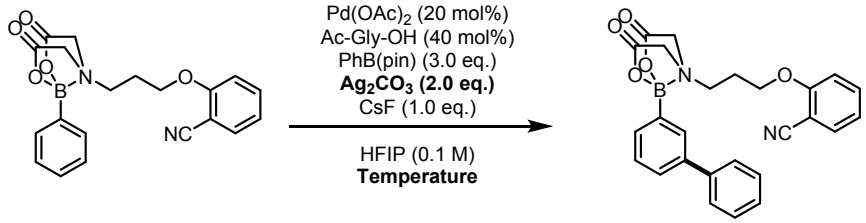


Entry	Base	Starting Material	Product
1	**CsF**	**34%**	**9%**
2	KF	26%	5%
3	Cs_2CO_3	21%	-
4	K_2CO_3	13%	-

Table S9: Screening for the effect of the base.

Temperature Screening

Ag_2CO_3 was then introduced as oxidant, with the screen investigating lowering the temperature of the reaction (**Table S10**).

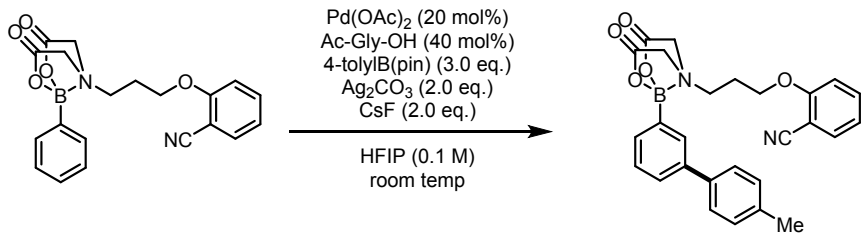


Entry	Temperature	Starting Material	Product	Di-functionalised Product
1	70 °C	32%	20%	5%
2	50 °C	25%	27%	10%
3	**25 °C**	**70%**	**28%**	**-**

Table S10: Screening for the effect of temperature.

Further Investigations into the base and alternative oxidants

With the knowledge that the reaction proceeded at room temperature, a screen of oxidants and bases was again performed. Cs_2CO_3 was elucidated as the optimal base at room temperature (**Table S11**).

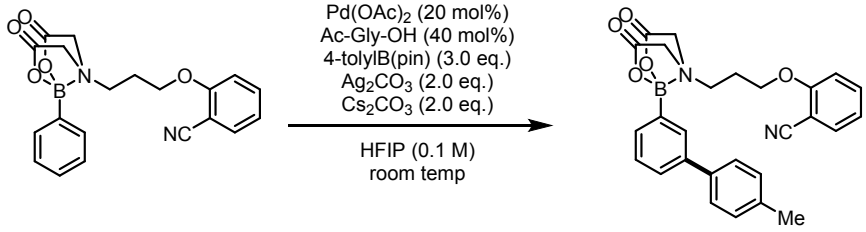


Entry	Change from Standard Conditions	Starting Material	Product
1	None	72%	22%
2	AgOAc as oxidant	68%	18%
3	Ag_2SO_4 as oxidant	80%	10%
4	No base	63%	19%
5	**Cs_2CO_3 as base**	**60%**	**30%**
6	K_3PO_4 as base	70%	3%
7	AgF as base	69%	16%

Table S11: Screen of oxidant/base combinations.

Investigations into Catalyst Poisoning

It was notable that no yields above 30% had been achieved. It was hypothesised that this might be due to catalyst poisoning. Consequently, subsequent reactions were performed with the addition of extra catalyst after the yield had plateaued (**Table S12**).



Entry	Change from Standard Conditions	Starting Material	Product
1	None	60%	30%
2	10% $Pd(OAc)_2$ + 10% $Pd(OAc)_2$ after 4 hours	68%	30%
3	20% $Pd(OAc)_2$ + 20% $Pd(OAc)_2$ after 4 hours	35%	50% (+15% di)

Table S12: Investigation of amount of catalyst.

The sequential addition of $Pd(OAc)_2$ 20% followed by 20% later achieved a synthetically useful yield of 50% of the *mono*-arylated product, and 15% of the *bis*-arylated product (total yield 65%), a catalyst turnover of around 1.5. It was speculated that the low turnover could reflect product inhibition, with C–H insertion into the product, followed by a second C–H insertion, forming an inactive *bis*-arylated Pd^{II} species (**Figure S11**).

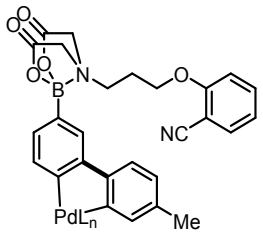
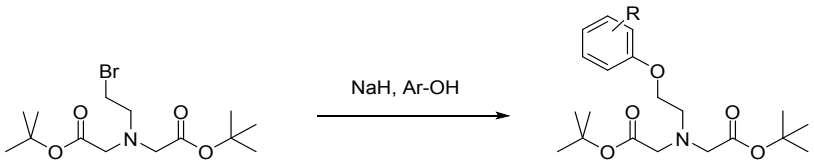


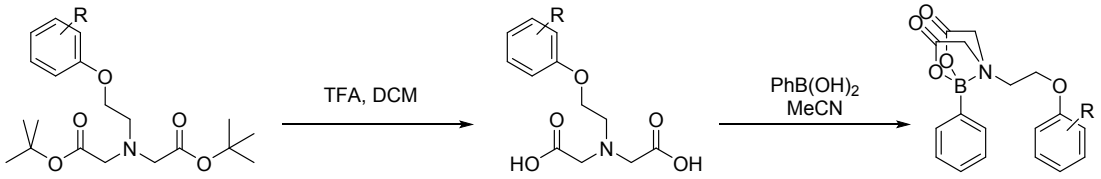
Figure S11: The possible unreactive bis-arylated Pd^{II} species causing product inhibition.

Synthesis of Directing Group Designs for Screening



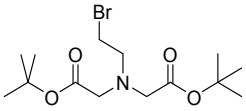
General Procedure A (alkylation with phenol compounds)

The appropriate phenol (1.1 eq.) was placed under an inert atmosphere, dissolved in anhydrous DMF (6.6 M) and cooled to 0 °C. Sodium hydride (60% in mineral oil, 1.2 eq.) was then added in portions over 5 minutes. The mixture was stirred for 30 minutes at 0 °C before the appropriate alkyl bromide (1 eq.) was added dropwise and the solution heated to 60 °C for 16 hours. The reaction was cooled to room temperature and slowly quenched with sat. aq. $NaHCO_3$ (1 mL). The reaction mixture was partitioned between Et_2O and sat. aq. $NaHCO_3$ and the layers separated. The organic fraction was further washed with sat. aq. $NaHCO_3$, before the combined aqueous phases were extracted with Et_2O. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo* to yield the desired product. Further purification *via* FCC was performed using Et_2O and hexanes if required.



General Procedure B (*tert*-butyl deprotection and boronic acid condensation).

The appropriate di-*tert* butyl ester (1 eq.) was placed under an inert atmosphere and dissolved in anhydrous $CHCl_2$ (0.5 M) and trifluoroacetic acid (10 eq.) added dropwise. The resulting solution was stirred at room temperature for 18 hours. On completion, the solvent was removed under vacuum, with MeCN added to azeotrope any excess trifluoroacetic acid. The crude material was added to a microwave vial, redissolved in MeCN:DMF (4:1, 0.4 M), phenylboronic acid (1 eq.) added and the vial sealed. The reaction mixture was heated to 95 °C for 90 minutes using microwave irradiation on a high absorption setting. The resulting mixture was dry loaded directly onto silica and purified using FCC (EtOAc and hexanes) to yield the desired product.



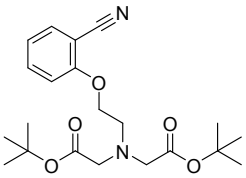
Di-*tert*-butyl 2,2'-((2-bromoethyl)azanediyl)diacetate

$NaHCO_3$ (7.68 g, 76.8 mmol) was placed under an atmosphere of N_2, anhydrous DMF (50 mL) and *tert*-butyl bromoacetate (10.2 mL, 69.2 mmol) added and the resulting suspension cooled to 0 °C. Ethanolamine (1.85 mL, 30.7 mmol) was added dropwise over a 5 minute period and the mixture stirred for 30 minutes at 0 °C before warming to room temperature and stirring for 18 hours. The reaction mixture was partitioned between Et_2O (150 mL) and sat. aq. $NaHCO_3$ (100 mL) and the layers separated. The organic fraction was further washed with sat. aq. $NaHCO_3$ (100 mL), before the combined aqueous phases were extracted with Et_2O (100 mL). The combined organic phases were washed with brine (100 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to yield the crude product as a yellow oil.

The crude product was dissolved in DCM (100 mL), PPh_3 (8.87 g, 33.8 mmol) added and the solution cooled to 0 °C. NBS (6.00 g, 33.8 mmol) was then added in portions over 10 minutes and the reaction mixture stirred at 0 °C for 1.5 hours. The solution was concentrated to an oil under vacuum, triturated with Et_2O and the precipitated $OPPh_3$ removed via filtration through silica. The filtrate was concentrated and purified *via* FCC (10% Et_2O in hexane) to yield the desired product as a clear oil (5.91 g, 16.8 mmol, 55%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.47 (s, 4H), 3.42 (t, *J* z= 7.4 Hz, 2H), 3.12 (t, *J* = 7.4 Hz, 2H), 1.46 (s, 18H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.4, 81.2, 56.7, 56.5, 30.2, 28.1.

The spectroscopic properties of the compound were consistent with the data pertaining to it in the literature (*J. Org. Chem.* 1993, 58, 1151-1158).



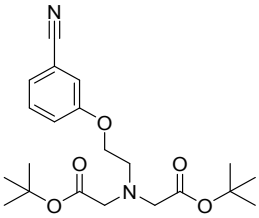
Di-*tert*-butyl 2,2'-((3-(2-cyanophenoxy)propyl)azanediyl)diacetate

General Procedure A: 2-cyanophenol (1.47 g, 4.00 mmol) was employed to obtain the desired product, which was isolated as a clear oil (1.43 g, 3.7 mmol, 92 %).

ν_{max}/cm^{-1} 2226, 1727, 1597, 1490, 1448, 1366, 1288, 1140, 752

HRMS (ES+ TOF) Calcd. for $C_{21}H_{31}N_2O_5$ ([M+H]$^+$): 391.2240. Found: 391.2228

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.48 (m, 2H), 7.05 – 6.95 (m, 2H), 4.27 (t, *J* = 5.8 Hz, 2H), 3.61 (s, 4H), 3.24 (t, *J* = 5.8 Hz, 2H), 1.47 (s, 18H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.88, 160.57, 134.28, 133.67, 120.72, 116.45, 112.21, 102.04, 81.15, 69.12, 57.35, 53.16, 28.15.



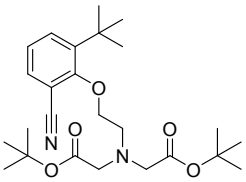
Di-*tert*-butyl 2,2'-((3-(3-cyanophenoxy)propyl)azanediyl)diacetate

General procedure A: 3-Cyanophenol (578 mg, 2.00 mmol) was employed to obtain the desired product, which was isolated as a yellow oil (558 mg, 1.43 mmol, 71%).

ν_{max}/cm^{-1} 2230, 1734, 1580, 1431, 1181, 1136, 793, 679

HRMS (ES+ TOF) Calcd. for $C_{21}H_{31}N_2O_5$ ([M+H]$^+$): 391.2240. Found: 391.2233

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (ddd, *J* = 8.2, 7.6, 0.7 Hz, 1H), 7.25 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.19 – 7.13 (m, 2H), 4.16 (t, *J* = 5.6 Hz, 2H), 3.57 (s, 4H), 3.20 (t, *J* = 5.6 Hz, 2H), 1.48 (s, 18H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 158.9, 130.3, 124.5, 119.7, 118.7, 117.7, 113.2, 81.2, 68.1, 57.1, 52.9, 28.2.



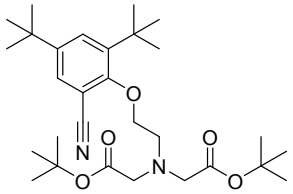
Di-*tert*-butyl 2,2'-((3-(2-(*tert*-butyl)-6-cyanophenoxy)propyl)azanediyl)diacetate

General procedure A: 2-Cyano-6-*tert*-butylphenol (530 mg, 3.03 mmol), synthesised using the literature procedure (*J. Org. Chem.* 2015, 80, 2, 1229-1234), was employed to obtain the desired product, which was isolated as a yellow oil (1.10 g, 2.47 mmol, 82%).

ν_{max}/cm^{-1} 2227, 1731, 1431, 1367, 1220, 1145, 988

HRMS (ES+ TOF) Calcd. for $C_{25}H_{39}N_2O_5$ ([M+H]$^+$): 447.2859. Found: 447.2874

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (ddd, *J* = 8.0, 1.8, 0.8 Hz, 1H), 7.46 (ddd, *J* = 7.6, 1.7, 0.8 Hz, 1H), 7.07 (td, *J* = 7.8, 0.8 Hz, 1H), 4.41 (td, *J* = 6.6, 0.8 Hz, 2H), 3.60 (d, *J* = 0.8 Hz, 4H), 3.35 (t, *J* = 6.5 Hz, 2H), 1.48 (d, *J* = 0.9 Hz, 18H), 1.40 (d, *J* = 0.8 Hz, 9H). The NMR spectra contains THF and Et_2O impurities.
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 161.1, 143.9, 132.2, 132.0, 123.3, 117.7, 106.4, 81.0, 73.5, 56.7, 54.1, 35.2, 30.4, 28.2. The NMR spectra contains THF and Et_2O impurities.



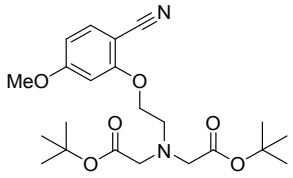
Di-*tert*-butyl 2,2'-((3-(2,4-di-*tert*-butyl-6-cyanophenoxy)propyl)azanediyl)diacetate

General procedure A: 2-Cyano-3,6-di-*tert*-butylphenol (231 mg, 1.00 mmol), synthesised using literature procedure (*J. Org. Chem.* 2015, 80, 2, 1229-1234), was employed to obtain the desired product, which was isolated as a yellow oil (450 mg, 0.90 mmol, 90%).

ν_{max}/cm^{-1} 2226, 1732, 1440, 1366, 1221, 1145, 988

HRMS (ES+ TOF) Calcd. for $C_{29}H_{47}N_2O_5$ ([M+H]$^+$): 503.3485. Found: 503.3498

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 2.5 Hz, 1H), 7.43 (d, *J* = 2.5 Hz, 1H), 4.38 (t, *J* = 6.5 Hz, 2H), 3.60 (s, 4H), 3.33 (t, *J* = 6.5 Hz, 2H), 1.48 (s, 18H), 1.40 (s, 9H), 1.31 (d, *J* = 1.9 Hz, 9H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 158.7, 146.0, 129.4, 128.8, 118.2, 105.7, 81.0, 73.4, 56.6, 54.1, 35.4, 31.2, 31.2, 30.5, 29.4, 28.2.



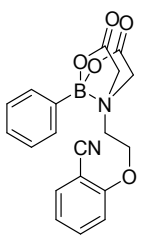
Di-*tert*-butyl 2,2'-((3-(2-cyano-5-methoxyphenoxy)propyl)azanediyl)diacetate

General procedure A: 2-Cyano-5-methoxyphenol (407 mg, 1.10 mmol), synthesised using the literature procedure (*J. Org. Chem.* 2015, 80, 2, 1229-1234), was employed to obtain the desired product, which was isolated as a yellow oil (412 mg, 0.98 mmol, 89%).

ν_{max}/cm^{-1} 2220, 1730, 1607, 1574, 1366, 1305, 1207, 1152, 1034

HRMS (ES + TOF) Calcd. for $C_{22}H_{33}N_2O_6$ ([M+H]$^+$): 421.2339. Found: 421.2339.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (dd, *J* = 8.4, 0.4 Hz, 1H), 6.55 – 6.50 (m, 2H), 4.24 (t, *J* = 5.9 Hz, 2H), 3.86 (s, 3H), 3.60 (s, 4H), 3.23 (t, *J* = 5.9 Hz, 2H), 1.47 (s, 18H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 164.5, 162.3, 134.7, 116.9, 106.4, 99.0, 94.2, 81.2, 69.1, 57.3, 55.7, 53.1, 28.2.



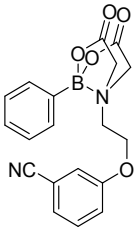
2-(2-(2,6-Dioxo-8-phenyltetrahydro-8H-4l4,8l4-[1,3,2]oxazaborolo[2,3-b][1,3,2]oxazaborol-4-yl)ethoxy)benzonitrile (2)

General procedure B: Di-*tert*-butyl 2,2'-((3-(2-cyanophenoxy)propyl)azanediyl)diacetate (702 mg, 1.79 mmol) was employed to obtain the desired product, which was isolated as an off-white solid (648 mg, 1.78 mmol, 99%).

v_{max}/cm^{-1} 2224, 1752, 1598, 1450, 1284, 1250, 1217, 1030, 998, 759.

HRMS (ES+ TOF) Calcd. for $C_{19}H_{18}BN_2O_5$ ([M+H]+): 365.1309. Found: 279.1029. This mass is in agreement with loss of the phenylboronic acid by fragmentation to reveal the iminodiacetic acid (Calculated mass for $C_{13}H_{15}N_2O_5$: 279.0981).

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.71 – 7.61 (m, 2H), 7.60 – 7.55 (m, 2H), 7.49 – 7.41 (m, 3H), 7.14 (td, *J* = 7.6, 0.9 Hz, 1H), 7.06 (dd, *J* = 8.6, 0.9 Hz, 1H), 4.38 – 4.29 (m, 4H), 4.14 (d, *J* = 17.3 Hz, 2H), 3.15 – 3.05 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.6, 159.5, 134.9, 133.7, 132.6, 129.5, 128.1, 121.9, 116.4, 112.4, 101.5, 63.9, 59.4, 57.0, 28.1.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 12.3.



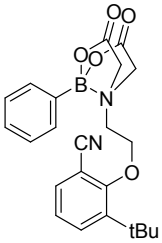
3-(2-(2,6-Dioxo-8-phenyltetrahydro-8H-4l4,8l4-[1,3,2]oxazaborolo[2,3-b][1,3,2]oxazaborol-4-yl)ethoxy)benzonitrile (6)

General procedure B: Di-*tert*-butyl 2,2'-((3-(3-cyanophenoxy)propyl)azanediyl)diacetate (514 mg, 1.31 mmol) was employed to obtain the desired product, which was isolated as a white solid (132 mg, 0.36 mmol, 28%).

v_{max}/cm^{-1} 2228, 1757, 1576, 1433, 1286, 1250, 1222, 1040, 998, 703

HRMS (ES- TOF) Calcd. for $C_{20}H_{18}BN_2O_7$ ([M-H]+HCO_2H): 409.1207. Found: 409.1220.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.59 – 7.53 (m, 2H), 7.52 – 7.42 (m, 4H), 7.40 – 7.36 (m, 1H), 7.30 (dd, *J* = 2.6, 1.4 Hz, 1H), 7.24 (ddd, *J* = 8.4, 2.7, 1.0 Hz, 1H), 4.27 (d, *J* = 17.1 Hz, 2H), 4.25 – 4.21 (m, 2H), 4.06 (d, *J* = 17.2 Hz, 2H), 3.04 (dd, *J* = 5.4, 4.4 Hz, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.6, 132.6, 130.7, 129.4, 128.1, 125.4, 119.9, 117.8, 113.3, 113.0, 63.5, 59.3, 57.2, 27.9.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 12.1.



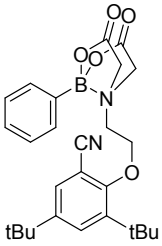
3-(*tert*-Butyl)-2-(2-(2,6-dioxo-8-phenyltetrahydro-8H-4l4,8l4-[1,3,2]oxazaborolo[2,3-b][1,3,2]oxazaborol-4-yl)ethoxy)benzonitrile (3)

General procedure B: Di-*tert*-butyl 2,2'-((3-(2-(*tert*-butyl)-6-cyanophenoxy)propyl)azanediyl) diacetate (334 mg, 0.75 mmol) was employed to obtain the desired product, which was isolated as a white solid (208 mg, 0.50 mmol, 66 %).

v_{max}/cm^{-1} 2228, 1757, 1433, 1268, 1220, 1028, 995, 846, 752, 702

HRMS (ES- TOF) Calcd. for $C_{24}H_{26}N_2O_7B$ ([M-H]+HCO_2H): 465.1833. Found: 465.1842.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.65 – 7.56 (m, 3H), 7.45 (d, *J* = 6.1 Hz, 3H), 7.25 (t, *J* = 7.8 Hz, 1H), 4.44 – 4.34 (m, 4H), 4.25 (d, *J* = 17.2 Hz, 2H), 3.15 (t, *J* = 5.0 Hz, 2H), 1.34 (s, 9H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.5, 159.4, 150.9, 144.1, 133.2, 132.7, 132.4, 129.5, 128.1, 125.0, 117.9, 70.1, 59.6, 58.1, 34.9, 30.0.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 12.4.



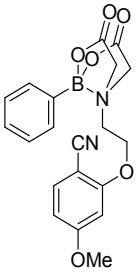
3,5-Di-*tert*-butyl-2-(2-(2,6-dioxo-8-phenyltetrahydro-8H-4l4,8l4-[1,3,2]oxazaborolo[2,3-b][1,3,2]oxazaborol-4-yl)ethoxy)benzonitrile (4)

General procedure B: Di-*tert*-butyl 2,2'-((3-(2,4-di-*tert*-butyl-6-cyanophenoxy)propyl)azanediyl) diacetate (312 mg, 0.62 mmol) was employed to obtain the desired product, which was isolated as a white solid (174 mg, 0.37 mmol, 60 %).

ν_{max}/cm^{-1} 2227, 1761, 1435, 1223, 1030, 997, 846, 703

HRMS (ES- TOF) Calcd. for $C_{28}H_{34}BN_2O_7$ ([M-H]+HCO_2H): 521.2459. Found: 521.2476.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.70 (d, *J* = 2.4 Hz, 1H), 7.62 (d, *J* = 2.5 Hz, 1H), 7.60 (m, 2H), 7.49 – 7.41 (m, 3H), 4.40 – 4.34 (m, 4H), 4.24 (d, *J* = 17.1 Hz, 2H), 3.13 (dd, *J* = 5.4, 4.4 Hz, 2H), 1.34 (s, 9H), 1.32 (s, 9H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.5, 157.1, 147.9, 143.2, 132.7, 130.4, 129.5, 129.1, 128.0, 118.1, 106.4, 69.9, 59.6, 58.1, 35.1, 34.5, 30.2, 30.0.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 12.4.



2-(2-(2,6-Dioxo-8-phenyltetrahydro-8H-4l4,8l4-[1,3,2]oxazaborolo[2,3-b][1,3,2]oxazaborol-4-yl)ethoxy)-4-methoxybenzonitrile (5)

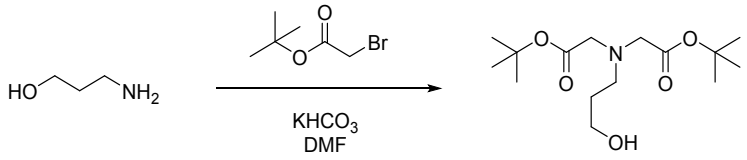
General procedure B: di-*tert*-butyl 2,2'-((3-(2-cyano-5-methoxyphenoxy)propyl)azanediyl)diacetate (222 mg, 0.52 mmol) was employed to obtain the desired product, which was isolated as a crystalline white solid (206 mg, 0.52 mmol, 100%).

ν_{max}/cm^{-1} 2221, 1759, 1606, 1434, 1267, 1206, 1030, 999, 756, 705.

HRMS (ES- TOF) Calcd. for $C_{20}H_{18}N_2O_6B$ ([M-H]$^-$): 393.1258. Found: 393.1260.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.62 – 7.54 (m, 3H), 7.48 – 7.41 (m, 3H), 6.68 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.55 (d, *J* = 2.3 Hz, 1H), 4.34 – 4.27 (m, 4H), 4.13 (d, *J* = 17.3 Hz, 2H), 3.86 (s, 3H), 3.12 – 3.05 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.6, 164.8, 161.2, 134.9, 132.6, 129.5, 128.1, 116.7, 107.2, 99.3, 93.5, 65.3, 64.0, 59.4, 57.0, 55.8.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 12.3.

Large Scale Synthesis of the MIDA-DG HCl salt (8)



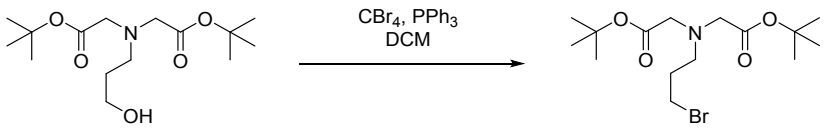
Di-*tert*-butyl 2,2'-((3-hydroxypropyl)azanediyl)diacetate

To a suspension of $KHCO_3$ (25.0 g, 250 mmol) in anhydrous DMF (170 mL) under N_2, was added *tert*-butyl bromoacetate (29.5 mL, 200 mmol) at 0 °C. 3-Aminopropan-1-ol (8.1 mL, 100 mmol) was subsequently added dropwise, the suspension stirred for 30 minutes at 0 °C then allowed to warm to room temperature and stirred until no *tert*-butyl bromoacetate was visible *via* TLC (around 6 hours). The reaction mixture was diluted with Et_2O (500 mL) and sat. aq. $NaHCO_3$ (300 mL) and the layers separated. The organic layer was washed with further $NaHCO_3$ (300 mL), the combined aqueous layers extracted with Et_2O (300 mL) and the organic extracts combined. The combined organic layers were then washed with brine (300 mL), dried with $MgSO_4$, filtered and concentrated *in vacuo* to yield the desired product as a clear oil (30.0 g, 99 mmol, 99%).

ν_{max}/cm^{-1} 3440, 2978, 2937, 1730, 1368, 1290, 1077, 1252, 1223, 1148, 1077, 846

HRMS (ES+ TOF) Calcd. for $C_{15}H_{30}NO_5$ ($[M+H]^+$): 304.2124. Found: 304.2126.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.37 (s, 1H), 3.84 – 3.78 (m, 2H), 3.41 (s, 4H), 2.90 – 2.82 (m, 2H), 1.69 (dp, *J* = 10.3, 5.5 Hz, 2H), 1.49 (s, 18H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.5, 81.5, 62.1, 55.8, 51.9, 28.6, 28.1.



Di-*tert*-butyl 2,2'-((3-bromopropyl)azanediyl)diacetate

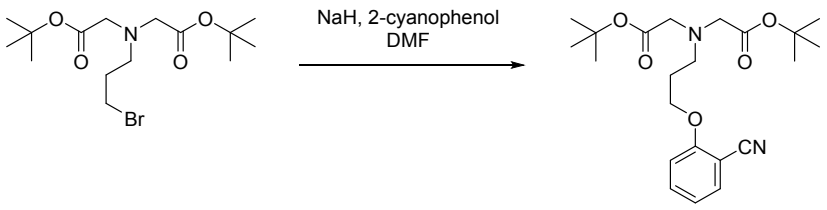
To di-*tert*-butyl 2,2'-((3-hydroxypropyl)azanediyl)diacetate (30.0 g, 99 mmol) in anhydrous DCM (170 mL), under N_2, at 0 °C was added PPh_3 (31.3 g, 119 mmol). CBr_4 (39.5 g, 119 mmol) was then added slowly in portions over 15 minutes. The resulting solution was stirred at 0 °C for 1 hour, until TLC indicated complete conversion. Et_2O (1250 mL) was added slowly to the reaction mixture at 0 °C to induce precipitation of a white solid. The suspension was stirred at 0 °C for a further half an hour before the precipitate was removed by filtration through cotton wool and the filtrate concentrated under vacuum. The residue was redissolved in Et_2O (200 mL) and the suspension filtered through silica and concentrated. This process was then repeated again to remove all remaining $OPPh_3$, yielding the desired product as a clear oil (36.1 g, 99 mmol, 100%).

ν_{max}/cm^{-1} 2978, 2937, 1737, 1457, 1368, 1252, 1152, 842

HRMS (ES+ TOF) Calcd. for $C_{15}H_{30}NO_5$ ($[M+H]^+$): 304.2124. Found: 304.2126.f

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.55 (t, *J* = 6.6 Hz, 2H), 3.45 (s, 4H), 2.88 (t, *J* = 6.8 Hz, 2H), 2.02 (p, *J* = 6.7 Hz, 2H), 1.49 (s, 18H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 81.1, 56.3, 52.6, 31.8, 31.4, 28.2.

The spectroscopic properties of the compound were consistent with the data pertaining to it in the literature (*Bioorg. Med. Chem. Lett.* 2008, 18, 5233-5237).



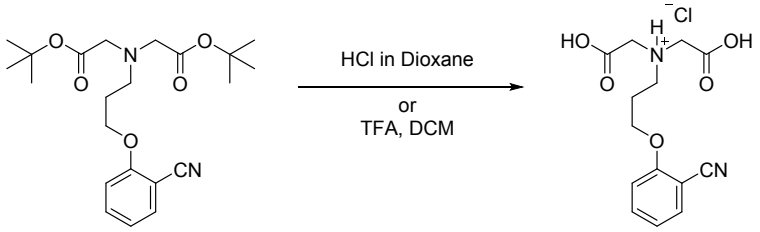
Di-*tert*-butyl 2,2'-((3-(2-cyanophenoxy)propyl)azanediyl)diacetate

To 2-cyanophenol (13.1 g, 110 mmol) in anhydrous DMF (500 mL) under N_2 at 0 °C was slowly added NaH (60% suspension in mineral oil) (4.4 g, 110 mmol) in small portions, causing effervescence. After addition, the reaction mixture was stirred for a further 30 minutes at 0 °C. To the suspension was added di-*tert*-butyl 2,2'-((3-bromopropyl)azanediyl)diacetate (13.1 g) as a solution in anhydrous DMF (120 mL). The reaction mixture was then heated to 60 °C and stirred for 3 hours. The reaction mixture was diluted with Et_2O (1500 mL) and sat. aq. $NaHCO_3$ (1000 mL) and the layers separated. The organic layer was washed with further $NaHCO_3$ (1000 mL), the combined aqueous layers extracted with Et_2O (1000 mL) and the organic extracts combined. The combined organic layers were then washed with brine (1500 mL), dried with $MgSO_4$, filtered and concentrated *in vacuo* to yield the desired product as a dark orange oil. The oil was dry loaded onto silica using DCM, and washed with hexanes to remove residual mineral oil. The product was then eluted using 40% EtOAc in hexane to yield the product as a clear yellow oil (33.5 g, 82.8 mmol, 84%).

ν_{max}/cm^{-1} 2227, 1735, 1493, 1451, 1367, 1289, 1255, 1145, 755

HRMS (ES+ TOF) Calcd. for $C_{22}H_{33}N_2O_5$ ([M+H]$^+$): 405.2389. Found: 405.2392.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.46 (m, 2H), 7.08 – 6.94 (m, 2H), 4.23 (t, *J* = 6.3 Hz, 2H), 3.46 (s, 4H), 2.95 (t, *J* = 6.7 Hz, 2H), 2.02 (p, *J* = 6.5 Hz, 2H), 1.47 (s, 18H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 160.8, 134.3, 133.7, 120.5, 116.5, 112.5, 102.0, 81.1, 66.8, 56.2, 50.8, 28.2, 27.6.



2,2'-((3-(2-Cyanophenoxy)propyl)azanediyl)diacetic acid hydrochloride salt (8)

To di-*tert*-butyl 2,2'-((3-(2-cyanophenoxy)propyl)azanediyl)diacetate (16.0 g, 39.6 mmol) was added HCl in dioxane (3.7 – 4.3 N, 99 mL) and the reaction stirred overnight at room temperature under a nitrogen atmosphere. An off-white precipitate was observed forming after stirring for 24 hours, indicating completion of the reaction. The suspension was diluted with Et_2O (~ 500 mL) and cooled to 0 °C for 2 hours. After this time, the precipitate was collected using Buchner filtration under a stream of nitrogen, washing with copious Et_2O.

NB: The hydrochloride salt of the product is highly hygroscopic when wet. If a stream of nitrogen is not used, a brown gum will quickly form when drying under air.

The off-white solid was collected and further dried at 40 °C under high vacuum overnight, yielding the desired MIDA-DG hydrochloride salt (11.9 g, 36.4 mmol, 92%).

ν_{max}/cm^{-1} 2229, 1733, 1599, 1495, 1450, 1416, 1379, 1290, 1200, 1118, 1081, 951, 872, 831, 757

HRMS (ES+ TOF) Calcd. for $C_{14}H_{17}N_2O_5$ ([M+H]$^+$): 293.1137. Found: 293.1142.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.75 – 7.70 (m, 1H), 7.67 (t, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 4.22 (t, *J* = 6.1 Hz, 2H), 4.10 (s, 4H), 3.34 (t, *J* = 7.7 Hz, 2H), 2.15 (t, *J* = 7.5 Hz, 2H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 168.8, 160.3, 135.6, 134.2, 121.7, 116.7, 113.6, 101.1, 66.6, 54.6, 52.9, 24.5.

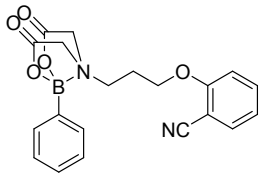
A small MeOH impurity is present in the NMR spectra.

2,2'-((3-(2-Cyanophenoxy)propyl)azanediyl)diacetic acid trifluoroacetic acid salt (8)

di-*tert*-butyl 2,2'-((3-(2-cyanophenoxy)propyl)azanediyl)diacetate (9.6 g, 23.8 mmol) was placed under an inert atmosphere and dissolved in anhydrous $CHCl_2$ (75 mL) and trifluoroacetic acid (13.6 mL, 10 eq.) added dropwise. The resulting solution was stirred at room temperature for 18 hours. On completion, the solvent was removed under vacuum, with MeCN added to azeotrope any excess trifluoroacetic acid, to yield the desired TFA salt as a highly hygroscopic orange solid (8.9 g, 21.9 mmol, 92%).

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.69 – 7.62 (m, 2H), 7.18 – 7.08 (m, 2H), 4.25 (t, *J* = 5.7 Hz, 2H), 4.19 (s, 4H), 3.67 – 3.52 (m, 2H), 2.34 – 2.21 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 166.8, 159.9, 158.6, 134.9, 133.7, 121.5, 116.2, 114.2, 112.9, 101.5, 66.1, 55.0, 54.7, 23.7
^{19}F NMR (377 MHz, Acetonitrile-d_3) δ -76.7 (s).

Synthesis of arylboronic acid MIDA-DG esters



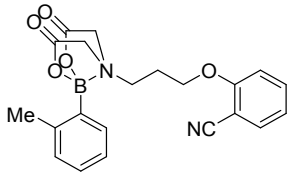
Phenylboronic acid MIDA-DG ester (7)

Phenylboronic acid (363 mg, 3.00 mmol) and the MIDA-DG hydrochloric acid salt (984 mg, 3.00 mmol) were dissolved in MeCN (30 mL) and refluxed for 24 hours. The reaction mixture was cooled to room temperature, dry loaded onto silica and purified *via* FCC (75% EtOAc in hexane).The product was isolated as an off-white solid (1.06 g, 2.70 mmol, 90%).

ν_{max}/cm^{-1} 2223, 1763, 1595, 1475, 1438, 1224, 1041, 1022, 754, 704

HRMS (ES+ TOF) Calcd. for $C_{20}H_{20}N_2O_5B$ ($[M+H]^+$): 379.1465. Found: 379.1481.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.63 – 7.55 (m, 2H), 7.54 – 7.50 (m, 2H), 7.41 – 7.37 (m, 3H), 7.07 (td, *J* = 7.6, 0.9 Hz, 1H), 6.99 (dd, *J* = 8.6, 0.9 Hz, 1H), 4.09 (d, *J* = 17.1 Hz, 2H), 4.02 (d, *J* = 17.1 Hz, 2H), 3.97 (t, *J* = 6.2 Hz, 2H), 2.86 – 2.79 (m, 2H), 2.15 – 2.05 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.5, 159.9, 134.8, 133.7, 132.5, 129.3, 128.0, 121.3, 116.1, 112.8, 101.4, 65.8, 58.9, 55.9, 23.8.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.8.



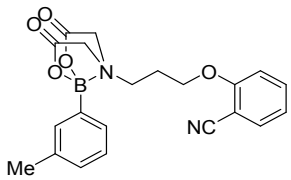
2-Methylphenylboronic acid MIDA-DG ester (13)

2-Methylphenylboronic acid (272 mg, 2.00 mmol) and the MIDA-DG trifluoracetic acid salt (812 mg, 2.00 mmol) were dissolved in MeCN (20 mL) and refluxed for 24 hours. The reaction mixture was cooled to room temperature, dry loaded onto silica and purified *via* FCC (75% EtOAc in hexane).The product was isolated as an off-white solid (685 mg, 1.70 mmol, 85%).

ν_{max}/cm^{-1} 2222, 1759, 1595, 1495, 1450, 1286, 1238, 1204, 1018, 857, 757.

HRMS (ES+ TOF) Calcd. For $C_{21}H_{21}BN_2O_5K$ ($[M + K]^+$): 431.1181. Found: 431.1183.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.63 – 7.55 (m, 2H), 7.44 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.28 (td, *J* = 7.5, 1.6 Hz, 1H), 7.23 – 7.15 (m, 2H), 7.07 (td, *J* = 7.6, 0.9 Hz, 1H), 7.02 – 6.98 (m, 1H), 4.09 (d, *J* = 17.2 Hz, 2H), 4.05 – 3.98 (m, 4H), 2.87 – 2.81 (m, 2H), 2.41 (s, 3H), 2.19 – 2.08 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.5, 159.9, 142.4, 134.8, 134.1, 133.7, 131.1, 129.4, 125.3, 121.3, 116.1, 112.7, 101.3, 65.7, 59.6, 55.9, 24.0, 22.2.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 12.5.



3-Methylphenylboronic acid MIDA-DG ester (14)

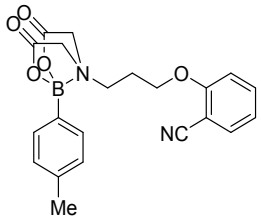
3-Methylphenylboronic acid (476 mg, 3.50 mmol) and the MIDA-DG trifluoracetic acid salt (1.42 g, 3.50 mmol) were dissolved in MeCN (35 mL) and refluxed for 6 hours. The reaction mixture was cooled to room temperature,

dry loaded onto silica and purified *via* FCC (washed with Et_2O then eluted with MeCN 50% in Et_2O).The product was isolated as a yellow crystalline solid (1.34 g, 3.38 mmol, 97%).

ν_{max}/cm^{-1} 2225, 1744, 1599, 1490, 1450, 1290, 1256, 1166, 1006, 864, 783, 753, 708.

HRMS (ES+ TOF) Calcd. For $C_{21}H_{21}BN_2O_5K$ ([M + K]$^+$): 431.1181. Found: 431.1178.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.63 – 7.58 (m, 1H), 7.58 – 7.54 (m, 1H), 7.34 – 7.28 (m, 2H), 7.26 (td, *J* = 7.3, 0.7 Hz, 1H), 7.23 – 7.17 (m, 1H), 7.07 (td, *J* = 7.6, 0.9 Hz, 1H), 6.98 (dd, *J* = 8.6, 1.1 Hz, 1H), 4.08 (d, *J* = 17.1 Hz, 2H), 4.02 (d, *J* = 17.1 Hz, 2H), 3.97 (t, *J* = 6.2 Hz, 2H), 2.86 – 2.80 (m, 2H), 2.34 (s, *J* = 0.7 Hz, 3H), 2.15 – 2.05 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.6, 159.9, 137.4, 134.8, 133.7, 133.1, 130.0, 129.5, 127.9, 121.3, 116.1, 112.7, 101.4, 65.8, 58.9, 55.9.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.8.



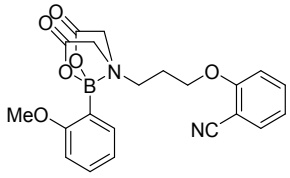
4-Methylphenylboronic acid MIDA-DG ester (15)

4-Methylphenylboronic acid (136 mg, 1.00 mmol) and the MIDA-DG trifluoracetic acid salt (406 mg, 1.00 mmol) were dissolved in MeCN (10 mL) and refluxed for 6 hours. The reaction mixture was cooled to room temperature, dry loaded onto silica and purified *via* FCC (washed with Et_2O then eluted with MeCN 50% in Et_2O).The product was isolated as an off-white solid (329 mg, 0.84 mmol, 84%).

ν_{max}/cm^{-1} 2225, 1767, 1595, 1476, 1279, 1044, 943, 869, 813, 764.

HRMS (ES+ TOF) Calcd. For $C_{21}H_{22}BN_2O_5$ ([M+H]$^+$): 393.1622. Found: 393.1639.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.63 – 7.55 (m, 2H), 7.42 – 7.37 (m, 2H), 7.22 – 7.17 (m, 2H), 7.07 (td, *J* = 7.6, 0.9 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 4.07 (d, *J* = 17.1 Hz, 2H), 4.03 – 3.96 (m, 4H), 2.86 – 2.78 (m, 2H), 2.34 (s, 3H), 2.14 – 2.05 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.6, 159.7, 139.1, 134.8, 133.7, 132.5, 128.7, 121.3, 116.1, 112.8, 101.4, 65.8, 58.8, 55.9, 23.8.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 12.0.



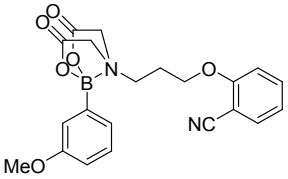
2-Methoxyphenylboronic acid MIDA-DG ester (10)

A microwave vial was charged with 2-methoxyphenylboronic acid (152 mg, 1.00 mmol), the MIDA-DG hydrochloric acid salt (328 mg, 1.00 mmol) and anhydrous MeCN (1 mL). The reaction mixture was irradiated in a microwave to 130 ˚C for 10 minutes before being allowed to cool to room temperature and concentrated *in vacuo*. To the resulting solid was added water (5 mL) and Et_2O (5 mL) and the suspension sonicated to cause trituration. After cooling to 0 °C, the resulting solid was collected, washed with ice cold water (2.5 mL) then ice cold Et_2O (2.5 mL) and air dried. The product was isolated as an off-white solid (188 mg, 0.46 mmol, 46%).

ν_{max}/cm^{-1} 2229, 1774, 1595, 1487,1453, 1316, 1230, 1029, 984, 749.

HRMS (ES+ TOF) Calcd. For $C_{21}H_{21}BN_2O_6K$ ([M + K]$^+$): 447.1130. Found: 447.1133.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.62 – 7.53 (m, 3H), 7.40 – 7.31 (m, 1H), 7.06 (td, *J* = 7.6, 0.9 Hz, 1H), 6.98 – 6.92 (m, 3H), 4.15 (d, *J* = 16.9 Hz, 2H), 4.02 (d, *J* = 17.0 Hz, 2H), 3.98 (t, *J* = 6.1 Hz, 2H), 3.80 (s, 3H), 3.06 – 2.99 (m, 2H), 2.15 – 2.06 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.7, 162.3, 159.8, 134.8, 134.3, 133.7, 131.0, 121.2, 120.5, 116.1, 112.5, 110.3, 101.3, 65.8, 60.6, 55.6, 54.6, 23.8.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.9.



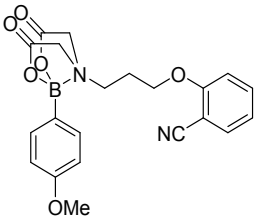
3-Methoxyphenylboronic acid MIDA-DG ester (11)

A microwave vial was charged with 3-methoxyphenylboronic acid (152 mg, 1.00 mmol), the MIDA-DG hydrochloric acid salt (328 mg, 1.00 mmol) and anhydrous MeCN (1 mL). The reaction mixture was irradiated in a microwave to 130 ˚C for 10 minutes before being allowed to cool to room temperature and concentrated *in vacuo*. To the resulting solid was added water (5 mL) and Et_2O (5 mL) and the suspension sonicated to cause trituration. After cooling to 0 °C, the resulting solid was collected, washed with ice cold water (2.5 mL) then ice cold Et_2O (2.5 mL) and air dried. The product was isolated as an off-white solid (304 mg, 0.75 mmol, 75%).

ν_{max}/cm^{-1} 2229, 1748, 1599, 1494, 1454, 1416, 1293, 1264, 1021, 999, 790, 757, 708

HRMS (ES+ TOF) Calcd. For $C_{21}H_{21}BN_2O_6K$ ([M + K]$^+$): 447.1130. Found: 447.1129.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.63 – 7.54 (m, 2H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.10 – 7.01 (m, 3H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.94 (ddd, *J* = 8.2, 2.7, 1.0 Hz, 1H), 4.09 (d, *J* = 17.1 Hz, 2H), 4.05 – 3.97 (m, 4H), 3.80 (s, 3H), 2.88 – 2.81 (m, 2H), 2.17 – 2.04 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.5, 159.9, 159.4, 134.8, 133.7, 129.3, 124.6, 121.3, 116.1, 115.0, 112.8, 101.4, 65.8, 58.9, 55.9, 54.7, 23.8. One Ar-C peak obscured by solvent peak.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.7.



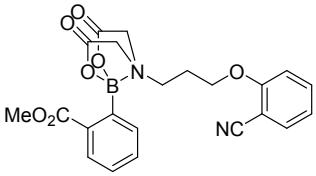
4-Methoxyphenylboronic acid MIDA-DG ester (12)

A microwave vial was charged with 4-methoxyphenylboronic acid (152 mg, 1.00 mmol), the MIDA-DG hydrochloric acid salt (328 mg, 1.00 mmol) and anhydrous MeCN (1 mL). The reaction mixture was irradiated in a microwave to 130 ˚C for 10 minutes before being allowed to cool to room temperature and concentrated *in vacuo*. To the resulting solid was added water (5 mL) and Et_2O (5 mL) and the suspension sonicated to cause trituration. Unfortunately, trituration proved unsuccessful. The solvents were removed under a stream of nitrogen, the residue dissolved in MeCN (5 mL), dry loaded onto silica and purified by FCC (75% EtOAc in hexane). The product was isolated as a white crystalline solid (266 mg, 0.65 mmol, 65%).

ν_{max}/cm^{-1} 2225, 1748, 1602, 1513, 1450, 1290, 1219, 1179, 1018, 984, 861, 824, 757.

HRMS (ES+ TOF) Calcd. For $C_{21}H_{21}BN_2O_6K$ ([M + K]$^+$): 447.1130. Found: 447.1138.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.63 – 7.54 (m, 2H), 7.45 – 7.40 (m, 2H), 7.07 (td, *J* = 7.6, 0.9 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 6.95 – 6.90 (m, 2H), 4.06 (d, *J* = 17.1 Hz, 2H), 4.02 – 3.96 (m, 4H), 3.79 (s, 3H), 2.86 – 2.78 (m, 2H), 2.14 – 2.04 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.5, 160.7, 159.9, 134.8, 133.9, 133.7, 121.3, 116.1, 113.5, 112.8, 101.4, 65.8, 58.8, 55.9, 54.7, 23.8.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 12.0.



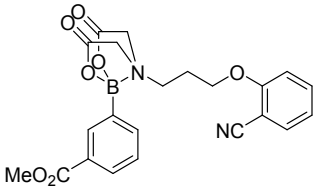
2-Methoxycarbonylphenylboronic acid MIDA-DG ester (16)

2-Methoxycarbonylphenylboronic acid (180 mg, 1.00 mmol) and the MIDA-DG hydrochloric acid salt (328 mg, 1.00 mmol) were dissolved in MeCN (10 mL) and refluxed for 16 hours. The reaction mixture was cooled to room temperature, dry loaded onto silica and purified *via* FCC (75% EtOAc in hexane).The product was isolated as a white crystalline solid (342 mg, 0.78 mmol, 78%).

ν_{max}/cm^{-1} 2225, 1756, 1715, 1595, 1491, 1450, 1290, 1260, 1197, 1133, 1006, 954, 865, 753

HRMS (ES+ TOF) Calcd. For $C_{22}H_{21}BN_2O_7Na$ ([M + Na]$^+$): 459.1340. Found: 459.1344.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.69 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.65 – 7.51 (m, 5H), 7.50 – 7.45 (m, 1H), 7.06 (tt, *J* = 7.6, 0.8 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 4.27 (d, *J* = 17.2 Hz, 2H), 4.06 – 3.99 (m, 5H), 3.82 (s, 4H), 3.19 (dd, *J* = 10.1, 6.1 Hz, 2H), 2.22 (dd, *J* = 9.9, 6.3 Hz, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 171.40, 168.87, 159.83, 137.13, 134.75, 134.72, 133.70, 130.34, 129.14, 128.44, 121.25, 116.01, 112.73, 101.37, 65.81, 61.28, 57.89, 52.37, 24.21.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 12.03.



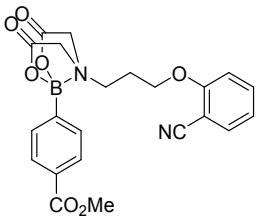
3-Methoxycarbonylphenylboronic acid MIDA-DG ester (17)

3-Methoxycarbonylphenylboronic acid (180 mg, 1.00 mmol) and the MIDA-DG hydrochloric acid salt (328 mg, 1.00 mmol) were dissolved in anhydrous MeCN (10 mL) and refluxed for 16 hours. The reaction mixture was then concentrated *in vacuo*. To the resulting residue was added water (5 mL) and Et_2O (5 mL) and the suspension sonicated to cause trituration. After cooling to 0 °C, the resulting solid was collected, washed with ice cold water (2.5 mL) then ice cold Et_2O (2.5 mL) and air dried. The product was isolated as an off-white solid (304 mg, 0.70 mmol, 70%).

ν_{max}/cm^{-1} 2229, 1767, 1707, 1599, 1495, 1446, 1290, 1215, 1006, 973, 865, 753, 705

HRMS (ES+ TOF) Calcd. For $C_{22}H_{21}BN_2O_7Na$ ([M + Na]$^+$): 459.1340. Found: 459.1339.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.13 (s, 1H), 8.01 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.75 (dt, *J* = 7.5, 1.4 Hz, 1H), 7.61 – 7.47 (m, 3H), 7.06 (td, *J* = 7.6, 0.9 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 4.12 (d, *J* = 17.2 Hz, 2H), 4.05 (d, *J* = 17.2 Hz, 2H), 3.98 (t, *J* = 6.2 Hz, 2H), 3.89 (s, 3H), 2.87 – 2.78 (m, 2H), 2.15 – 2.05 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.4, 166.9, 159.8, 137.2, 134.7, 133.6, 133.2, 130.2, 129.8, 128.3, 121.3, 116.0, 112.7, 101.4, 65.7, 59.1, 56.2, 51.7, 23.8.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.6.



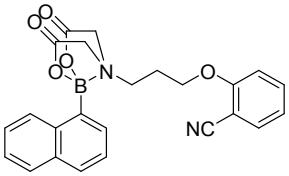
4-Methoxycarbonylphenylboronic acid MIDA-DG ester (18)

4-Methoxycarbonylphenylboronic acid (180 mg, 1.00 mmol) and the MIDA-DG hydrochloric acid salt (328 mg, 1.00 mmol) were dissolved in MeCN (10 mL) and refluxed for 16 hours. The reaction mixture was cooled to room temperature, dry loaded onto silica and purified *via* FCC (washed with Et_2O then eluted with EtOAc).The product was isolated as a white crystalline solid (336 mg, 0.77 mmol, 77%).

ν_{max}/cm^{-1} 2225, 1759, 1715, 1599, 1491, 1450, 1394, 1275, 1219, 1111, 1044, 999, 842, 764, 708

HRMS (ES+ TOF) Calcd. For $C_{22}H_{21}BN_2O_7K$ ($[M + K]^+$): 475.1079. Found: 475.1082.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.99 – 7.94 (m, 2H), 7.66 – 7.61 (m, 2H), 7.61 – 7.53 (m, 2H), 7.05 (td, *J* = 7.6, 0.9 Hz, 1H), 7.00 – 6.94 (m, 1H), 4.11 (d, *J* = 17.1 Hz, 2H), 4.05 (d, *J* = 17.2 Hz, 2H), 3.98 (t, *J* = 6.2 Hz, 2H), 3.89 (s, 3H), 2.86 – 2.80 (m, 2H), 2.14 – 2.04 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.4, 166.8, 159.8, 134.7, 133.6, 132.7, 130.9, 128.6, 121.3, 116.1, 112.7, 101.4, 65.7, 59.0, 56.1, 51.7, 23.8.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.5.



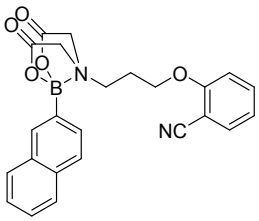
1-Napthylboronic acid MIDA-DG ester (22)

1-Napthylboronic acid (172 mg, 1.00 mmol) and the MIDA-DG trifluoroacetic acid salt (408 mg, 1.00 mmol) were dissolved in MeCN (13 mL) and refluxed for 16 hours. The reaction mixture was cooled to room temperature, dry loaded onto silica and purified *via* FCC (washed with Et_2O then eluted with EtOAc).The product was isolated as a white crystalline solid (249 mg, 0.58 mmol, 58%).

ν_{max}/cm^{-1} 2225, 1748, 1599, 1491, 1454, 1290, 1260, 1234, 1170, 1103, 1013, 173, 854, 753, 708.

HRMS (ES- TOF) Calcd. for $C_{25}H_{22}BN_2O_7$ ($[M-H]+HCO_2H$): 473.1520. Found: 473.1530.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.26 (dt, *J* = 8.5, 0.9 Hz, 1H), 7.97 – 7.88 (m, 2H), 7.71 (dd, *J* = 6.9, 1.3 Hz, 1H), 7.59 – 7.45 (m, 5H), 7.02 (td, *J* = 7.6, 0.8 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 4.16 (d, *J* = 17.2 Hz, 2H), 4.09 (d, *J* = 17.2 Hz, 2H), 3.81 (t, *J* = 6.3 Hz, 2H), 2.90 – 2.82 (m, 2H), 2.07 (dtd, *J* = 11.1, 8.0, 7.1, 5.4 Hz, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.6, 159.8, 136.4, 134.7, 133.9, 133.6, 133.5, 130.4, 129.1, 127.2, 126.2, 125.3, 125.3, 121.2, 116.0, 112.7, 101.3, 65.6, 59.2, 55.4, 23.9.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 12.6.



2-Napthylboronic acid MIDA-DG ester

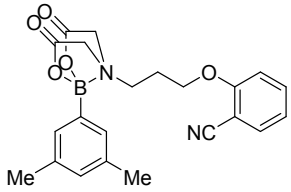
2-Napthylboronic acid (172 mg, 1.00 mmol) and the MIDA-DG trifluoroacetic acid salt (408 mg, 1.00 mmol) were dissolved in MeCN (13 mL) and refluxed for 16 hours. The reaction mixture was cooled to room temperature,

dry loaded onto silica and purified *via* FCC (washed with Et_2O then eluted with EtOAc).The product was isolated as a white crystalline solid (307 mg, 0.72 mmol, 72%).

ν_{max}/cm^{-1} 2222, 1744, 1595, 1491, 1450, 1290, 1260, 1208, 1185, 1003, 951, 857, 824, 746

HRMS (ES- TOF) Calcd. for $C_{25}H_{22}BN_2O_7$ ([M-H]+HCO_2H): 473.1520. Found: 473.1534.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.08 (d, *J* = 1.2 Hz, 1H), 7.97 – 7.91 (m, 1H), 7.91 – 7.86 (m, 2H), 7.61 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.57 – 7.45 (m, 4H), 7.00 (td, *J* = 7.6, 0.9 Hz, 1H), 6.88 (dd, *J* = 8.6, 0.9 Hz, 1H), 4.15 (d, *J* = 17.1 Hz, 2H), 4.07 (d, *J* = 17.1 Hz, 2H), 3.91 (t, *J* = 6.2 Hz, 2H), 2.90 – 2.82 (m, 2H), 2.15 – 2.06 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.6, 159.8, 134.7, 134.0, 133.6, 133.1, 129.2, 128.4, 127.6, 127.2, 126.4, 125.9, 121.2, 116.1, 112.7, 101.3, 65.7, 59.0, 56.0, 23.9.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 12.1.



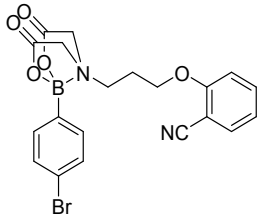
3,5-Dimethylphenylboronic acid MIDA-DG ester (23)

3,5-Dimethylphenylboronic acid (150 mg, 1.00 mmol) and the MIDA-DG trifluoroacetic acid salt (408 mg, 1.00 mmol) were dissolved in MeCN (13 mL) and refluxed for 16 hours. The reaction mixture was cooled to room temperature, dry loaded onto silica and purified *via* FCC (washed with Et_2O then eluted with EtOAc).The product was isolated as a white crystalline solid (318 mg, 0.78 mmol, 78%).

ν_{max}/cm^{-1} 2225, 1744, 1595, 1491, 1450, 1290, 1182, 1018, 939, 876, 846, 753, 708

HRMS (ES- TOF) Calcd. for $C_{23}H_{24}BN_2O_7$ ([M-H]+HCO_2H): 451.1677. Found: 451.1693.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.64 – 7.53 (m, 2H), 7.11 (s, 2H), 7.07 (td, *J* = 7.6, 0.9 Hz, 1H), 7.02 (s, 1H), 6.98 (d, *J* = 8.5 Hz, 1H), 4.07 (d, *J* = 17.1 Hz, 2H), 4.03 – 3.95 (m, 4H), 2.87 – 2.79 (m, 2H), 2.32 – 2.28 (m, 5H), 2.14 – 2.04 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.6, 159.9, 137.3, 134.8, 133.6, 130.8, 130.2, 121.3, 116.1, 112.7, 101.4, 65.8, 58.9, 55.9, 23.8, 20.5.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 12.0.



4-Bromophenylboronic acid MIDA-DG ester (20)

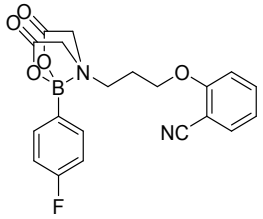
4-Bromophenylboronic acid (201 mg, 1.00 mmol) and the MIDA-DG trifluoroacetic acid salt (408 mg, 1.00 mmol) were dissolved in MeCN (13 mL) and refluxed for 16 hours. The reaction mixture was cooled to room temperature, dry loaded onto silica and purified *via* FCC (washed with Et_2O then eluted with EtOAc).The product was isolated as a white crystalline solid (350 mg, 0.77 mmol, 77%).

ν_{max}/cm^{-1} 2222, 1759, 1584, 1495, 1454, 1386, 1290, 1260, 1219, 1044, 1003, 869, 813, 760

HRMS (ES- TOF) Calcd. for $C_{21}H_{19}BN_2O_7Br$ ([M-H]+HCO_2H): 501.0469. Found: 501.0466.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.63 – 7.55 (m, 2H), 7.55 – 7.51 (m, 2H), 7.45 – 7.40 (m, 2H), 7.08 (td, *J* = 7.6, 0.9 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 4.09 (d, *J* = 17.1 Hz, 2H), 4.06 – 3.98 (m, 4H), 2.88 – 2.79 (m, 2H), 2.15 – 2.05 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.7, 165.2, 140.1, 139.9, 139.0, 136.3, 128.8, 126.6, 121.4, 118.0, 106.7, 71.0, 64.3, 61.4, 29.1.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.6.



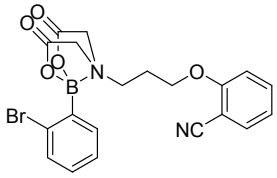
4-Fluorophenylboronic acid MIDA-DG ester (21)

4-Fluorophenylboronic acid (140 mg, 1.00 mmol) and the MIDA-DG trifluoroacetic acid salt (408 mg, 1.00 mmol) were dissolved in MeCN (13 mL) and refluxed for 16 hours. The reaction mixture was cooled to room temperature, dry loaded onto silica and purified *via* FCC (washed with Et_2O then eluted with EtOAc).The product was isolated as a white crystalline solid (274 mg, 0.69 mmol, 69%).

ν_{max}/cm^{-1} 225, 1767, 1595, 1476, 1402, 1256, 1215, 1044, 1001, 943, 872, 835, 764

HRMS (ES+ TOF) Calcd. For $C_{20}H_{19}BN_2O_5F$ ([M + H]$^+$): 397.1371. Found: 397.1377.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.63 – 7.56 (m, 2H), 7.56 – 7.51 (m, 2H), 7.14 – 7.05 (m, 3H), 7.00 (d, *J* = 8.4 Hz, 1H), 4.08 (d, *J* = 17.1 Hz, 2H), 4.04 – 3.98 (m, 4H), 2.86 – 2.78 (m, 2H), 2.15 – 2.04 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.4, 162.6, 159.9, 134.8, 134.7, 133.7, 121.3, 116.1, 114.9, 114.7, 112.7, 101.4, 65.7, 58.9, 56.0, 23.8.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.6.
^{19}F NMR (377 MHz, Acetonitrile-d_3) δ -76.5, -114.0 (q, *J* = 7.2 Hz). Trifluoroacetic acid impurity remaining.



2-Bromophenylboronic acid MIDA-DG ester (19)

2-Bromophenylboronic acid (201 mg, 1.00 mmol) and the MIDA-DG trifluoroacetic acid salt (408 mg, 1.00 mmol) were dissolved in MeCN (13 mL) and refluxed for 16 hours. The reaction mixture was cooled to room temperature, dry loaded onto silica and purified *via* FCC (washed with Et_2O then eluted with EtOAc).The product was isolated as a white crystalline solid (372 mg, 0.81 mmol, 81%).

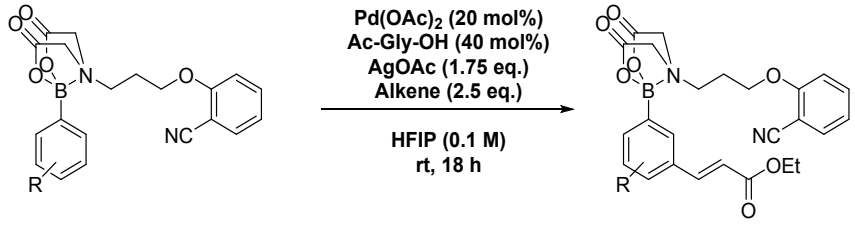
ν_{max}/cm^{-1} 2222, 1767, 1491, 1424, 1293, 1200, 1125, 1059, 1018, 954, 861, 760

HRMS (ES- TOF) Calcd. for $C_{21}H_{19}BN_2O_7Br$ ([M-H]+HCO_2H): 501.0469. Found: 501.0479.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.70 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.63 – 7.54 (m, 3H), 7.38 (td, *J* = 7.4, 1.2 Hz, 1H), 7.29 (ddd, *J* = 7.9, 7.3, 1.9 Hz, 1H), 7.07 (td, *J* = 7.6, 0.9 Hz, 1H), 7.02 – 6.96 (m, 1H), 4.23 (d, *J* = 17.2 Hz, 2H), 4.09 (d, *J* = 17.2 Hz, 2H), 4.02 (t, *J* = 6.1 Hz, 2H), 3.11 – 3.03 (m, 2H), 2.23 – 2.13 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.5, 159.8, 136.5, 134.7, 133.7 (2Ar-C), 131.4, 127.9, 127.0, 121.3, 116.1, 112.6, 101.3, 65.6, 61.2, 56.8, 24.1.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.8.

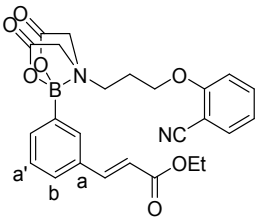
Alkenylation of arylboronic acid MIDA-DG esters

General Procedure for the C–H alkenylation of aryl boronic acid MIDA-DG esters:



A 20 mL vial was charged with arylboronic acid MIDA-DG ester (1.0 eq.), AgOAc (1.75 eq.), Ac-Gly-OH (40 mol%) and $Pd(OAc)_2$ (20 mol%). The vial was then charged with HFIP (0.1 M) and the corresponding alkene coupling partner (2.5 eq.) was added. The vial was sealed and stirred at room temperature for 18 hours. The reaction mixture was diluted with MeCN (~5 mL) and dry loaded onto a silica column. The column was washed with Et_2O (100 mL) before the products were subsequently eluted with 1:1 MeCN:Et_2O. The eluent was concentrated under vacuum to yield the alkenylated products as an inseparable mixture of regio-isomers. The corresponding yields of each isomer were calculated using ^{1}H NMR analysis.

NB: The high polarity of MIDA-DG containing compounds precludes their separation using normal phase FCC. As such, 'catch and release' purification was used to isolate mixtures of mono and di-functionalised and regioisomeric mixtures, with starting material if full conversion was not achieved. These mixtures were weighed and the yields of the constituent products calculated using ^{1}H NMR in combination with molecular weights and the mass of the solids. All the C–H functionalisation products were later derivatised to the pinacol boronate esters and purified to allow unambiguous characterisation.



3-(Ethyl prop-2-enoate)phenylboronic acid MIDA-DG ester (7a)

Phenylboronic acid MIDA-DG ester (151 mg, 0.4 mmol) was employed to yield the product as an off-white solid (147 mg, 75% total yield: **a**: 55%, **b**: 8%, **a**+**a'**: 8%, **a**+**b**: 4% as determined by ^{1}H NMR).

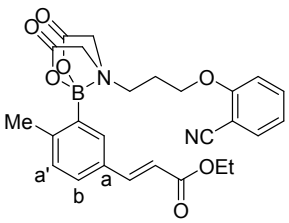
Characterisation data for major isomer:

HRMS (ES+ TOF) Calcd. for $C_{25}H_{26}N_2O_7B$ ([M + H]$^+$): 477.1833. Found: 477.1841.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.75 – 7.64 (m, 3H), 7.61 – 7.54 (m, 3H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.05 (td, *J* = 7.6, 0.9 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.53 (d, *J* = 16.1 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.11 (d, *J* = 17.1 Hz, 2H), 4.04 (d, *J* = 17.1 Hz, 2H), 3.98 (t, *J* = 6.2 Hz, 2H), 2.87 – 2.81 (m, 2H), 2.14 – 2.06 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.4, 166.58, 159.9, 144.5, 143.78, 134.8, 134.6, 134.0, 133.6, 133.1, 132.8, 132.5, 128.6, 128.6, 121.3, 119.2, 118.3, 116.1, 112.7, 101.4, 65.7, 60.2, 59.0, 56.1, 29.4, 23.8, 13.7. Unable to distinguish ^{13}C peaks between regioisomers.

^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.6.

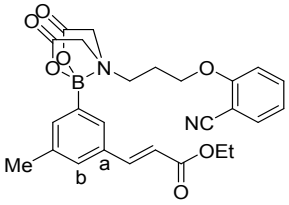


2-Methyl-5-(ethyl prop-2-enoate)phenylboronic acid MIDA-DG ester (13a)

2-Methylphenylboronic acid MIDA-DG ester (118 mg, 0.3 mmol) was employed to yield the product as an off-white solid (97 mg, 54% total yield: **a**: 43%, **b**: 3%, **a'**: 4%, **a**+**b** and **a'**+**b**: 4%, **SM**: 13% as determined by ^{1}H NMR).
Characterisation data for major isomer:

HRMS (ES+ TOF) Calcd. for $C_{26}H_{27}N_2O_7BNa$ ([M + Na]$^+$): 513.1809. Found: 513.1824.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.67 (d, *J* = 16.0 Hz, 1H), 7.62 (d, *J* = 2.1 Hz, 1H), 7.61 – 7.54 (m, 3H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.08 – 7.04 (m, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.45 (d, *J* = 16.0 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.12 (d, *J* = 17.2 Hz, 2H), 4.04 (d, *J* = 15.1 Hz, 2H), 4.00 (t, *J* = 5.2 Hz, 2H), 2.88 – 2.81 (m, 2H), 2.44 (s, 3H), 2.16 – 2.10 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.4, 166.7, 159.9, 145.4, 144.5, 134.8, 133.6, 131.8, 131.4, 128.4, 121.3, 116.1, 112.7, 101.4, 65.7, 60.1, 59.8, 59.6, 56.1, 24.0, 22.2, 13.7. Unable to distinguish ^{13}C peaks between regioisomers.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 12.5.

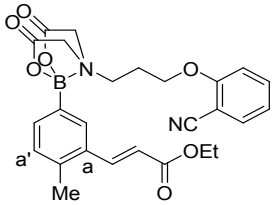


3-Methyl-5-(ethyl prop-2-enoate)phenylboronic acid MIDA-DG ester (14a)

3-Methylphenylboronic acid MIDA-DG ester (118 mg, 0.3 mmol) was employed to yield the product as an off-white solid (99 mg, 66% total yield: **a**: 42%, **b**: 21%, **a**+**b**: 3%, as determined by ^{1}H NMR).
Characterisation data for major isomer:

HRMS (ES+ TOF) Calcd. for $C_{26}H_{27}N_2O_7BNa$ ([M + Na]$^+$): 513.1809. Found: 513.1818.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.66 (d, *J* = 16.1 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.50 (s, 1H), 7.49 (s, 1H), 7.38 (s, 1H), 7.05 (td, *J* = 7.6, 0.9 Hz, 1H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 4.11 (d, *J* = 17.1 Hz, 2H), 4.03 (d, *J* = 17.0 Hz, 2H), 3.98 (t, *J* = 5.5 Hz, 2H), 2.89 – 2.80 (m, 2H), 2.37 (s, 3H), 2.14 – 2.05 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.4, 166.6, 166.6, 159.9, 159.8, 144.7, 141.7, 141.5, 138.3, 137.1, 135.4, 135.0, 134.7, 134.0, 133.7, 133.6, 130.4, 130.1, 129.1, 125.9, 121.3, 119.5, 118.0, 116.1, 112.7, 101.4, 65.8, 60.3, 60.2, 59.0, 56.1, 29.4, 23.8, 23.8, 20.4, 18.9, 13.7. Unable to distinguish ^{13}C peaks between regioisomers.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.8.



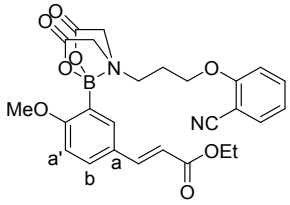
4-Methyl-3-(ethyl prop-2-enoate)phenylboronic acid MIDA-DG ester (15a)

4-Methylphenylboronic acid MIDA-DG ester (118 mg, 0.3 mmol) was employed to yield the product as an off-white solid (95 mg, 50% total yield: **a**: 43%, **a**+**a'**: 7%, **SM**: 16%, as determined by ^{1}H NMR).
Characterisation data for major isomer:

HRMS (ES+ TOF) Calcd. for $C_{26}H_{27}N_2O_7BNa$ ([M + Na]$^+$): 513.1809. Found: 513.1814.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.66 (d, *J* = 16.1 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.52 – 7.47 (m, 2H), 7.38 (s, 1H), 7.05 (td, *J* = 7.6, 0.9 Hz, 1H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 4.11 (d, *J* = 17.1 Hz, 2H), 4.03 (d, *J* = 17.0 Hz, 2H), 3.98 (t, *J* = 6.1 Hz, 2H), 2.90 – 2.80 (m, 2H), 2.36 (s, 3H), 2.14 – 2.05 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.4, 166.6, 159.9, 144.7, 141.7, 138.3, 137.1, 135.4, 135.0, 134.7, 134.0, 133.7, 133.6, 130.4, 130.1, 129.1, 125.9, 121.3, 119.5, 118.0, 116.1, 112.7, 101.4, 65.8, 60.3, 60.2, 59.0, 56.1, 29.4, 23.8, 20.4, 18.9, 13.7. Unable to distinguish ^{13}C peaks between regioisomers.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.8.

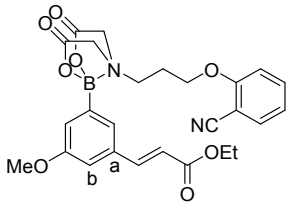


2-Methoxy-5-(ethyl prop-2-enoate)phenylboronic acid MIDA-DG ester (10a)

2-Methoxyphenylboronic acid MIDA-DG ester (122 mg, 0.3 mmol) was employed to yield the product as an off-white solid (121 mg, 79% total yield: **a**: 58%, **b**: 15%, **a**+**b**: 6%, as determined by ^{1}H NMR).
Characterisation data for major isomer:

HRMS (ES+ TOF) Calcd. for $C_{26}H_{27}N_2O_8BNa$ ([M + Na]$^+$): 529.1758. Found: 529.1760.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.79 (d, *J* = 2.3 Hz, 1H), 7.68 – 7.48 (m, 4H), 7.04 (td, *J* = 7.6, 0.8 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 4.22 (d, *J* = 7.1 Hz, 2H), 4.15 (d, *J* = 17.0 Hz, 2H), 4.04 (d, *J* = 17.0 Hz, 2H), 3.99 (t, *J* = 5.9 Hz, 2H), 3.85 (s, 3H), 3.08 – 2.99 (m, 2H), 2.10 (dt, *J* = 10.4, 5.8 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.6, 166.8, 164.1, 159.7, 144.3, 135.0, 134.7, 133.7, 133.7, 131.0, 126.8, 121.2, 120.9, 118.7, 116.1, 115.7, 112.5, 110.9, 109.4, 101.2, 65.7, 60.3, 60.0, 55.7, 55.6, 55.1, 54.9, 23.8, 13.7. Unable to distinguish ^{13}C peaks between regioisomers.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.7.

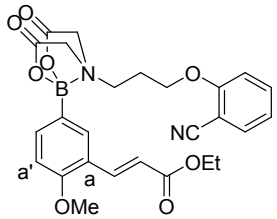


3-Methoxy-5-(ethyl prop-2-enoate)phenylboronic acid MIDA-DG ester (11a)

3-Methoxyphenylboronic acid MIDA-DG ester (122 mg, 0.3 mmol) was employed to yield the product as an off-white solid (92 mg, 33% total yield: **a**: 23%, **b**: 10%, **SM**: 35% as determined by ^{1}H NMR).
Characterisation data for major isomer:

HRMS (ES+ TOF) Calcd. for $C_{26}H_{27}N_2O_8BNa$ ([M + Na]$^+$): 529.1758. Found: 529.1760.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.92 (d, *J* = 16.2 Hz, 1H), 7.63 – 7.53 (m, 2H), 7.12 (s, 1H), 7.10 – 7.04 (m, 3H), 7.03 (dt, *J* = 3.4, 1.1 Hz, 1H), 7.01 – 6.97 (m, 1H), 6.56 (d, *J* = 16.2 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.11 (d, *J* = 17.1 Hz, 2H), 4.04 (d, *J* = 13.1 Hz, 2H), 4.01 – 3.97 (m, 2H), 3.92 (s, 3H), 2.91 – 2.82 (m, 2H), 2.15 – 2.06 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.5, 168.4, 159.9, 159.4, 144.4, 139.2, 134.7, 133.7, 129.3, 128.3, 125.4, 124.7, 124.6, 123.7, 121.3, 120.0, 118.8, 118.5, 116.1, 115.0, 113.4, 112.8, 101.4, 65.8, 60.2, 60.1, 59.1, 59.0, 58.9, 56.0, 55.9, 55.3, 55.0, 54.7, 23.8, 13.7. Unable to distinguish ^{13}C peaks between regioisomers.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.7.

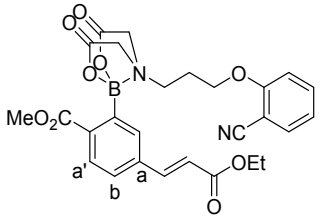


4-Methoxy-3-(ethyl prop-2-enoate)phenylboronic acid MIDA-DG ester (12a)

4-Methoxyphenylboronic acid MIDA-DG ester (122 mg, 0.3 mmol) was employed to yield the products as an off-white solid (53 mg, 34% total yield: **a**: 30%, **a**+**a'**: 4%, as determined by ^{1}H NMR).
Characterisation data for major isomer:

HRMS (ES+ TOF) Calcd. for $C_{26}H_{27}N_2O_8BNa$ ([M + Na]$^+$): 529.1758. Found: 529.1767.

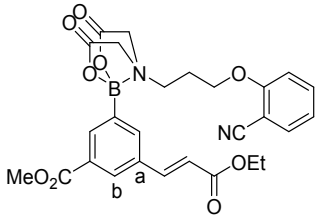
^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.89 (d, *J* = 16.2 Hz, 1H), 7.67 (d, *J* = 1.9 Hz, 1H), 7.61 – 7.50 (m, 3H), 7.08 – 7.00 (m, 2H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.58 (d, *J* = 16.2 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.10 (d, *J* = 17.1 Hz, 2H), 4.04 – 3.97 (m, 4H), 3.90 (s, 3H), 2.89 – 2.81 (m, 2H), 2.10 (ddt, *J* = 12.1, 8.1, 5.3 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.5, 167.0, 166.6, 159.9, 159.3, 139.8, 138.4, 136.2, 134.7, 134.4, 133.6, 133.5, 128.7, 128.2, 122.6, 121.3, 120.4, 118.8, 116.1, 113.7, 112.7, 111.2, 101.4, 65.8, 60.3, 60.1, 59.0, 56.1, 55.3, 23.8, 13.7. Unable to distinguish ^{13}C peaks between regioisomers.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.9.



2-Methoxycarbonyl-5-(ethyl prop-2-enoate)phenylboronic acid MIDA-DG ester (16a)
2-Methoxycarbonylphenylboronic acid MIDA-DG ester (131 mg, 0.3 mmol) was employed to yield the products as a white mixture of solids(139 mg, 34% total yield: **a**: 16%, **b**: 11%, **a'**: 7%, **SM**: 65%, as determined by ^{1}H NMR). The reaction was repeated using 0.2 mmol of MIDA-DG ester for an extended time of 48 hours. The product was isolated as a white solid (96 mg, 61% total yield: **a**: 32%, **b**:10%, **a'**: 13%, **di**: 6%, **SM**: 32%, as determined by ^{1}H NMR).
Characterisation data for major isomer:

HRMS (ES+ TOF) Calcd. for $C_{27}H_{27}N_2O_9BNa$ ([M + Na]$^+$): 557.1707. Found: 557.1707.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.88 (d, *J* = 1.7 Hz, 1H), 7.71 (m, 2H), 7.67 – 7.61 (m, 1H), 7.60 – 7.51 (m, 2H), 7.09 – 7.01 (m, 1H), 7.01 – 6.96 (m, 1H), 6.59 (d, *J* = 16.1 Hz, 1H), 4.28 (d, *J* = 17.1 Hz, 2H), 4.08 – 3.99 (m, 7H), 3.83 (s, 3H), 3.26 – 3.13 (m, 2H), 2.28 – 2.13 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 170.9, 168.8, 166.3, 159.8, 143.3, 140.7, 138.4, 137.1, 135.7, 134.9, 134.7, 133.7, 130.4, 129.4, 129.1, 129.0, 128.6, 128.3, 127.9, 127.6, 121.3, 120.9, 120.1, 116.0, 112.7, 101.4, 65.8, 61.3, 60.4, 57.9, 52.5, 52.4, 24.2, 13.6. Unable to distinguish ^{13}C peaks between regioisomers.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 12.0.

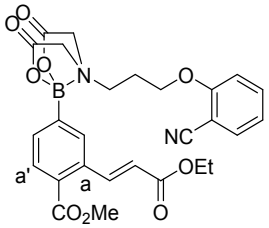


3-Methoxycarbonyl-5-(ethyl prop-2-enoate)phenylboronic acid MIDA-DG ester (17a)
3-Methoxycarbonylphenylboronic acid MIDA-DG ester (131 mg, 0.3 mmol) was employed to yield the product as a white solid (137 mg, 32% total yield: **a**: 29%, **b**: 3%, **SM**: 66% as determined by ^{1}H NMR). The reaction was repeated using 0.2 mmol of MIDA-DG ester for an extended time of 48 hours. The products was isolated as a white solid (93 mg, 59% total yield: **a**: 49%, **b**:10%, **SM**: 34%, as determined by ^{1}H NMR).
Characterisation data for major isomer:

HRMS (ES+ TOF) Calcd. for $C_{27}H_{27}N_2O_9BNa$ ([M + Na]$^+$): 557.1707. Found: 557.1702.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.22 (t, *J* = 1.8 Hz, 1H), 8.13 (dt, *J* = 2.6, 1.4 Hz, 1H), 7.94 (d, *J* = 1.4 Hz, 1H), 7.75 (d, *J* = 16.1 Hz, 1H), 7.61 – 7.51 (m, 2H), 7.06 – 7.02 (m, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.61 (d, *J* = 16.1 Hz, 1H),

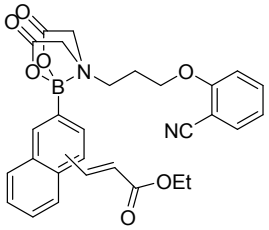
4.24 (q, *J* = 7.1 Hz, 2H), 4.15 (d, *J* = 17.1 Hz, 2H), 4.06 (d, *J* = 17.1 Hz, 2H), 3.99 (t, *J* = 6.1 Hz, 2H), 3.91 (s, 3H), 2.89 – 2.80 (m, 2H), 2.10 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.3, 166.4, 159.8, 143.4, 137.2, 136.7, 136.4, 134.8, 134.7, 134.6, 133.6, 133.6, 133.2, 130.6, 130.2, 129.6, 128.3, 127.4, 121.3, 119.6, 116.0, 112.7, 101.4, 65.7, 60.3, 59.2, 59.1, 59.1, 56.3, 56.2, 56.2, 51.9, 51.7, 23.8, 23.8, 13.6. Unable to distinguish ^{13}C peaks between regioisomers.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.5.



4-Methoxycarbonyl-3-(ethyl prop-2-enoate)phenylboronic acid MIDA-DG ester (18a)
4-Methoxycarbonylphenylboronic acid MIDA-DG ester (131 mg, 0.3 mmol) was employed to yield the product as a white solid (138 mg, 22% total yield: **a**: 22%, **SM**: 78%, as determined by ^{1}H NMR). The reaction was repeated using 0.1 mmol of MIDA-DG ester for an extended time of 48 hours. The product was isolated as a white solid (49 mg, 52% total yield: **a**: 49%, **a+a'**: 3%, **SM**: 47%, as determined by ^{1}H NMR).
Characterisation data for major isomer:

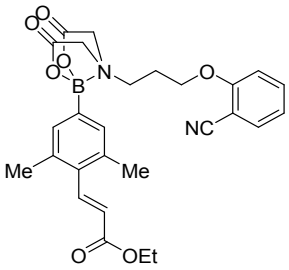
HRMS (ES+ TOF) Calcd. for $C_{27}H_{27}N_2O_9BNa$ ([M + Na]$^+$): 557.1707. Found: 557.1705.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.34 (d, *J* = 16.0 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.82 – 7.78 (m, 1H), 7.63 (dq, *J* = 7.8, 1.5 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.04 (tdd, *J* = 7.6, 2.2, 0.9 Hz, 1H), 6.95 (d, *J* = 8.5 Hz, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.15 (d, *J* = 17.2 Hz, 2H), 4.07 (d, *J* = 17.1 Hz, 2H), 3.98 (dt, *J* = 7.3, 6.2 Hz, 2H), 3.89 (s, 3H), 2.90 – 2.79 (m, 2H), 2.17 – 2.04 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.4, 168.4, 167.1, 166.8, 166.4, 159.9, 159.8, 143.5, 140.6, 135.2, 134.7, 133.8, 133.6, 133.6, 132.7, 132.5, 132.1, 130.9, 130.7, 129.9, 128.6, 121.3, 120.8, 116.1, 116.1, 112.7, 112.7, 101.4, 65.7, 65.6, 63.8, 60.4, 59.2, 59.1, 56.3, 56.1, 52.0, 51.7, 28.1, 23.9, 23.8, 13.7, 13.6. Unable to distinguish ^{13}C peaks between regioisomers.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.4.



Alkenylated 2-napythphenylboronic acid MIDA-DG ester (22a)
2-Napthylboronic acid MIDA-DG ester (128 mg, 0.3 mmol) was employed to yield the products as a white solid (99 mg). The product gave a complex mixture of regio and mono or di isomers. The yield calculation and characterisation were performed after forming the pinacol boronate ester to allow separation and easier elucidation. Please see the next section (*Synthesis of arylboronic acid pinacol esters*) for the relevant yield and characterisation data.

HRMS (ES+ TOF) Calcd. for $C_{29}H_{28}N_2O_7B$ ([M + H]$^+$): 527.1990. Found: 527.1988.

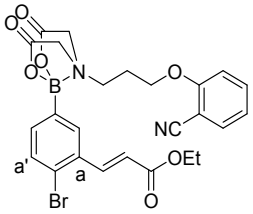


3,5-Dimethyl-4-(ethyl prop-2-enoate)phenylboronic acid MIDA-DG ester (23a)

3,5-Dimethylphenylboronic acid MIDA-DG ester (122 mg, 0.3 mmol) was employed to yield the products as a white solid after 48 hours (115 mg, 40% yield, **SM**: 45%, as determined by ^{1}H NMR).
Characterisation data for major isomer:

HRMS (ES+ TOF) Calcd. for $C_{27}H_{30}N_2O_7B$ ([M + H]$^+$): 505.2146. Found: 505.2144.

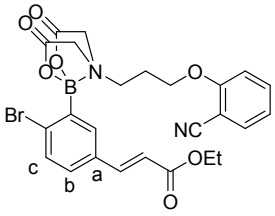
^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.82 (d, *J* = 16.4 Hz, 1H), 7.63 – 7.54 (m, 2H), 7.22 (s, 2H), 7.06 (td, *J* = 7.6, 0.8 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.10 (d, *J* = 16.4 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 4.09 (d, *J* = 17.0 Hz, 2H), 4.04 – 3.96 (m, 4H), 2.91 – 2.78 (m, 2H), 2.33 (s, 6H), 2.15 – 2.05 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.5, 166.3, 159.8, 142.8, 137.3, 136.1, 134.7, 133.6, 130.2, 123.9, 121.3, 116.0, 112.7, 101.4, 65.8, 60.3, 59.0, 56.0, 23.8, 20.2, 13.6.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.9.



4-Bromo-3-(ethyl prop-2-enoate)phenylboronic acid MIDA-DG ester (20a)
4-Bromophenylboronic acid MIDA-DG ester (137 mg, 0.3 mmol) was employed to yield the product as an off-white solid after 48 hours (136 mg, 69% total yield, **a**: 55%, **a+a'**: 14%, **SM**: 16%, as determined by ^{1}H NMR).
Characterisation data for major isomer:

HRMS (ES+ TOF) Calcd. for $C_{25}H_{24}N_2O_7BBrNa$ ([M + Na]$^+$): 577.0758. Found: 577.0760.

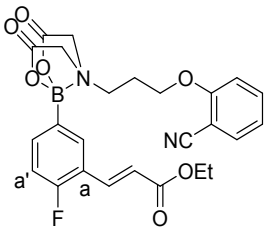
^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.95 (d, *J* = 16.0 Hz, 1H), 7.80 (d, *J* = 1.8 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.42 (dt, *J* = 8.0, 2.2 Hz, 1H), 7.06 (td, *J* = 7.6, 1.0 Hz, 1H), 7.00 – 6.96 (m, 1H), 6.53 (d, *J* = 15.9 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 4.12 (d, *J* = 17.1 Hz, 2H), 4.09 – 3.97 (m, 4H), 2.91 – 2.83 (m, 2H), 2.16 – 2.06 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.3, 166.1, 166.0, 159.9, 142.7, 142.3, 135.7, 135.4, 134.8, 134.6, 133.8, 133.7, 133.6, 133.6, 132.9, 132.3, 131.0, 126.1, 122.4, 121.5, 121.3, 116.1, 112.7, 101.4, 65.7, 60.6, 60.5, 59.3, 59.1, 59.0, 56.5, 56.3, 56.1, 23.9, 23.9, 23.8, 13.6. Unable to distinguish ^{13}C peaks between regioisomers.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.5.



2-Bromo-5-(ethyl prop-2-enoate)phenylboronic acid MIDA-DG ester (19a)
2-Bromophenylboronic acid MIDA-DG ester (137 mg, 0.3 mmol) was employed to yield the product as an off-white solid after 48 hours (142 mg, 49% total yield, **a**: 32%, **b**: 13%, **c**: 3%, **di**: 1%, **SM**: 42%, as determined by ^{1}H NMR).
Characterisation data for major isomer:

HRMS (ES+ TOF) Calcd. for $C_{25}H_{24}N_2O_7BBrNa$ ([M + Na]$^+$): 577.0758. Found: 577.0777.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.86 (d, *J* = 2.4 Hz, 1H), 7.76 – 7.66 (m, 1H), 7.65 – 7.48 (m, 4H), 7.10 – 7.02 (m, 1H), 7.01 – 6.95 (m, 1H), 6.51 (d, *J* = 16.1 Hz, 1H), 4.28 – 4.18 (m, 4H), 4.14 – 4.05 (m, 2H), 4.02 (t, *J* = 6.1 Hz, 2H), 3.11 – 3.03 (m, 2H), 2.24 – 2.11 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.5, 166.3, 166.1, 159.8, 143.9, 143.2, 138.1, 136.7, 136.5, 134.8, 134.3, 133.7, 133.2, 131.3, 130.0, 129.7, 127.9, 127.5, 127.0, 121.3, 119.1, 116.1, 112.6, 101.3, 65.6, 61.5, 61.2, 60.3, 56.8, 24.1, 13.6. Unable to distinguish ^{13}C peaks between regioisomers.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.7.

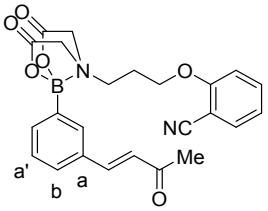


4-Fluoro-3-(ethyl prop-2-enoate)phenylboronic acid MIDA-DG ester (21a)

4-Fluorophenylboronic acid MIDA-DG ester (119 mg, 0.3 mmol) was employed to yield the product as an off-white solid after 48 hours (101 mg, 54% total yield, **a**: 43%, **a+a'**: 11%, **SM**: 15%, as determined by ^{1}H NMR).
Characterisation data for major isomer:

HRMS (ES+ TOF) Calcd. for $C_{25}H_{25}N_2O_7BF$ ([M + Na]$^{+}$): 495.1739. Found: 495.1750.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.80 – 7.73 (m, 2H), 7.62 – 7.50 (m, 3H), 7.17 (dd, *J* = 11.2, 8.3 Hz, 1H), 7.05 (td, *J* = 7.6, 0.9 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.60 (d, *J* = 16.2 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.11 (d, *J* = 17.1 Hz, 2H), 4.08 – 3.96 (m, 4H), 2.88 – 2.82 (m, 4H), 2.15 – 2.05 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.3, 166.4, 159.9, 136.8 (d, *J* = 2.7 Hz), 136.5, 136.4, 134.7, 134.7, 134.0, 134.0, 133.7, 133.6, 121.3, 121.1, 121.0, 116.1, 115.7, 115.5, 112.7, 101.4, 65.7, 60.4, 59.2, 59.0, 58.9, 56.2, 56.0, 23.8, 13.6.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.5.
^{19}F NMR (377 MHz, Acetonitrile-d_3) δ -115.9 (dt, *J* = 12.8, 7.1 Hz).

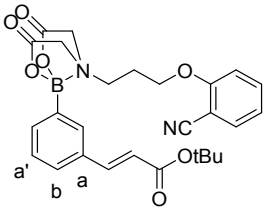


3-(But-3-ene-2-enone)phenylboronic acid MIDA-DG ester (7b)

Phenylboronic acid MIDA-DG ester (113 mg, 0.3 mmol) was employed to yield the product as a white solid (93 mg, 69% total yield: **a**: 59%, **b**: 8%, **a+a'**: 2%, as determined by ^{1}H NMR).
Characterisation data for major isomer:

HRMS (ES- TOF) Calcd. for $C_{25}H_{24}N_2O_8B$ ([M + HCOO]$^{-}$): 491.1626. Found: 491.1632.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.75 (s, 1H), 7.68 (dt, *J* = 7.8, 1.6 Hz, 1H), 7.65 – 7.55 (m, 4H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.05 (tt, *J* = 7.6, 0.8 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.77 (d, *J* = 16.4 Hz, 1H), 4.12 (d, *J* = 17.0 Hz, 2H), 4.05 (d, *J* = 17.1 Hz, 2H), 3.98 (t, *J* = 6.1 Hz, 2H), 2.89 – 2.82 (m, 2H), 2.34 (s, 3H), 2.14 – 2.06 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 198.2, 168.4, 159.9, 143.3, 134.8, 134.6, 134.3, 133.7, 133.6, 133.0, 132.5, 128.7, 128.6, 128.0, 127.7, 127.2, 121.3, 116.1, 112.7, 101.4, 65.7, 59.0, 56.1, 26.7, 23.8. Unable to distinguish ^{13}C peaks between regioisomers.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.6.

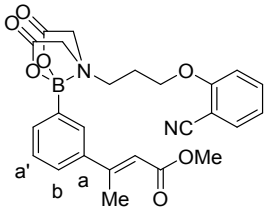


3-(*tert*-Butyl prop-2-enoate)phenylboronic acid MIDA-DG ester (7c)

Phenylboronic acid MIDA-DG ester (113 mg, 0.3 mmol) was employed to yield the product as a white solid (119 mg, 58% total yield: **a**: 46%, **b**: 7%, **a+a'**: 3%, **a+b**: 2%, **SM**: 26% as determined by ^{1}H NMR).
Characterisation data for major isomer:

HRMS (ES- TOF) Calcd. for $C_{28}H_{30}N_2O_9B$ ([M + HCOO]$^{-}$): 549.2044. Found: 549.2054.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.71 – 7.63 (m, 2H), 7.62 – 7.51 (m, 4H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.10 – 7.03 (m, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 4.11 (d, *J* = 17.1 Hz, 2H), 4.03 (d, *J* = 17.1 Hz, 2H), 3.98 (t, *J* = 6.2 Hz, 2H), 2.87 – 2.80 (m, 2H), 2.15 – 2.06 (m, 2H), 1.53 (s, 9H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.5, 168.4, 159.7, 143.7, 134.8, 134.3, 133.7, 133.6, 132.6, 132.5, 128.5, 128.0, 127.5, 121.3, 120.0, 116.1, 112.8, 109.8, 65.8, 59.0, 56.1, 27.4, 23.8. Unable to distinguish ^{13}C peaks between regioisomers.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.7.

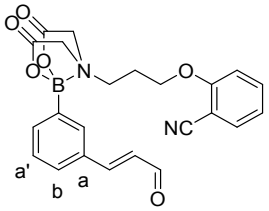


3-(4-Methoxy-4-oxobut-2-en-2-yl)phenylboronic acid MIDA-DG ester (7d)

Phenylboronic acid MIDA-DG ester (113 mg, 0.3 mmol) was employed to yield the product as a white solid (48 mg, 16% total yield: **a**: 12%, **b**: 3%, **a+a'**: 1%, **SM**: 21%, as determined by ^{1}H NMR).
Characterisation data for major isomer:

HRMS (ES+ TOF) Calcd. for $C_{25}H_{26}N_2O_7B$ ([M + H]$^+$): 477.1833. Found: 477.1849.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.64 – 7.56 (m, 3H), 7.56 – 7.53 (m, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.06 (td, *J* = 7.6, 0.8 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.17 (q, *J* = 1.3 Hz, 1H), 4.11 (d, *J* = 17.0 Hz, 2H), 4.03 (d, *J* = 17.1 Hz, 2H), 3.99 – 3.96 (m, 2H), 3.72 (s, 3H), 2.88 – 2.79 (m, 2H), 2.56 (s, 3H), 2.16 – 2.06 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 170.4, 168.5, 168.5, 141.5, 134.8, 133.7, 133.6, 133.4, 132.5, 130.3, 129.3, 128.2, 128.0, 127.4, 121.3, 116.4, 112.7, 106.7, 101.4, 65.8, 65.8, 59.0, 58.9, 56.1, 55.9, 23.8, 23.8, 17.2. Unable to distinguish 13C peaks between regioisomers.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.8.

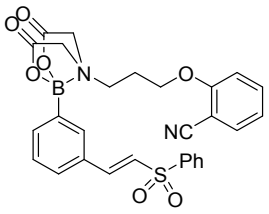


3-(Prop-2-enal)phenylboronic acid MIDA-DG ester (7i)

Phenylboronic acid MIDA-DG ester (113 mg, 0.3 mmol) was employed to yield the product as a white solid (111 mg, 65% total yield: **a**: 60%, **b**: 5%, **SM**: 24%, as determined by ^{1}H NMR).
Characterisation data for major isomer:

HRMS (ES+ TOF) Calcd. for $C_{23}H_{22}N_2O_6B$ ([M + H]$^+$): 433.1571. Found: 433.1581.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 9.69 (d, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 1.6 Hz, 1H), 7.71 (dt, *J* = 7.9, 1.5 Hz, 1H), 7.66 (d, *J* = 16.0 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.05 (tt, *J* = 7.6, 0.9 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.77 (dd, *J* = 16.0, 7.7 Hz, 1H), 4.12 (d, *J* = 17.0 Hz, 2H), 4.05 (d, *J* = 17.0 Hz, 2H), 3.99 (t, *J* = 5.9 Hz, 2H), 2.89 – 2.83 (m, 2H), 2.15 – 2.06 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 194.0, 168.4, 153.2, 135.4, 134.8, 133.7, 133.6, 133.2, 132.5, 129.3, 129.0, 128.7, 128.5, 128.0, 128.0, 121.3, 116.1, 112.7, 101.4, 65.7, 59.1, 56.1, 23.8. Unable to distinguish ^{13}C peaks between regioisomers.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.6.



3-(2-(Phenylsulfonyl)vinyl)phenylboronic acid MIDA-DG ester (7h)

Phenylboronic acid MIDA-DG ester (113 mg, 0.3 mmol) was employed to yield the product as a white solid (113 mg, 35% total yield: **a**: 30%, **b**: 5%, **SM**: 49%, as determined by ^{1}H NMR).

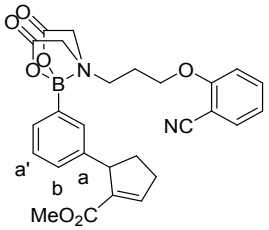
Characterisation data for major isomer:

HRMS (ES+ TOF) Calcd. for $C_{28}H_{26}N_2O_7BS$ ($[M + H]^+$): 545.1554. Found: 545.1564.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.98 – 7.93 (m, 2H), 7.74 – 7.68 (m, 3H), 7.67 – 7.55 (m, 6H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 15.5 Hz, 1H), 7.04 (td, *J* = 7.6, 0.8 Hz, 1H), 6.94 (dt, *J* = 8.4, 0.8 Hz, 1H), 4.11 (d, *J* = 17.1 Hz, 2H), 4.03 (d, *J* = 17.1 Hz, 2H), 3.96 (t, *J* = 6.1 Hz, 2H), 2.82 (ddd, *J* = 11.3, 4.7, 3.1 Hz, 2H), 2.15 – 2.05 (m, 2H).

^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.4, 159.8, 142.7, 141.1, 135.4, 133.6, 133.5, 133.2, 132.3, 129.5, 129.5, 129.4, 128.7, 127.6, 127.4, 121.2, 116.1, 101.4, 65.7, 59.1, 56.1, 23.8. Unable to distinguish ^{13}C peaks between regioisomers.

^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.8.



3-(2-(2-(Methoxycarbonyl)cyclopent-2-en-1-yl)phenylboronic acid MIDA-DG ester (7e)

Phenylboronic acid MIDA-DG ester (113 mg, 0.3 mmol) was employed to yield the product as a white solid (125 mg, 67% total yield: **a**: 46%, **b**: 21%, **SM**: 22%, as determined by ^{1}H NMR).

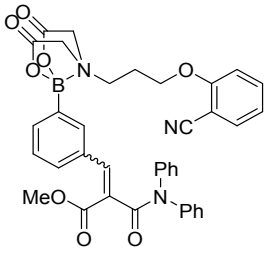
Characterisation data for major isomer:

HRMS (ES- TOF) Calcd. for $C_{28}H_{28}N_2O_9B$ ($[M + HCOO]^-$): 547.1888. Found: 547.1900.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.63 – 7.55 (m, 2H), 7.34-7.28 (m, 2H), 7.18 (dt, *J* = 7.1, 2.1 Hzj, 1H), 7.13 – 7.04 (m, 2H), 7.00 (dt, *J* = 8.6, 3.0 Hz, 1H), 6.95 (dp, *J* = 6.7, 1.9 Hz, 1H), 4.16 – 4.09 (m, 1H), 4.08 – 4.00 (m, 4H), 3.99-3.92 (m, 2H), 3.51 (s, 3H), 2.87 – 2.77 (m, 2H), 2.69 – 2.58 (m, 1H), 2.56 – 2.44 (m, 2H), 2.14 – 2.05 (m, 2H), 1.88 – 1.74 (m, 1H).

^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.5, 164.8, 159.9, 145.1, 138.8, 134.8, 133.6, 132.5, 131.3, 130.3, 129.3, 129.1, 128.0, 126.6, 121.3, 116.1, 112.8, 101.4, 65.8, 65.8, 58.9, 56.0, 50.7, 50.0, 33.8, 31.9, 23.8. Unable to distinguish ^{13}C peaks between regioisomers.

^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.9.

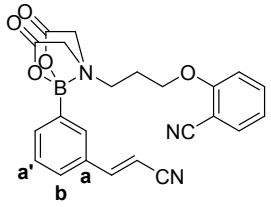


1-(Methoxycarbonyl)-1-(bisphenylamido)Ethene alkenylated phenyboronic acid MIDA-DG ester (7f)

Phenylboronic acid MIDA-DG ester (113 mg, 0.3 mmol) was employed, with only 1.2 equivalents of the coupling partner (accessed using the method described in *J. Org. Chem.* 2016, 81, 9947-9956), to yield the product as a white solid (156 mg, 0.24 mmol, 79% as a 6 : 1 ratio of *meta*:*para* isomers as determined by ^{1}H NMR). The *E:Z* ratio is unknown.
Characterisation data for major isomer:

HRMS (ES+ TOF) Calcd. for $C_{37}H_{33}N_3O_8B$ ([M + H]$^+$): 658.2361. Found: 658.2374.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.75 (d, *J* = 1.5 Hz, 1H), 7.70 – 7.61 (m, 2H), 7.60 – 7.50 (m, 3H), 7.46 – 7.42 (m, 6H), 7.42 – 7.36 (m, 2H), 7.34 – 7.26 (m, 3H), 7.18 (dd, *J* = 8.3, 6.4 Hz, 2H), 7.04 (td, *J* = 7.7, 1.0 Hz, 1H), 6.93 (dd, *J* = 8.3, 1.2 Hz, 3H), 4.05 (dd, *J* = 5.2, 3.5 Hz, 4H), 3.89 (t, *J* = 6.2 Hz, 2H), 3.83 (s, 1H), 3.80 (s, 3H), 2.80 (dd, *J* = 10.2, 5.9 Hz, 2H), 2.12 – 2.01 (m, 2H). Integrals corresponding to aromatic protons are combined with the *para* isomer.
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.4, 168.4, 166.1, 165.3, 164.9, 159.8, 142.9, 142.2, 141.8, 141.1, 134.9, 134.7, 134.2, 133.9, 133.7, 133.4, 133.2, 133.1, 132.5, 130.5, 129.3, 129.2, 129.2, 129.1, 128.7, 128.2, 127.7, 127.6, 127.1, 126.9, 126.6, 121.3, 116.1, 112.7, 101.4, 65.7, 59.0, 58.9, 56.0, 56.0, 52.2, 51.7, 23.8. Unable to distinguish ^{13}C peaks between regioisomers.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.7.



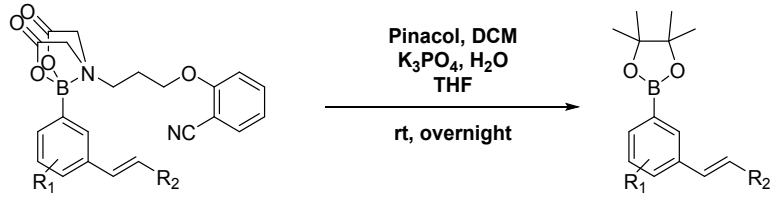
3-(2-Cyanovinyl)phenylboronic acid MIDA-DG ester (7g)
Phenylboronic acid MIDA-DG ester (113 mg, 0.3 mmol) was employed, with only 2 equivalents of the vinyl cyanide, to yield the product as a white solid after 48 hours (104 mg, 58% total yield: **a**: 50%, **b**: 8%, **SM**: 26%, as determined by ^{1}H NMR). The *meta* and *para* products were a mixture of *E* and *Z* isomers both in a 1.2 :1.0 ratio respectively.
Characterisation data for major isomer:

HRMS (ES+ TOF) Calcd. for $C_{23}H_{21}N_3O_5B$ ([M + H]$^+$): 430.1574. Found: 430.1586.

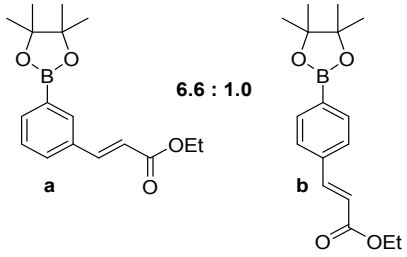
Aromatic peaks that could not be assigned to a certain stereoisomer are labelled: ***E or Z***
Peaks that overlap for both isomers are labelled: ***E and Z***, and the integral corresponding to one isomer given.
^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.88 (d, *J* = 1.4 Hz, 1H, ***E or Z***), 7.66 (d, *J* = 1.6 Hz, 1H, ***E or Z***), 7.63 – 7.55 (m, 2H, ***E and Z***), 7.52 – 7.49 (m, 1H, ***E or Z***), 7.44 (t, *J* = 7.6 Hz, 1H, ***E or Z***), 7.34 (d, *J* = 12.1 Hz, 1H, ***Z***), 7.07 (dddd, *J* = 8.5, 7.6, 1.9, 0.9 Hz, 1H, ***E and Z***), 6.97 (d, *J* = 8.5 Hz, 1H, ***E and Z***), 6.13 (d, *J* = 16.8 Hz, 1H, ***E***), 5.62 (d, *J* = 12.1 Hz, 1H, ***Z***), 4.11 (d, *J* = 17.1 Hz, 2H, ***E and Z***), 4.04 (d, *J* = 18.6 Hz, 2H, ***E and Z***), 4.01 – 3.96 (m, 2H, ***E and Z***), 2.89 – 2.79 (m, 2H, ***E or Z***), 2.15 – 2.05 (m, 2H, ***E or Z***).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.5, 168.4, 159.8, 150.8, 149.2, 135.3, 134.9, 133.5, 133.3, 132.5, 132.0, 129.3, 129.2, 128.7, 128.6, 128.1, 128.0, 126.9, 121.3, 116.1, 112.7, 101.3, 96.4, 95.4, 65.8, 65.7, 59.0, 56.1, 56.0, 23.8. Unable to distinguish ^{13}C peaks between regioisomers.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.8.

Synthesis of arylboronic acid pinacol esters

General procedure for the synthesis of aryl boronic acid pinacol esters from the corresponding MIDA-DG ester:



To a 20 mL vial was added the alkenylated boronic acid MIDA-DG mixture (1 eq.), pinacol (1 eq.) and K_3PO_4 (3 eq.). The mixture was suspended in DCM (0.1 M), THF (1 M) and water (0.2 M), the vial sealed and stirred at 40 °C for 16 hours. The reaction mixture was then cooled to room temperature, diluted with water (1.5 mL), the organic layer separated and the aqueous layer further extracted with DCM (2 × 3 mL). The organic mixture was concentrated and purified *via* FCC (10% EtOAc in hexane) to yield the desired mono-alkenylated aryl boronic acid pinacol ester.

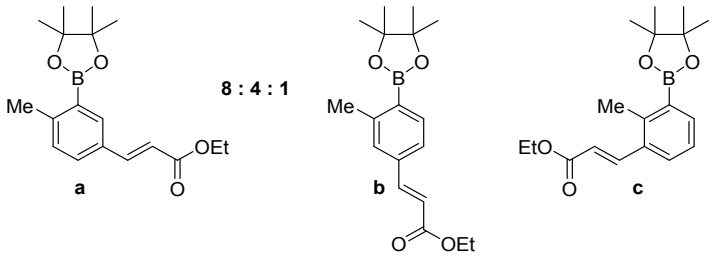


Ethyl (E)-3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (9)

The corresponding alkenylated boronic acid MIDA-DG ester (0.26 mmol) was used as a mixture of regioisomers to yield the mono-alkenylated pinacol boronate esters as a white solid. The ratio of *meta* (**a**) : *para* (**b**) in the isolated mixture was 6.6 : 1.0 (53 mg, 0.17 mmol, 67%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (td, *J* = 1.4, 0.7 Hz, 1H, **a**), 7.83 (dt, *J* = 7.3, 1.2 Hz, 1H, **a** and **b**), 7.73 (d, *J* = 16.0 Hz, 1H, **a** and **b**), 7.65 – 7.58 (m, 1H, **a**), 7.54 (d, *J* = 7.9 Hz, 1H, **b**), 7.41 (t, *J* = 7.6 Hz, 1H, **a**), 6.56 – 6.48 (m, 1H, **a** and **b**), 4.28 (q, *J* = 7.1 Hz, 2H, **a** and **b**), 1.40 – 1.32 (m, 18H **a** and **b**).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.0 (**a** and **b**), 144.5 (**a**), 144.4 (**b**), 136.9 (**b**), 136.5 (**a**), 135.2 (**b**), 134.7 (**b**), 134.4 (**a**), 133.8 (**a**), 131.2, 130.8 (**a**), 128.3 (**a**), 127.2 (**b**), 119.2 (**b**), 118.4 (**a**), 84.0 (**a** and **b**), 60.5 (**b**), 60.4 (**a**), 24.9 (**a** and **b**), 14.3 (**a** and **b**).
^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.9.

The characterisation data is in agreement with that reported in the literature (*Org. Lett.* 2015, 17, 5792-5795).



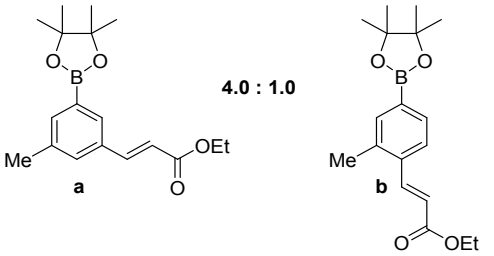
Ethyl (E)-3-(4-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (13a-pin)

The corresponding alkenylated boronic acid MIDA-DG ester (0.09 mmol) was used as a mixture of regioisomers to yield the mono-alkenylated pinacol boronate esters as a clear glassy solid. The ratio of *meta* (**a**) : *para* (**b**) : *meta* (**c**) in the isolated mixture was 8 : 4 : 1 (28 mg, 0.09 mmol, 100%).

HRMS (APCI +) Calcd. for $C_{18}H_{26}O_4B$ ($[M + H]^+$): 317.1919. Found: 317.1909.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 15.8 Hz, 1H, **c**), 7.96 (d, *J* = 2.0 Hz, 1H, **a**), 7.79 (d, *J* = 7.6 Hz, 1H, **b** and **c**), 7.75 – 7.66 (d, *J* = 15.8 Hz, 1H, **a**), 7.67 (d, , *J* = 15.8 Hz, 1H, **b**), 7.61 (dd, J = 7.8, 1.4 Hz, 1H, **c**), 7.49 (dd,

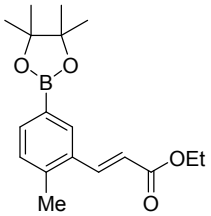
J = 7.9, 2.1 Hz, 1H, **a**), 7.35 (d, *J* = 1.7 H, 1H, **b**), 7.33 (s, 1H, **a**), 7.20 (d, *J* = 7.9 Hz, 1H, **a**, **b**, and **c**), 6.49 (d, *J* = 15.8 Hz, 1H, **b**), 6.46 (d, *J* = 15.8 Hz, 1H, **a**), 6.33 (d, *J* = 15.8 Hz, 1H, **c**), 4.28 (qd, *J* = 7.1, 2.6 Hz, 2H, **a**, **b**, and **c**), 2.65 (s, 3H, **c**), 2.57 (s, 3H, **a** and **b**), 1.43 – 1.30 (m, 15H, **a**, **b**, and **c**).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.2 (**a**), 167.0 (**b** and **c**), 147.6 (**a**), 145.4 (**b)**, 144.6 (**a**), 144.6 (**b** and **c**), 137.6 (**b**), 136.5 (**c**), 136.4 (**b**), 135.8 (**a**), 131.0 (**a**), 130.8 (**c**), 130.4 (**a**), 130.2 (**a**), 129.8 (**c** and **b**), 129.4 (**a**), 129.0 (**c**), 125.4 (**c**), 124.7 (**c**), 124.2 (**b**), 118.9 (**b**), 117.1 (**a**), 83.7 (**a**, and **c**), 83.6 (**b**), 60.5 (**b**), 60.3 (**a** and **c**), 24.9 (**a**, **b**, and **c**), 22.2 (**a** and **c**), 22.2 (**b**), 14.4 (**a**, **b**, and **c**).
^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.3.



Ethyl (E)-3-(3-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (14a-pin)
The corresponding alkenylated boronic acid MIDA-DG ester (0.26 mmol) was used as a mixture of regioisomers to yield the mono-alkenylated pinacol boronate esters as a clear glassy solid. The ratio of *meta* (**a**) : *para* (**b**) in the isolated mixture was 4.0 : 1.0 (48 mg, 0.15 mmol, 58%).

HRMS (APCI +) Calcd. for $C_{18}H_{26}O_4B$ ([M + H]$^+$): 317.1919. Found: 317.1920.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 15.9 Hz, 1H, **b**), 7.84 – 7.80 (m, 1H, **a**), 7.74 – 7.63 (m, 2H, **a** and **b**), 7.57 (d, *J* = 7.8 Hz, 1H, **b**), 7.44 (td, *J* = 1.7, 0.8 Hz, 1H, **a**), 6.50 (d, *J* = 16.0 Hz, 1H, **a**), 6.42 (d, *J* = 15.9 Hz, 1H, **b**), 4.27 (q, *J* = 7.1 Hz, 2H, **a** and **b**), 2.46 (s, 4H, **b**), 2.39 (s, 3H, **a**), 1.39 – 1.32 (m, 15H, **a** and **b**).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.1 (**a**), 167.0 (**b**), 144.7 (**a**), 142.1 (**b**), 137.8 (**b**), 137.3 (**a**), 137.1 (**a**), 136.7 (**b**), 135.3 (**b**), 133.9 (**b**), 132.6 (**a**), 131.8 (**b**), 131.7 (**a**), 131.5 (**a**), 125.6 (**b**), 120.1 (**b**), 118.2 (**a**), 84.0 (**a**), 84.0 (**b**), 60.5 (**b**), 60.4 (**a**), 24.9 (**a** and **b**), 21.1 (**a**), 19.6 (**b**), 14.3 (**a** and **b**).
^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.1.

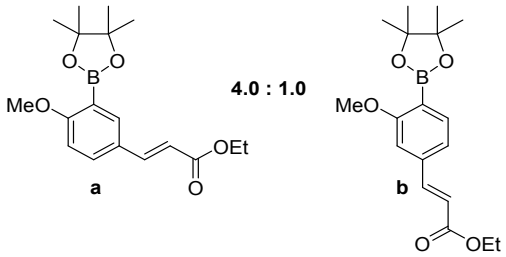


Ethyl (E)-3-(2-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (15a-pin)
The corresponding alkenylated boronic acid MIDA-DG ester (0.13 mmol) was used as a mixture of regioisomers to yield the pinacol boronate ester as a clear glassy solid (28 mg, 0.09 mmol, 69%).

ν_{max}/cm^{-1} 2978, 1715, 1636, 1607, 1357, 1320, 1260, 1163, 965, 857, 708

HRMS (APCI +) Calcd. for $C_{18}H_{26}O_4B$ ([M + H]$^+$): 317.1919. Found: 317.1921.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 1.2 Hz, 1H), 8.00 (d, *J* = 15.9 Hz, 1H), 7.72 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 6.50 (d, *J* = 15.8 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.48 (s, 3H), 1.37 (d, *J* = 1.8 Hz, 15H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.1, 142.1, 140.8, 136.2, 133.0, 132.9, 130.2, 119.5, 83.9, 60.4, 24.9, 20.1, 14.4.
^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.8.

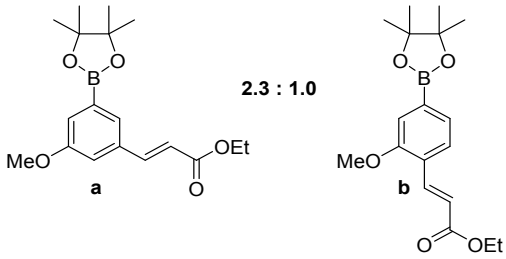


Ethyl (E)-3-(4-methoxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (10a-pin)

The corresponding alkenylated boronic acid MIDA-DG ester (0.21 mmol) was used as a mixture of regioisomers to yield the mono-alkenylated pinacol boronate esters as a clear glassy solid. The ratio of *meta* (**a**) : *para* (**b**) in the isolated mixture was 4.0 : 1.0 (17 mg, 0.05 mmol, 25%).

HRMS (APCI +) Calcd. for $C_{18}H_{26}O_5B$ ([M + H]$^+$): 333.1868. Found: 333.1860.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 2.4 Hz, 1H, **a**), 7.73 – 7.64 (m, 1H, **a** and 2H, **b**), 7.58 (dd, *J* = 8.7, 2.4 Hz, 1H, **a**), 7.13 (dd, *J* = 7.6, 1.3 Hz, 1H, **b**), 6.99 (d, *J* = 1.3 Hz, 1H, **b**), 6.88 (d, *J* = 8.6 Hz, 1H, **a**), 6.49 (d, *J* = 16.0 Hz, 1H, **b**), 6.37 (d, *J* = 16.0 Hz, 1H, **a**), 4.32 – 4.22 (m, 2H, **a** and **b**), 3.88 (s, 3H, **a** and **b**), 1.39 – 1.32 (m, 15H, **a** and **b**).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.4 (**a**), 166.9 (**b**), 165.8 (**a**), 164.4 (**b**), 144.5 (**b**), 144.2 (**a**), 138.4 (**b**), 137.1 (**b**), 136.8 (**a**), 132.7 (**a**), 129.8 (**b**), 126.6 (**a**), 120.2 (**b**), 119.1 (**b**), 115.7 (**a**), 110.6 (**a**), 109.4 (**b**), 83.7 (**a**), 83.7 (**b**), 60.6 (**b**), 60.3 (**a**), 55.9(**a**), 55.8 (**b**), 24.8 (**a** and **b**), 14.4 (**a**), 14.3 (**b**).
^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.6.

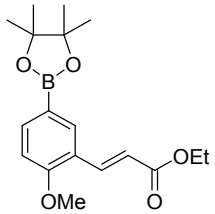


Ethyl (E)-3-(3-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (11a-pin)

The corresponding alkenylated boronic acid MIDA-DG ester (0.10 mmol) was used as a mixture of regioisomers to yield the mono-alkenylated pinacol boronate esters as a clear glassy solid. The ratio of *meta* (**a**) : *para* (**b**) in the isolated mixture was 2.3 : 1.0 (18 mg, 0.05 mmol, 50%).

HRMS (APCI +) Calcd. for $C_{18}H_{26}O_5B$ ([M + H]$^+$): 333.1868. Found: 333.1867.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 16.2 Hz, 1H, **a**), 7.69 (d, *J* = 16.0 Hz, 1H, **b**), 7.64 – 7.59 (m, 1H, **b**), 7.53 (d, *J* = 7.6 Hz, 1H, **a**), 7.42 (dd, *J* = 7.5, 1.0 Hz, 1H, **a**), 7.37 – 7.32 (m, 1H, **a** and **b**), 7.15 (dd, *J* = 2.7, 1.6 Hz, 1H, **b**), 6.59 (d, *J* = 16.2 Hz, 1H, **a**), 6.50 (d, *J* = 16.0 Hz, 1H, **b**), 4.28 (qd, *J* = 7.2, 2.0 Hz, 2H, **a** and **b**), 3.95 (s, 3H, **a**), 3.87 (d, *J* = 2.0 Hz, 3H, **b**), 1.36 (m, 15H, **a** and **b**).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.4 (**a**), 167.0 (**b**), 159.4 (**b**), 157.6 (**a**), 144.4 (**b**), 139.9 (**a**), 135.3 (**b**), 128.1 (**a**), 127.1 (**a** and **b**), 126.1 (**a**), 120.9 (**b**), 119.7 (**a**), 118.7 (**b**), 116.7 (**b**), 116.7 (**a**), 84.1 (**b**), 84.1 (**a**), 60.5 (**b**), 60.4 (**a**), 55.6 (**a**), 55.4 (**b**), 24.9 (**a** and **b**), 14.4 (**a**), 14.3 (**b**).
^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.8.



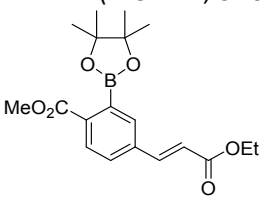
Ethyl (E)-3-(2-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (12a-pin)

The corresponding alkenylated boronic acid MIDA-DG ester (0.09 mmol) was used as a mixture of regioisomers to yield the pinacol boronate ester as a clear glassy solid (15 mg, 0.05 mmol, 50%).

v_{max}/cm^{-1} 2978, 1707, 1632, 1603, 1357, 1249, 1163, 1126, 1025, 988, 854, 671

HRMS (APCI +) Calcd. for $C_{18}H_{26}O_5B$ ([M + H]$^+$): 333.1868. Found: 333.1856.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 7.98 (m, 2H), 7.81 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 6.62 (d, *J* = 16.2 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.93 (s, 3H), 1.36 (d, *J* = 3.3 Hz, 15H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 160.7, 139.8, 138.3, 135.8, 122.9, 118.9, 110.4, 83.8, 60.3, 55.5, 24.9, 14.4.
^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.0.

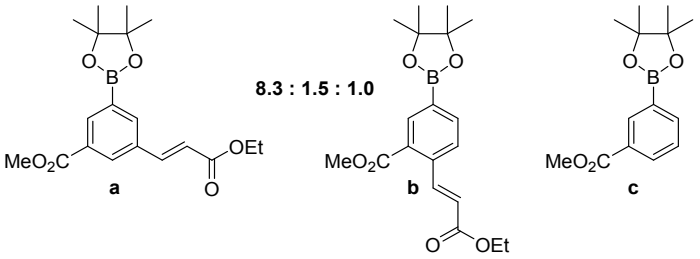


Methyl (E)-3-(3-ethoxy-3-oxoprop-1-en-1-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (16a-pin)

The 2-methoxycarbonylphenylboronic acid MIDA-DG ester proved particularly hard to deprotect and, as such, more forcing conditions were required to access the pinacol ester.
The corresponding alkenylated boronic acid MIDA-DG ester (0.09 mmol) was used as a mixture of regioisomers . The boronic acid was dissolved in THF (1 mL) in a microwave vial, K_3PO_4 (3.0 eq.) and pinacol (1.0 eq.) added and the vial sealed. The reaction mixture was heated to 90 °C for one hour, cooled to room temperature, filtered and purified using preparative TLC to yield the mono-alkenylated pinacol boronate ester as a clear glassy solid (3 mg, 0.01 mmol, 10%). *The isolated sample contained a 10% impurity believed to be the* para *functionalised isomer.*

HRMS (APCI +) Calcd. for $C_{19}H_{26}O_6B$ ([M + H]$^+$): 361.1817. Found: 361.1822.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 16.1 Hz, 1H), 7.65 (d, *J* = 1.8 Hz, 1H), 7.57 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 3H), 1.46 (s, 12H), 1.36 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.9, 166.6, 143.3, 137.5, 134.6, 131.7, 129.3, 128.5, 120.5, 84.3, 60.7, 52.5, 24.9, 14.3.
^{11}B NMR (160 MHz, Chloroform-*d*) δ 31.4.



Methyl (E)-3-(3-ethoxy-3-oxoprop-1-en-1-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (17a-pin)

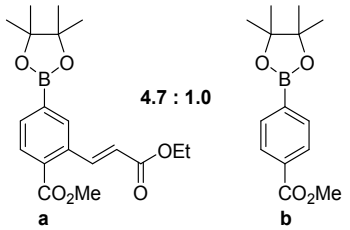
The corresponding alkenylated boronic acid MIDA-DG ester (0.09 mmol) was used as a mixture of regioisomers to yield the mono-alkenylated pinacol boronate esters as a clear glassy solid. The ratio of *meta* (**a**) : *para* (**b**) : starting material (**c**) in the isolated mixture was 8.3 : 1.5 : 1.0 (14 mg, 0.04 mmol, 44%).

HRMS (APCI +) Calcd. for $C_{19}H_{26}O_6B$ ([M + H]$^+$): 361.1817. Found: 361.1821.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 – 8.41 (m, 1H, **a**, **b**, and **c**), 8.38 (d, *J* = 1.3 Hz, 1H, **b**), 8.29 (t, *J* = 1.8 Hz, 1H, **a**), 8.16 (t, *J* = 1.4 Hz, 1H, **a** and **c**), 8.00 (dt, *J* = 7.4, 1.3 Hz, 1H, **c**), 7.96 (dd, *J* = 7.7, 1.3 Hz, 1H, **b**), 7.75 (d, *J* = 16.0 Hz, 1H, **a**), 7.62 (d, *J* = 7.8 Hz, 1H, **b**), 7.47 (t, *J* = 7.6 Hz, 1H, **c**), 6.59 (d, *J* = 16.0 Hz, 1H, **a**), 6.36 (d, *J* = 15.9 Hz, 1H, **b**), 4.29 (q, *J* = 7.2 Hz, 2H, **a** and **b**), 3.98 – 3.91 (m, 3H, **a**, **b**, and **c**), 1.47 – 1.26 (m, 15H, **a**, **b**, and **c**).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7 (**a**), 166.6 (**a**), 143.5 (**b**), 143.4 (**a**), 139.2 (**b**), 138.4 (**a**), 137.2 (**a**), 137.0 (**b**), 135.8 (**b**), 134.3 (**a**), 131.6 **(a)**, 130.4 (**a**), 119.6 (**a**), 84.4 (**a** and **b**), 84.3 (**c**), 60.6 (**a** and **b**), 52.3 (**a** and **b**), 24.9 (**a**, **b**, and **c**), 14.3 (**a** and **b**). Unable to fully characterise ^{13}C for **b** and **c**.
^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.5.

The characterisation data for **c** is in agreement with that reported in the literature (*Angew. Chem. Int. Ed.* 2018, 57, 16721-16726).



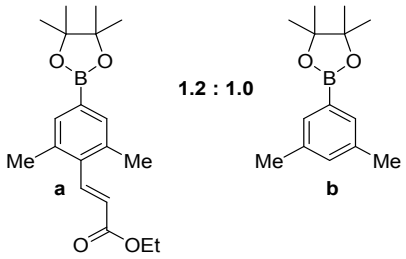
Methyl (E)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (18a-pin)

The corresponding alkenylated boronic acid MIDA-DG ester (0.07 mmol) was used as a mixture of regioisomers to yield the pinacol boronate ester as clear glassy solids. The ratio of product (**a**) : non-alkenylated material (**b**) in the isolated mixture was 4.7 : 1.0 (15 mg, 0.04 mmol (**a**), 51%).

HRMS (APCI +) Calcd. for $C_{19}H_{26}O_6B$ ([M + H]$^+$): 361.1817. Found: 361.1809.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 (d, *J* = 15.9 Hz, 1H, **a**), 8.06 (s, 1H, **a**), 8.04 (d, *J* = 8.4 Hz, 2H, **b**), 7.95 (d, *J* = 7.7 Hz, 1H, **a**), 7.89 (d, *J* = 8.3 Hz, 2H, **b**), 7.86 (dd, *J* = 7.8, 1.2 Hz, 1H, **a**), 6.43 (d, *J* = 15.9 Hz, 1H, **a**), 4.29 (q, *J* = 7.1 Hz, 2H, **a**), 3.96 (s, 3H, **a**), 3.94 (s, 3H, **b**), 1.41 – 1.33 (m, 15H, **a** and 12H, **b**).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.3 (**a**), 166.7 (**a**), 143.5 (**a**), 135.4 (**a)**, 135.3 (**a)**, 134.7 (**b**), 134.3 (**a)**, 132.0 (**a)**, 129.8 (**a)**, 128.6 (**b**), 121.2 (**a)**, 84.4 (**a)**, 60.5 (**a)**, 52.4 (**a)**, 24.9 (**a)**, 14.3 (**a)**.
^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.9.

The characterisation data for **b** is in agreement with that reported in the literature (*J. Am. Chem. Soc*. 2017, 139, 607-610).



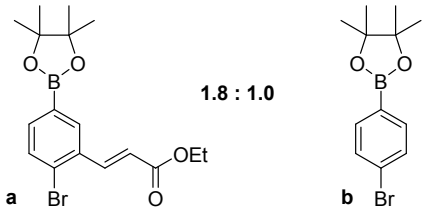
Ethyl (E)-3-(2,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23a-pin)

The corresponding alkenylated boronic acid MIDA-DG ester (0.12 mmol) was used as a mixture with the non-alkenylated starting material to yield the pinacol boronate esters as a clear glassy solid. The ratio of product (**a**) : non-alkenylated material (**b**) in the isolated mixture was 1.2 : 1.0 (38 mg, 0.06 mmol (**a**), 50%).

HRMS (APCI +) Calcd. for $C_{19}H_{28}O_4B$ ([M + H]$^+$): 331.2075. Found: 331.2074.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 16.4 Hz, 1H, **a**), 7.54 (s, 2H, **a**), 7.47 (s, 2H, **b**), 7.13 (s, 1H, **b**), 6.11 (d, *J* = 16.4 Hz, 1H, **a**), 4.31 (q, *J* = 7.2 Hz, 2H, **a**), 2.38 (s, 6H, **a**), 2.35 (s, 6H, **b**), 1.37 (d, *J* = 1.6 Hz, 15H, **a** and 12H, **b**).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7 (**a**), 143.2 (**a**), 137.2 (**b**), 137.0 (**a**), 135.8 (**a**), 134.4 (**a**), 133.0 (**b**), 132.4 (**b**), 124.3 (**a**), 83.9 (**a**), 83.7 (**b**), 60.6 (**a**), 24.9 (**a** and **b**), 21.2 (**b**), 20.8 (**a**)f, 14.3 (**a**).
^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.1.

The characterisation data for **b** is in agreement with that reported in the literature (*Org. Lett.* 2018, 20, 5564-5568).



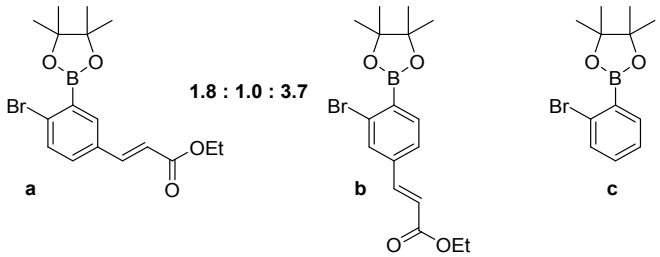
Ethyl (E)-3-(2-bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (20a-pin)

The corresponding alkenylated boronic acid MIDA-DG ester (0.17 mmol) was used as a mixture with the non-alkenylated starting material to yield the pinacol boronate esters as a clear glassy solid. The ratio of product (**a**) : non-alkenylated material (**b**) in the isolated mixture was 1.8 : 1.0 (28 mg, 0.05 mmol (**a**), 29%). The mixture also contained a small impurity believed to correspond to *ortho* alkenylated 4-bromophenylboronic acid, that could not be fully characterised.

HRMS (TOF ES-) Calcd. for $C_{17}H_{21}O_4BBr$ ([M − H]$^-$): 379.0716. Found: 379.0735.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 8.02 (m, 2H, **a**), 7.68 (d, *J* = 8.3 Hz, 2H, **b**), 7.63 (m, 2H, **a**), 7.55 – 7.50 (m, 2H, **b**), 6.52 (d, *J* = 16.0 Hz, 1H, **a**), 4.30 (q, *J* = 7.1 Hz, 2H, **a**), 1.36 (d, *J* = 3.7 Hz, 15H, **a** and 12H **b**).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.5 (**a**), 142.9, 142.8 (**a**), 137.1 (**a**), 136.3 (**b**), 134.2 (**a**), 134.0 (**a**), 133.4, 132.9 (**a**), 131.1, 131.0 (**b**), 128.7 (**a**), 127.8, 127.7, 126.2 (**b**), 121.3 (**a**), 121.1, 84.3 (**a**), 84.0 (**b**), 60.7 (**a**), 24.9 (**a** and **b**), 14.3 (**a**). Peaks that are unassigned are believed to correspond to the 2-alkenylated 4-bromophenylboronic acid pinacol ester.
^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.9.

The characterisation data for **b** is in agreement with that reported in the literature (*J. Org. Chem.* 2018, 83, 12831-12837).



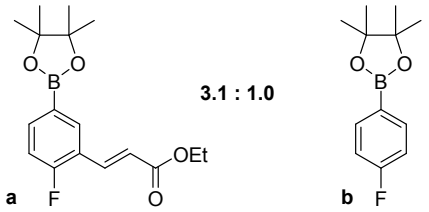
Ethyl (E)-3-(2-bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (19a-pin)

The corresponding alkenylated boronic acid MIDA-DG ester (0.14 mmol) was used as a mixture with the non-alkenylated starting material to yield the pinacol boronate esters as a clear glassy solid. The ratio of product (**a**) : non-alkenylated material (**b**) : starting material (**c**) in the isolated mixture was 1.8 : 1.0 : 3.0 (13 mg, 0.01 mmol (**a**), 0.01 (**b**), 12% yield).

HRMS (APCI +) Calcd. for $C_{19}H_{26}O_6B$ ([M + H]$^+$): 381.0867. Found: 381.0869.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 15.9 Hz, 1H, **b**), 7.68 – 7.60 (m, 2H, **a** and 1H, **c**), 7.59 – 7.52 (m, 1H, **a,** 1H, **b** and 1H, **c**), 7.44 – 7.38 (m, 1H, **a** and 2H, **b**), 7.31 (m, 1H, **c**), 7.26 (m, 1H, **c**), 6.47 (d, *J* = 16.0 Hz, 1H, **a**), 6.41 (d, *J* = 15.9 Hz, 1H, **b**), 4.30 (app. p, *J* = 7.3 Hz, 2H, **a** and **b**), 1.40 (s, 12H, **a, b**, and **c**), 1.38 – 1.34 (m, 3H, **a** and **b**).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.3 (**a**), 143.2 (**a**), 136.4 (**c**), 132.6 (**c**), 132.1 (**a**), 131.9 (**c**), 129.4 (**a**), 128.0 (**c**), 127.8 (**b**), 127.7 (**a**), 126.3 (**c**), 121.2 (**b**), 119.0 (**a**), 84.3 (**a**, **b**, and **c**), 60.7 (**b**), 60.7 (**a**), 24.8 (**a**, **b**, and **c**), 14.3 (**a** and **b**). Unable to fully characterise the ^{13}C data for **b**.
^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.8.

The characterisation data for **c** is in agreement with that reported in the literature (*Angew. Chem. Int. Ed.* 2017, 56, 7078-7082).



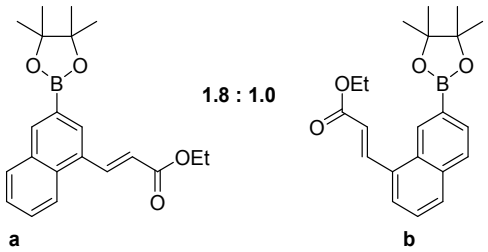
Ethyl (E)-3-(2-fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (21a-pin)

The corresponding alkenylated boronic acid MIDA-DG ester (0.13 mmol) was used as a mixture with the non-alkenylated starting material to yield the pinacol boronate esters as a clear glassy solid. The ratio of product (**a**) : non-alkenylated material (**b**) in the isolated mixture was 3.1 : 1.0 (27 mg, 0.07 mmol (**a**), 54%).

HRMS (APCI +) Calcd. for $C_{17}H_{23}O_4B$ ([M + H]$^+$): 321.1668. Found: 321.1671.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (dd, *J* = 8.0, 1.7 Hz, 1H, **a**), 7.85 (d, *J* = 16.3 Hz, 1H, **a**), 7.81 (m, 1H, **a** and 2H, **b**), 7.14 – 7.04 (m, 1H, **a** and 2H, **b**), 6.63 (d, *J* = 16.2 Hz, 1H, **a**), 4.29 (q, *J* = 7.1 Hz, 2H, **a**), 1.36 (m, 15H, **a** and 12H, **b**).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.8 (**a**), 165.1 (d, *J* = 250.4 Hz, **b**), 163.4 (d, *J* = 258.2 Hz, **a**), 138.3 (d, *J* = 9.0 Hz, **a**), 137.0 (m, **a** and **b**), 136.0 (d, *J* = 3.1 Hz, **a**), 122.0 (d, *J* = 11.2 Hz, **a**), 120.9 (d, *J* = 6.0 Hz, **a**), 115.7 (d, *J* = 21.2 Hz, **a**), 114.8 (d, *J* = 20.2 Hz, **b**), 84.2 (**a**), 83.9 (**b**), 60.6 (**a**), 24.9 (**a** and **b**), 14.3 (**a**).
^{19}F NMR (377 MHz, Chloroform-*d*) δ -108.4 (**b**), -110.5 (**a**).
^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.6.

The characterisation data for **b** is in agreement with that reported in the literature (*Angew. Chem. Int. Ed.* 2018, 57, 16832-16836).

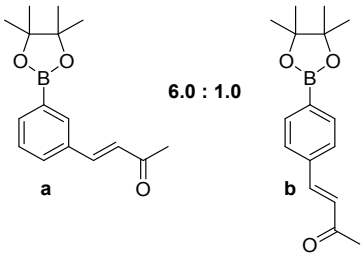


Ethyl (E)-3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-1-yl)acrylate (22a-pin)

The corresponding alkenylated boronic acid MIDA-DG ester (0.3 mmol) was used as a mixture of regioisomers to yield the mono-alkenylated pinacol boronate esters as a colourless solid. The ratio of *meta* (**a**) : *para* (**b**) in the isolated mixture was 1.8 : 1.0, **a** : **b** (22 mg, 0.06 mmol, 21% over 2 steps from the 2-naphtylboronic acid MIDA-DG ester).

HRMS (TOF ES+) Calcd. for $C_{21}H_{26}O_4B$ ([M + H]$^+$): 353.1924. Found: 353.1931.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.70 (s, 1H, **b**), 8.68 (d, *J* = 15.7 Hz, 1H, **b**), 8.54 (d, *J* = 15.7 Hz, 1H, **a**), 8.42 (s, 1H, **a**), 8.22 (dd, *J* = 8.6, 1.1 Hz, 1H, **a**), 8.17 (t, *J* = 0.9 Hz, 1H, **a**), 7.96 – 7.86 (m, 1H, **a** and 2H, **b**), 7.78 (dt, *J* = 7.2, 0.9 Hz, 1H, **b**), 7.64 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H, **a**), 7.59 – 7.49 (m, 1H, **a** and **b**), 6.66 (d, *J* = 15.7 Hz, 1H, **a**), 6.57 (d, *J* = 15.7 Hz, 1H, **b**), 4.39 – 4.30 (m, 2H, **a** and **b**), 1.42 (s, 12H, **a** and **b**), 1.41 – 1.38 (m, 3H, **a** and **b**).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.0 (**a** and **b**), 141.9 (**a**), 141.6 (**a**), 138.5 (**a**), 135.2 (**b**), 133.0 (**b**), 132.9 (**b**), 132.6 (**a**), 131.5 (**b**), 131.3 (**b**), 130.9 (**a**), 130.3 (**b**), 129.8 (**a**), 129.5 (**a**), 128.0 (**a**), 127.8 (**b**), 126.5 (**b**), 126.2 (**a**), 124.9 (**b**), 123.3 (**a**), 122.5 (**b**), 121.0 (**a** and **b**), 84.2 (**a**), 84.1 (**b**), 60.6 (**b**), 60.6 (**a**), 24.9 (**a** and **b**), 14.4 (**a** and **b**).
^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.2.



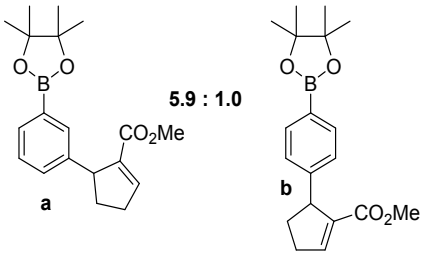
(E)-4-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)but-3-en-2-one (7b-pin)

The corresponding alkenylated boronic acid MIDA-DG ester (0.20 mmol) was used as a mixture of regioisomers to yield the mono-alkenylated pinacol boronate esters as a white solid. The ratio of *meta* (**a**) : *para* (**b**) in the isolated mixture was 6.0 : 1.0 (26 mg, 0.10 mmol, 50%).

HRMS (APCI +) Calcd. for $C_{16}H_{22}O_3B$ ([M + H]$^+$): 273.1657. Found: 273.1657.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 7.99 (m, 1H, **a**), 7.85 (dt, *J* = 7.3, 1.2 Hz, 1H, **a**), 7.65 (dt, *J* = 8.0, 1.7 Hz, 1H, **a** and 2H, **b**), 7.60 – 7.50 (m, 1H, **a** and 3H, **b**), 7.43 (t, *J* = 7.5 Hz, 1H, **a**), 6.79 (d, *J* = 16.4 Hz, 1H, **a**), 6.78 (d, *J* = 16.1 Hz, 1H, **b**), 2.41 (s, 3H, **b**), 2.40 (s, 3H, **a**), 1.38 (s, 12H, **a** and **b**).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.4 (**a**), 198.4 (**b**), 143.4 (**a**), 143.3 (**b**), 136.8 (**a** and **b**), 135.3 (**b**), 134.8 (**a**), 133.8 (**a**), 130.9 (**a**), 128.4 (**a**), 127.9 (**b**), 127.4 (**b**), 127.3 (**a**), 84.1 (**a**), 84.1 (**b**), 27.6 (**b**), 27.5 (**a**), 24.9 (**a** and **b**).
^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.6.

The characterisation data for **b** is in agreement with that reported in the literature (*Angew. Chem. Int. Ed.* 2017, 56, 2022-2025).

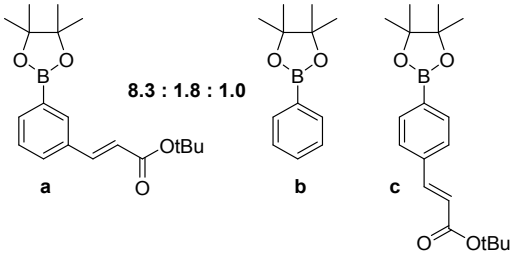


Methyl 5-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)cyclopent-1-ene-1-carboxylate (7e-pin)

The corresponding alkenylated boronic acid MIDA-DG ester (0.20 mmol) was used as a mixture of regioisomers to yield the mono-alkenylated pinacol boronate esters as a white solid. The ratio of *meta* (**a**) : *para* (**b**) in the isolated mixture was 5.9 : 1.0 (28 mg, 0.09 mmol, 45%).

HRMS (APCI +) Calcd. for $C_{19}H_{26}O_4B$ ([M + H]$^+$): 329.1919. Found: 329.1903.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.74 (m, 2H, **b**), 7.66 (dt, *J* = 8.2, 1.3 Hz, 2H, **a**), 7.33 – 7.27 (m, 1H, **a**), 7.25 (dt, *J* = 7.7, 1.7 Hz, 1H, **a**), 7.20 (d, *J* = 8.1 Hz, 2H, **b**), 7.03 (td, *J* = 2.4, 1.6 Hz, 1H, **a** and **b**), 4.18 (ddq, *J* = 8.2, 4.3, 2.3, 1.8 Hz, 1H, **a** and **b**), 3.61 (d, *J* = 2.1 Hz, 3H, **a** and **b**), 2.79 – 2.63 (m, 1H, **a** and **b**), 2.62 – 2.47 (m, 2H, **a** and **b**), 2.01 – 1.85 (m, 1H, **a** and **b**), 1.36 (d, *J* = 5.5 Hz, 12H, **a** and **b**).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.2 (**a**), 165.1 (**b**), 148.5 (**b**), 145.2 (**a** and **b**), 144.3 (**a**), 139.1 (**a**), 139.0 (**b**), 135.0 (**b**), 133.6 (**a**), 132.8 (**a**), 129.7 (**a**), 127.8 (**a**), 126.4 (**b**), 83.7 (**a**), 83.6 (**b**), 51.3 (**a** and **b**), 50.3 (**b**), 50.1 (**a**), 34.2 (**a**), 34.1 (**b**), 32.3 (**b**), 32.2 (**a**), 24.9 (**b**), 24.9 (**a**).
^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.9.



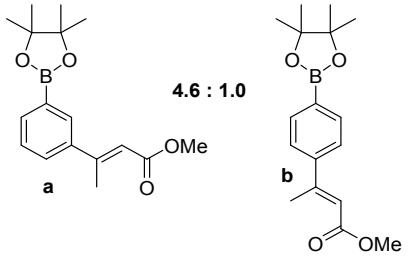
***tert*-Butyl (E)-3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (7c-pin)**

The corresponding alkenylated boronic acid MIDA-DG ester (0.15 mmol) was used as a mixture of regioisomers to yield the mono-alkenylated pinacol boronate esters as a white solid. The ratio of *meta* (**a**) : phenylboronic acid pinacol ester (**b**) : *para* (**c**) in the isolated mixture was 8.3 : 1.8 : 1.0 (36 mg, 0.10 mmol, 65%).

HRMS (APCI +) Calcd. for $C_{19}H_{28}O_4B$ ($[M + H]^+$): 331.2080. Not found. Found: 257.1334 corresponding to loss of *tert*-butanol anion fragment C_4H_9O. Calcd. for $C_{15}H_{18}O_3B$ ($[M- C_4H_9O]^+$):257.1344.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.97 (m, 1H, **a**), 7.86 – 7.79 (m, 2H, **a, b** and **c**), 7.66 – 7.58 (m, 2H, **a**), 7.55 – 7.51 (d, *J* = 7.9 Hz, 2H, **c**), 7.51 – 7.45 (m, 1H, **b**), 7.43 – 7.36 (m, 1H, **a** and **b**), 6.45 (d, *J* = 16.0 Hz, 1H, **a** and **c**), 1.55 (s, 9H, **a** and **c**), 1.37 (d, *J* = 2.2 Hz, 15H, **a**, **b**, and **c**).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.3 (**a** and **c**), 143.5 (**a**), 143.4 (**c**), 137.2 (**c**), 136.3 (**a**), 135.2 (**c**), 134.7 (**b**), 134.2 (**a**), 134.0 (**a**), 131.3 (**b**), 130.8 (**a**), 128.2 (**a**), 127.7 (**b**), 127.2 (**c**), 121.1 (**c**), 120.3 (**a**), 84.0 (**a** and **c**), 83.8 (**b**), 80.6 (**c**), 80.4 (**a**), 28.2 (**a** and **c**), 24.9 (**a**, **b**, and **c**).
^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.0.

The characterisation data for **b** is in agreement with that reported in the literature (*Chem. Comm.*, 2018, 54, 13969-13972).

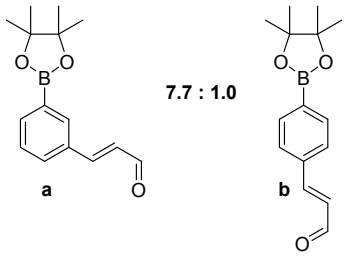


Methyl (E)-3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)but-2-enoate (7d-pin)

The corresponding alkenylated boronic acid MIDA-DG ester (0.05 mmol) was used as a mixture of regioisomers to yield the mono-alkenylated pinacol boronate esters as a white solid. The ratio of *meta* (**a**) : *para* (**b**) in the isolated mixture was 4.6 : 1.0 (4 mg, 0.01 mmol, 20%).

HRMS (APCI +) Calcd. for $C_{17}H_{24}O_4B$ ($[M + H]^+$): 303.1762. Found: 303.1762.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.91 (m, 1H, **a**), 7.86 – 7.79 (m, 1H, **a** and 2H, **b**), 7.58 (ddd, *J* = 7.9, 2.1, 1.3 Hz, 1H, **a**), 7.52 – 7.47 (m, 2H, **b**), 7.41 (ddd, *J* = 7.9, 7.3, 0.6 Hz, 1H, **a**), 6.19 (q, *J* = 1.3 Hz, 1H, **a** and **b**), 3.78 (s, 3H, **a** and **b**), 2.62 (d, *J* = 1.3 Hz, 3H, **a**), 2.60 (d, *J* = 1.3 Hz, 3H, **b**), 1.38 (d, *J* = 1.4 Hz, 12H, **a** and **b**).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.3 (**a**), 156.1 (**a**), 141.5 (**a**), 135.4 (**a**), 134.9 (**b**), 134.7 (**b**), 132.6 (**a**), 129.2 (**a**), 127.9 (**a**), 125.6 (**b**), 117.2 (**b**), 116.7 (**a**), 84.0 (**a**), 51.1 (**a**), 24.9 (**a**), 18.1 (**a**). Unable to fully characterise ^{13}C for **b**.
^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.9.



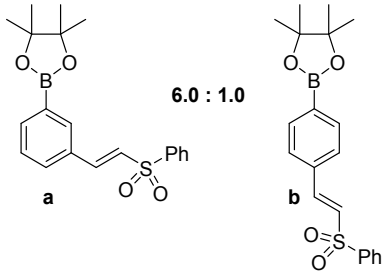
(*E*)-3-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylaldehyde (7i-pin)

The corresponding alkenylated boronic acid MIDA-DG ester (0.19 mmol) was used as a mixture of regioisomers to yield the mono-alkenylated pinacol boronate esters as a white solid. The ratio of *meta* (**a**) : *para* (**b**) in the isolated mixture was 7.7 : 1.0 (24 mg, 0.09 mmol, 47%).

HRMS (APCI +) Calcd. for $C_{15}H_{21}O_3B$ ($[M + H]^+$): 259.1500. Found: 259.1506.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.74 (d, *J* = 7.7 Hz, 1H, **b**), 9.72 (d, *J* = 7.7 Hz, 1H, **a**), 8.03 (s, 1H, **a**), 7.92 – 7.84 (m, 1H, **a** and 2H, **b**), 7.68 (dt, *J* = 7.8, 1.6 Hz, 1H, **a**), 7.61 – 7.55 (m, 2H, **b**), 7.51 (d, *J* = 16.0 Hz, 1H, **a** and **b**), 7.46 (t, *J* = 7.6 Hz, 1H, **a**), 6.79 (dd, *J* = 16.0, 7.7 Hz, 1H, **a** and **b**), 1.38 (d, *J* = 2.5 Hz, 12H, **a** and **b**).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.7 (**a** and **b**), 152.8 (**a**), 152.5 (**b**), 137.6 (**a**), 136.4 (**b**), 135.4 (**b**), 135.2 (**a**), 133.4 (**a**), 130.9 (**a**), 129.3 (**b**), 128.6 (**a**), 128.5 (**a**), 127.6 (**b**), 84.2 **(a** and **b**), 24.9 **(a** and **b**).
^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.8.

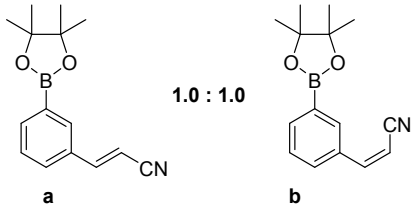
The characterisation data for **b** is in agreement with that reported in the literature (*Angew. Chem. Int. Ed.* 2018, 57, 12819-12823).



(*E*)-4,4,5,5-Tetramethyl-2-(3-(2-(phenylsulfonyl)vinyl)phenyl)-1,3,2-dioxaborolane (7h-pin)
The corresponding alkenylated boronic acid MIDA-DG ester (0.11 mmol) was used as a mixture of regioisomers to yield the mono-alkenylated pinacol boronate esters as a white solid. The ratio of *meta* (**a**) : *para* (**b**) in the isolated mixture was 6.0 : 1.0 (15 mg, 0.04 mmol, 36%).

HRMS (APCI +) Calcd. for $C_{20}H_{24}O_4BS$ ([M + H]$^+$): 371.1483. Found: 371.1481.

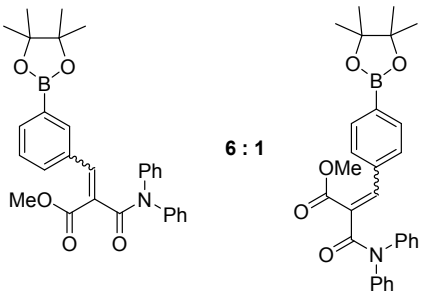
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (m, 3H, **a**, 2H, **b**), 7.89 – 7.81 (m, 1H, **a**, 2H, **b**), 7.72 (d, *J* = 15.4 Hz, 1H, **a** and **b**), 7.67 – 7.61 (m, 1H, **a**), 7.61 – 7.54 (m, 3H, **a** and **b**), 7.52 – 7.47 (m, 2H, **b**), 7.43 (t, *J* = 7.6 Hz, 1H, **a**), 6.94 (d, *J* = 15.5 Hz, 1H, **a**), 6.93 (d, *J* = 15.5 Hz, 1H, **b**), 1.36 (s, 12H, **a** and **b**).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.4 (**a**), 142.3 (**b**), 140.8 (**b**), 137.4 (**a**), 135.4 (**b**), 134.5 (**a**), 133.5 (**b**), 133.4 (**a**), 131.8 (**a**), 131.6 (**a**), 129.4 (**a**), 129.3 (**a**), 128.5 (**a**), 128.1 (**b**), 127.7 (**a**), 127.4 (**a**), 84.2 (**a** and **b**), 24.9 (**a** and **b**). Unable to assign all carbons for **b**.
^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.6.



(*E*)-3-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylonitrile (7g-pin)
The corresponding alkenylated boronic acid MIDA-DG ester (0.17 mmol) was used as a mixture of regioisomers to yield the mono-alkenylated pinacol boronate esters as a white solid. The ratio of *cis* (**a**) : *trans* (**b**) in the isolated mixture was 1.0 : 1.0 (30 mg, 0.12 mmol, 69%). The products contained some small impurities corresponding to the *para*-alkenylated pinacol esters.

HRMS (TOF ES+) Calcd. for $C_{15}H_{19}NO_2B$ ([M + H]$^+$): 256.1503. Found: 256.1507.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (dt, *J* = 7.8, 1.7 Hz, 1H, **b**), 8.01 – 7.95 (m, 1H, **b**), 7.90 (dddd, *J* = 9.8, 5.2, 2.2, 1.2 Hz, 2H, **a and b**), 7.86 – 7.78 (m, 1H, **a**), 7.55 (dt, *J* = 7.7, 1.7 Hz, 1H, **a**), 7.49 (t, *J* = 7.7 Hz, 1H, **a**), 7.47 – 7.38 (m, 2H, **a and b**), 7.18 (d, *J* = 12.1 Hz, 1H, **b**), 5.97 (d, *J* = 16.7 Hz, 1H, **a**), 5.47 (d, *J* = 12.1 Hz, 1H, **b**), 1.38 (d, *J* = 3.4 Hz, 24H, **a and b**).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.6 (**a**), 148.8 (**b**), 137.5 (**a or b**), 137.2 (**a or b**), 136.6 (**b**), 134.7 (**a**), 133.6 (**a**), 133.0 (**b**), 132.9 (**a**), 130.3 (**a or b**), 130.1 (**a or b**), 128.5 (**a or b**), 128.4 (**a or b**), 118.2 (**a**), 117.3 (**b**), 96.4 (**b**), 95.1 (**a**), 84.2 (**a or b**), 84.2 (**a or b**), 24.9 (**a and b**). Not all ^{13}C peaks could be exactly assigned to **a or b**.
^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.8.



Methyl 2-(diphenylcarbamoyl)-3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (7f-pin)

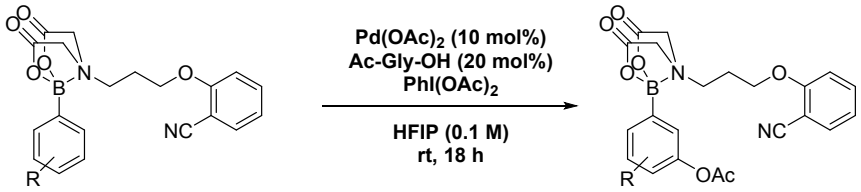
The corresponding alkenylated boronic acid MIDA-DG ester (0.24 mmol) was used as a mixture of regioisomers to yield the mono-alkenylated pinacol boronate esters as a white solid (42 mg, 0.04 mmol, 36%). The product contained a 15% impurity consisting of the *para* substituted isomer (not characterised). The geometry of the double bond is unknown but presumed to be cis.

HRMS (TOF ES+) Calcd. for $C_{29}H_{31}NO_5B$ ($[M + H]^+$): 484.2290. Found: 484.2303

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 8.02 (m, 1H), 7.88 (dt, *J* = 7.4, 1.3 Hz, 1H), 7.62 (dt, *J* = 7.9, 1.6 Hz, 1H), 7.48 (s, 1H), 7.45 (dd, *J* = 8.5, 1.4 Hz, 2H), 7.41 – 7.33 (m, 2H), 7.28 – 7.17 (m, 2H), 7.15 – 7.09 (m, 2H), 6.85 – 6.81 (m, 2H), 3.87 (d, *J* = 1.2 Hz, 3H), 1.39 (s, 12H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.2, 165.2, 143.5, 141.9, 141.3, 136.8, 136.3, 135.9, 133.0, 132.4, 128.9, 127.6, 126.4, 84.1, 52.5, 25.0.
^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.9.

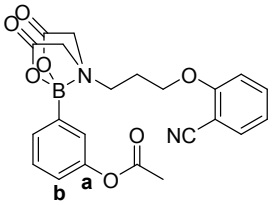
Acetoxylation of aryl boronic acid MIDA-DG esters

General Procedure for the C–H Acetoxylation of aryl boronic acid MIDA-DG esters



A vial was charged with arylboronic acid MIDA-DG ester (1.0 eq.), $PhI(OAc)_2$ (1.2 eq.), Ac-Gly-OH (20 mol%), $Pd(OAc)_2$ (10 mol%) and HFIP (0.1 M). The vial was sealed and stirred at 40 °C for 24 hours. The reaction mixture was diluted with MeCN (~5 mL), dry loaded onto a silica column and purified via 'catch and release' purification: washing with copious Et_2O to remove by-products then eluting using EtOAc as eluent.

NB: The high polarity of MIDA-DG containing compounds precludes their separation using normal phase FCC. As such, 'catch and release' purification was used to isolate mixtures of mono and di-functionalised and regioisomeric mixtures, with starting material if full conversion was not achieved. These mixtures were weighed and the yields of the constituent products calculated using ^{1}H NMR in combination with molecular weights and the mass of the solids. All the C–H functionalisation products were later derivatised to the corresponding phenols and purified to allow unambiguous characterisation.



3-Acetoxyphenylboronic acid MIDA-DG ester (7k)

Phenylboronic acid MIDA-DG ester (113 mg, 0.3 mmol) was employed to yield the product as an off-white solid (100 mg, total yield: 70% **a**: 61% **b**: 9% with 7% SM remaining, as determined by ^{1}H NMR).

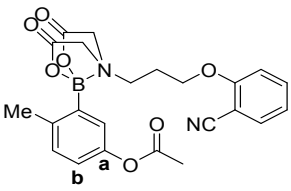
Characterisation data for major isomer:

HRMS (TOF ES+) Calcd. for $C_{22}H_{22}N_2O_7B$ ([M+H]$^+$): 437.1520. Found: 437.1536.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.64 – 7.55 (m, 2H), 7.46 – 7.36 (m, 2H), 7.23 (dd, *J* = 2.6, 1.1 Hz, 1H), 7.15 – 7.10 (m, 1H), 7.07 (td, *J* = 7.6, 0.9 Hz, 1H), 7.03 – 6.96 (m, 1H), 4.10 (d, *J* = 17.1 Hz, 2H), 4.03 (d, *J* = 17.1 Hz, 2H), 3.97 (t, *J* = 6.2 Hz, 2H), 2.90 – 2.81 (m, 2H), 2.25 (s, 3H), 2.15 – 2.06 (m, 2H).

^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 169.6, 168.4, 159.9, 150.9, 134.8, 133.8, 133.6, 132.5, 129.9, 129.3, 128.0, 125.7, 122.8, 121.3, 116.1, 112.8, 101.4, 65.8, 59.0, 56.1, 55.9, 23.8, 20.3. Unable to distinguish ^{13}C peaks between regioisomers.

^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.6.



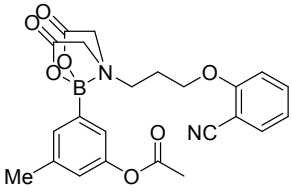
2-Methyl-5-acetoxyphenylboronic acid MIDA-DG ester (13b)

2-Methylphenylboronic acid MIDA-DG ester (78 mg, 0.2 mmol) was employed to yield the product as a yellow solid (43 mg, total yield: 48% **a**: 38%, **b**: 10% as determined by ^{1}H NMR).

Characterisation data for major isomer:

HRMS (TOF ES+) Calcd. for $C_{23}H_{24}N_2O_7B$ ([M+H]$^+$): 451.1677. Found: 451.1674.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.64 – 7.55 (m, 2H), 7.22 – 7.18 (m, 1H), 7.14 (d, *J* = 2.5 Hz, 1H), 7.07 (td, *J* = 7.5, 0.8 Hz, 1H), 7.02 – 6.97 (m, 2H), 4.11 (d, *J* = 17.2 Hz, 2H), 4.07 – 3.98 (m, 4H), 2.90 – 2.83 (m, 2H), 2.40 (s, 3H), 2.23 (s, 3H), 2.18 – 2.10 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 169.7, 168.4, 159.9, 148.7, 139.9, 135.5, 134.8, 133.6, 132.2, 127.0, 124.0, 122.6, 121.3, 118.5, 116.1, 112.7, 101.4, 65.7, 59.8, 56.1, 24.0, 22.1, 21.5, 20.3. Unable to distinguish ^{13}C peaks between regioisomers.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 12.3.



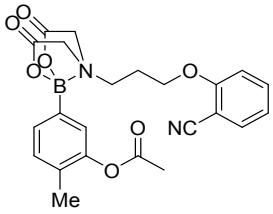
3-Methyl-5-acetoxyphenylboronic acid MIDA-DG ester (14b)

3-Methylphenyl5boronic acid MIDA-DG ester (78 mg, 0.2 mmol) was employed to yield the product as a white solid (56 mg, 62%).

ν_{max}/cm^{-1} 2956, 2225, 1748, 1599, 1491, 1445, 1282, 1208, 1178, 1014, 945, 865, 757, 708.

HRMS (TOF ES+) Calcd. for $C_{23}H_{24}N_2O_7B$ ([M+H]$^+$): 451.1677. Found: 451.1674.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.63 – 7.55 (m, 2H), 7.21 (dt, *J* = 1.8, 0.9 Hz, 1H), 7.07 (td, *J* = 7.6, 0.9 Hz, 1H), 7.03 – 6.97 (m, 2H), 6.93 (ddd, *J* = 2.3, 1.6, 0.8 Hz, 1H), 4.09 (d, *J* = 17.1 Hz, 2H), 4.03 (d, *J* = 17.1 Hz, 2H), 3.98 (t, *J* = 6.2 Hz, 2H), 2.89 – 2.82 (m, 2H), 2.35 (s, 3H), 2.23 (s, 3H), 2.15 – 2.06 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 169.6, 168.4, 159.9, 150.9, 139.5, 134.8, 133.6, 130.6, 123.3, 122.6, 121.3, 116.2, 112.8, 101.4, 65.8, 59.0, 56.1, 23.8, 20.4, 20.3.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.6.

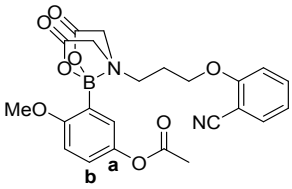


4-Methyl-3-acetoxyphenylboronic acid MIDA-DG ester (15b)

4-Methylphenylboronic acid MIDA-DG ester (78 mg, 0.2 mmol) was employed to yield the product as an off-white solid (26 mg, 12%, **SM**: 11% as determined by ^{1}H NMR). The isolated mixture also contained an unknown impurity that was removed after deprotection and oxidation of the boronic acid.

HRMS (TOF ES+) Calcd. for $C_{23}H_{24}N_2O_7B$ ([M+H]$^+$): 451.1677. Found: 451.1672.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.64 – 7.54 (m, 2H), 7.42 – 7.37 (m, 1H), 7.26 – 7.22 (m, 1H), 7.15 (s, 1H), 7.08 (ddt, *J* = 8.2, 6.7, 0.8 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 4.08 (d, *J* = 17.1 Hz, 2H), 4.02 (d, *J* = 17.1 Hz, 2H), 3.99 – 3.96 (m, 2H), 2.88 – 2.81 (m, 2H), 2.19 (s, 3H), 2.16 (s, 3H), 2.13 – 2.07 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.6, 168.4, 159.9, 149.6, 139.1, 134.8, 133.7, 132.6, 130.9, 130.1, 126.0, 121.3, 112.8, 65.8, 58.9, 56.0, 26.7, 23.8.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.9.

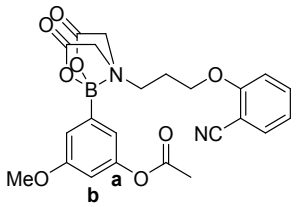


2-Methoxy-5-acetoxyphenylboronic acid MIDA-DG ester (10b)

2-Methoxyphenylboronic acid MIDA-DG ester (82 mg, 0.2 mmol) was employed to yield the product as a yellow solid (35.3 mg, total yield: 28% **a**: 17%, **b**: 11% **SM:** 18% as determined by ^{1}H NMR).
Characterisation data for major isomer:

HRMS (TOF ES+) Calcd. for $C_{23}H_{24}N_2O_8B$ ([M+H]$^+$): 467.1626. Found: 451.1627.

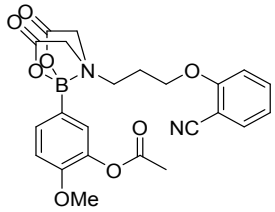
^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.62 – 7.54 (m, 2H), 7.10 – 7.03 (m, 2H), 7.00 – 6.92 (m, 2H), 6.73 – 6.70 (m, 1H), 4.15 (d, *J* = 17.0 Hz, 2H), 4.06 – 3.97 (m, 4H), 3.78 (s, 3H), 3.09 – 2.99 (m, 2H), 2.26 (s, 3H), 2.17 – 2.07 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 169.3, 168.8, 168.7, 163.2, 162.3, 159.8, 153.5, 139.5, 135.0, 134.8, 134.5, 134.3, 133.7, 131.0, 127.3, 123.7, 121.2, 120.5, 116.1, 113.7, 112.6, 112.5, 111.1, 110.3, 104.8, 101.2, 65.8, 59.2, 55.7, 55.6, 55.5, 55.2, 55.0, 54.6, 23.9, 23.8, 20.3, 20.3. Unable to distinguish ^{13}C peaks between regioisomers.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.6.



3-Methoxy-5-acetoxyphenylboronic acid MIDA-DG ester (11b)
3-Methoxyphenylboronic acid MIDA-DG ester (122 mg, 0.3 mmol) was employed to yield the product as a yellow solid (76 mg, Total yield: 54% **a:** 35%, **b**: 19% as determined by ^{1}H NMR).
Characterisation data for major isomer:

HRMS (TOF ES+) Calcd. for $C_{23}H_{24}N_2O_8B$ ([M+H]$^+$): 467.1626. Found: 467.1624.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.64 – 7.55 (m, 2H), 7.08 (td, *J* = 7.1, 6.7, 0.9 Hz, 1H), 7.01 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.92 (dd, *J* = 2.4, 1.0 Hz, 1H), 6.80 (dd, *J* = 2.1, 1.0 Hz, 1H), 6.70 (t, *J* = 2.3 Hz, 1H), 4.09 (d, *J* = 17.1 Hz, 2H), 4.04 – 3.97 (m, 4H), 3.80 (s, 3H), 2.88 (dt, *J* = 11.4, 4.4 Hz, 2H), 2.24 (s, 3H), 2.16 – 2.07 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.4, 159.9, 134.8, 133.6, 129.3, 125.0, 122.6, 121.3, 117.8, 116.2, 116.2, 114.8, 112.8, 112.8, 109.0, 65.8, 59.0, 58.9, 56.0, 55.9, 55.5, 55.1, 23.9, 23.8, 20.3, 19.8. Unable to distinguish ^{13}C peaks between regioisomers.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.3.

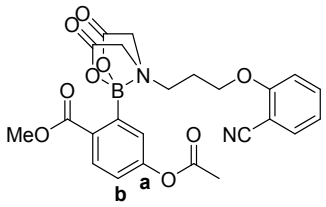


4-Methoxy-3-acetoxyphenylboronic acid MIDA-DG ester (12b)
4-Methoxyphenylboronic acid MIDA-DG ester (122 mg, 0.3 mmol) was employed to yield the products as a yellow solid (62 mg, 0.04 mmol, 44%).

ν_{max}/cm^{-1} 2926, 2225, 1752, 1599, 1513, 1449, 1290, 1260, 1200, 1126, 1044, 1006, 591, 865, 813, 757.

HRMS (TOF ES+) Calcd. for $C_{23}H_{24}N_2O_8B$ ([M+H]$^+$): 467.1626. Found: 467.1642.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.64 – 7.54 (m, 2H), 7.36 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.16 (d, *J* = 1.8 Hz, 1H), 7.11 – 7.05 (m, 2H), 7.01 (dd, *J* = 8.5, 0.8 Hz, 1H), 4.07 (d, *J* = 17.1 Hz, 2H), 4.03 – 3.96 (m, 4H), 3.81 (s, 3H), 2.89 – 2.81 (m, 2H), 2.24 (s, 3H), 2.16 – 2.05 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.9, 168.4, 159.9, 152.2, 139.7, 134.8, 133.7, 131.4, 126.8, 121.3, 116.1, 112.8, 112.4, 101.4, 65.8, 58.9, 56.0, 55.4, 23.8, 19.8.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.8.



2-Methoxycarbonyl-5-acetoxyphenylboronic acid MIDA-DG ester (16b)

2-Methoxycarbonylphenylboronic acid MIDA-DG ester (44 mg, 0.1 mmol) was employed to yield the product as a yellow solid after an extended reaction time of 48 hours (35 mg, total yield: 40% **a**: 33%, **b**: 7% **SM:** 36% as determined by ^{1}H NMR).

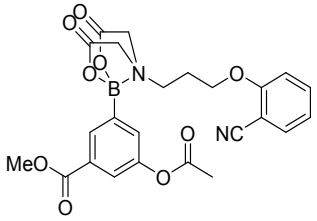
Characterisation data for major isomer:

HRMS (TOF ES+) Calcd. for $C_{24}H_{24}N_2O_9B$ ([M+H]$^+$): 495.1575. Found: 495.1574.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.72 (d, *J* = 8.4 Hz, 1H), 7.65 – 7.51 (m, 2H), 7.42 (d, *J* = 2.4 Hz, 1H), 7.21 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.06 (m, 1H), 7.00 (m, 1H), 4.29 (d, *J* = 17.1 Hz, 2H), 4.07 – 3.98 (m, 4H), 3.82 (s, 3H), 3.25 – 3.14 (m, 2H), 2.28 (s, 3H), 2.25 – 2.18 (m, 2H).

^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 171.4, 170.5, 169.3, 168.9, 168.8, 168.6, 159.8, 152.5, 137.1, 136.4, 134.7, 134.3, 133.7, 131.6, 130.5, 130.4, 130.2, 129.3, 128.5, 128.1, 124.3, 122.6, 121.3, 116.1, 112.7, 101.4, 101.3, 65.8, 61.5, 61.3, 60.4, 57.9, 57.6, 52.4, 24.2, 20.4, 19.9. Unable to distinguish ^{13}C peaks between regioisomers.

^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 12.0.



3-Methoxycarbonyl-5-acetoxyphenylboronic acid MIDA-DG ester (17b)

3-Methoxycarbonylphenylboronic acid MIDA-DG ester (44 mg, 0.1 mmol) was employed to yield the product as a yellow solid after an extended reaction time of 48 hours (40 mg, **product**: 36%, **SM**: 50% as determined by ^{1}H NMR).

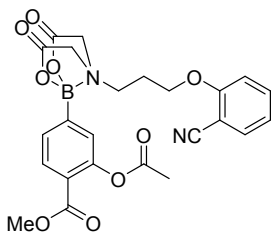
Characterisation data for major isomer:

HRMS (TOF ES+) Calcd. for $C_{24}H_{24}N_2O_9B$ ([M+H]$^+$): 495.1575. Found: 495.1572.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.01 – 7.99 (m, 1H), 7.72 (dd, *J* = 2.4, 1.5 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.48 – 7.46 (m, 1H), 7.05 (tdd, *J* = 7.6, 2.6, 0.9 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 4.13 (d, *J* = 17.2 Hz, 2H), 4.06 (d, *J* = 17.2 Hz, 2H), 3.98 (t, *J* = 6.1 Hz, 2H), 3.89 (s, 3H), 2.90 – 2.79 (m, 2H), 2.27 (s, 3H), 2.11 (dddd, *J* = 11.1, 9.6, 7.2, 4.9 Hz, 2H).

^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 169.5, 168.4, 168.3, 166.9, 166.1, 159.9, 159.8, 150.9, 137.2, 134.7, 133.6, 133.6, 133.3, 131.4, 130.5, 130.4, 130.2, 129.8, 128.3, 123.6, 123.5, 121.3, 116.1, 116.0, 112.7, 112.7, 101.4, 101.4, 65.7, 59.2, 59.1, 56.3, 56.2, 51.9, 51.7, 23.9, 23.8, 20.3. Unable to distinguish ^{13}C peaks between regioisomers.

^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.46.



4-Methoxycarbonyl-3-acetoxyphenylboronic acid MIDA-DG ester (18b)

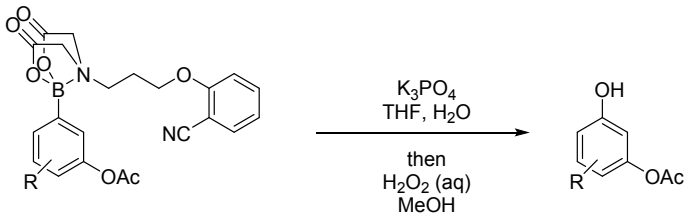
4-Methoxycarbonylphenylboronic acid MIDA-DG ester (44 mg, 0.1 mmol) was employed to yield the product as a yellow solid after an extended reaction time of 48 hours (31 mg, **product**: 21%, **SM**: 48% as determined by ^{1}H NMR).
Characterisation data for major isomer:

HRMS (TOF ES+) Calcd. for $C_{24}H_{23}N_2O_9BNa([M+Na]^+)$: 517.1394. Found: 517.1407.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.94 (d, *J* = 7.7 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.50 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.30 (d, *J* = 1.3 Hz, 1H), 7.06 (td, *J* = 7.6, 0.8 Hz, 1H), 6.98 (d, *J* = 9.0 Hz, 1H), 4.13 (d, *J* = 17.1 Hz, 2H), 4.07 (d, *J* = 14.2 Hz, 2H), 3.98 (t, *J* = 6.3 Hz, 2H), 3.84 (s, 3H), 2.90 – 2.84 (m, 2H), 2.28 (s, 3H), 2.10 (m, 2H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 170.7, 169.6, 168.4, 168.3, 166.8, 159.9, 159.8, 150.0, 134.7, 133.6, 133.6, 132.7, 130.9, 130.9, 130.2, 128.6, 128.4, 127.8, 124.2, 123.6, 121.3, 121.3, 116.2, 116.1, 112.8, 112.7, 101.4, 65.6, 60.0, 59.1, 59.0, 56.2, 56.1, 51.9, 51.7, 23.8, 23.8, 20.2, 20.2, 13.5. Unable to distinguish ^{13}C peaks between regioisomers.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.4.

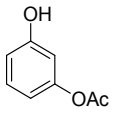
Oxidised Acetoxylated Phenols

General Procedure for the oxidation of C–H Acetoxylated Products



General procedure for the oxidation of boronic acid MID-DG esters:

To a 20 mL vial was added the acetoxylated boronic acid MIDA-DG mixture (1 eq.), K_3PO_4 (2.2 eq.) or NaOH (3 eq.). The mixture was dissolved in THF (0.05 M), and H_2O_2 (30% v/v aq., 5 mL / mmol) added. The reaction mixture was stirred at room temperature until complete conversion of the SM (checked by TLC). The reaction mixture was diluted with brine (5.0 mL) and DCM (10 mL). The organic layer was separated, concentrated under vacuum and purified via preparative TLC to yield the desired product.

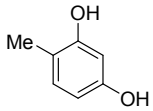


3-Hydroxyphenyl acetate

The corresponding acetoxylated boronic acid MIDA-DG ester (0.3 mmol) (as a mixture of regioisomers) and K_3PO_4 were employed to yield the desired phenol as a clear glassy solid (8 mg, 0.05 mmol, 18%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (t, *J* = 8.1 Hz, 1H), 6.69 (dddd, *J* = 12.2, 8.1, 2.3, 0.9 Hz, 2H), 6.61 (t, *J* = 2.3 Hz, 1H), 5.48 (s, 1H), 2.32 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.8, 156.6, 151.5, 130.1, 113.7, 109.2, 105.4, 21.2.

The characterisation data for the compound is in agreement with that reported in the literature (*Org. Biomol. Chem.,* 2011, 9, 8119-8121).



2,4-Dihydroxytoluene

Methyl 2,4-dihydroxytoluene was synthesised by oxidation/de-acetoxylation of 2-Methyl-5-acetoxyphenylboronic acid MIDA-DG ester and 4-Methyl-3-acetoxyphenylboronic acid MIDA-DG ester.

From 2-methyl-5-acetoxyphenylboronic acid MIDA-DG ester

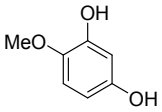
The corresponding acetoxylated boronic acid MIDA-DG ester (0.07 mmol) (as a mixture of regioisomers) and NaOH were employed to yield the desired phenol as a glassy solid (2.5 mg, 0.02 mmol, 29%).

From 4-methyl-3-acetoxyphenylboronic acid MIDA-DG ester

The corresponding acetoxylated boronic acid MIDA-DG ester (0.02 mmol) (as a mixture of regioisomers) and NaOH were employed to yield the desired phenol as a glassy solid (1.6 mg, 0.01 mmol, 65%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.95 (d, *J* = 9.0 Hz, 1H), 6.33 (dq, *J* = 5.1, 2.5 Hz, 2H), 2.16 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.8, 154.6, 131.4, 115.7, 107.5, 102.6, 14.9.

The characterisation data for the compound is in agreement with that reported in the literature (*Eur. J. Med. Chem.* 143, 2018, 1428-1435).

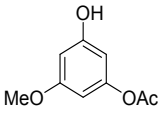


2,4-Dihyrdoxyanisole

The corresponding acetoxylated 2-methoxyphenylboronic acid MIDA-DG ester (0.03 mmol) (as a mixture of regioisomers) was used as a mixture of regioisomers to yield the desired phenol as a clear oil (1.5 mg, 0.01 mmol, 33%).

^{1}H NMR (400 MHz, Methanol-d_4) δ 6.74 (d, *J* = 8.7 Hz, 1H), 6.34 (d, *J* = 2.8 Hz, 1H), 6.23 (dd, *J* = 8.7, 2.8 Hz, 1H), 3.77 (s, 3H).
^{13}C NMR (101 MHz, Methanol-d_4) δ 153.0, 148.5, 142.5, 114.5, 106.5, 104.4, 57.4.

The characterisation data for the compound is in agreement with that reported in the literature (*J. Agric. Food Chem.* 2008, 56, 6809-6817).

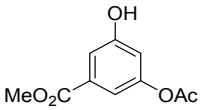


3-Hydroxy-5-methoxyphenyl acetate

The corresponding acetoxylated boronic acid MIDA-DG ester (0.21 mmol) (as a mixture of regioisomers) and K_3PO_4 were employed to yield the desired phenol as a clear oil (20 mg, 0.11 mmol, 52%).

HRMS (TOF ES+) Calcd. for $C_9H_{11}O_4$ ([M+H]$^+$): 183.0652. Found: 183.0655.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.30 (t, *J* = 2.2 Hz, 1H), 6.26 (t, *J* = 2.1 Hz, 1H), 6.23 (t, *J* = 2.1 Hz, 1H), 5.21 (s, 1H), 3.78 (s, 3H), 2.30 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.4, 161.3, 157.0, 152.2, 101.9, 100.3, 99.4, 55.5, 21.2.



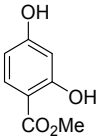
Methyl 3-acetoxy-5-hydroxybenzoate

The corresponding acetoxylated boronic acid MIDA-DG ester (0.04 mmol) (as a mixture of regioisomers) and K_3PO_4 were employed to yield the desired phenol as a clear oil (4 mg, 0.02 mmol, 50%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (dd, *J* = 2.4, 1.3 Hz, 1H), 7.34 (dd, *J* = 2.1, 1.3 Hz, 1H), 6.82 (t, *J* = 2.3 Hz, 1H), 5.63 (s, 1H), 3.90 (s, 3H), 2.31 (s, 3H).

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.31 (dd, *J* = 2.4, 1.4 Hz, 1H), 7.19 (dd, *J* = 2.2, 1.4 Hz, 1H), 6.76 (t, *J* = 2.3 Hz, 1H), 3.88 (s, 4H), 2.27 (s, 3H).
^{13}C NMR (101 MHz, Methanol-d_4) δ 170.8, 167.7, 159.9, 153.1, 133.2, 114.8, 114.7, 52.8, 20.9.

The characterisation data for the compound is in agreement with that reported in the literature (*ChemMedChem*, 2015, 10, 116-133).



Methyl 2,4-dihydroxybenzoate

Methyl 2,4-dihydroxybenzoate was synthesised by oxidation/de-acetoxylation of 2-Methoxycarbonyl-5-acetoxyphenylboronic acid MIDA-DG ester and 4-Methoxycarbonyl-3-acetoxyphenylboronic acid MIDA-DG ester.

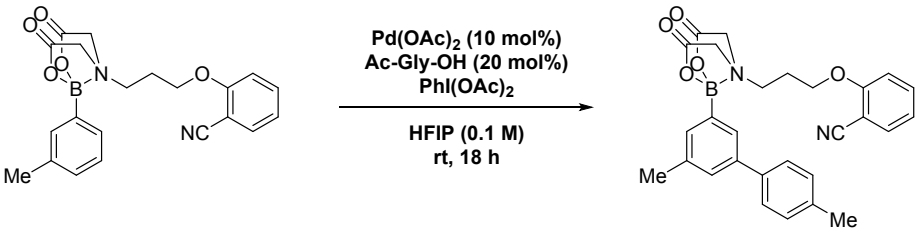
From 2-methoxycarbonyl-5-acetoxyphenylboronic acid MIDA-DG ester:
The corresponding acetoxylated boronic acid MIDA-DG ester (0.04 mmol) (as a mixture of regioisomers) and K_3PO_4 were employed to yield the desired phenol as a glassy solid (2.2 mg, 0.01 mmol, 33%).

From 4-methoxycarbonyl-3-acetoxyphenylboronic acid MIDA-DG ester:
The corresponding acetoxylated boronic acid MIDA-DG ester (0.21 mmol) (as a mixture of regioisomers) and K_3PO_4 were employed to yield the desired phenol as a glassy solid (12 mg, 0.07 mmol, 34%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.72 (s, 1H), 10.48 (s, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 6.37 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.30 (d, *J* = 2.3 Hz, 1H), 3.84 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 170.01, 164.67, 163.13, 132.07, 108.82, 104.42, 102.94, 52.49.

The characterisation data for the compound is in agreement with that reported in the literature (*Org. Lett.* 2018, 20, 708-711).

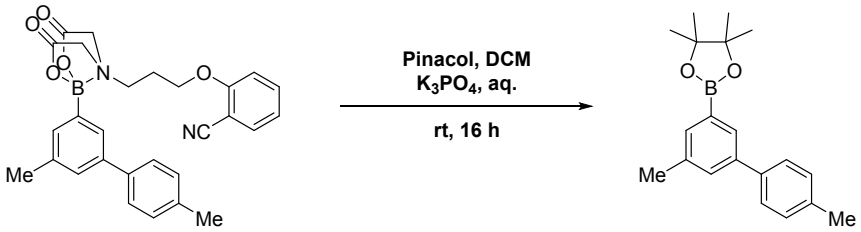
C–H Arylations



3-Methyl-5-(4-methylphenyl)phenylboronic acid MIDA-DG ester

A 20 mL vial was charged with 3-methylphenylboronic acid MIDA-DG ester (78.4 mg, 0.20 mmol), 4-methylphenylboronic acid pinacol ester (90.3 mg, 2.0 eq.), Ag_2CO_3 (110 mg, 2.0 eq.), Cs_2CO_3 (130 mg, 2.0 eq.), Ac-Gly-OH (9.4 mg, 40 mol%) and $Pd(OAc)_2$ (9.0 mg, 20 mol%). HFIP (2.0 mL, 0.1 M) was then added, the vial sealed and the suspension stirred at room temperature for 4 hours. After this time, further $Pd(OAc)_2$ (9.0 mg, 20 mol%) was added, the vial resealed and stirring continued for 14 further hours. The reaction mixture was diluted with MeCN (~5 mL) and dry loaded onto a silica column. The column was washed with Et_2O (50 mL) before the products were eluted with MeCN:Et_2O (1:1) (50 mL). The solvent was removed to yield the crude product/starting material mixture as an off white solid (71 mg, crude yield, calculated from ^{1}H NMR: **product:** 52%, **SM**: 26%).

HRMS (TOF ES+) Calcd. for $C_{28}H_{28}N_2O_5B$ ([M+H]$^+$): 483.2086. Found: 483.2098.



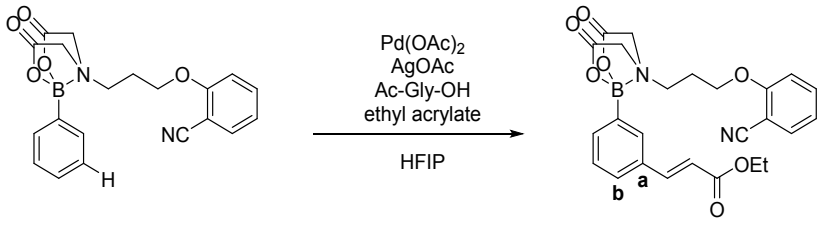
2-(4',5-Dimethyl-[1,1'-biphenyl]-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24)

A 20 mL vial was charged with the crude 3-methyl-5-(4-methylphenyl)phenylboronic acid MIDA-DG ester product (0.155 mmol from ^{1}H NMR) mixture and K_3PO_4 (99 mg, 3.0 eq.) and pinacol (18 mg, 1.0 eq.) were added. The solids were dissolved in DCM (1.55 mL), H_2O (0.8 mL) and THF (0.15 mL) and the biphasic mixture stirred overnight. The reaction mixture was diluted with brine (5 mL) and DCM (5 mL), the phases separated and the aqueous further extracted with DCM (2 × 5 mL). The organic phases were combined, dried over MgSO4, filtered and concentrated in vacuo. The crude product was purified using FCC (10% Et2O in hexanes) to yield the product as a white solid (19 mg, 0.06 mmol, 40% yield, 32% over two steps). *The reaction mixture contained a 10% inseparable impurity believed to correspond to the 3-methyl-4-(4-phenylmethyl)phenylboronic acid pinacol ester.*

HRMS (TOF ES+) Calcd. for $C_{20}H_{26}O_2B$ ([M+H]$^+$): 309.2020. Found: 309.2032.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (dt, *J* = 1.8, 0.8 Hz, 1H), 7.64 (qd, *J* = 1.8, 1.2 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.53 (td, *J* = 1.9, 0.8 Hz, 1H), 7.28 – 7.24 (m, 3H), 2.45 (d, *J* = 0.7 Hz, 3H), 2.42 (s, 3H), 1.39 (d, *J* = 1.0 Hz, 15H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.3, 137.6, 136.8, 135.4, 134.1, 130.7, 130.5, 129.3, 127.1, 83.8, 24.9, 21.4, 21.1. ^{13}C NMR peaks were unambiguously assigned using HMBC and HSQC.
^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.0.

Large Scale C–H Alkenylation of Phenylboronic acid MIDA-DG ester



A 100 mL round-bottomed flask was charged with phenylboronic acid MIDA-DG ester (1.51 g, 4.00 mmol), AgOAc (1.17 g, 1.75 eq.), Ac-Gly-OH (187 mg, 40 mol%) and $Pd(OAc)_2$ (180 mg, 20 mol%). The flask was evacuated and flushed with nitrogen three times before HFIP (40 mL, 0.1 M) and the corresponding alkene coupling partner (1.09 mL, 2.5 eq.) were added. The vial was sealed and stirred at room temperature for 18 hours. The reaction mixture was diluted with MeCN (40 mL) and dry loaded onto a silica column. The column was washed with copius Et_2O before the products were subsequently eluted with MeCN:Et_2O (1:1, 250 mL). The solvent was removed under vacuum to yield the desired product as a crystalline white solid (1.45g, 62% total yield, **a**: 43%, **b**: 7%, **a+a:** 7%, **a+b:** 5%, **SM:** 15%).

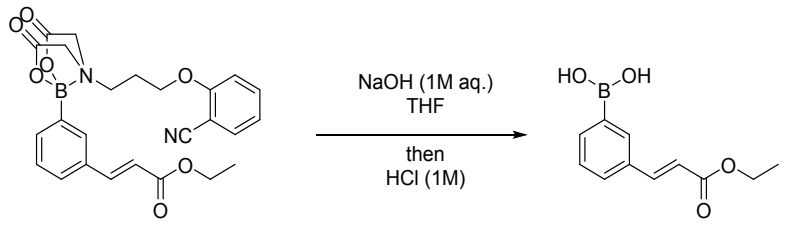
The reaction was repeated on a 3 mmol scale, and left for 24 hours to drive the reaction to completion. The product was isolated as a crystalline white solid (1.25 g, 81% total yield, **a**: 56%, **b**: 8%, **a+a:** 10%, **a+b:** 7%).

The average yield for the two repeats was: 72% total yield

The characterisation data was in agreement with that reported within this supporting information.

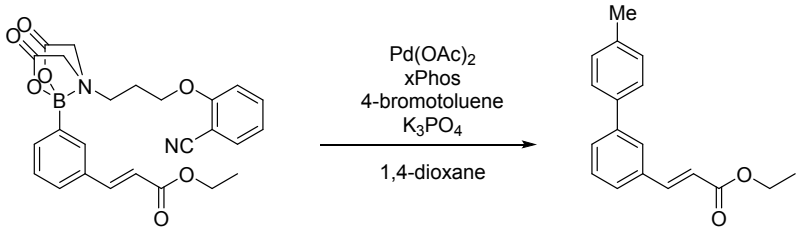
C-H Activation Product Derivatisations

General procedure for removal and recovery of the MIDA-DG:



To a mixture of C–H alkenylated products [168 mg, 0.36 mmol (0.20 mmol *meta*, 0.16 mmol *para, meta-meta di, meta-para di* and *non-alkenylated*)] was added THF (3.25 mL) and NaOH (1 M aq., 1.1 mL, 3 eq.). The mixture was stirred for 10 minutes at room temperature until no starting materials were observed by TLC (EtOAc). The reaction was acidified using HCl (1 M, aq.) (2.2 mL), the THF removed under reduced pressure at 30 °C for 10 minutes and the resulting suspension diluted with H_2O (11 mL) and Et_2O (13 mL). The layers were separated and the aqueous phase further extracted with Et_2O (2 × 13 mL). The combined organic phases were dried with $MgSO_4$ and concentrated to give a crude mixture of boronic acids that were immediately used in the next step.

The aqueous phase was collected and concentrated under a steady stream of nitrogen overnight. The resulting solid was dissolved in MeCN, filtered to remove the NaCl and concentrated under vacuo to yield the MIDA-DG hydrochloride (118 mg, 0.36 mmol, 100%) as an off-white solid.

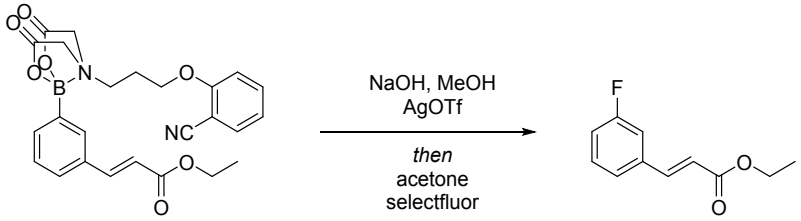


Ethyl (E)-3-(4'-methyl-[1,1'-biphenyl]-3-yl)acrylate (26)

Following the **general procedure for removal and recovery of the MIDA-DG** (84 mg, 0.18 mmol, 0.10 mmol *meta*), the crude boronic acid (1.2 eq.), $Pd(OAc)_2$ (3.3 mg, 10 mol%), xphos (14.1 mg, 20 mol%) and K_3PO_4 (94 mg, 3.0 eq.) were added to a 20 mL vial and placed under an atmosphere of nitrogen. Degassed 1,4-dioxane (1.5 mL) and 4-bromotoluene (18 μL, 0.15 mmol, 1.0 eq.) were then added and the reaction mixture stirred under N_2 at 75 °C for 18 hours. The reaction mixture was dry loaded on to silica and purified via FCC (5% EtOAc in hexane) to yield the desired product (13.0 mg, 0.05 mmol, 48%) as a colourless oil. *The product contains a 6% impurity believed to be ethyl (E)-3-(4'-methyl-[1,1'-biphenyl]-4-yl)acrylate.*

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 16.1 Hz, 1H), 7.72 (t, *J* = 1.8 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.51 – 7.43 (m, 4H), 7.29 – 7.25 (m, 2H), 6.50 (d, *J* = 16.0 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.0, 144.6, 141.9, 137.5, 134.9, 129.6, 129.3, 128.9, 127.0, 126.7, 126.5, 118.5, 60.6, 21.1, 14.4.

The characterisation data for the compound is in agreement with that reported in the literature (*J. Am. Chem. Soc.* 2019, 141, 1903-1907).



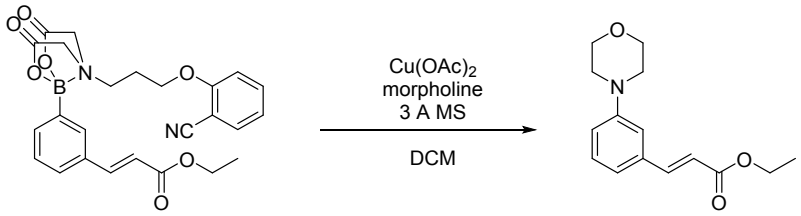
Ethyl (E)-3-(3-fluorophenyl)acrylate (27)

The method described in *Org. Lett.* 2009, 11, 2860-2863 was used for the fluorination of the boronic acid.

Following the **general procedure for removal and recovery of the MIDA-DG** (168.0 mg, 0.36 mmol, 0.20 mmol *meta*), the crude boronic acid (1.0 eq.) and NaOH (14.2 mg, 1.0 eq.) were dissolved in MeOH (1.8 mL) and stirred at room temperature for 15 minutes. The mixture was then cooled to 0 °C and AgOTf (182.5 mg, 2.0 eq.) added. The reaction mixture was then stirred for 30 minutes at 0 °C then concentrated under a stream of nitrogen, still at 0 °C. The MeOH was further removed by azeotroping with acetone (2 × 1.8 mL) at 0 °C. Once dry, molecular sieves (3 Å, 180 mg) and selectfluor (132.0 mg, 1.05 eq.) were added, dissolved in acetone (3.6 mL), stirred at 0 °C for 5 minutes then warmed to room temperature. The reaction mixture was dry loaded onto silica and purified via FCC (5% EtOAc in hexane). The appropriate fractions were combined and concentrated to yield the desired product (23.0 mg, 0.12 mmol, 59%) as a colourless oil. *The product contains a 10% impurity believed to be ethyl cinnamate from protodeboronation during the reaction.*

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 16.0 Hz, 1H), 7.39 – 7.31 (m, 1H), 7.29 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.24 – 7.18 (m, 1H), 7.07 (tdd, *J* = 8.1, 2.5, 1.0 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H).
^{19}F NMR (377 MHz, Chloroform-*d*) δ -112.6 (q, *J* = 8.6 Hz).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.6, 163.0 (d, *J* = 246.8 Hz), 143.2 (d, *J* = 1.9 Hz), 136.7 (d, *J* = 7.7 Hz), 130.4 (d, *J* = 8.1 Hz), 124.0, 119.7, 117.1 (d, *J* = 21.6 Hz), 114.3 (d, *J* = 22.3 Hz), 60.7, 14.3.

The characterisation data for the compound is in agreement with that reported in the literature (*Synth. Commun.* 2018, 48, 1482-1486).



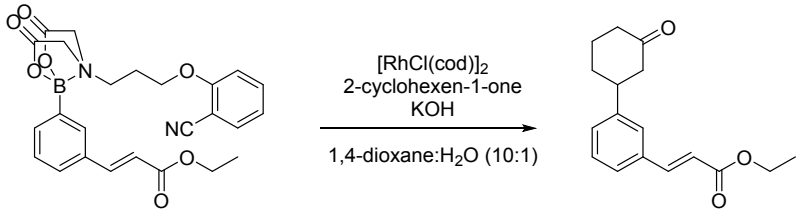
Ethyl (E)-3-(3-morpholinophenyl)acrylate (30)

Following the **general procedure for removal and recovery of the MIDA-DG** (168.0 mg, 0.36 mmol, 0.20 mmol *meta*), the crude boronic acid (1.2 eq.), $Cu(OAc)_2$ (27.3 mg, 1 eq.) and molecular sieves (3 Å, 50 mg) were added to a 4 mL vial. The solids were dissolved in DCM (1 mL) and morpholine (13 mL, 1 eq.) added. The reaction mixture was stirred under air, at room temperature, overnight. After completion, the reaction mixture was dry loaded onto silica and purified via FCC (15% EtOAc in hex) to yield the product (24.0 mg, 0.09 mmol, 46%) as a colourless oil.

ν_{max}/cm^{-1} 2974, 1707, 1636, 1595, 1491, 1446, 1305, 1267, 1238, 1174, 1122, 1036, 980, 891, 857, 783, 682

HRMS (TOF ES+) Calcd. for $C_{15}H_{20}NO_3$ ([M+H]$^+$): 262.1438. Found: 262.1445.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.63 (d, *J* = 16.0 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.15 (t, *J* = 2.1 Hz, 1H), 7.11 – 7.07 (m, 1H), 6.98 (ddd, *J* = 8.3, 2.6, 0.9 Hz, 1H), 6.49 (d, *J* = 16.0 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.80 – 3.74 (m, 4H), 3.19 – 3.11 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 166.6, 152.0, 144.8, 144.1, 135.2, 129.6, 119.2, 118.1, 114.9, 66.4, 60.2, 48.8, 13.6.



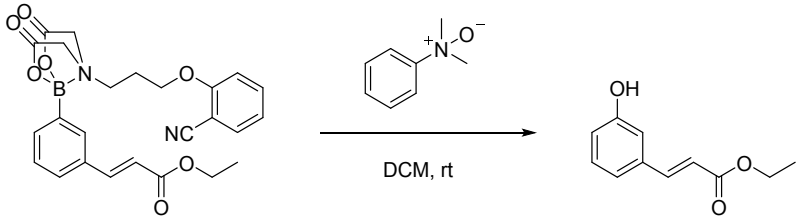
Ethyl (E)-3-(3-(3-oxocyclohexyl)phenyl)acrylate (28)

Following the **general procedure for removal and recovery of the MIDA-DG** (84.0 mg, 0.18 mmol, 0.1 mmol *meta*), the crude boronic acid (1.2 eq.) and $[RhCl(cod)]_2$ (3.7 mg, 5 mol%) were place under a nitrogen atmosphere. A solution of 1,4-dioxane:H_2O (10:1, 1.5 mL) and KOH (8.4 mg, 1.0 eq.) was degassed for 15 minutes using nitrogen before being added to the boronic acid and catalyst. 2-Cyclohexen-1-one (14.5 µl, 1.0 eq.) was added and the mixture stirred at room temperature overnight. After completion, the reaction mixture was dry loaded directly onto silica and purified via FCC (30% EtOAc in hexanes). The appropriate fractions were combined and concentrated to yield the product (20 mg, 0.07 mmol, 49%) as a colourless oil.

ν_{max}/cm^{-1} 2933, 1703, 1636, 1446, 1368, 1312, 1264, 1223, 1163, 1096, 1036, 984, 865, 798, 693

HRMS (TOF ES+) Calcd. for $C_{17}H_{21}O_3$ ($[M+H]^+$): 273.1485. Found: 273.1488.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 16.0 Hz, 1H), 7.43 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.26 (dt, *J* = 7.6, 1.5 Hz, 1H), 6.46 (d, *J* = 16.1 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.05 (tt, *J* = 11.7, 4.0 Hz, 1H), 2.67 – 2.34 (m, 4H), 2.24 – 2.07 (m, 2H), 1.98 – 1.71 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.6, 166.9, 145.0, 144.4, 134.9, 129.3, 128.6, 126.4, 126.3, 118.5, 60.6, 48.8, 44.6, 41.2, 32.7, 25.5, 14.3.



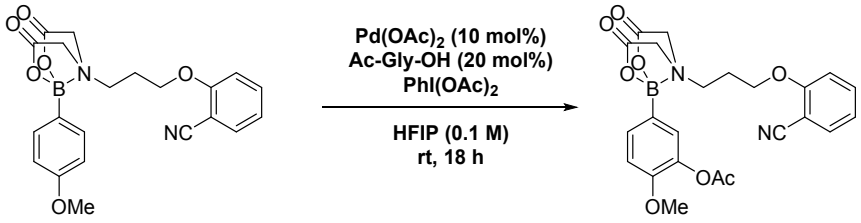
Ethyl (E)-3-(3-hydroxyphenyl)acrylate (29)

Following the **general procedure for removal and recovery of the MIDA-DG** (84.0 mg, 0.18 mmol, 0.1 mmol *meta*), the crude boronic acid (1 eq.) and *N,N*-dimethylaniline-*N*-oxide (29.6 mg, 1.2 eq.) were dissolved in DCM (1 mL) and stirred at room temperature. After completion by TLC (15% EtOAc in hexane), roughly 30 minutes, the reaction mixture was dry loaded onto silica and purified via FCC (15% EtOAc in hexane). The appropriate fractions were combined and concentrated to yield the product (10 mg, 0.05 mmol, 52%) as a colourless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 16.0 Hz, 1H), 7.30 – 7.21 (m, 1H), 7.09 (dt, *J* = 8.0, 1.3 Hz, 1H), 7.02 (t, *J* = 2.0 Hz, 1H), 6.91 – 6.85 (m, 1H), 6.41 (d, *J* = 16.1 Hz, 1H), 5.75 (br. s, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.3, 156.2, 144.6, 135.9, 130.1, 120.7, 118.5, 117.5, 114.6, 60.8, 14.3.

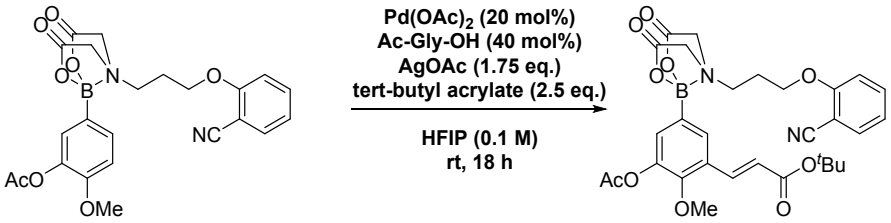
The characterisation data for the compound is in agreement with that reported in the literature (*J. Am. Chem. Soc.* 2019, 141, 1903-1907).

Iterative C–H Functionalisation / Cross Coupling Sequence



4-Methoxy-3-acetoxyphenylboronic acid MIDA-DG ester (12b)

A 20 mL vial was charged with arylboronic acid MIDA-DG ester (354 mg, 0.87 mmol), $PhI(OAc)_2$ (335 mg, 1.2 eq.), Ac-Gly-OH (20 mg, 20 mol%), $Pd(OAc)_2$ (20 mg, 10 mol%) and HFIP (8.7 mL). The vial was sealed and stirred at room temperature for 18 hours. The reaction mixture was diluted with MeCN (~5 mL), dry loaded onto a silica column and purified via 'catch and release' purification (washed with copious Et_2O, then elute with a similar amount of EtOAc) to yield the acetoxylated product as an off-white solid (218 mg, 0.47 mmol, 54%). The characterisation data was in agreement with that reported for the same compound above.

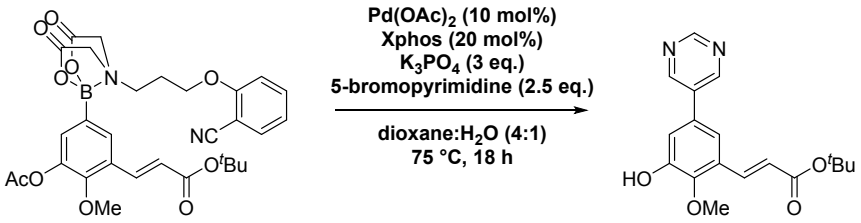


3-Acetoxy-4-methoxy-5-(*tert*-butyl prop-2-enoate)phenylboronic acid MIDA-DG ester

A 20 mL vial was charged with the acetoxylated arylboronic acid MIDA-DG ester (161 mg, 0.35 mmol), AgOAc (100 mg, 1.75 eq.), Ac-Gly-OH (16 mg, 40 mol%) and $Pd(OAc)_2$ (16 mg, 20 mol%). The vial was evacuated and flushed with nitrogen three times before HFIP (3.45 mL) and the *tert*-butyl acrylate (125 μL, 2.5 eq.) were added. The vial was sealed and stirred at room temperature for 23 hours. The reaction mixture was diluted with MeCN (~5 mL) and dry loaded onto a silica column. The column was washed with Et_2O (100 mL) before the products were subsequently eluted with copious EtOAc. The EtOAc was removed under vacuum to yield the alkenylated products as an off white solid (158 mg, 0.209 mmol, 61%). The isolated product contained a 21% (0.07 mmol) impurity corresponding to the starting material that could not be separated from the product.

HRMS (TOF ES+) Calcd. for $C_{30}H_{33}N_2O_{10}BNa$ ($[M+Na]^+$): 615.2126. Found: 615.2128.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.81 – 7.74 (m, 1H), 7.64 – 7.54 (m, 3H), 7.27 (d, *J* = 1.7 Hz, 1H), 7.10 – 7.05 (m, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 6.50 (d, *J* = 16.2 Hz, 1H), 4.11 (d, *J* = 17.1 Hz, 2H), 4.06 – 3.96 (m, 4H), 3.82 (s, 3H), 2.92 – 2.82 (m, 2H), 2.31 (s, 3H), 2.11 (dtd, *J* = 11.6, 4.0, 2.2 Hz, 2H), 1.53 (s, 9H).
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 169.1, 168.3, 165.9, 160.0, 151.6, 143.9, 137.4, 134.8, 133.6, 129.8, 129.4, 129.0, 122.1, 121.3, 116.1, 112.8, 101.4, 80.2, 65.9, 61.4, 59.1, 56.2, 27.4, 23.9, 20.1.
^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.4.



***tert*-Butyl (E)-3-(3-hydroxy-2-methoxy-5-(pyrimidin-5-yl)phenyl)acrylate (32)**

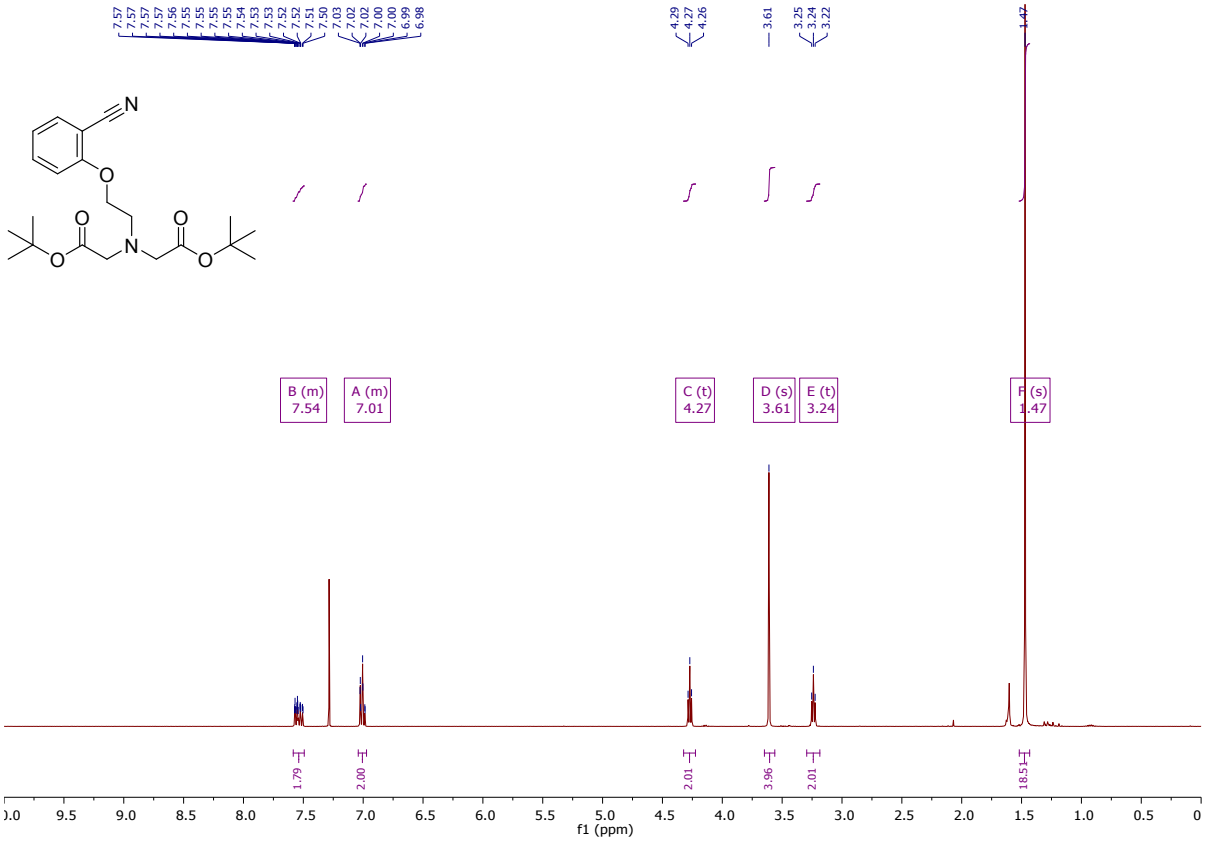
A 20 mL vial was charged with the acetoxylated and alkenylated boronic acid MIDA-DG (0.28 mmol, 0.209 acetoxylated and alkenylated product, 0.07 mmol acetoxylated material, 1.2 eq.). $Pd(OAc)_2$ (5.3 mg, 10 mol%), XPhos (22.4 mg, 20 mol%) and 5-bromopyrimidine (37.5 mg, 1.0 eq.) were added and the vial sealed and placed under a nitrogen atmosphere. The mixture was suspended in degassed 1,3-dioxane (0.24 mL) and a degassed solution of K_3PO_4 (150 mg, 3.0 eq.) in H_2O (0.6 mL) subsequently added. The mixture was heated to 75 °C for 18 hours. On completion, the mixture was diluted with brine (3 mL) and extracted with DCM (3 × 6 mL). The organic phases were combined, dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified using preparative TLC (50% Et2O in hexanes) to yield the desired product (27 mg, 0.082 mmol, 35%) as a clear glassy solid.

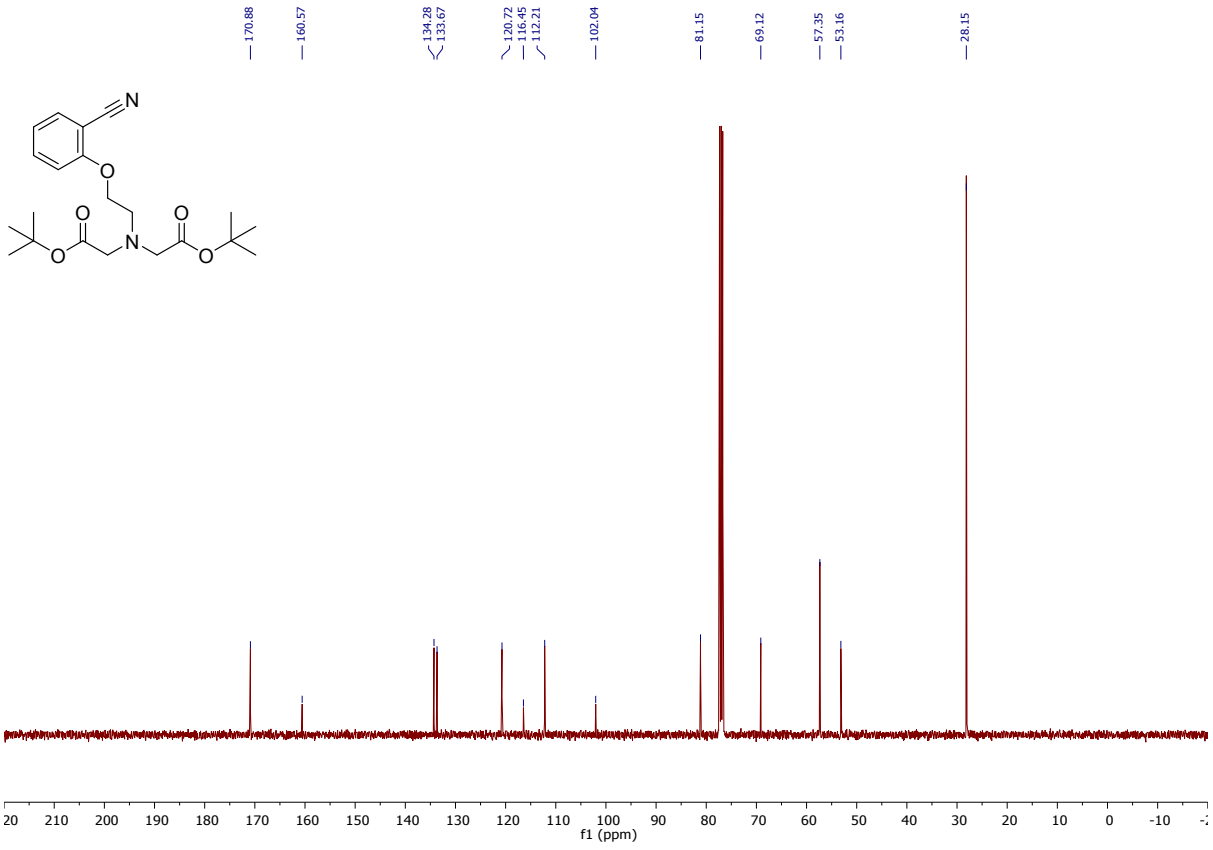
ν_{max}/cm^{-1} 2930m 1703, 1636, 1580, 1416, 1368, 1312, 1252, 1215, 1152, 992, 902, 854, 992

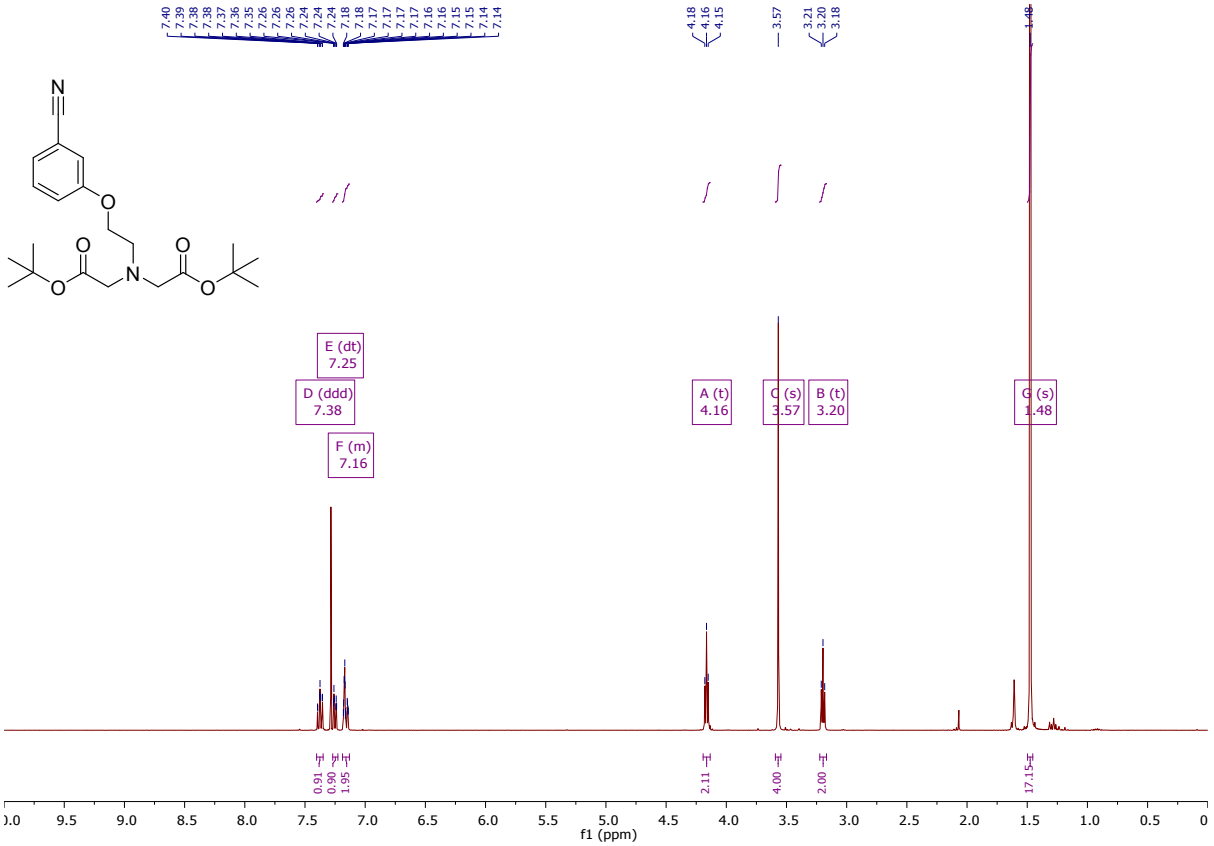
HRMS (APCI +) Calcd. for $C_{18}H_{21}N_2O_4$ ($[M+H]^+$): 329.1496. Found: 329.1495.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.24 (s, 1H), 8.95 (s, 3H), 7.85 (d, *J* = 16.1 Hz, 1H), 7.28 (s, 1H), 7.22 (d, *J* = 2.2 Hz, 1H), 6.54 (d, *J* = 16.1 Hz, 1H), 6.10 (s, 1H), 3.91 (s, 3H), 1.58 (s, 10H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.0, 157.6, 154.8, 150.2, 136.9, 133.5, 131.3, 129.1, 123.1, 117.9, 115.4, 115.0, 81.0, 62.6, 28.2.

Directing Group NMR Spectra



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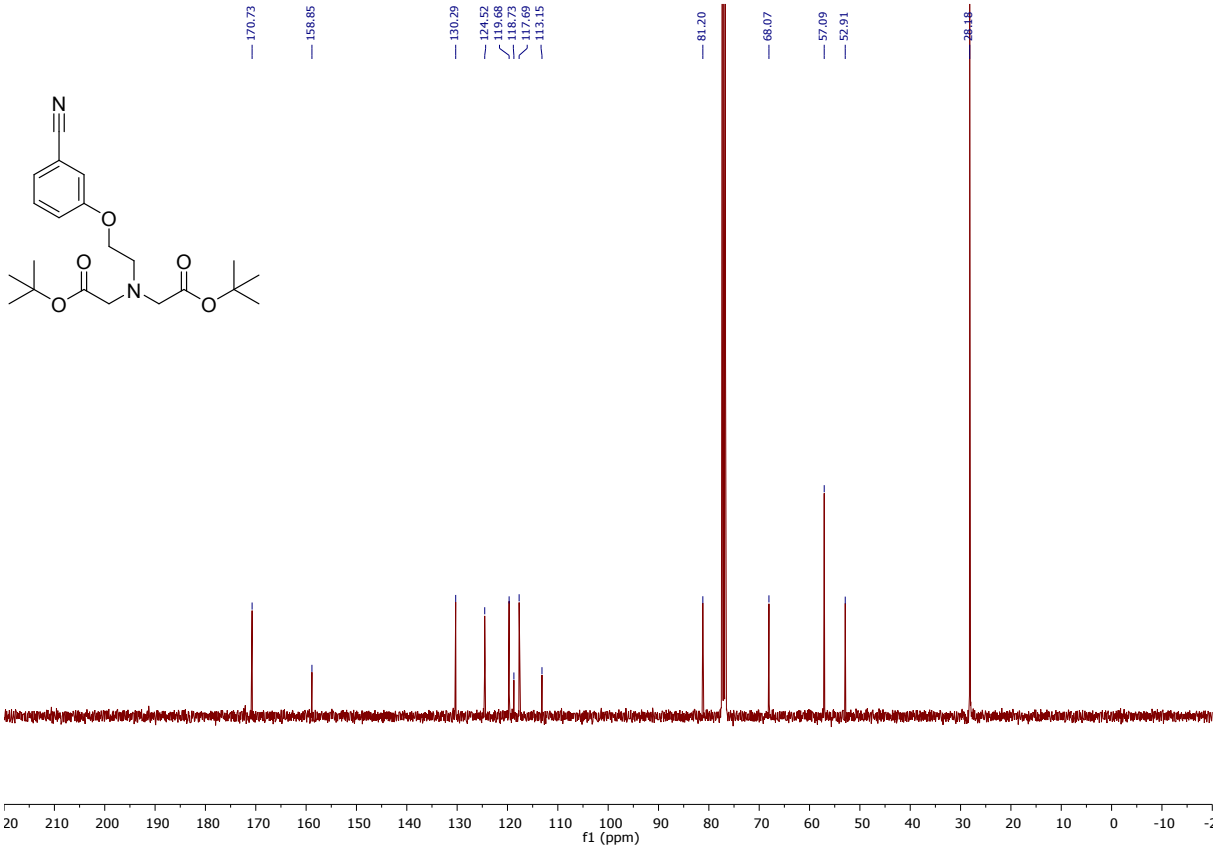
f1 (ppm)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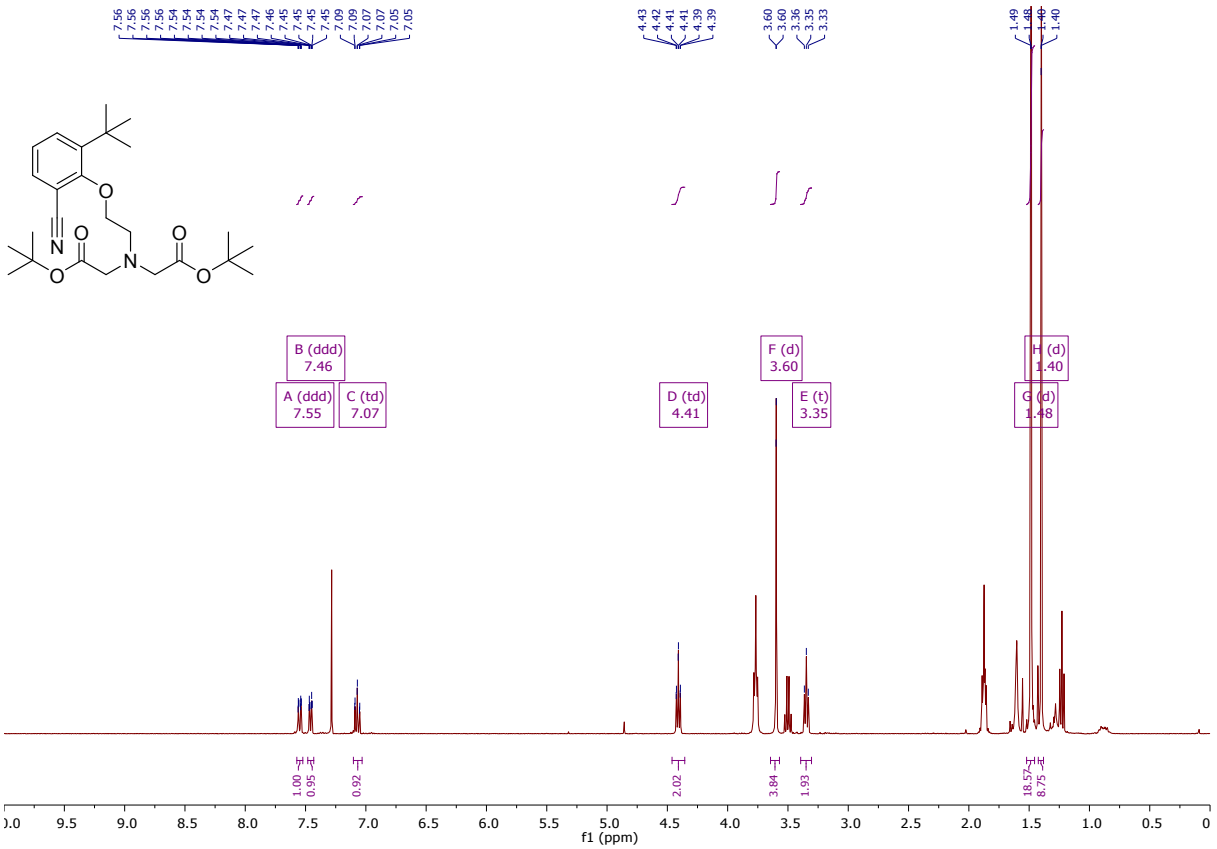
f1 (ppm)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G (d)
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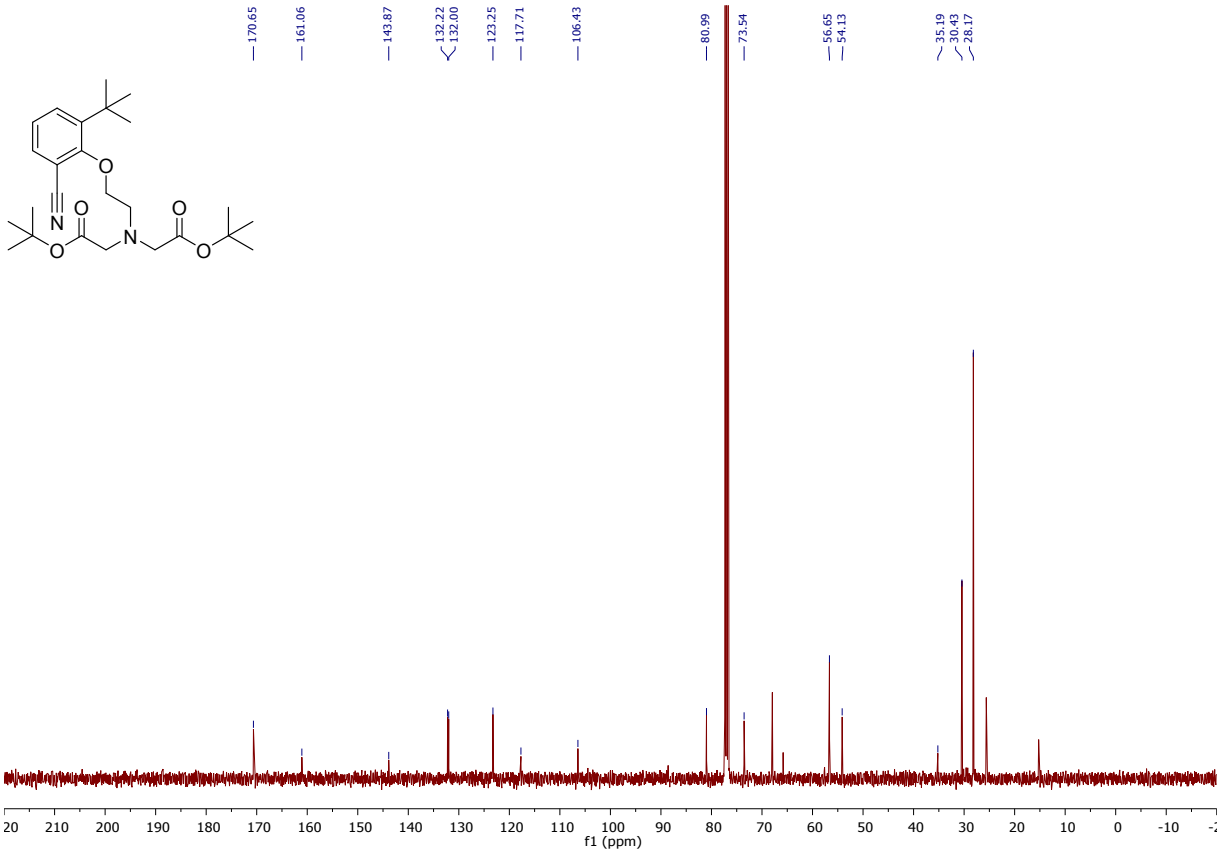
f1 (ppm)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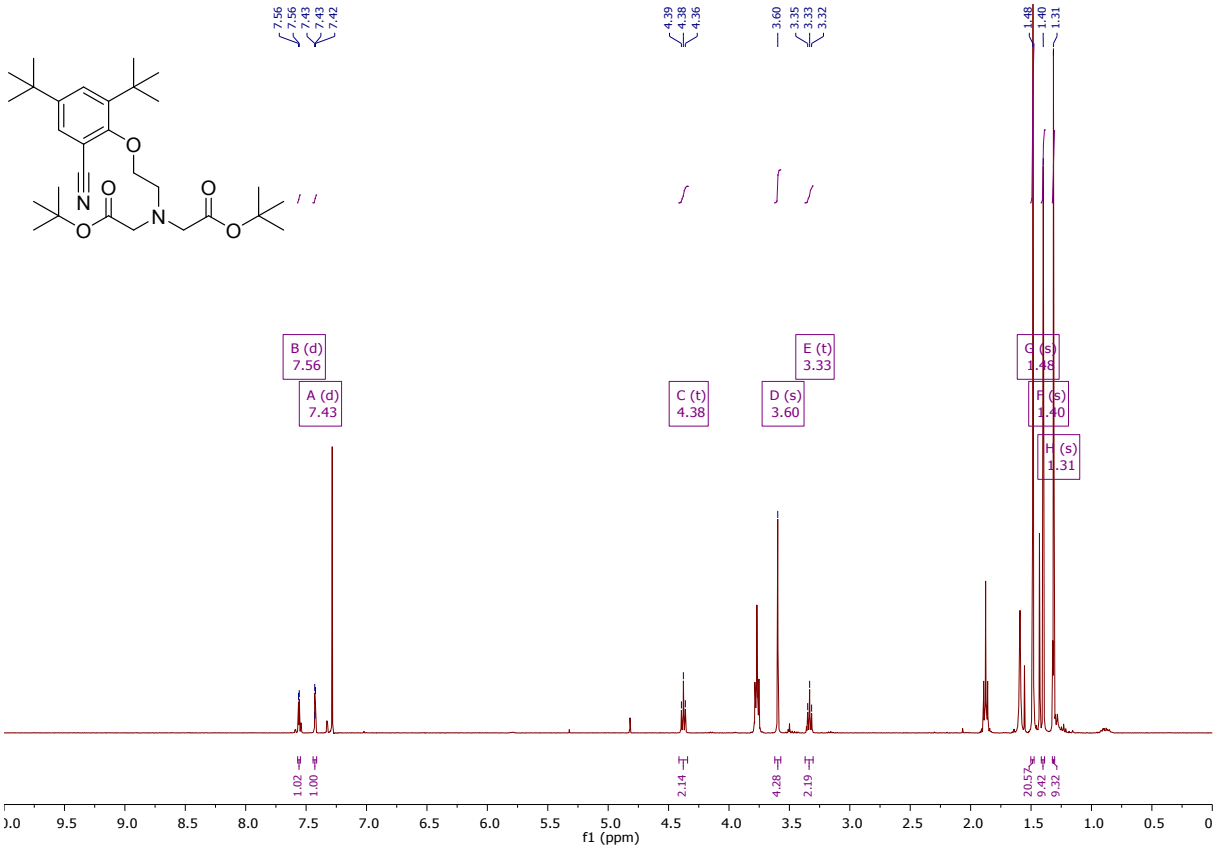
f1 (ppm)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1.40
1.31
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A (d)
7.43
C (t)
4.38
D (s)
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E (t)
3.33
G (s)
1.48
F (s)
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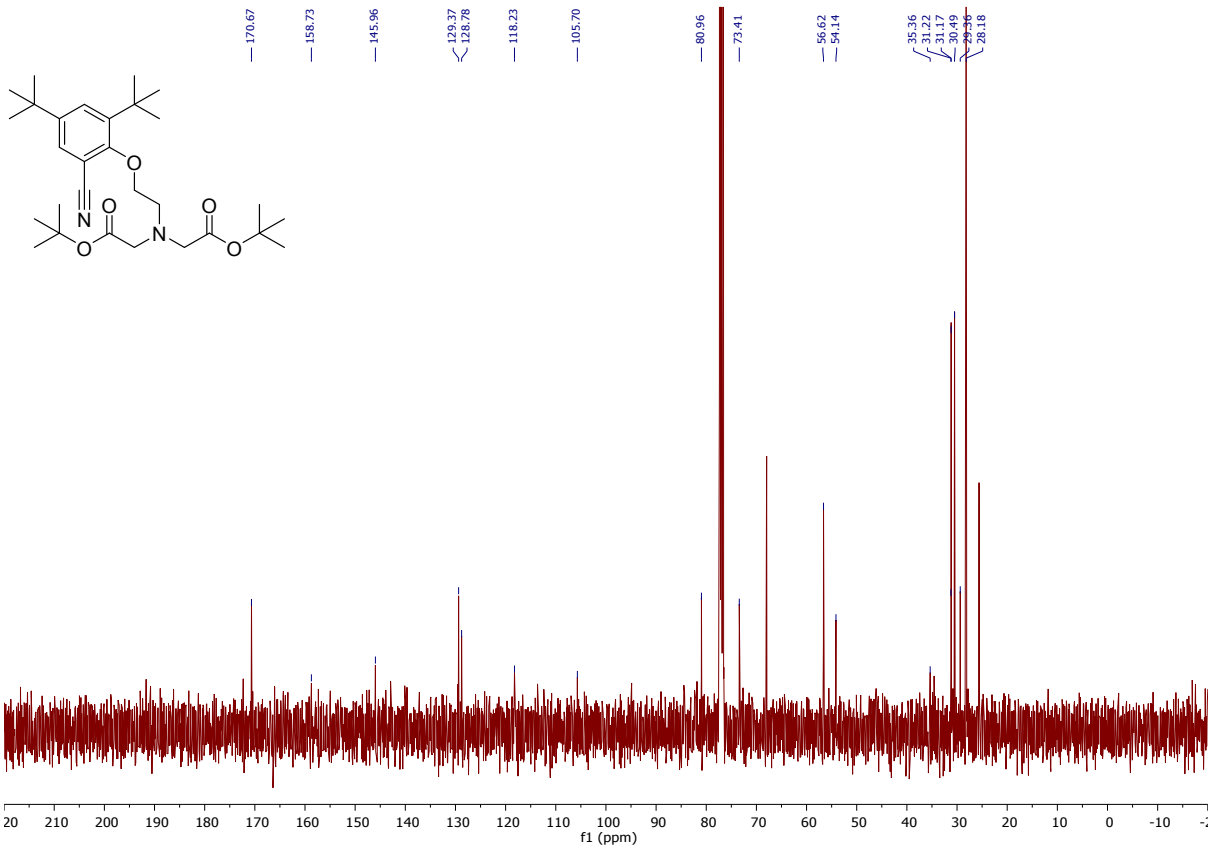
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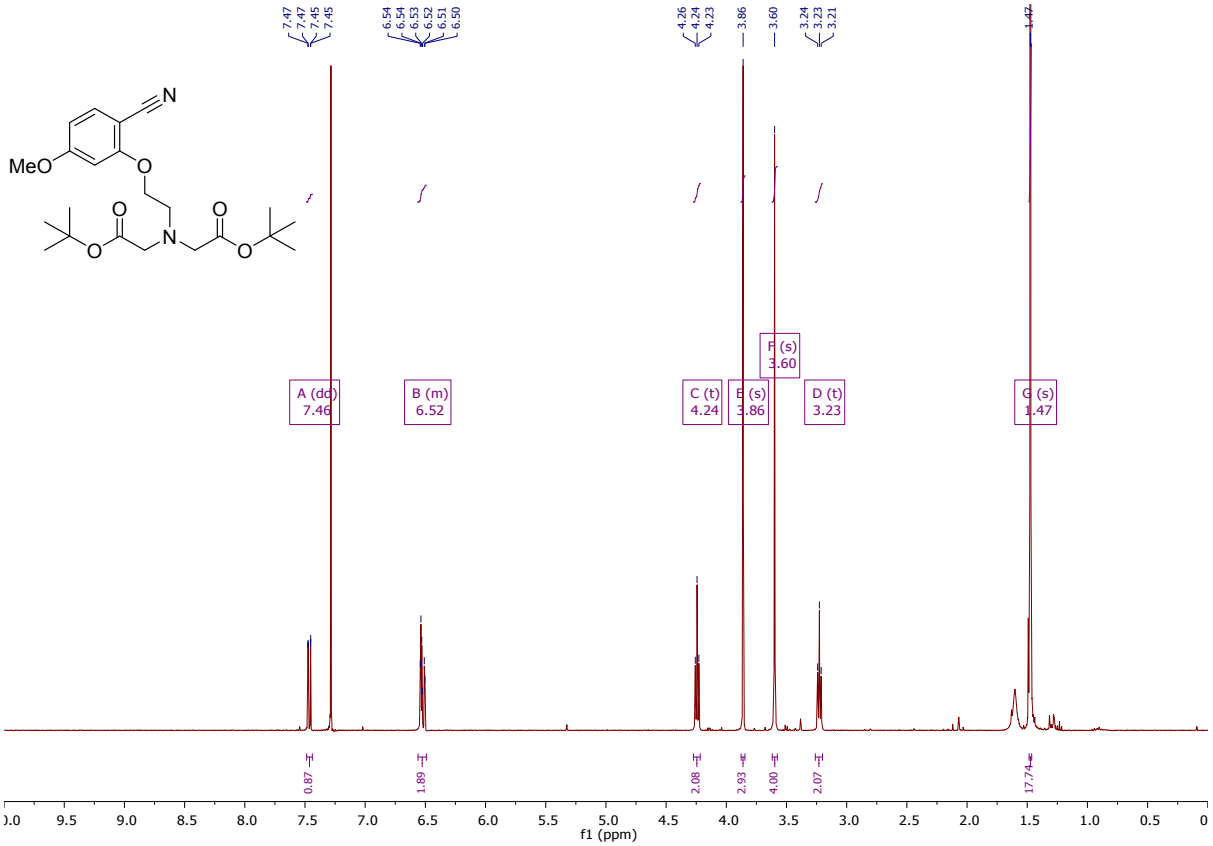
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B (m)
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C (t)
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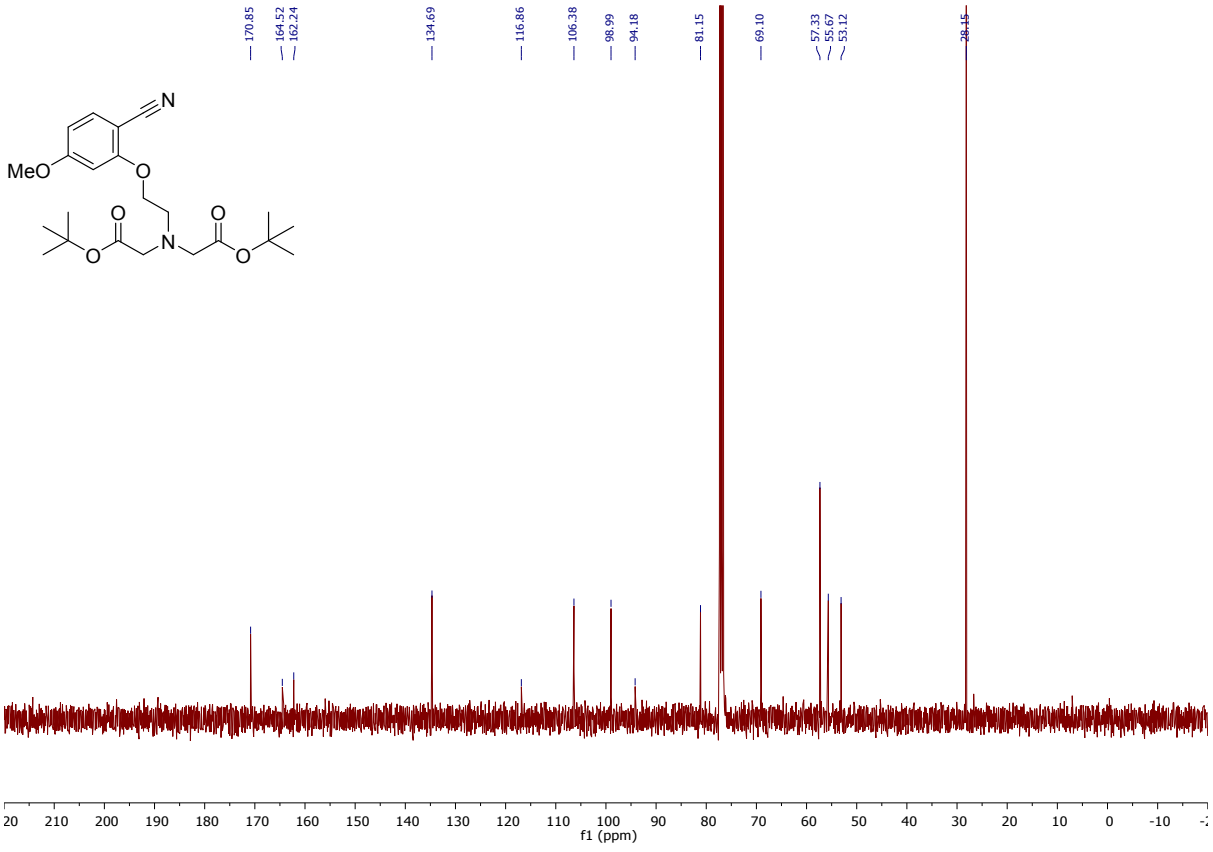
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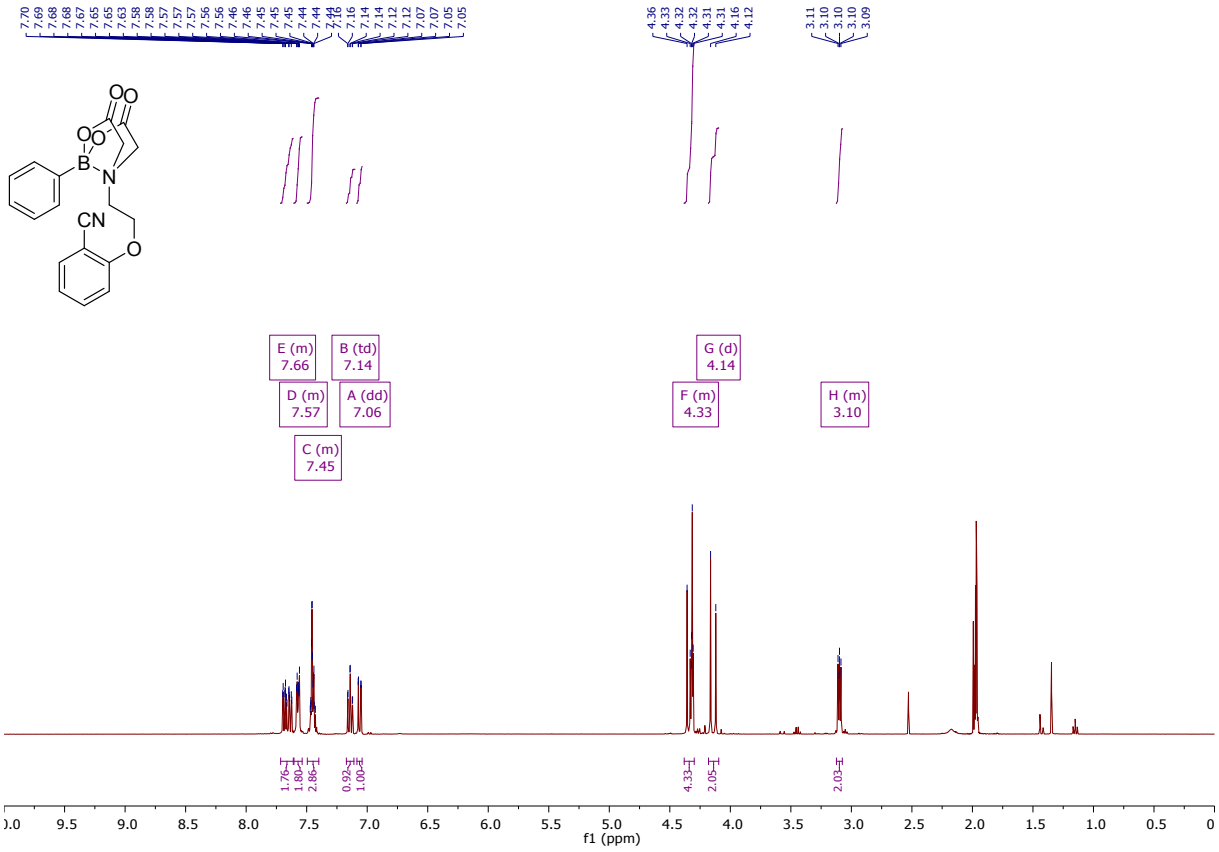
f1 (ppm)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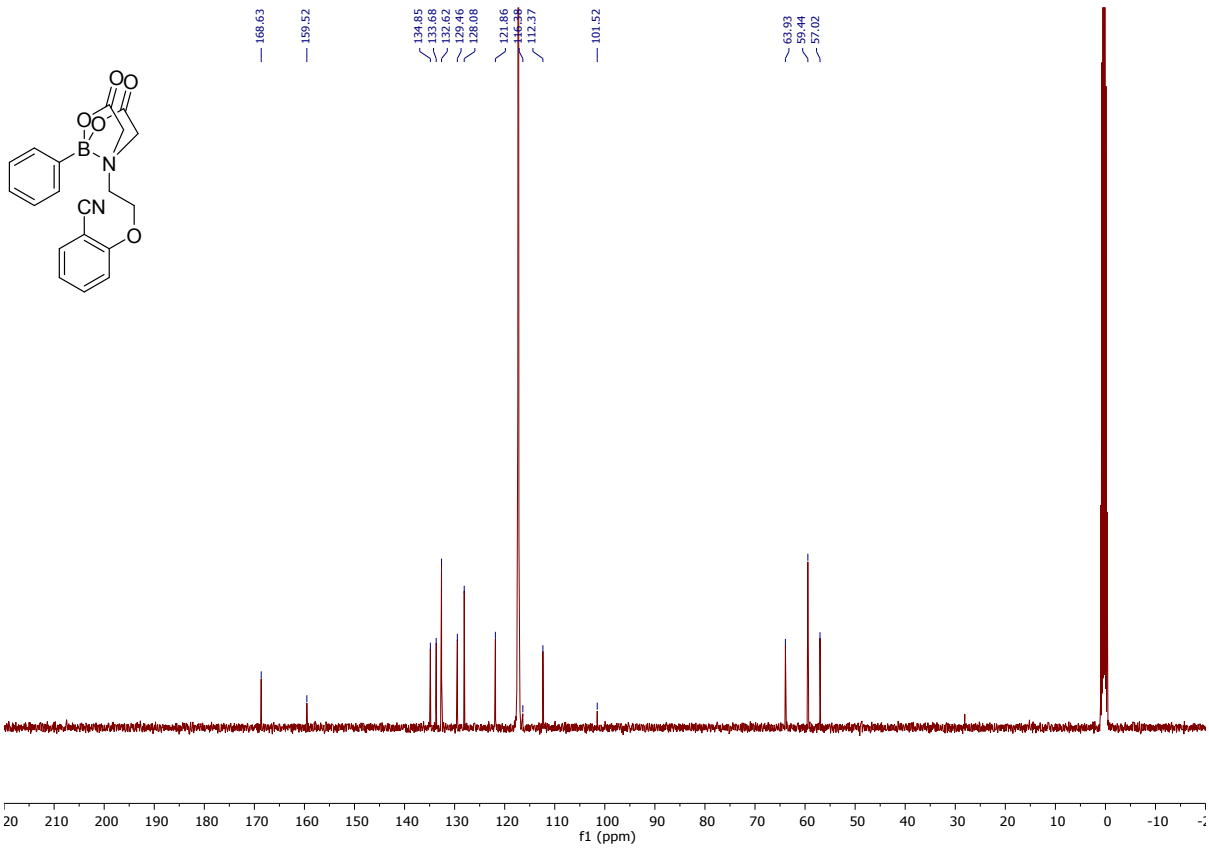
f1 (ppm)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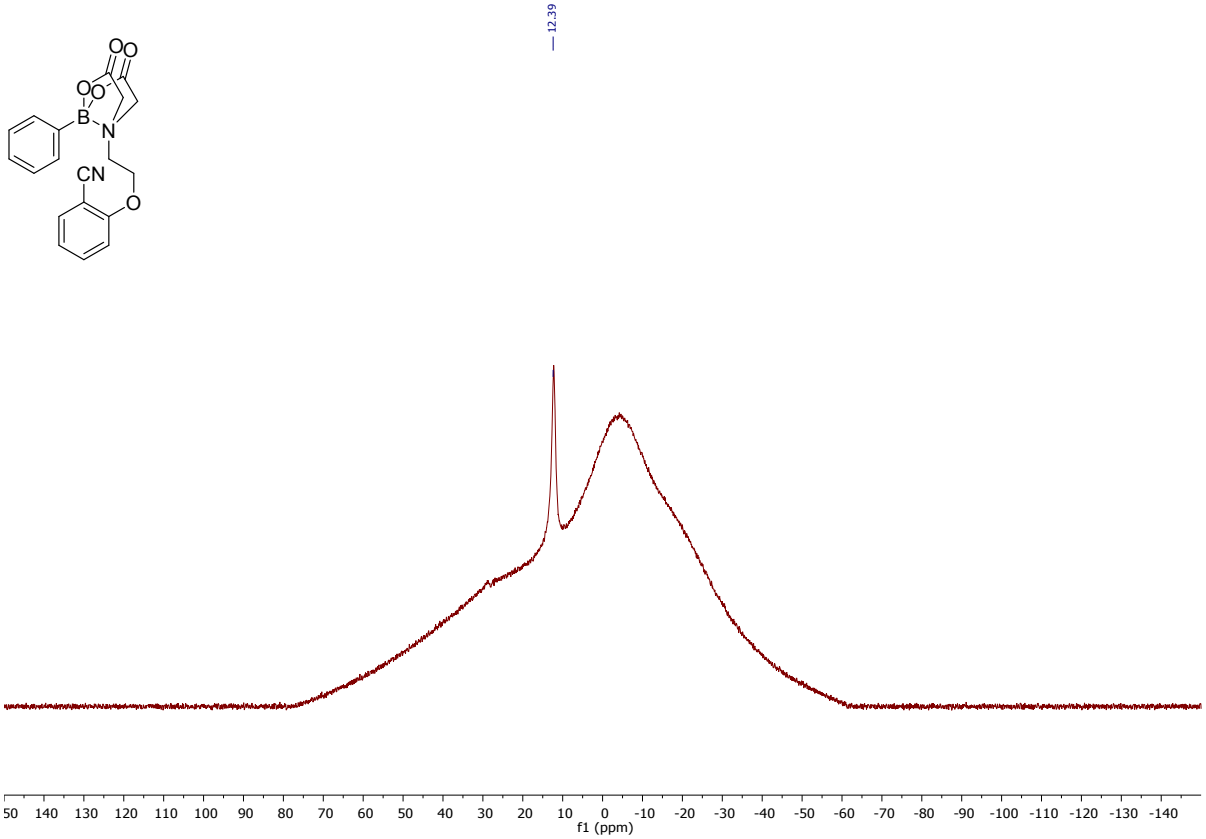
57.02
f1 (ppm)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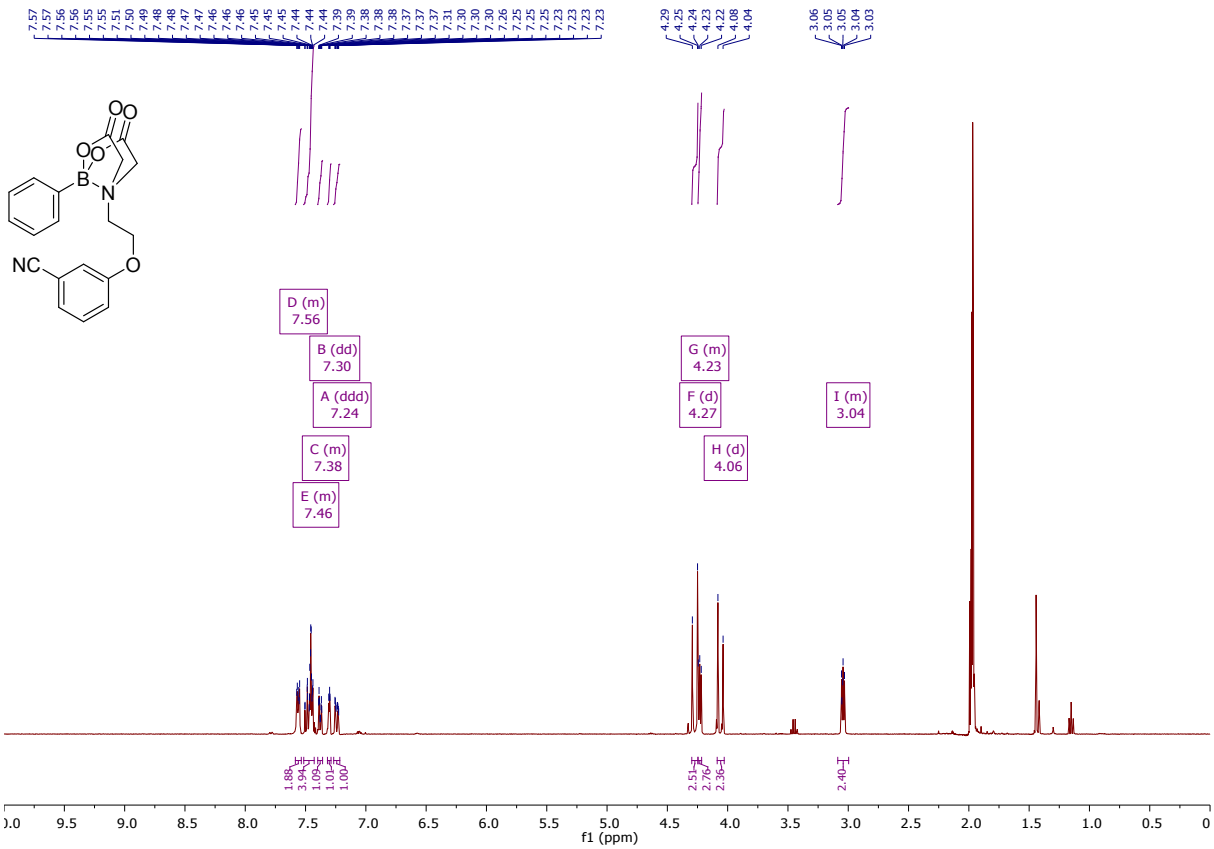
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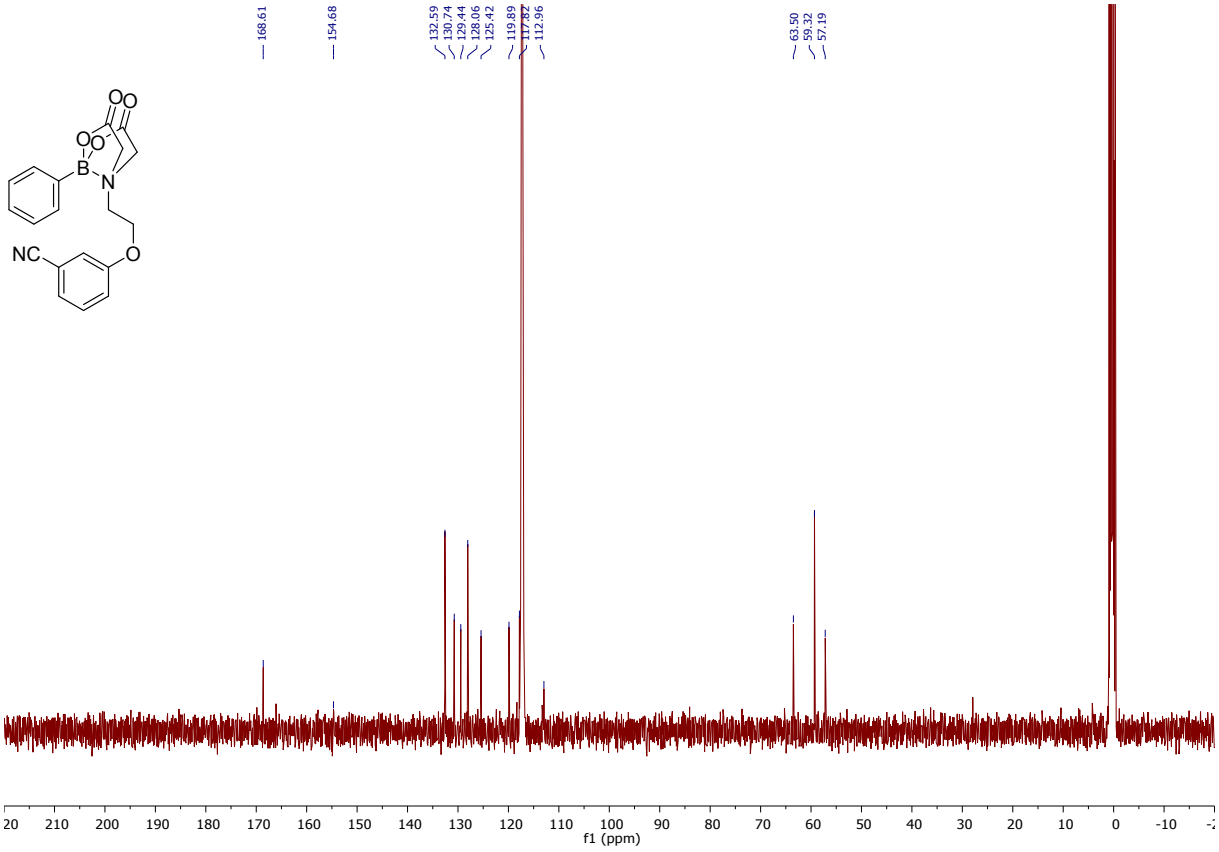
f1 (ppm)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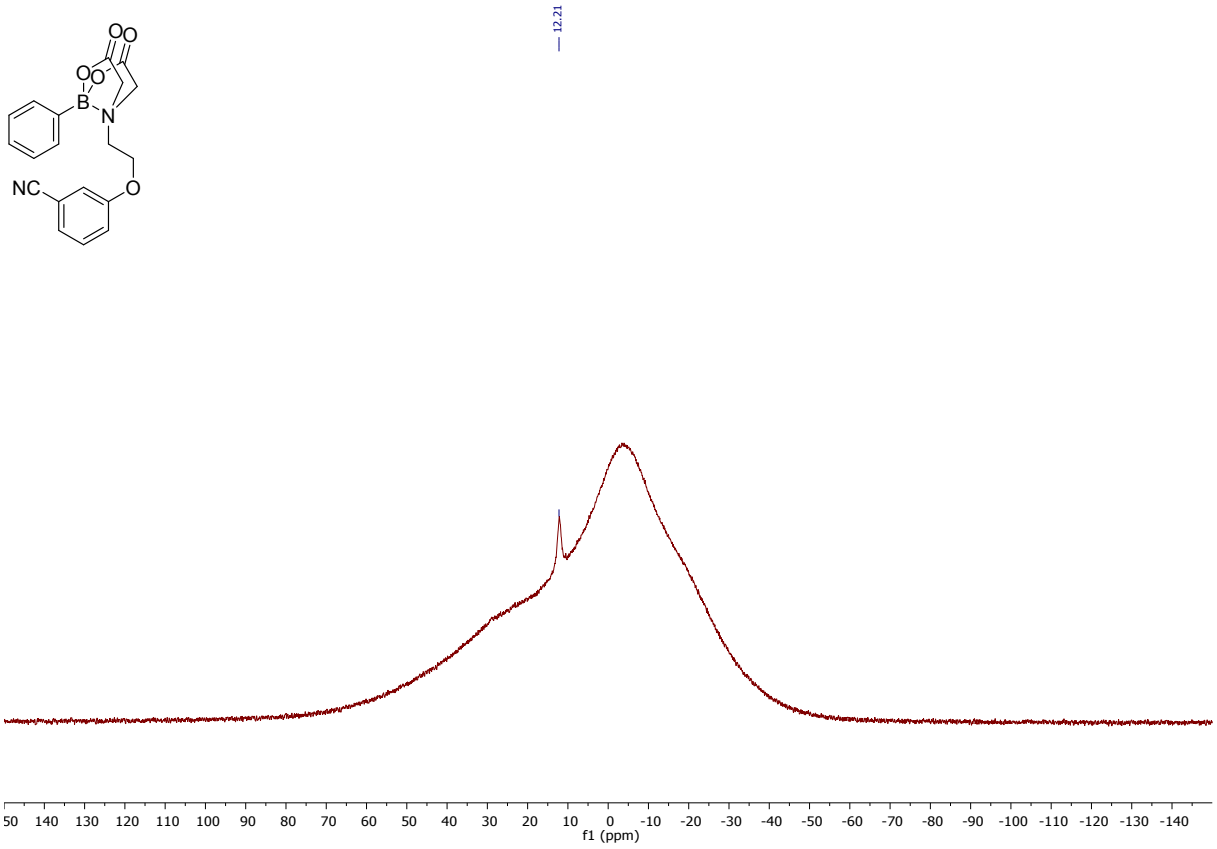
NC
O
B
N
f1 (ppm)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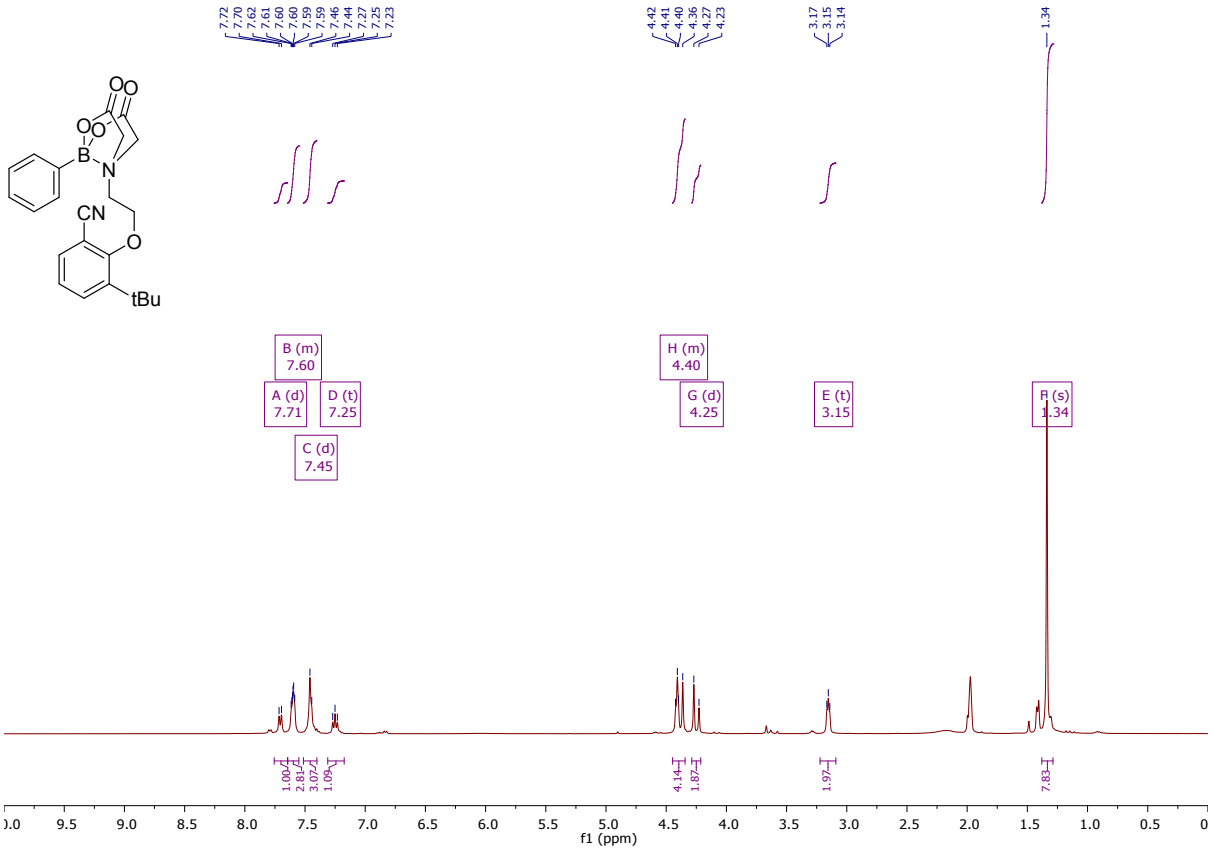
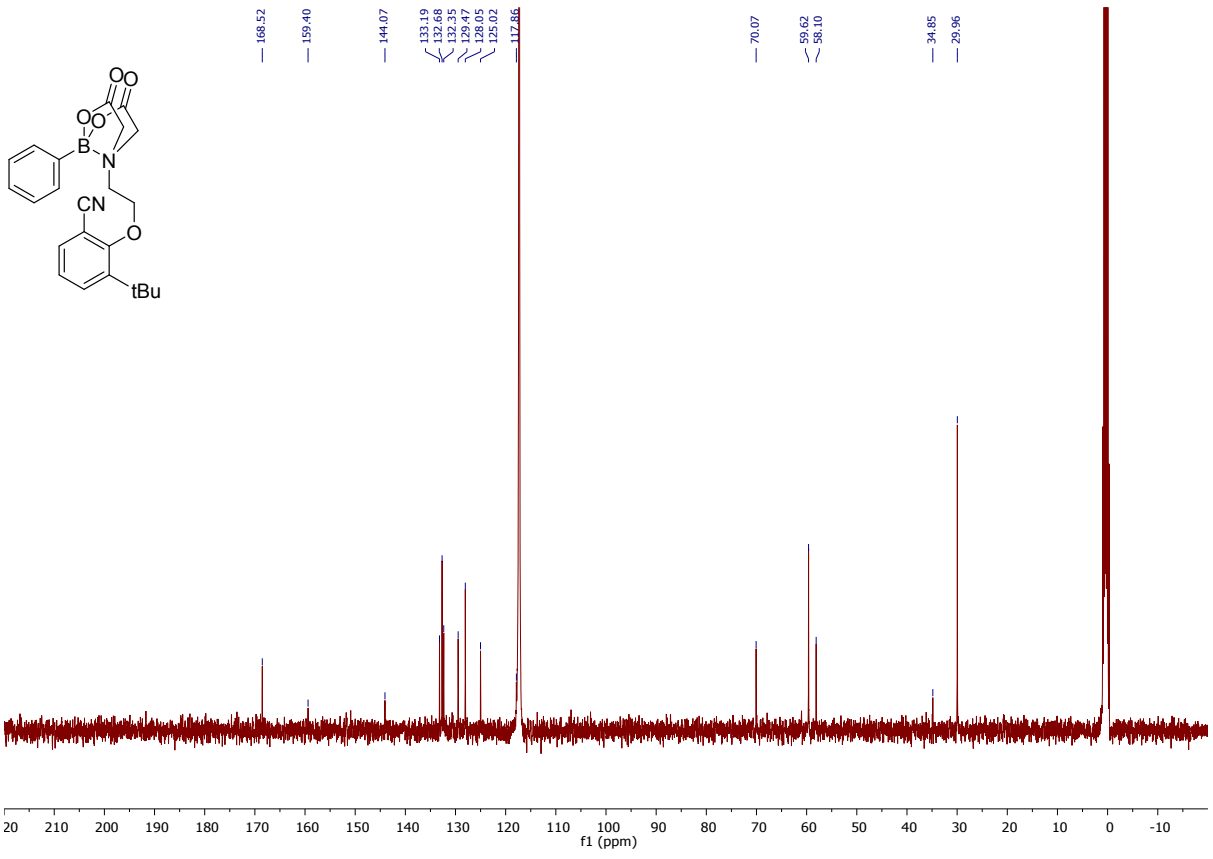
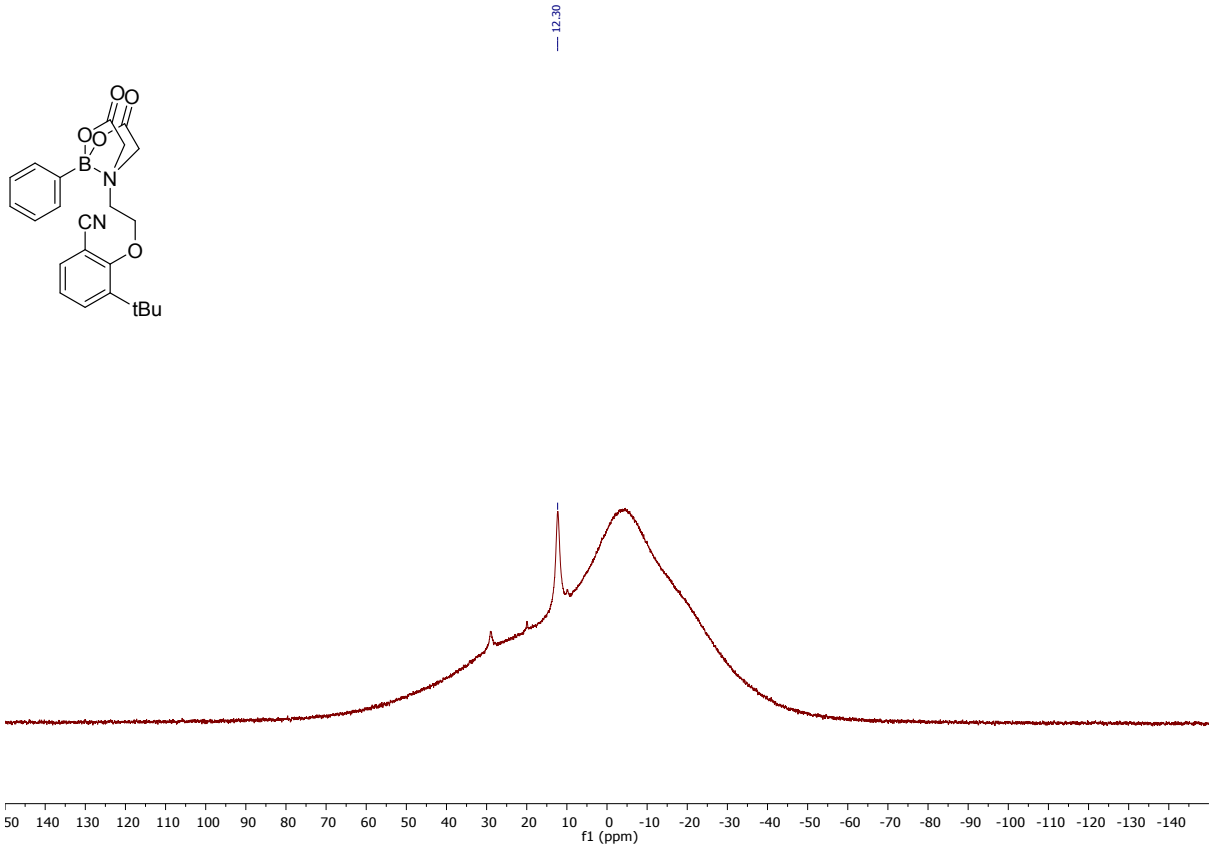
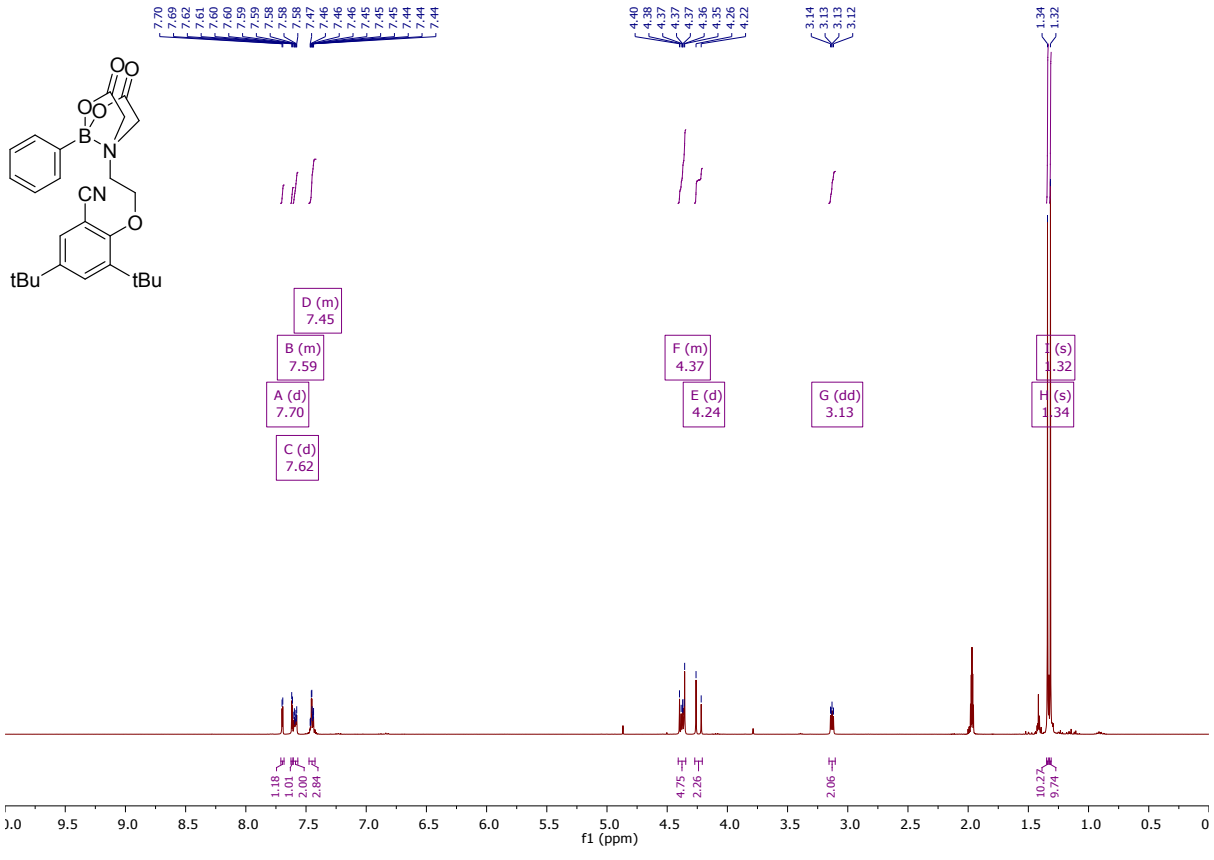
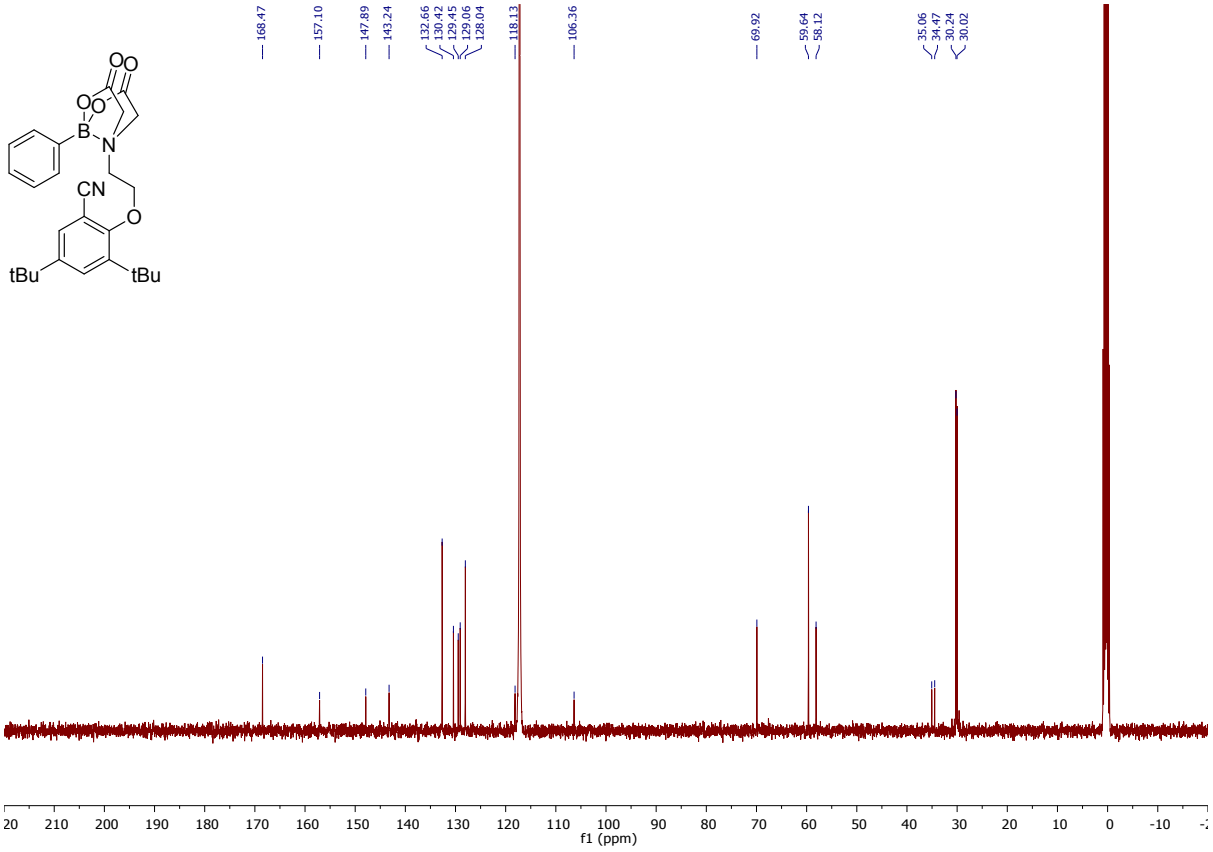
B
N
f1 (ppm)

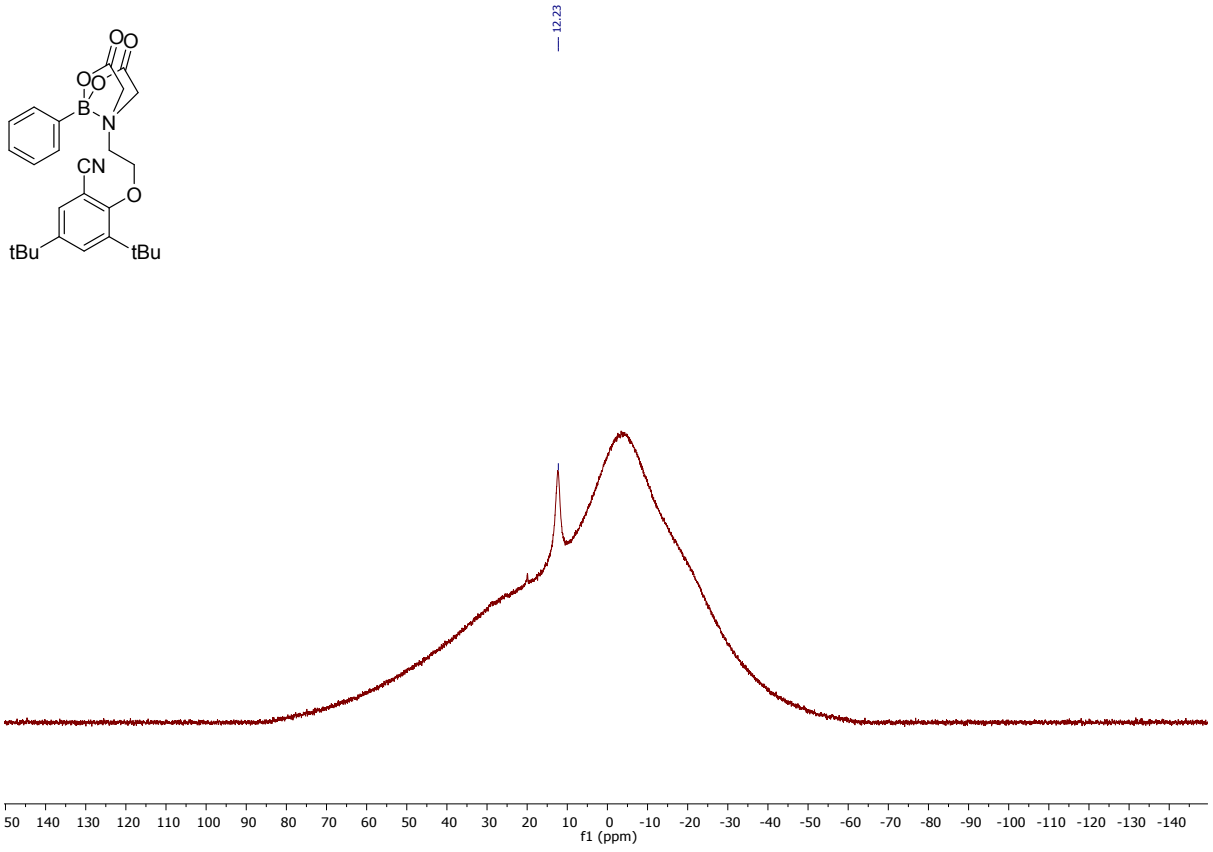

7.72
7.70
7.62
7.61
7.60
7.60
7.59
7.59
7.46
7.44
7.27
7.25
7.23
4.42
4.41
4.40
4.36
4.27
4.23
3.17
3.15
3.14
1.34
B (m)
7.60
A (d)
7.71
D (t)
7.25
C (d)
7.45
H (m)
4.40
G (d)
4.25
E (t)
3.15
F (s)
1.34
1.00
2.81
3.07
1.09
4.14
1.87
1.97
7.83
f1 (ppm)

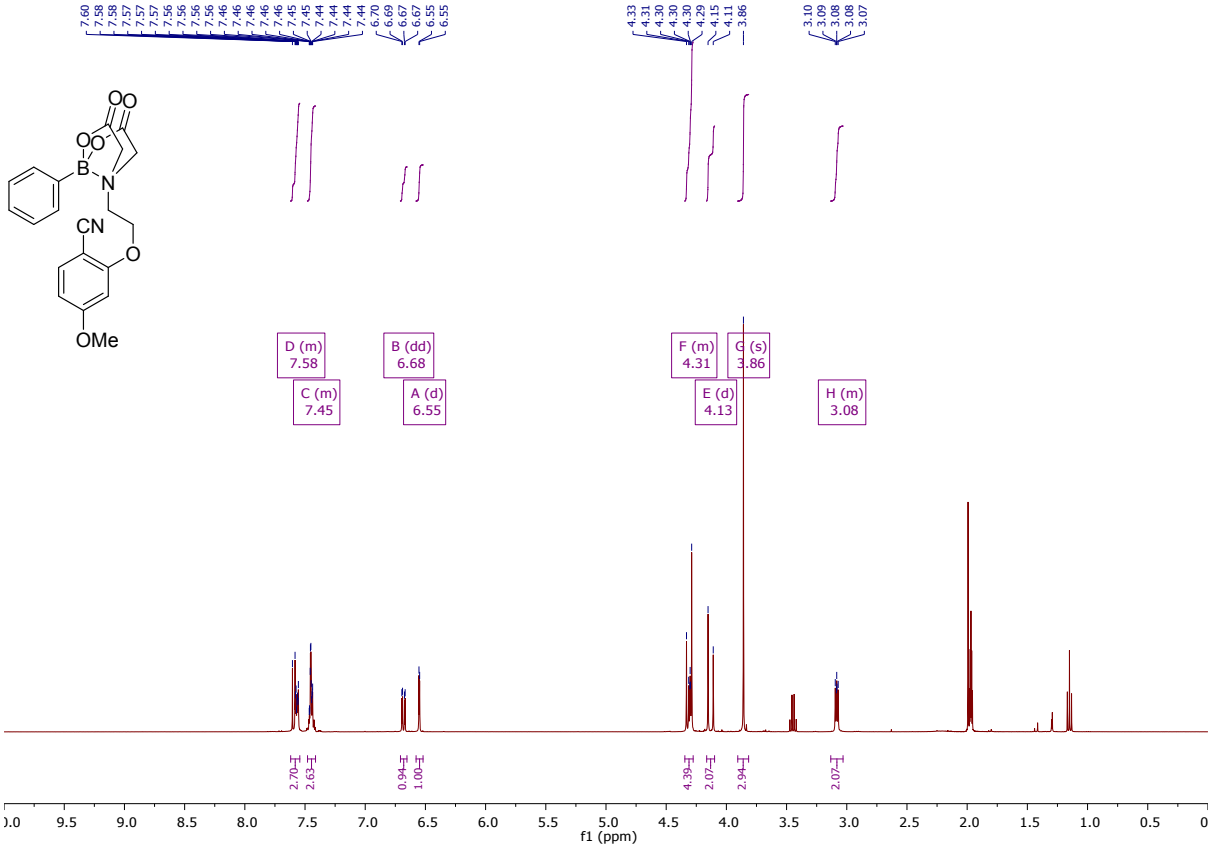

168.52
159.40
144.07
133.19
132.68
132.35
129.47
128.05
125.02
117.86
70.07
59.62
58.10
34.85
29.96
f1 (ppm)

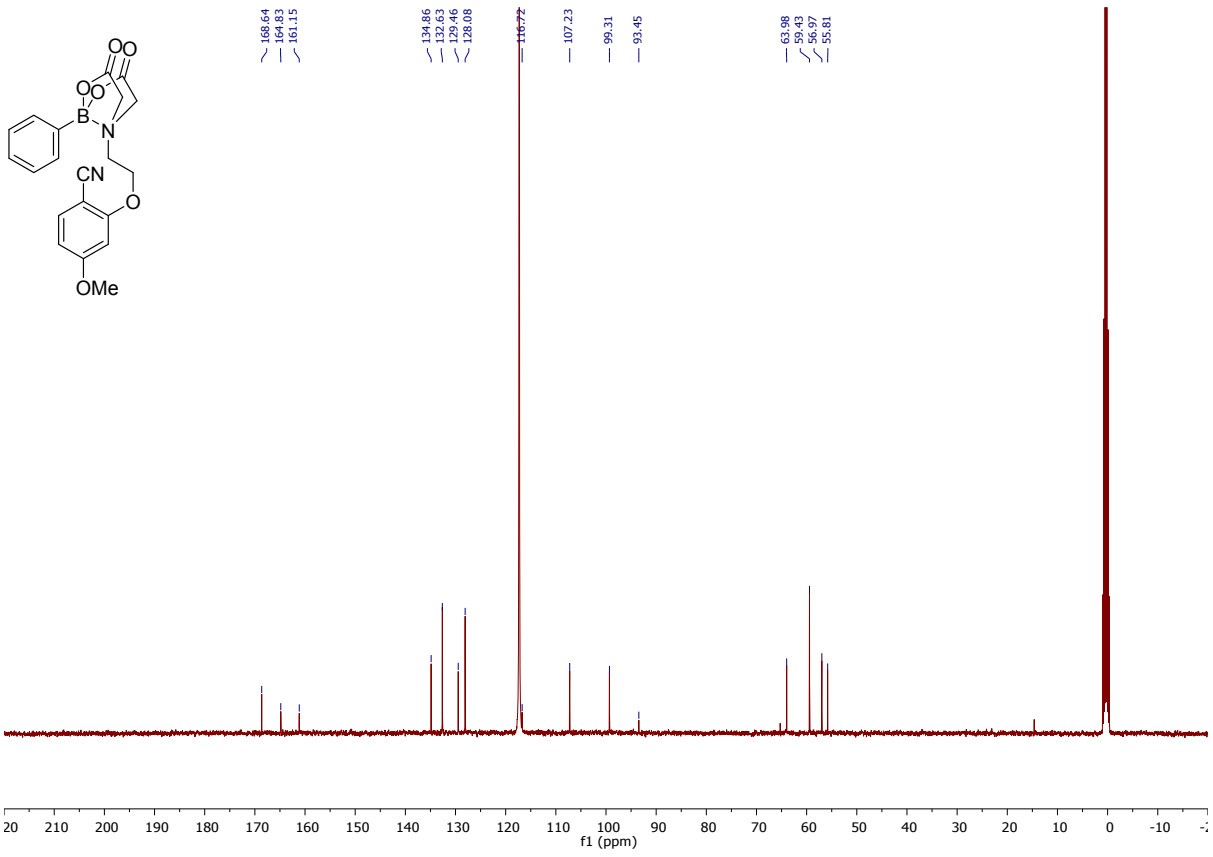

12.30
f1 (ppm)

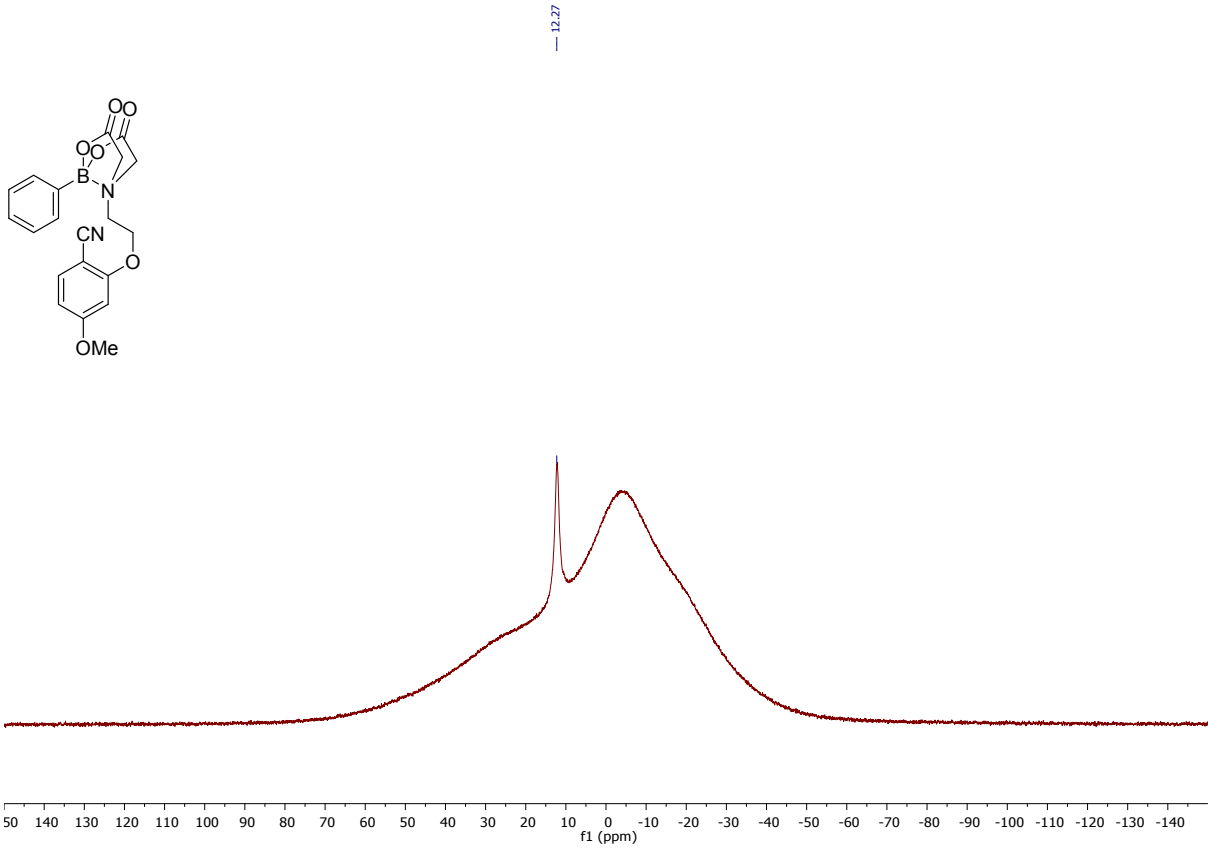

D (m) 7.45
B (m) 7.59
A (d) 7.70
C (d) 7.62
F (m) 4.37
E (d) 4.24
G (dd) 3.13
I (s) 1.32
H (s) 1.34
f1 (ppm)

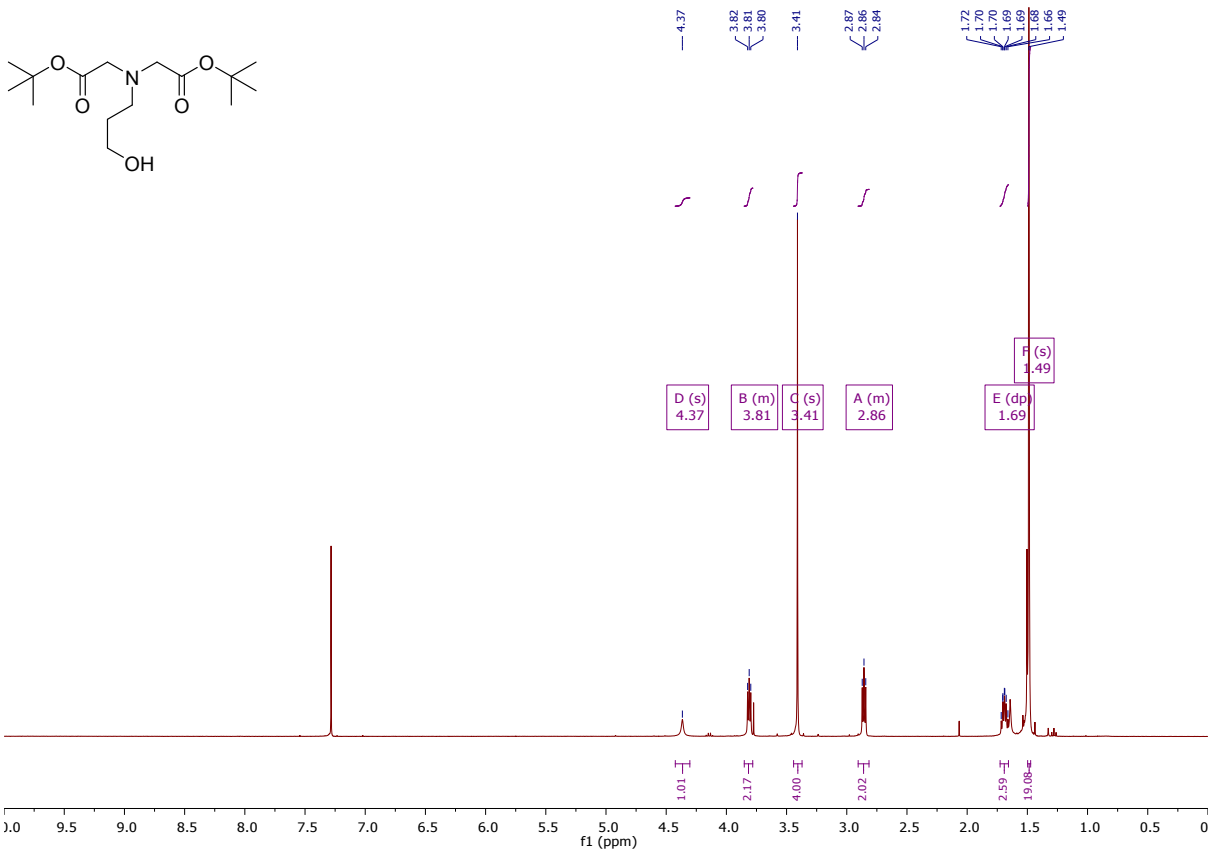

168.47
157.10
147.89
143.24
132.66
130.42
129.45
129.06
128.04
118.13
106.36
69.92
59.64
58.12
35.06
34.47
30.24
30.02
O
O
O
O
B
N
CN
O
tBu
tBu
f1 (ppm)

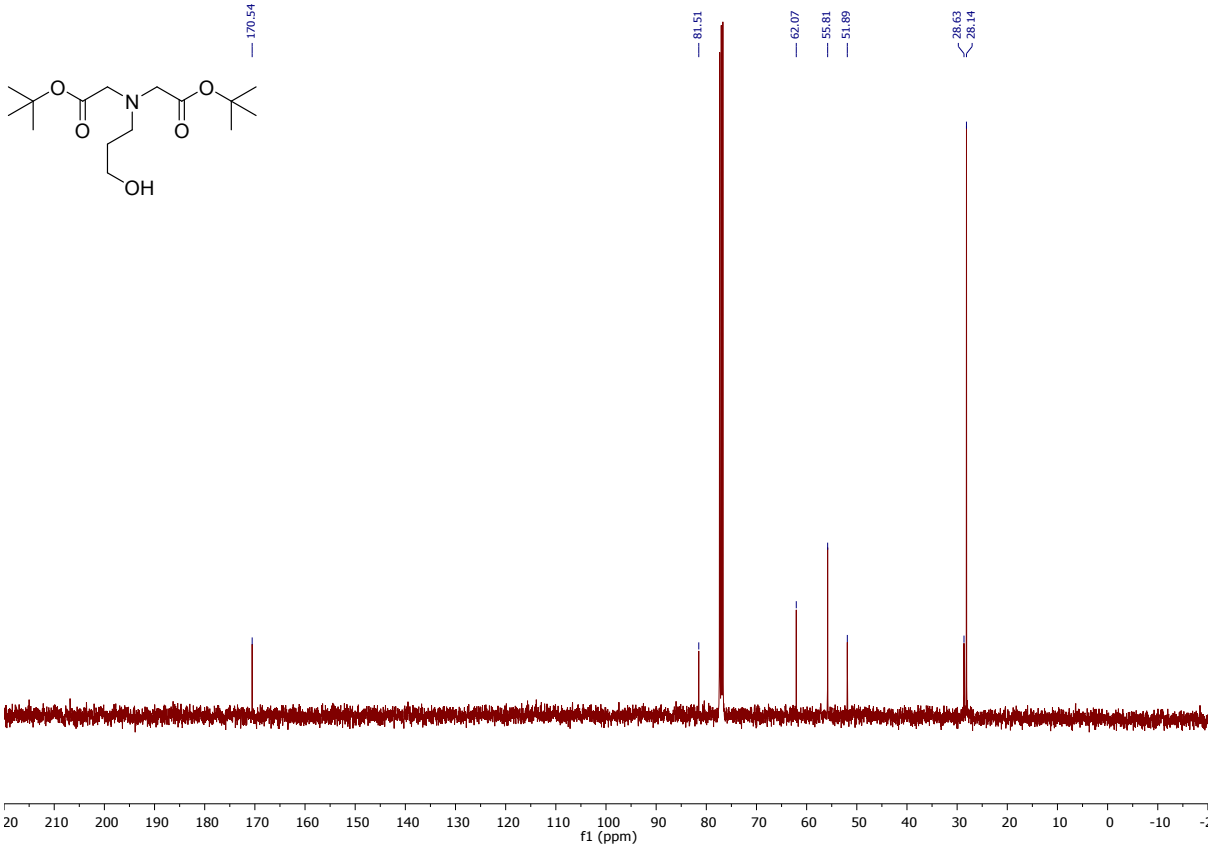

12.23
O
O
O
O
B
N
CN
O
tBu
tBu
f1 (ppm)

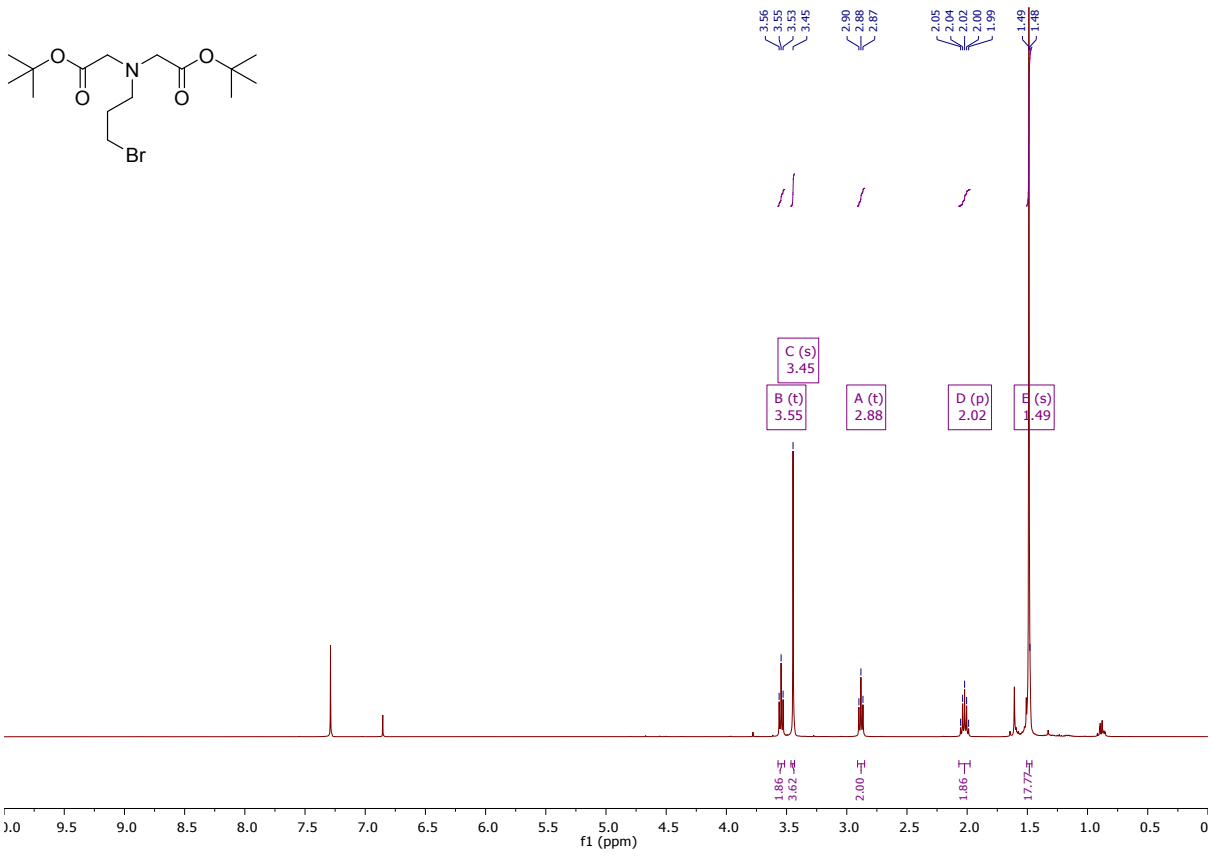

7.60 7.58 7.58 7.58 7.57 7.57 7.57 7.56 7.56 7.56 7.56 7.46 7.46 7.46 7.46 7.46 7.45 7.44 7.44 7.44 7.44 6.70 6.69 6.67 6.67 6.55 6.55
4.33 4.31 4.30 4.30 4.30 4.29 4.15 4.11 3.86
3.10 3.09 3.08 3.08 3.07
O O O O B N CN O OMe
D (m) 7.58
C (m) 7.45
B (dd) 6.68
A (d) 6.55
F (m) 4.31
E (d) 4.13
G (s) 3.86
H (m) 3.08
2.70 2.63 0.94 1.00 4.39 2.07 2.94 2.07
f1 (ppm)

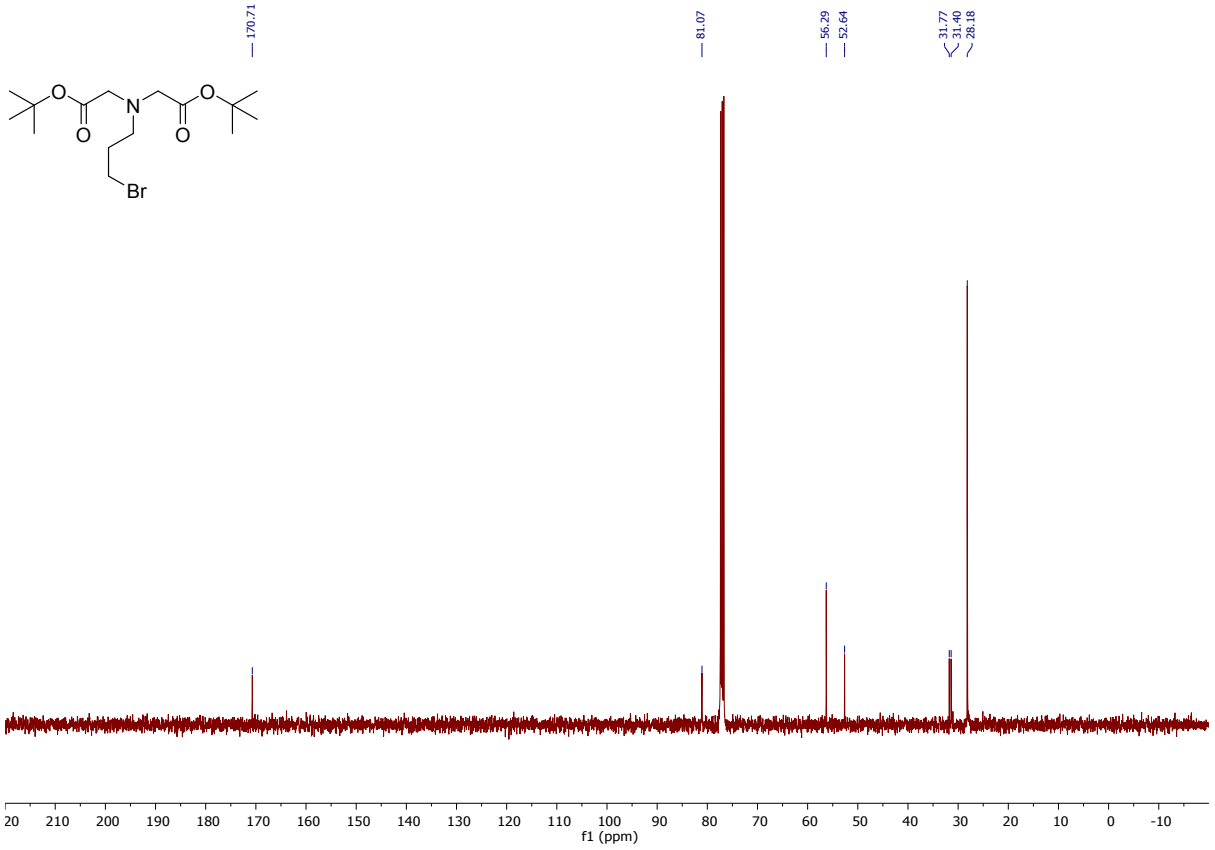

168.64 164.83 161.15 134.86 132.63 129.46 128.08 116.72 107.23 99.31 93.45 63.98 59.43 56.97 55.81
O O O O B N CN O OMe
f1 (ppm)

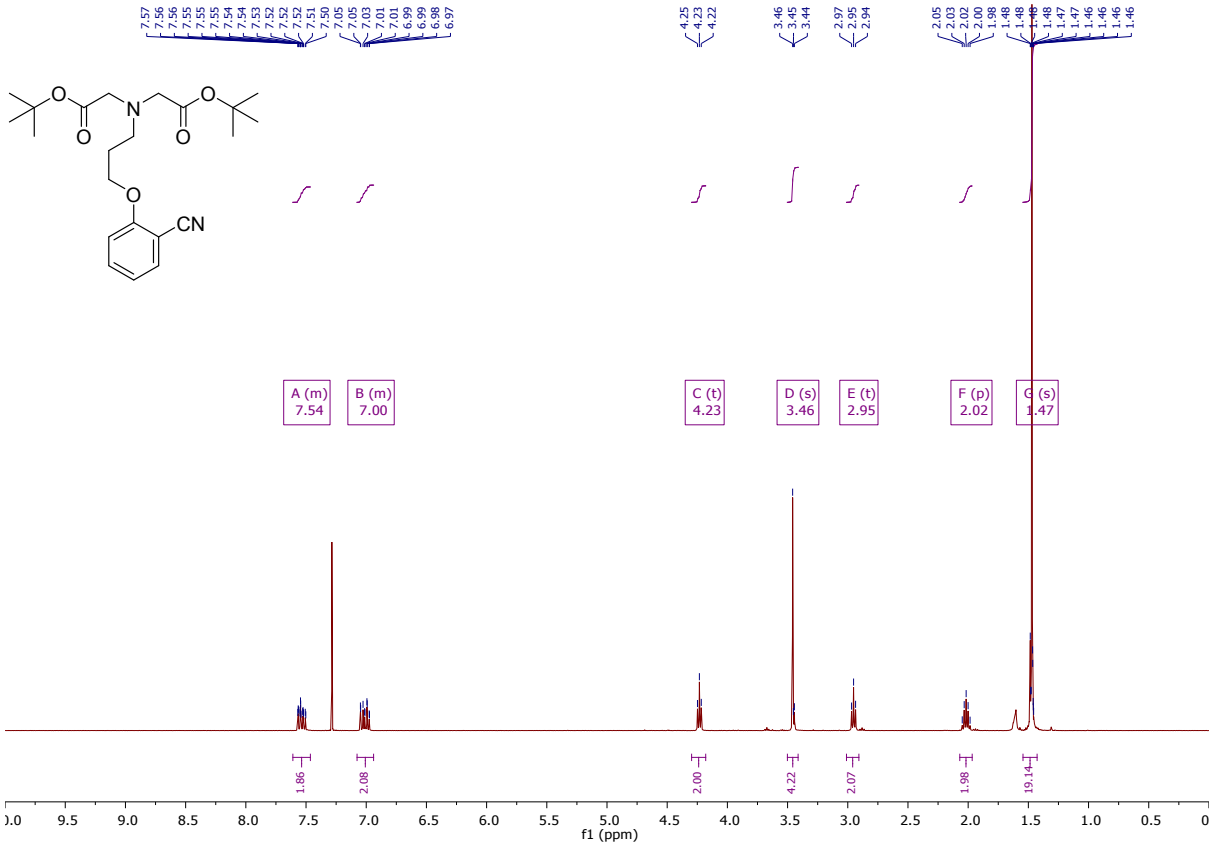

12.27
CN
O
OMe
f1 (ppm)

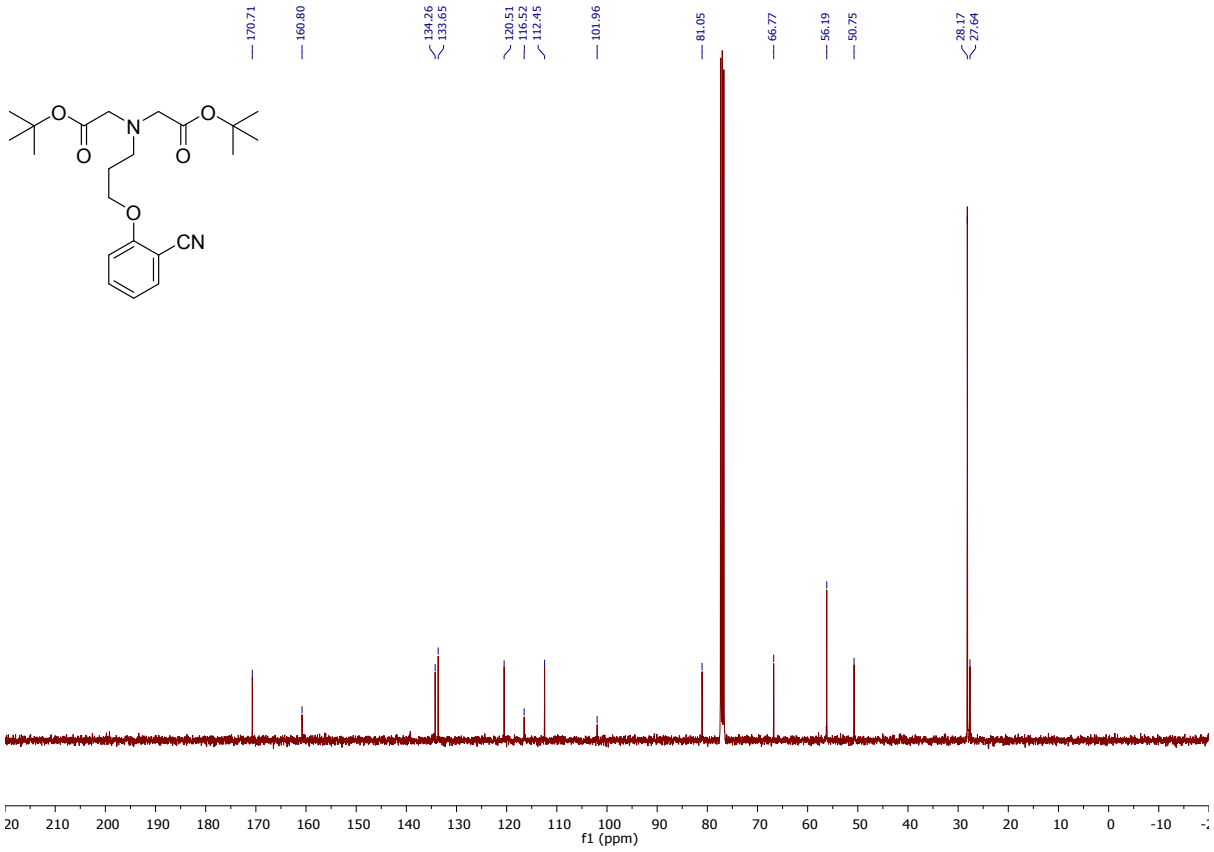

4.37
3.82
3.81
3.80
3.41
2.87
2.86
2.84
1.72
1.70
1.70
1.69
1.69
1.68
1.66
1.49
D (s) 4.37
B (m) 3.81
C (s) 3.41
A (m) 2.86
E (dp) 1.69
F (s) 1.49
OH
1.01
2.17
4.00
2.02
2.59
19.08
f1 (ppm)

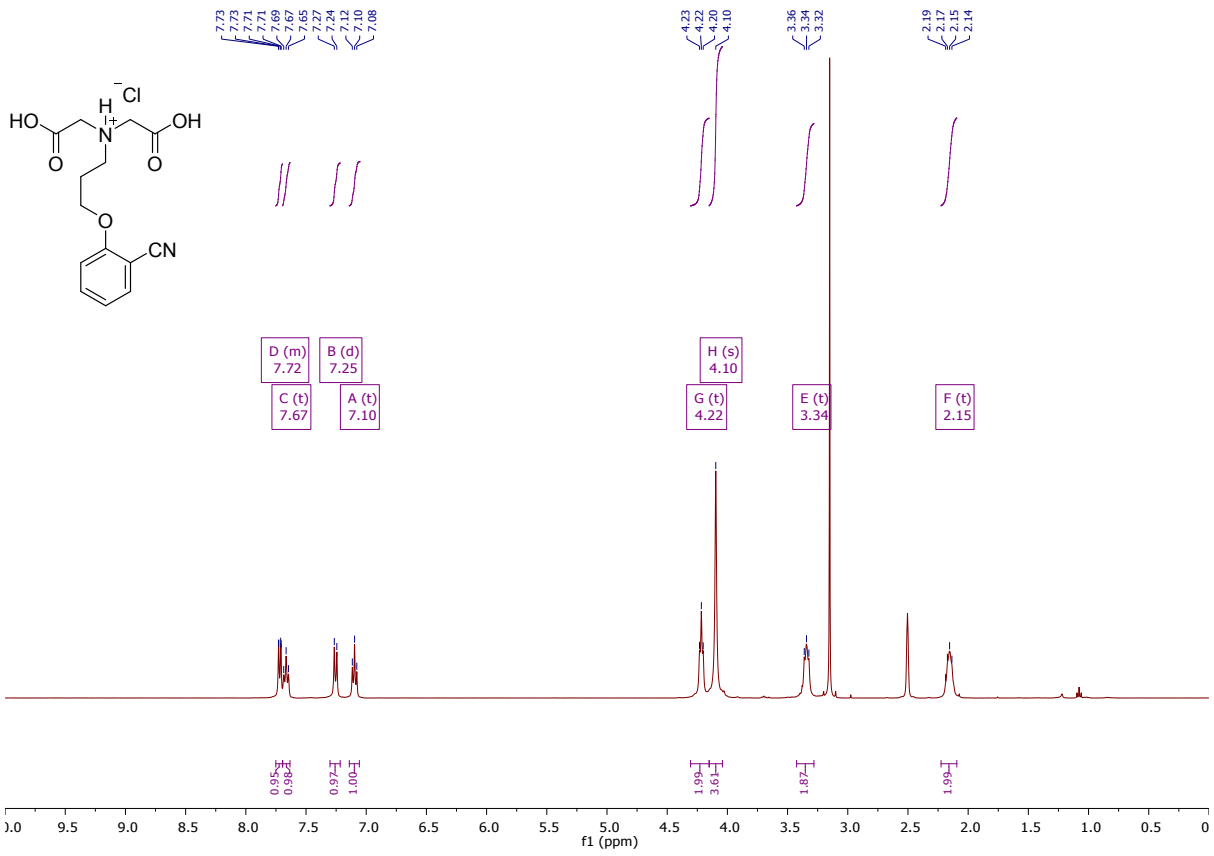

170.54
81.51
62.07
55.81
51.89
28.63
28.14
OH
f1 (ppm)

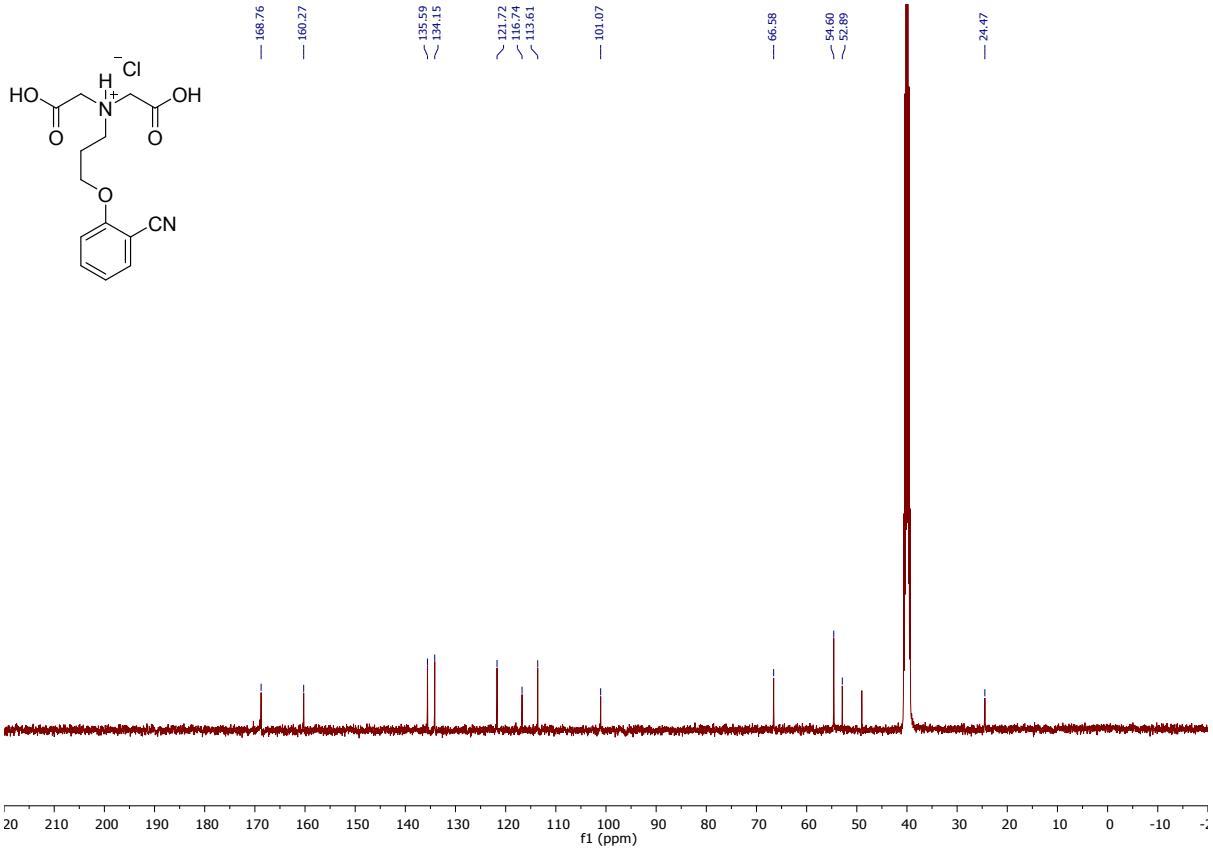

3.56
3.55
3.53
3.45
2.90
2.88
2.87
2.05
2.04
2.02
2.00
1.99
1.49
1.48
C (s) 3.45
B (t) 3.55
A (t) 2.88
D (p) 2.02
E (s) 1.49
1.86
3.62
2.00
1.86
17.77
Br
f1 (ppm)

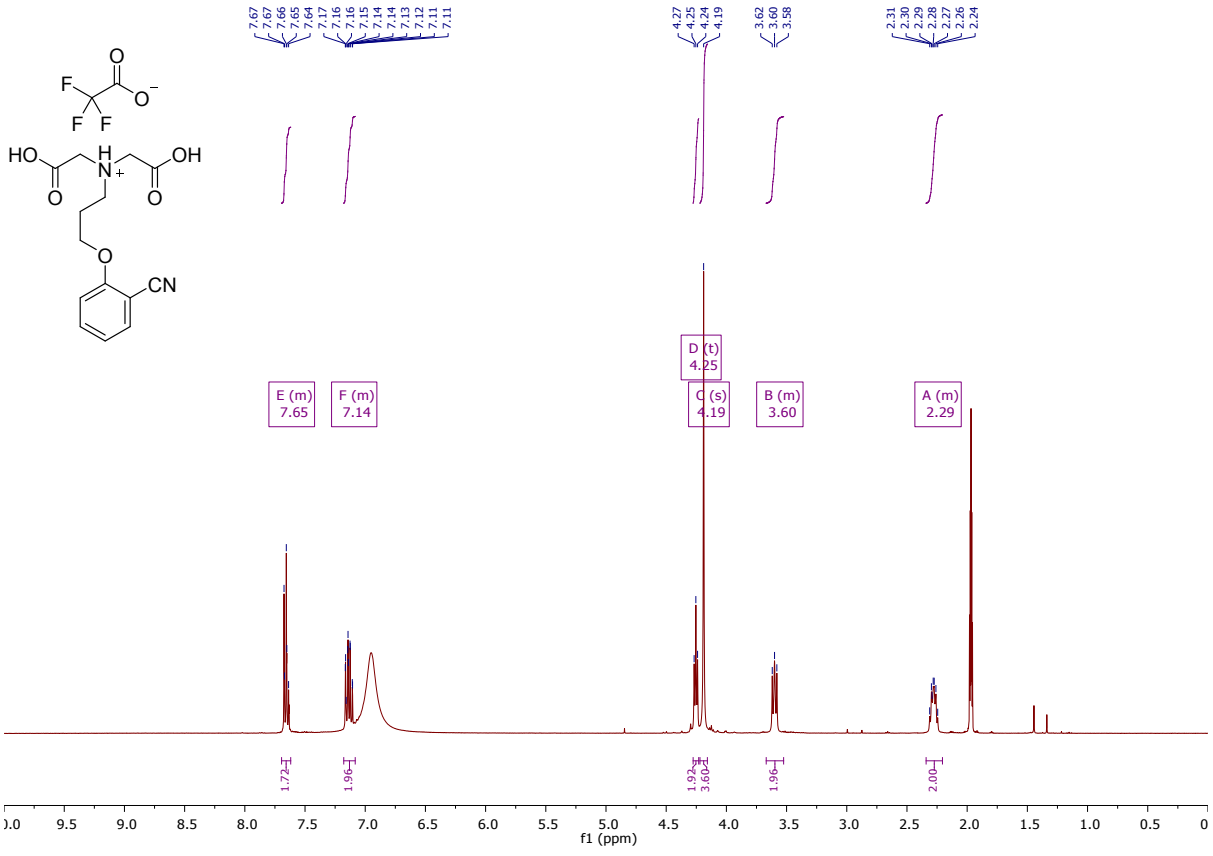

170.71
81.07
56.29
52.64
31.77
31.40
28.18
O
O
N
O
O
Br
f1 (ppm)

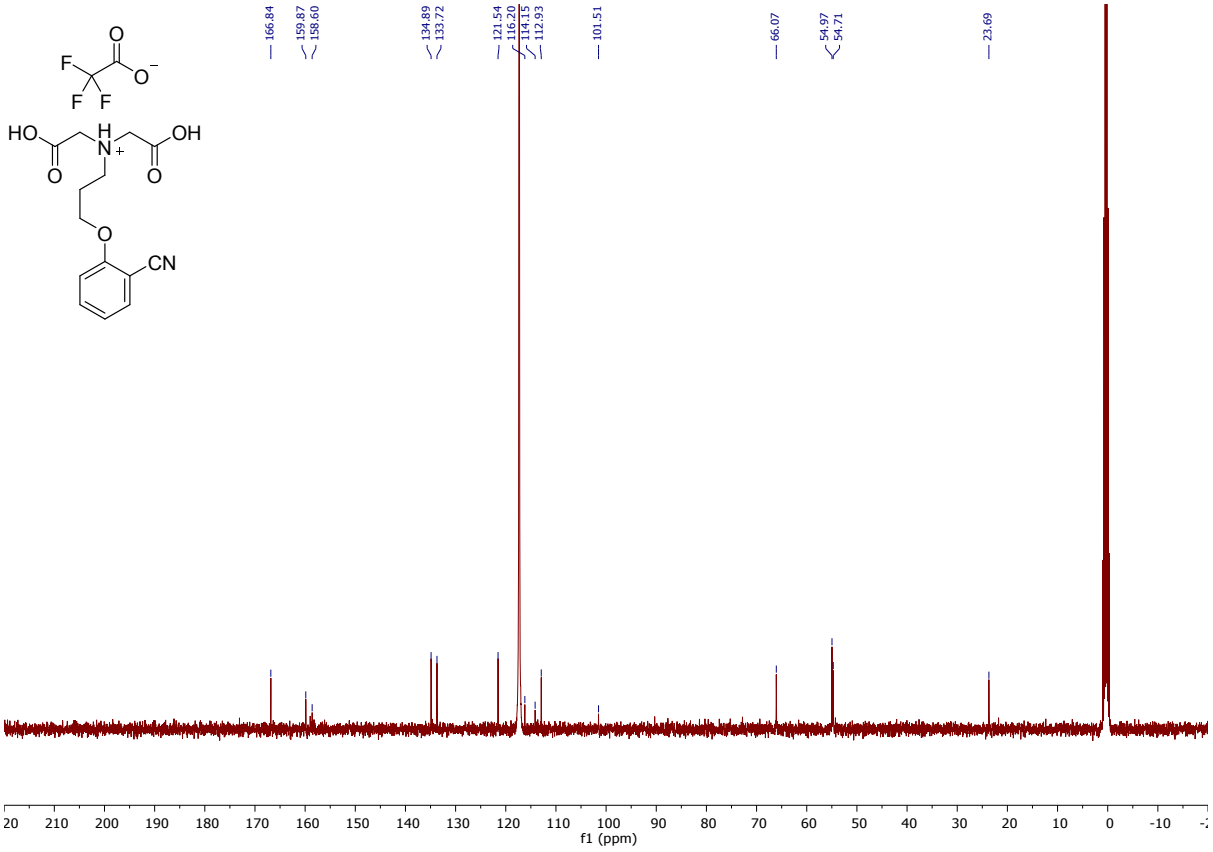

7.57
7.56
7.56
7.55
7.55
7.55
7.54
7.54
7.53
7.52
7.52
7.52
7.51
7.50
7.05
7.05
7.03
7.01
7.01
6.99
6.99
6.98
6.97
4.25
4.23
4.22
3.46
3.45
3.44
2.97
2.95
2.94
2.05
2.03
2.02
2.00
1.98
1.48
1.48
1.48
1.47
1.47
1.46
1.46
1.46
1.46
O
O
N
O
O
O
CN
A (m)
7.54
B (m)
7.00
C (t)
4.23
D (s)
3.46
E (t)
2.95
F (p)
2.02
G (s)
1.47
1.86
2.08
2.00
4.22
2.07
1.98
19.14
f1 (ppm)

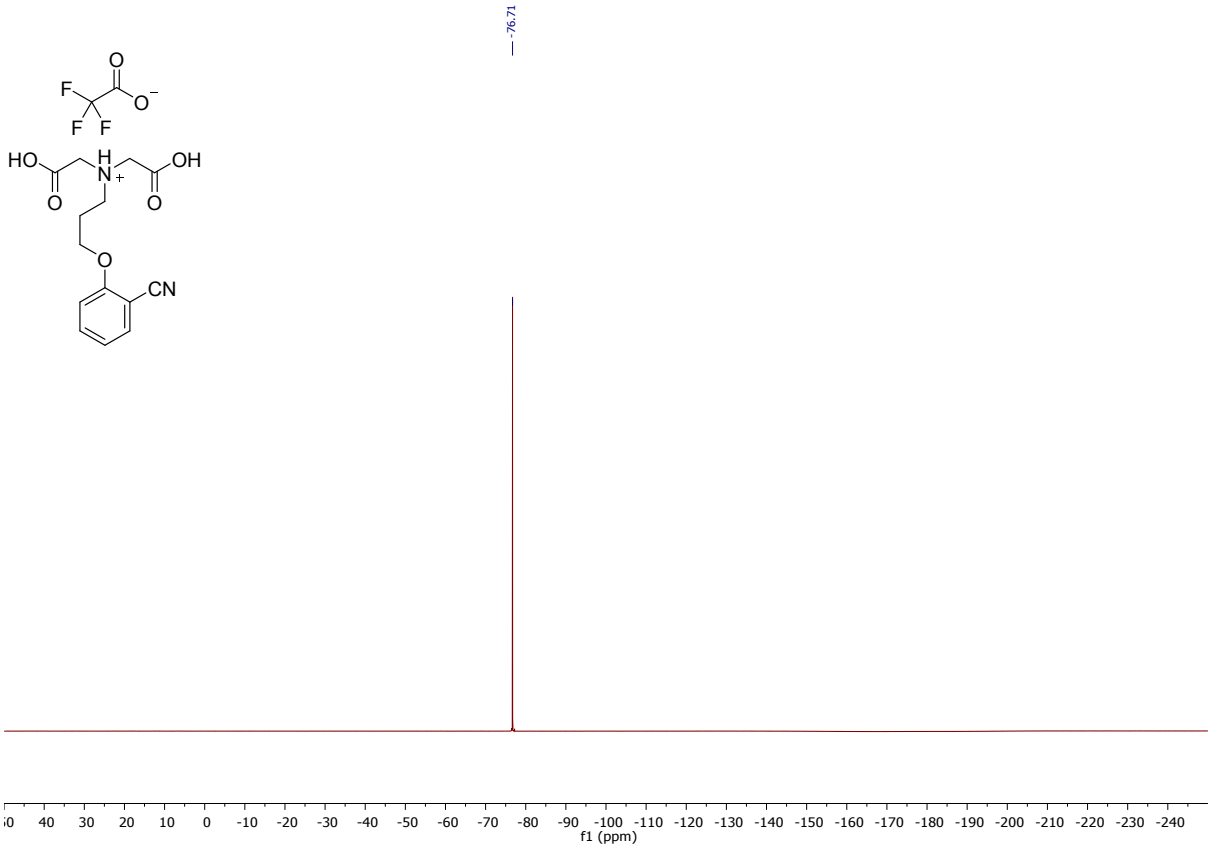

170.71
160.80
134.26
133.65
120.51
116.52
112.45
101.96
81.05
66.77
56.19
50.75
28.17
27.64
O
N
O
O
O
O
CN
f1 (ppm)


7.73
7.73
7.71
7.71
7.69
7.67
7.65
7.27
7.24
7.12
7.10
7.08
4.23
4.22
4.20
4.10
3.36
3.34
3.32
2.19
2.17
2.15
2.14
H
Cl
HO
OH
N
O
O
O
O
CN
D (m)
7.72
B (d)
7.25
H (s)
4.10
C (t)
7.67
A (t)
7.10
G (t)
4.22
E (t)
3.34
F (t)
2.15
0.95
0.98
0.97
1.00
1.99
3.61
1.87
1.99
f1 (ppm)

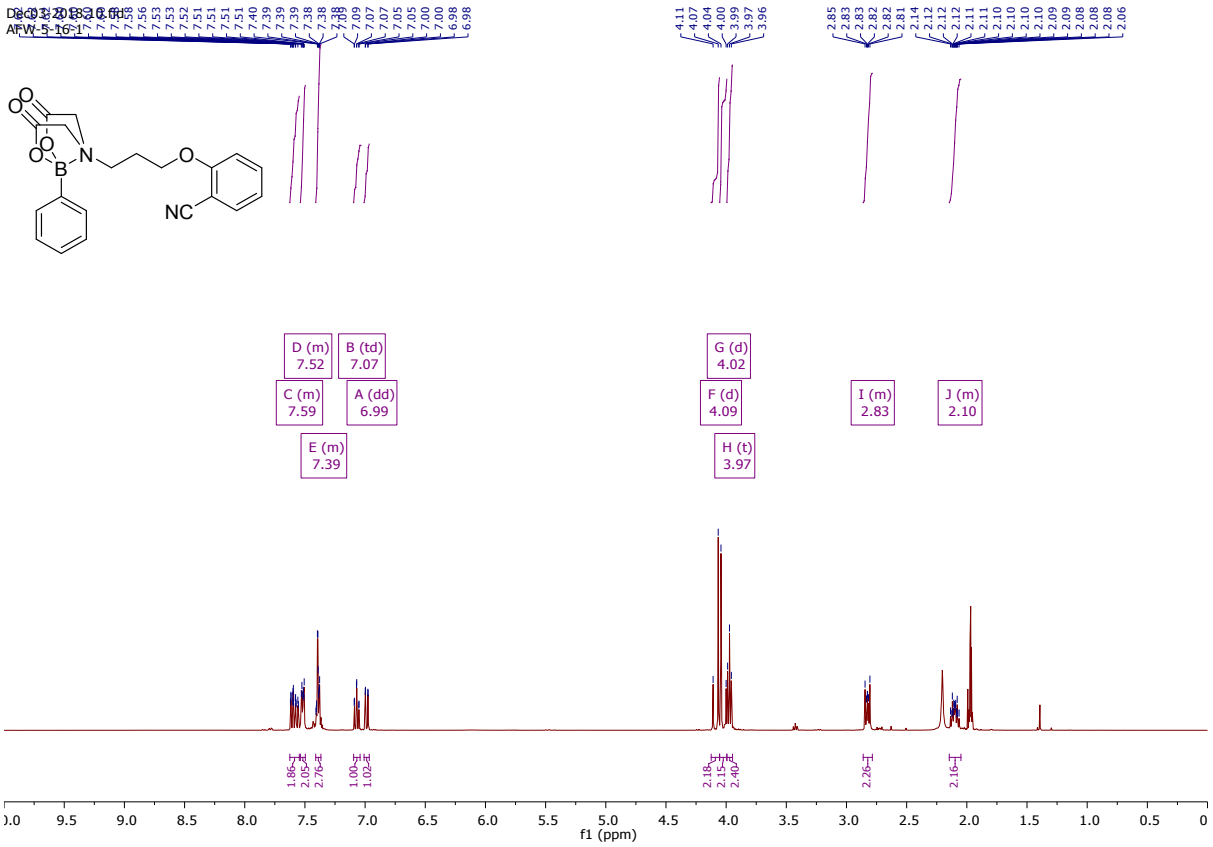

168.76
160.27
135.59
134.15
121.72
116.74
113.61
101.07
66.58
54.60
52.89
24.47
Cl
HO
OH
O
CN
f1 (ppm)

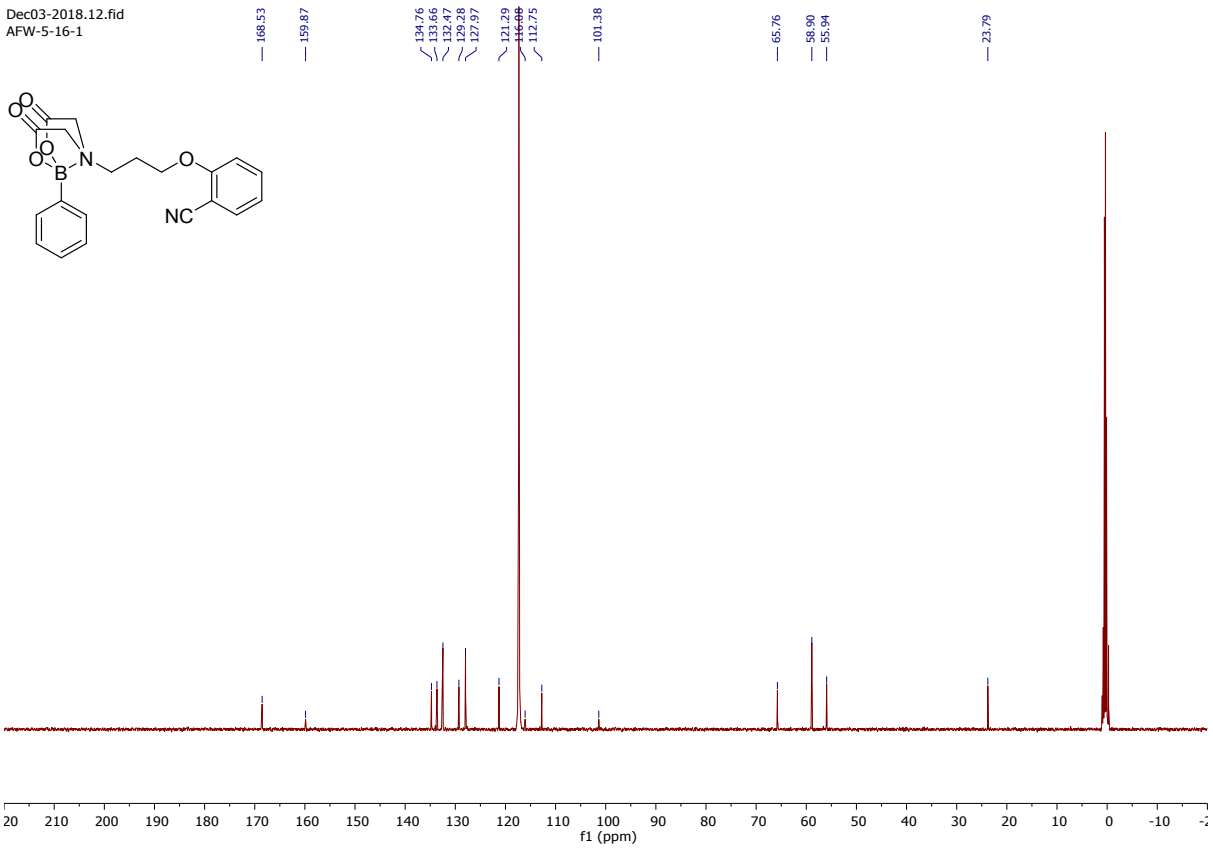

7.67
7.66
7.65
7.64
7.17
7.16
7.15
7.14
7.13
7.12
7.11
4.27
4.25
4.24
4.19
3.62
3.60
3.58
2.31
2.30
2.29
2.28
2.27
2.26
2.24
F
O
HO
OH
CN
D (t)
4.25
E (m)
7.65
F (m)
7.14
C (s)
4.19
B (m)
3.60
A (m)
2.29
1.72
1.96
1.92
3.60
1.96
2.00
f1 (ppm)

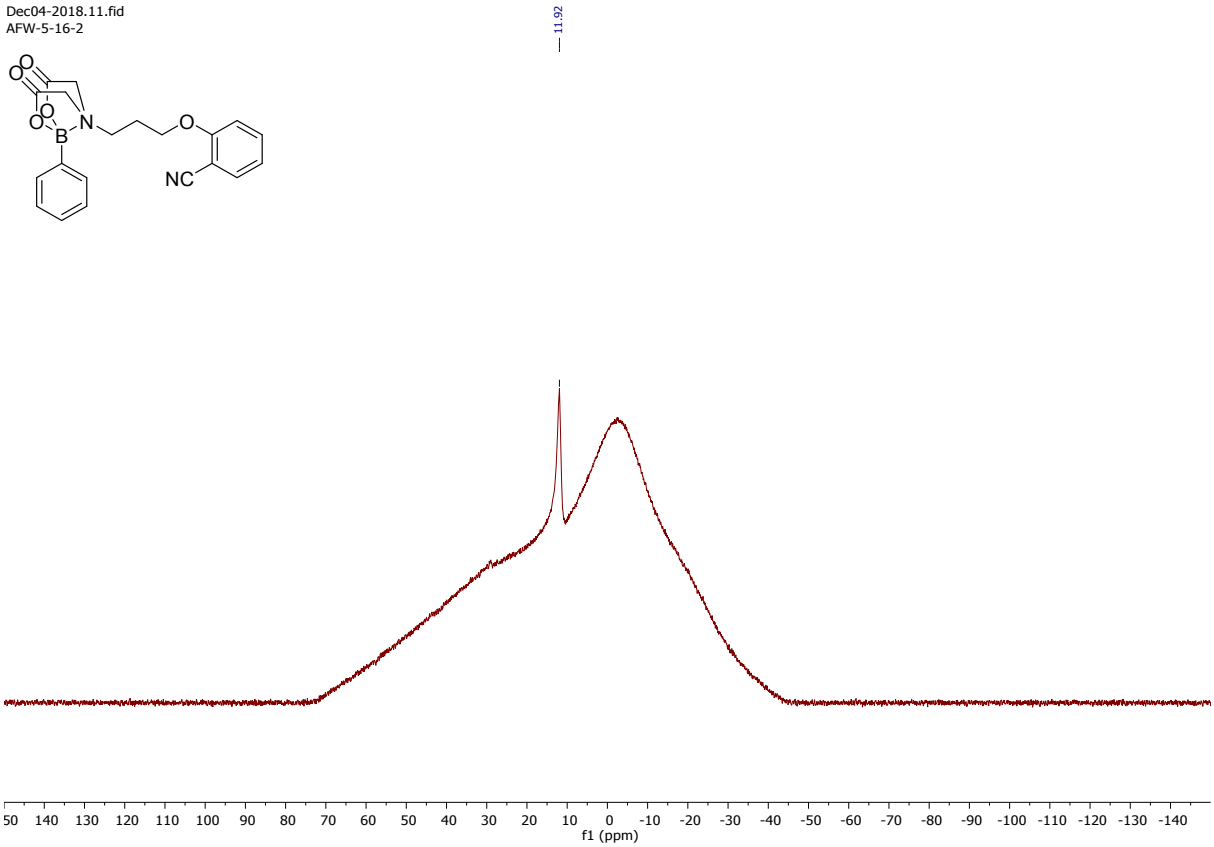

166.84
159.87
158.60
134.89
133.72
121.54
116.20
114.15
112.93
101.51
66.07
54.97
54.71
23.69
f1 (ppm)

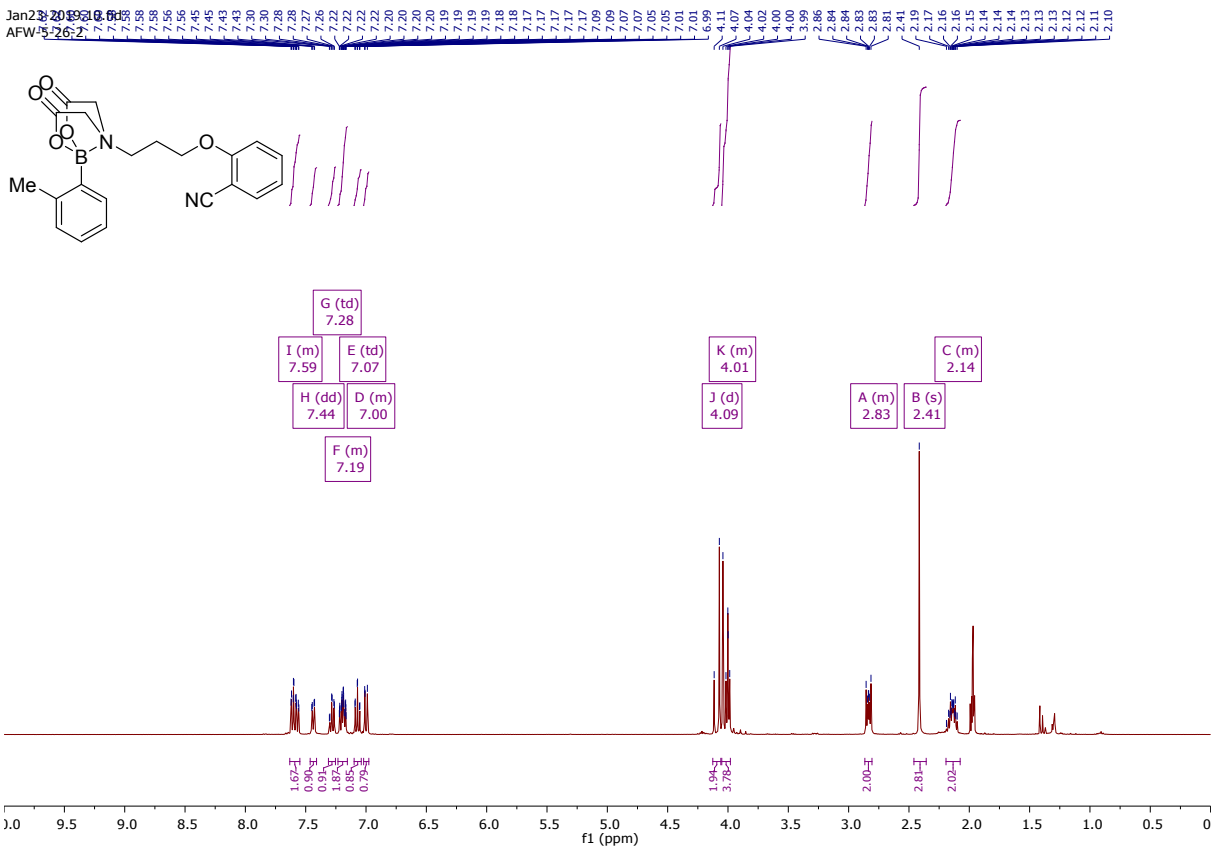

-76.71
f1 (ppm)

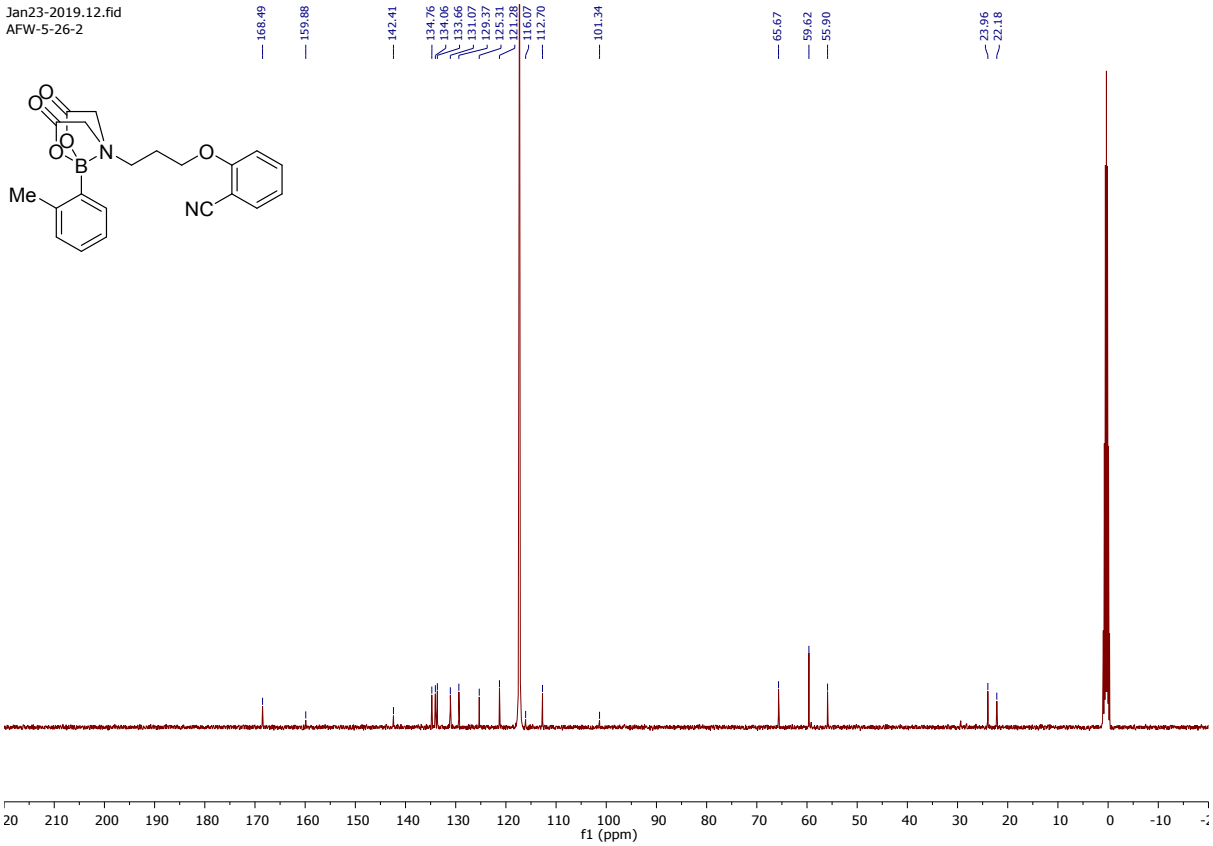
Aryl boronic acid MIDA-DG ester NMR Spectra

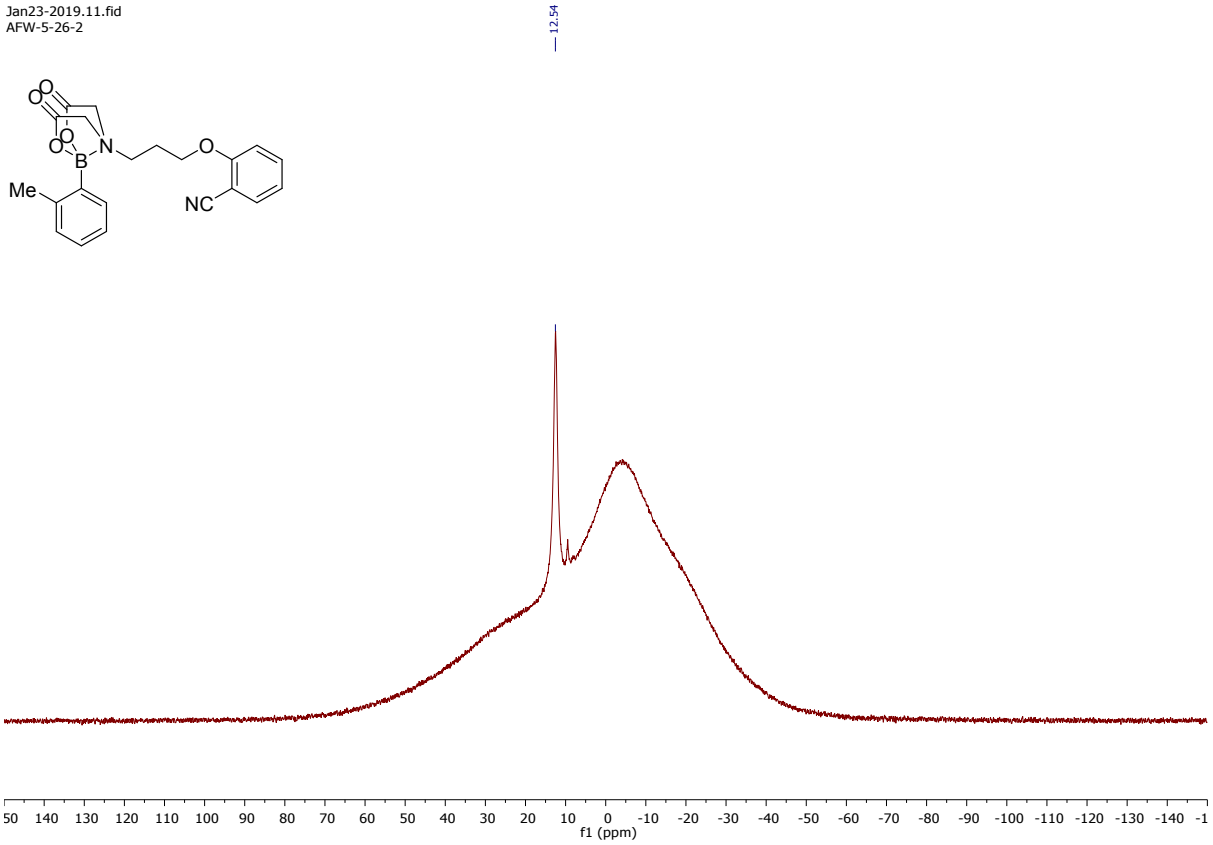


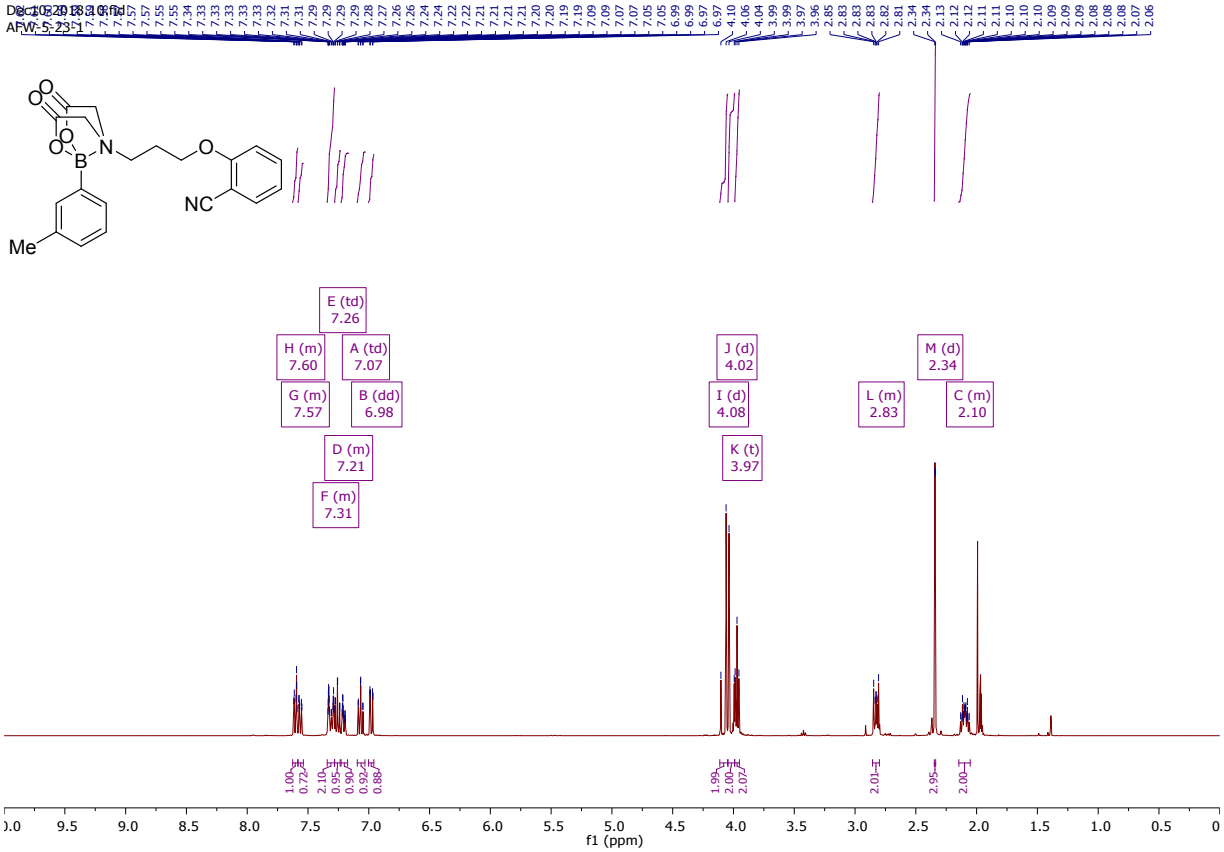


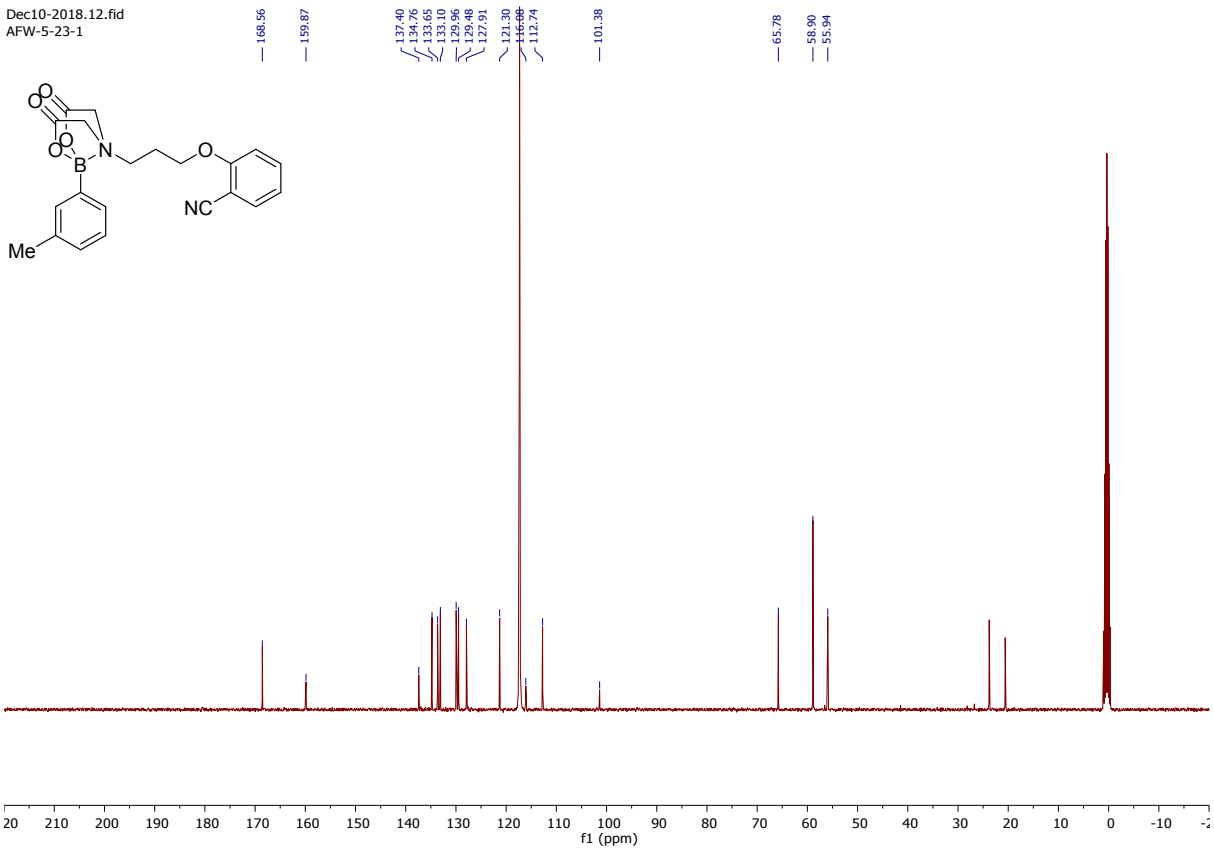

Dec04-2018.11.fid
AFW-5-16-2
11.92
f1 (ppm)


Me
G (td) 7.28
I (m) 7.59
E (td) 7.07
H (dd) 7.44
D (m) 7.00
F (m) 7.19
K (m) 4.01
J (d) 4.09
A (m) 2.83
B (s) 2.41
C (m) 2.14
f1 (ppm)

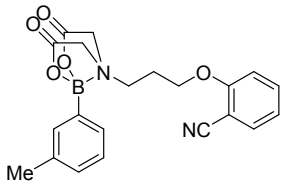

Jan23-2019.12.fid
AFW-5-26-2
168.49
159.88
142.41
134.76
134.06
133.66
131.07
129.37
125.31
121.28
116.07
112.70
101.34
65.67
59.62
55.90
23.96
22.18
O
O
O
O
B
N
O
Me
NC
f1 (ppm)


Jan23-2019.11.fid
AFW-5-26-2
12.54
O
O
O
O
B
N
O
Me
NC
f1 (ppm)

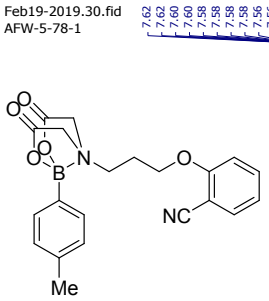

Dec10-2018.10.fid
AFW-5-23-1
E (td) 7.26
H (m) 7.60
A (td) 7.07
G (m) 7.57
B (dd) 6.98
D (m) 7.21
F (m) 7.31
J (d) 4.02
I (d) 4.08
K (t) 3.97
L (m) 2.83
M (d) 2.34
C (m) 2.10
f1 (ppm)

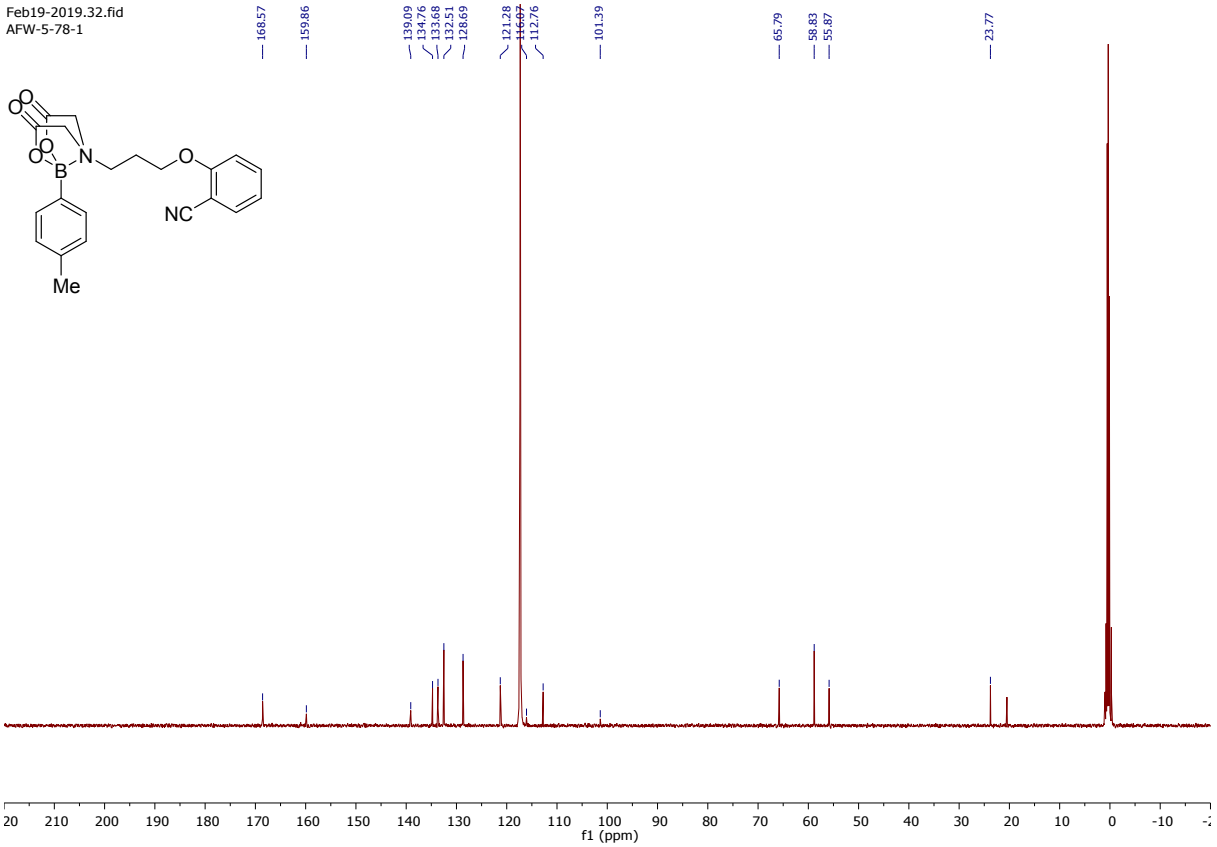

Dec10-2018.12.fid
AFW-5-23-1
168.56
159.87
137.40
134.76
133.65
133.10
129.96
129.48
127.91
121.30
116.88
112.74
101.38
65.78
58.90
55.94
f1 (ppm)

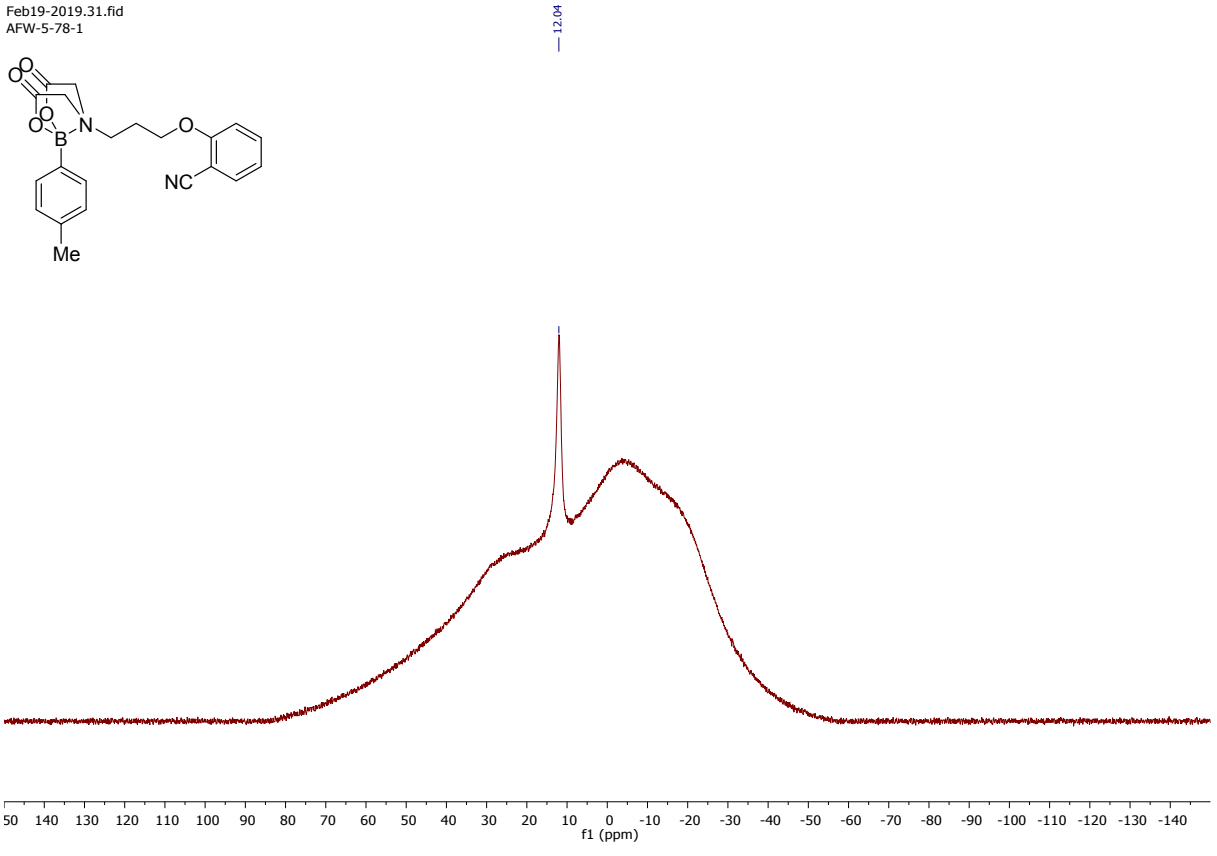
Dec10-2018.11.fid
AFW-5-23-1

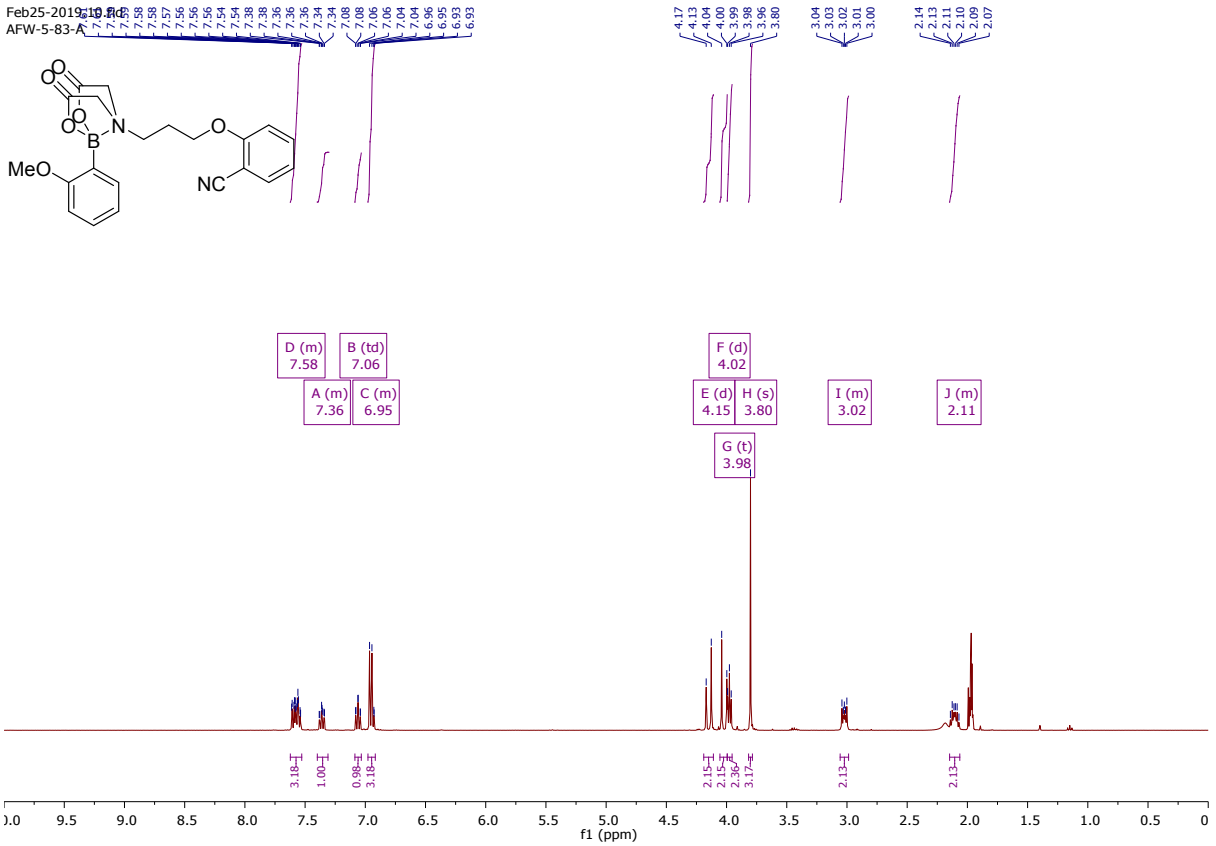


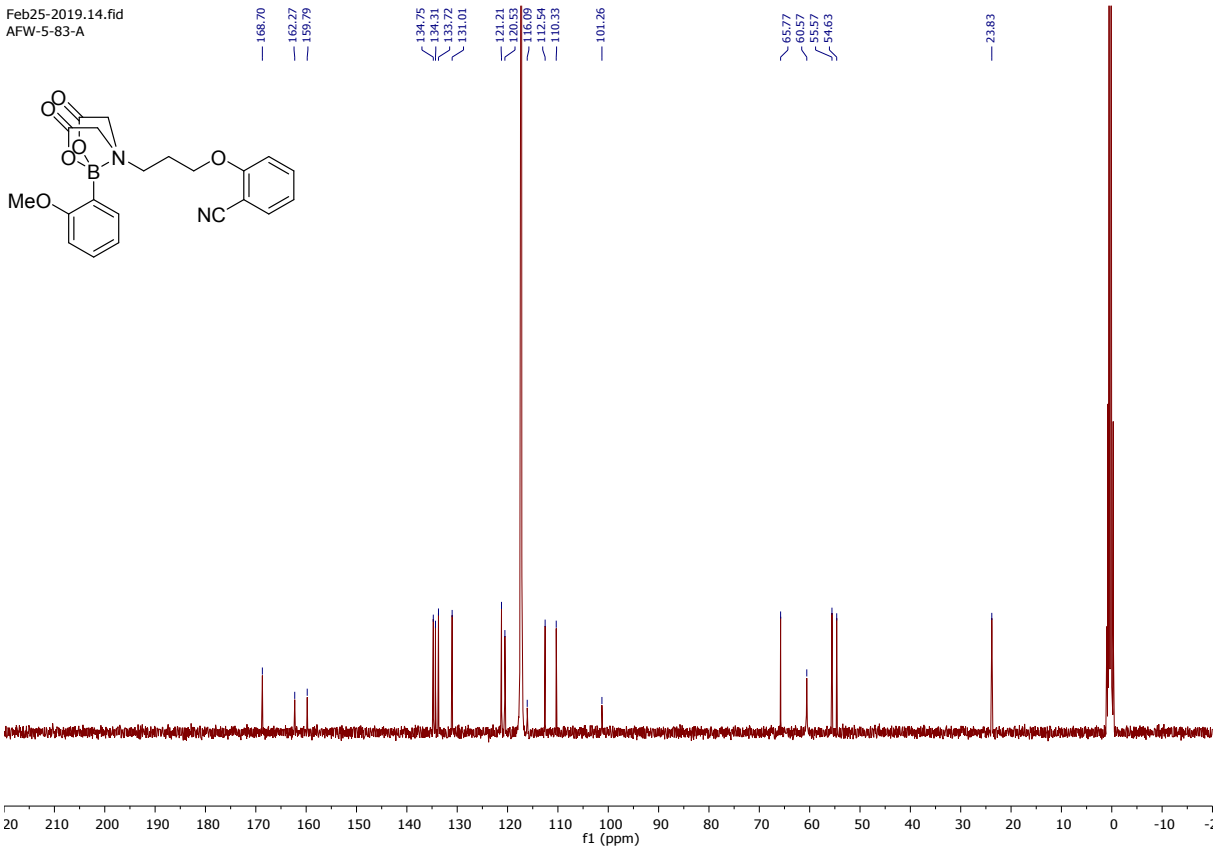
Feb19-2019.30.fid
AFW-5-78-1

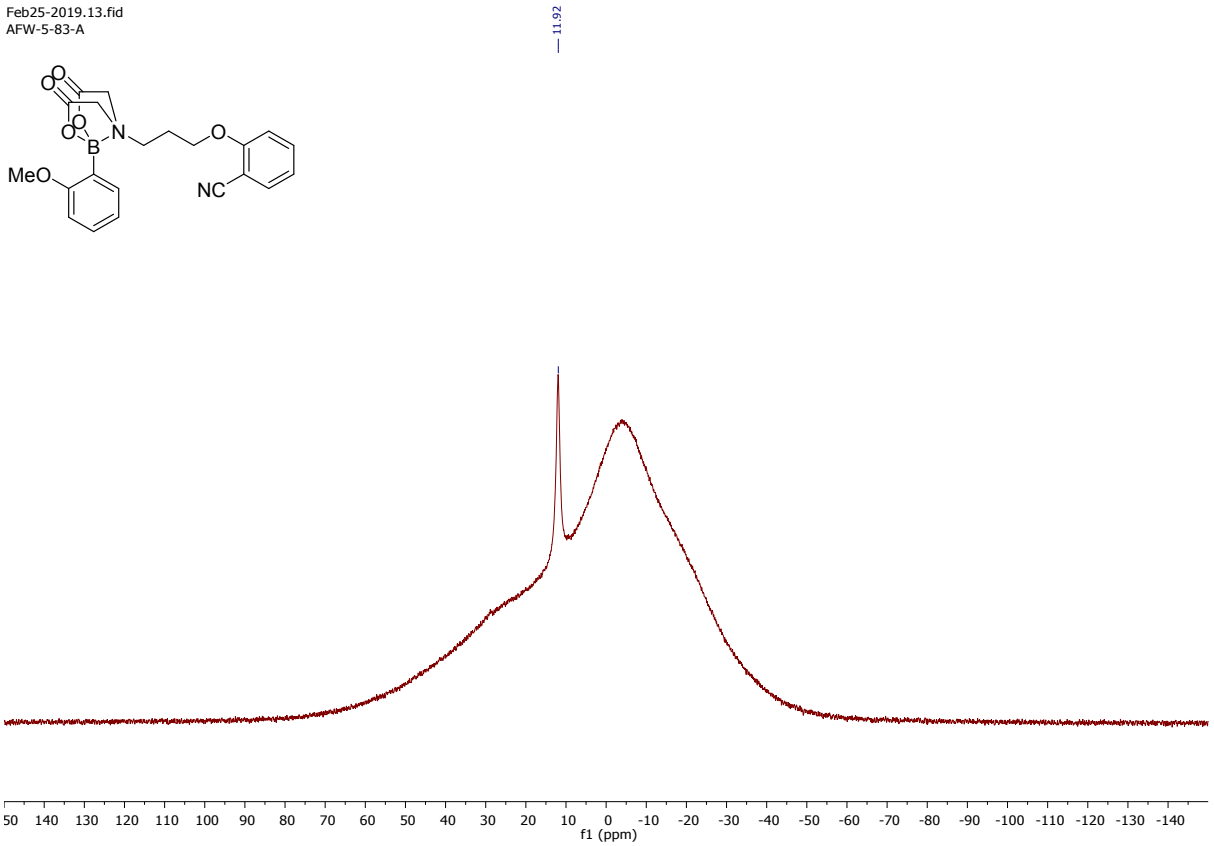


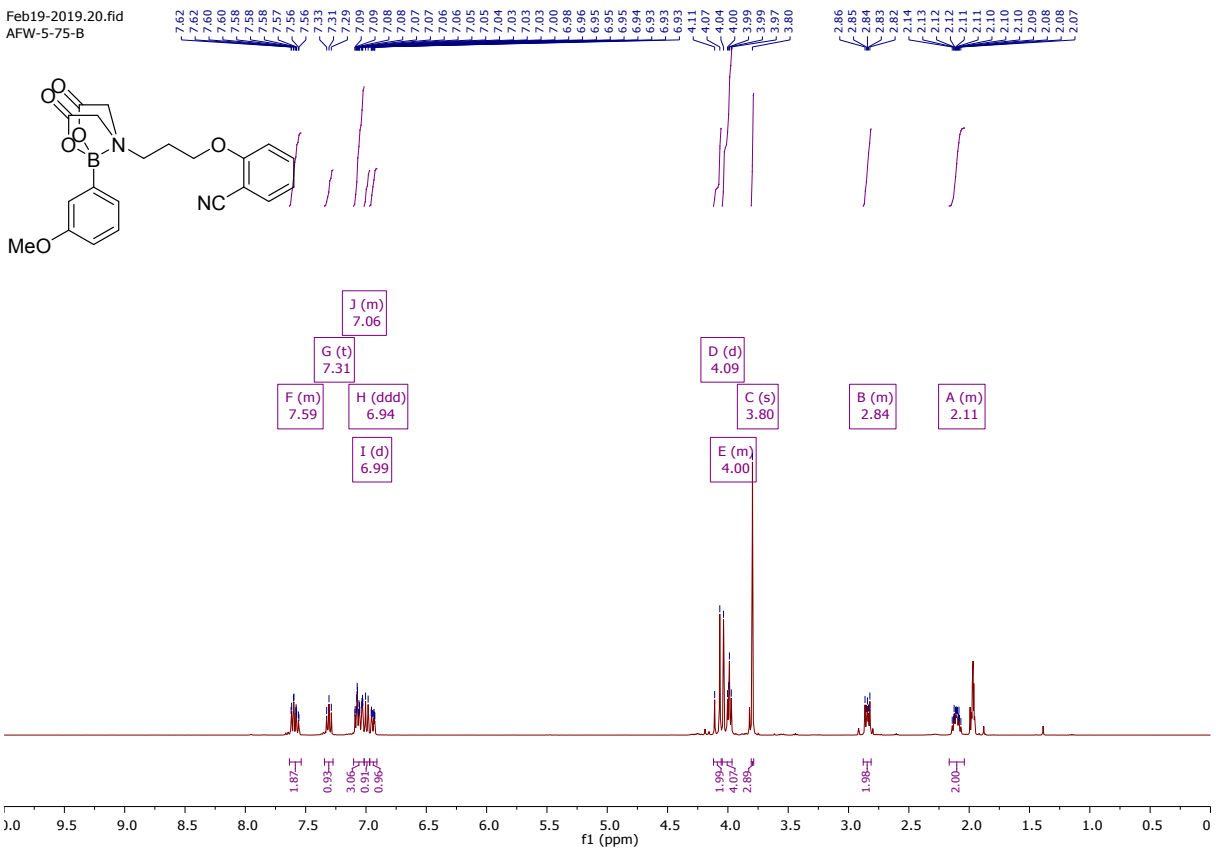

Feb19-2019.32.fid
AFW-5-78-1
168.57
159.86
139.09
134.76
133.68
132.51
128.69
121.28
116.07
112.76
101.39
65.79
58.83
55.87
23.77
O
O
O
B
N
O
NC
Me
f1 (ppm)

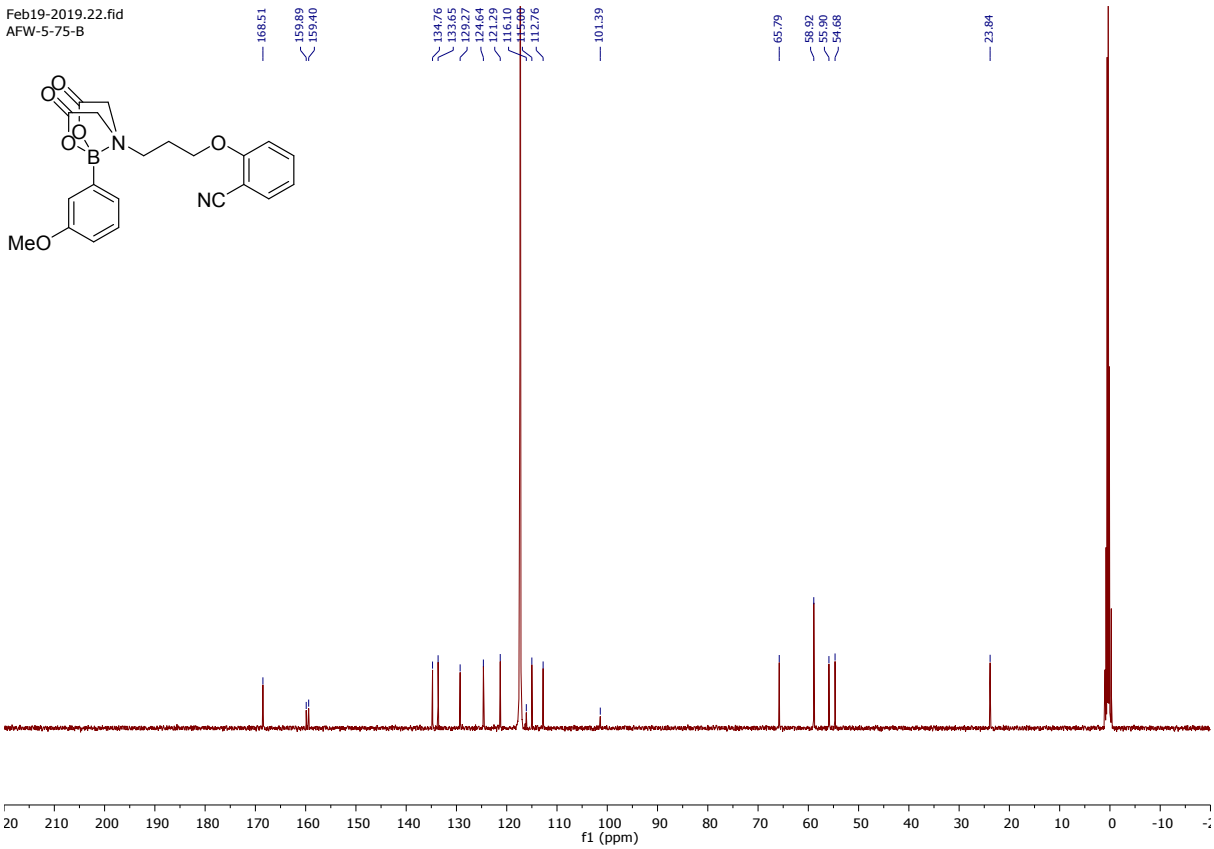

Feb19-2019.31.fid
AFW-5-78-1
12.04
O
O
O
B
N
O
NC
Me
f1 (ppm)

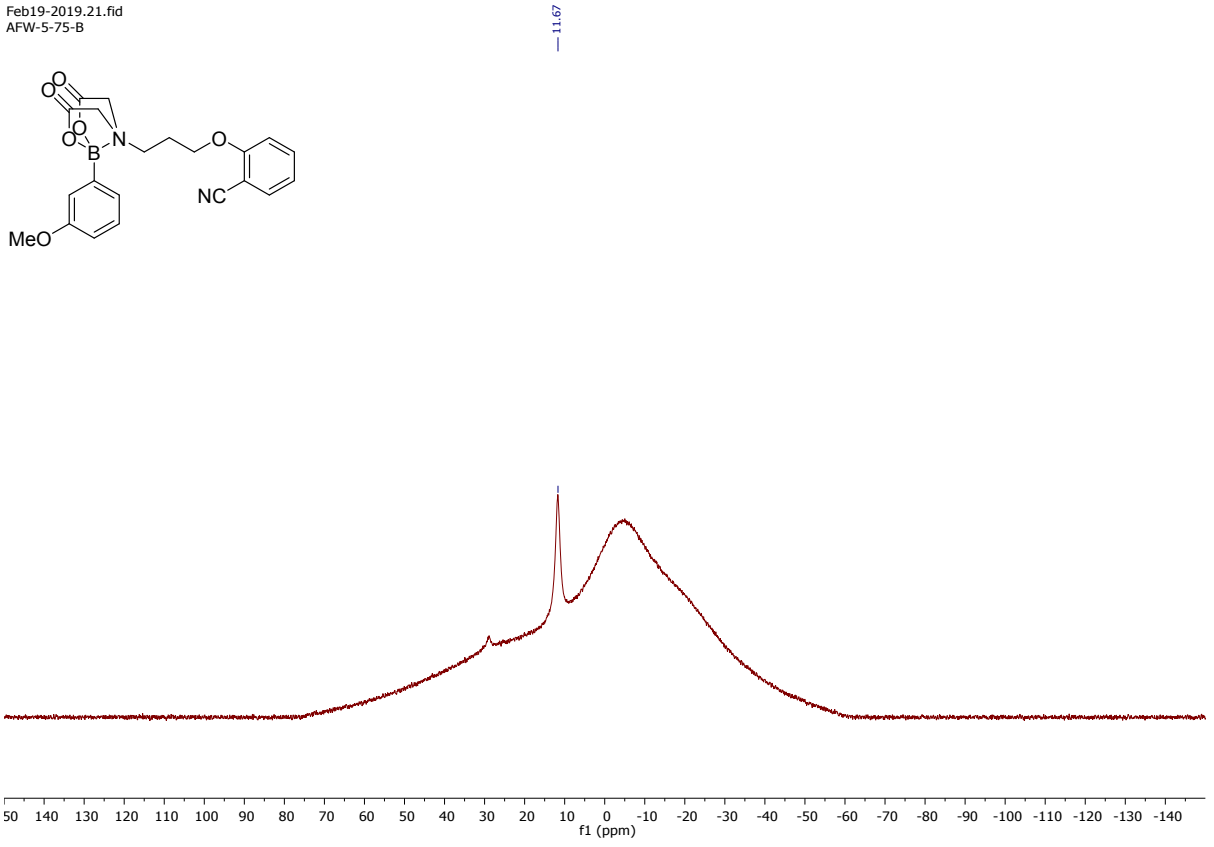

Feb25-2019.14.fid
AFW-5-83-A
MeO
NC
D (m) 7.58
B (td) 7.06
A (m) 7.36
C (m) 6.95
F (d) 4.02
E (d) 4.15
H (s) 3.80
G (t) 3.98
I (m) 3.02
J (m) 2.11
f1 (ppm)

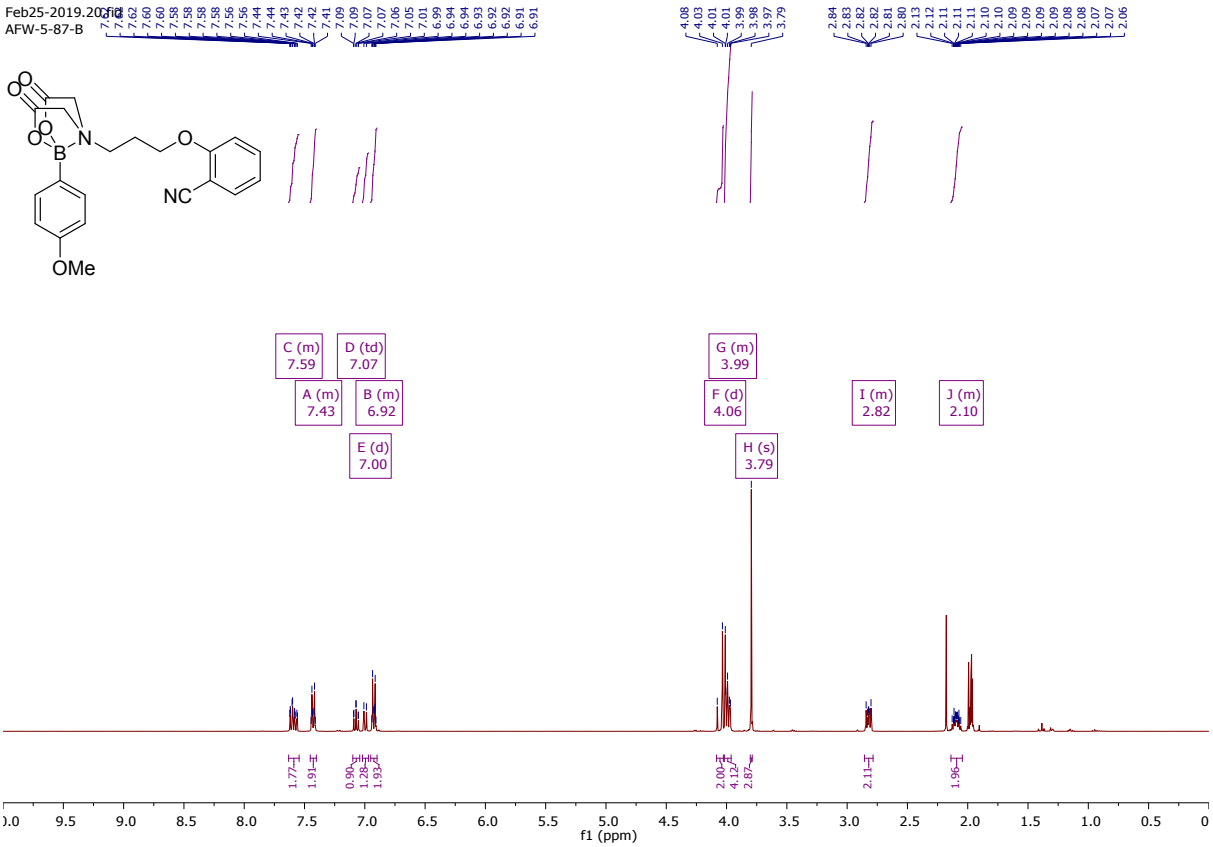

Feb25-2019.14.fid
AFW-5-83-A
MeO
NC
f1 (ppm)

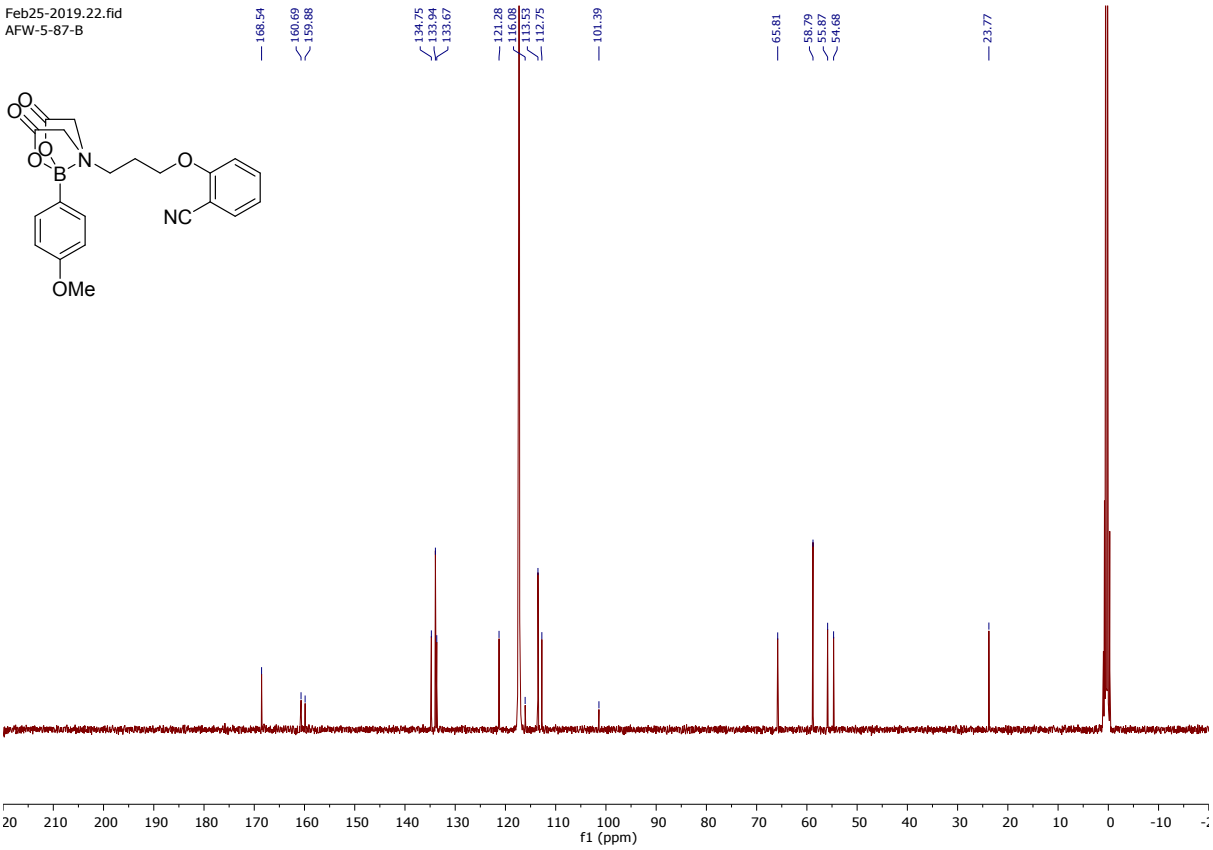

Feb25-2019.13.fid
AFW-5-83-A
11.92
MeO
NC
f1 (ppm)


Feb19-2019.20.fid
AFW-5-75-B
MeO
NC
J (m) 7.06
G (t) 7.31
F (m) 7.59
H (ddd) 6.94
I (d) 6.99
D (d) 4.09
C (s) 3.80
E (m) 4.00
B (m) 2.84
A (m) 2.11
f1 (ppm)

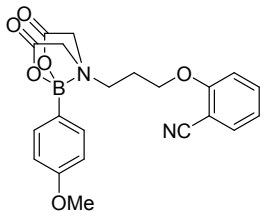

Feb19-2019.22.fid
AFW-5-75-B
168.51
159.89
159.40
134.76
133.65
129.27
124.64
121.29
116.10
115.86
112.76
101.39
65.79
58.92
55.90
54.68
23.84
O
O
O
O
B
N
O
NC
MeO
f1 (ppm)

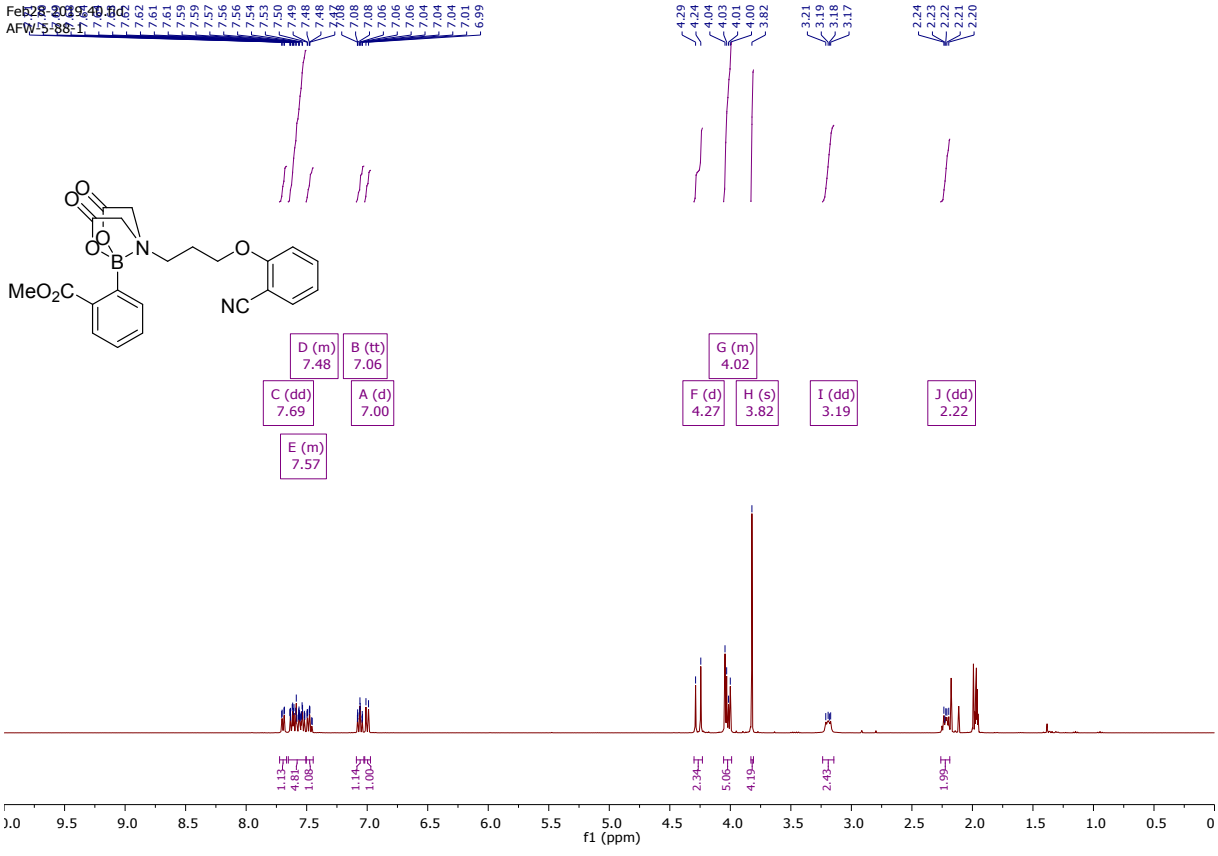

Feb19-2019.21.fid
AFW-5-75-B
11.67
O
O
O
O
B
N
O
NC
MeO
f1 (ppm)

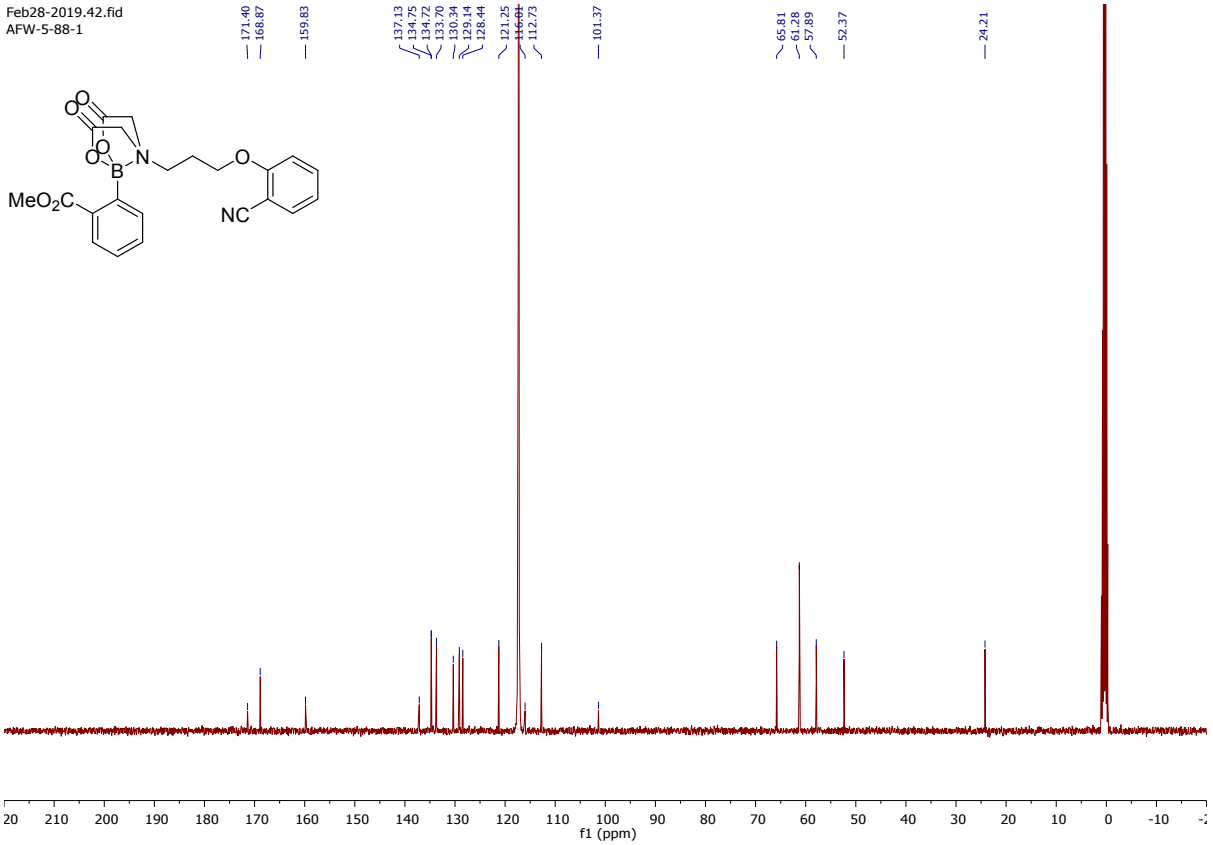

Feb25-2019.20.fid
AFW-5-87-B
C (m) 7.59
D (td) 7.07
A (m) 7.43
B (m) 6.92
E (d) 7.00
G (m) 3.99
F (d) 4.06
H (s) 3.79
I (m) 2.82
J (m) 2.10
f1 (ppm)

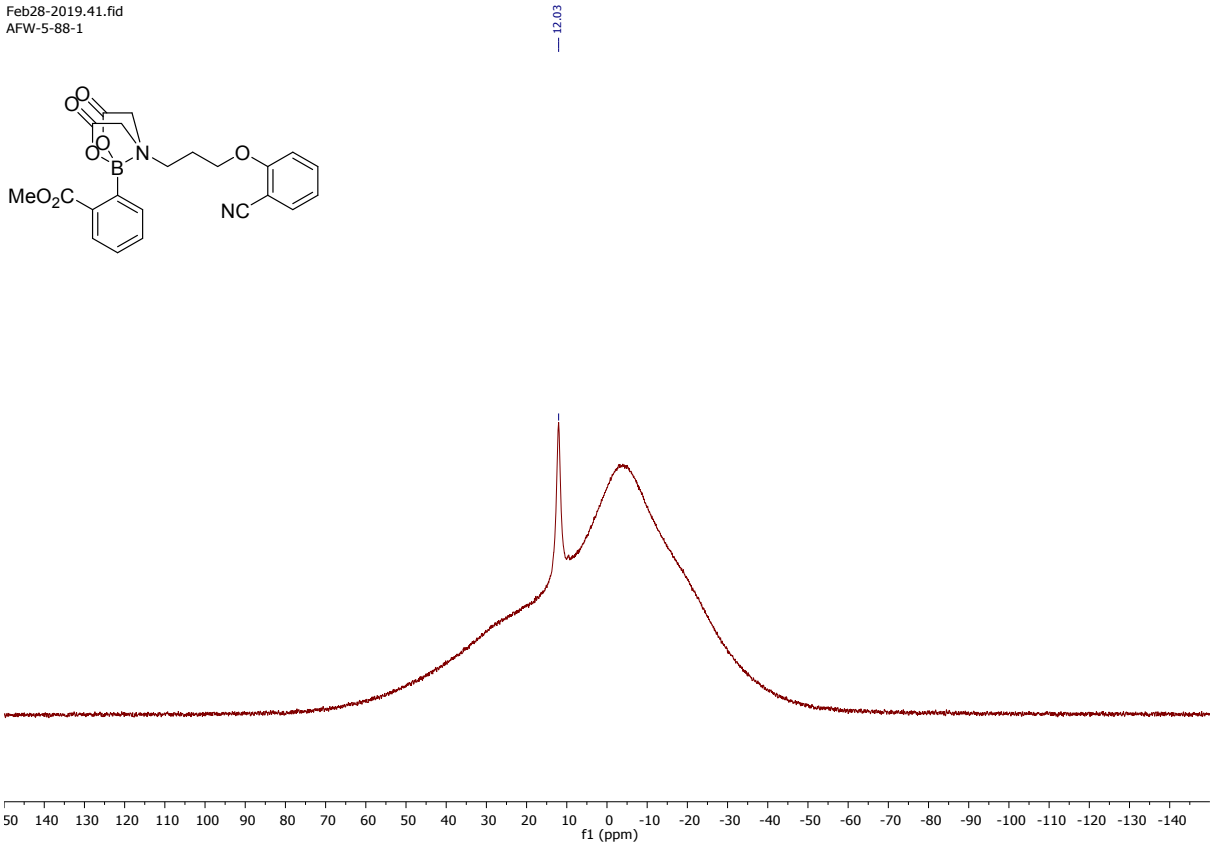

Feb25-2019.22.fid
AFW-5-87-B
f1 (ppm)

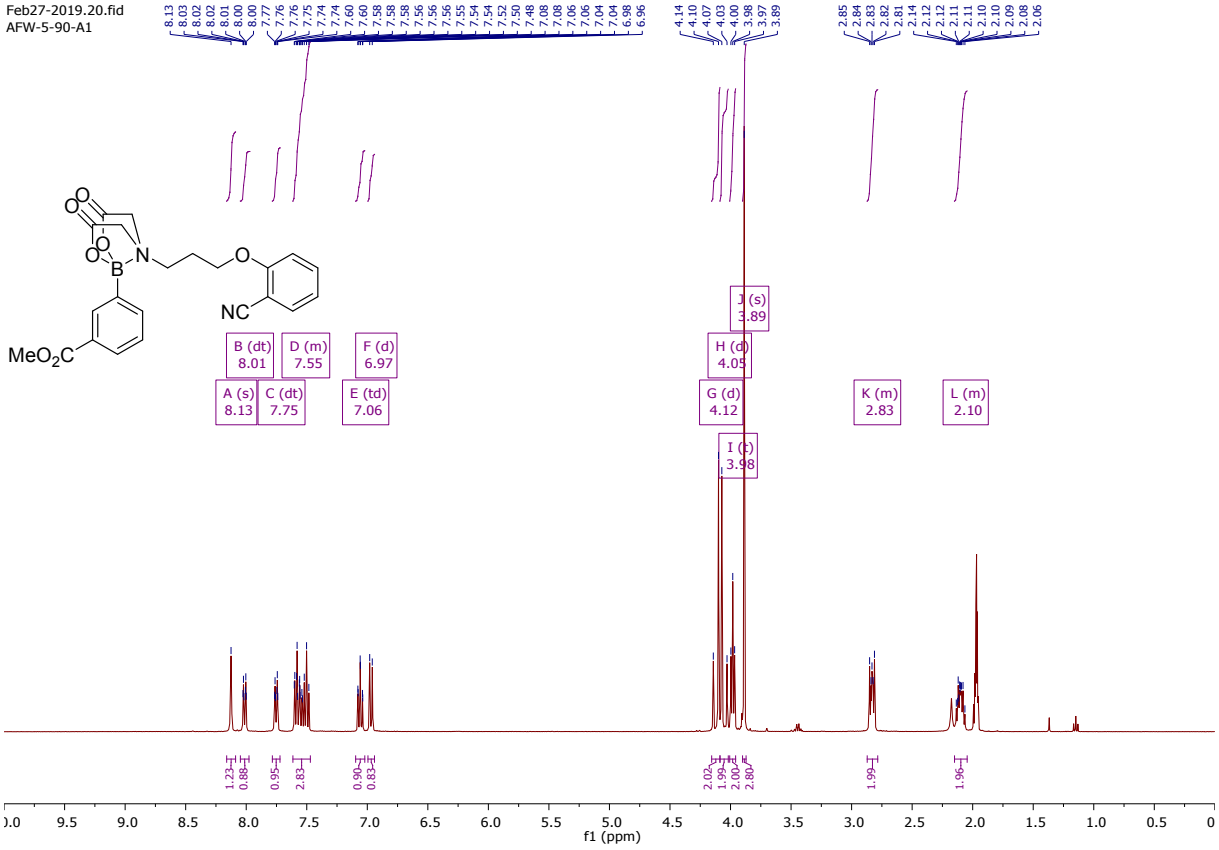
Feb25-2019.21.fid
AFW-5-87-B

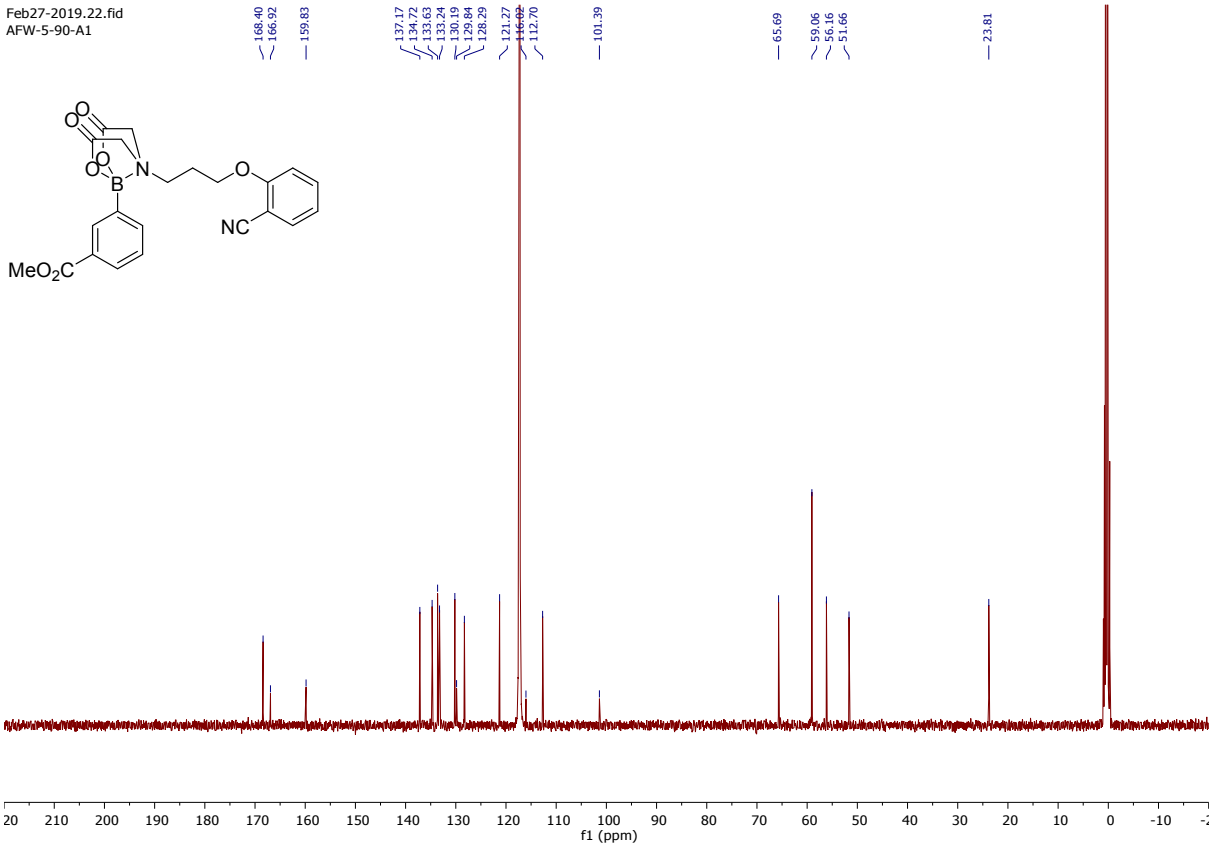




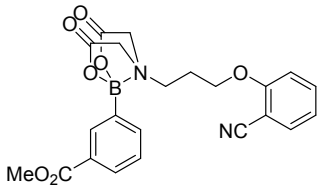

Feb28-2019.42.fid
AFW-5-88-1
171.40
168.87
159.83
137.13
134.75
134.72
133.70
130.34
129.14
128.44
121.25
116.01
112.73
101.37
65.81
61.28
57.89
52.37
24.21
MeO2C
NC
f1 (ppm)


Feb28-2019.41.fid
AFW-5-88-1
12.03
MeO2C
NC
f1 (ppm)

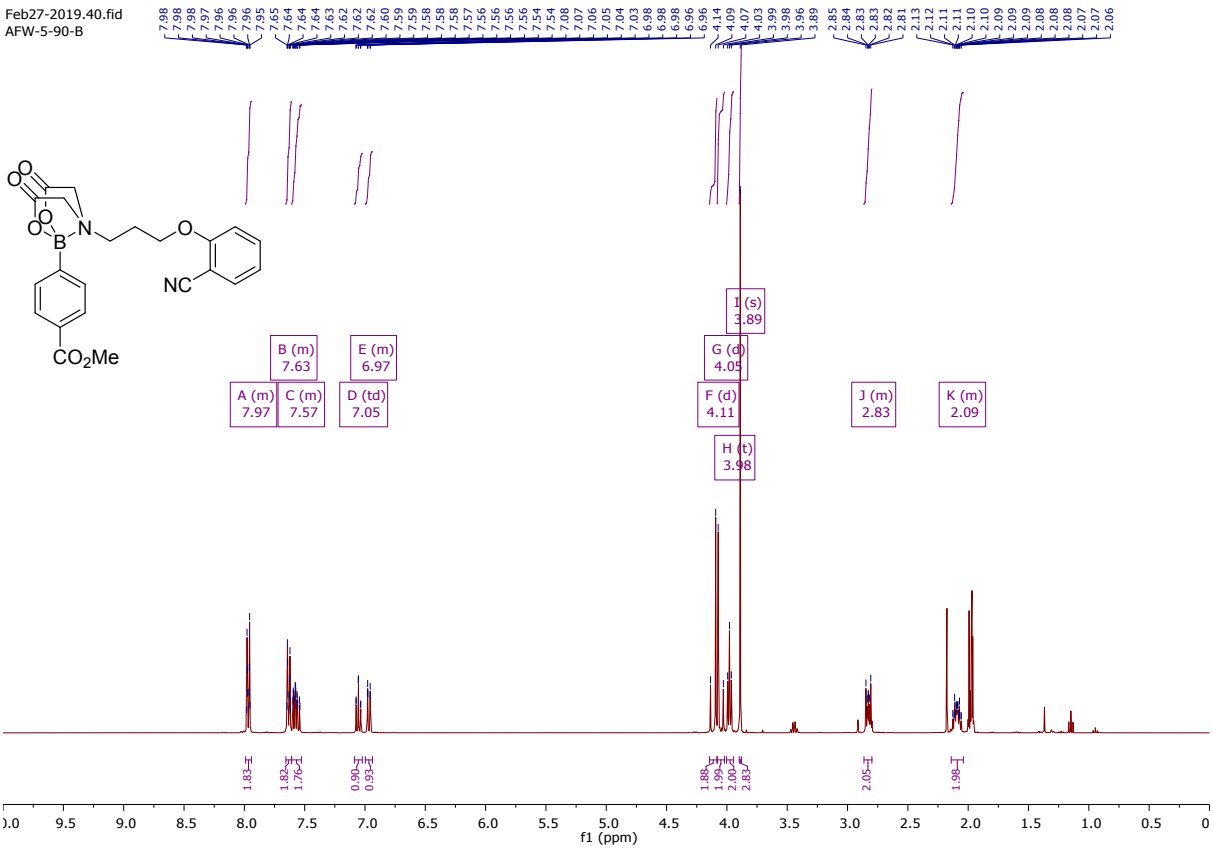

Feb27-2019.20.fid
AFW-5-90-A1
A (s) 8.13
B (dt) 8.01
C (dt) 7.75
D (m) 7.55
E (td) 7.06
F (d) 6.97
G (d) 4.12
H (d) 4.05
I (t) 3.98
J (s) 3.89
K (m) 2.83
L (m) 2.10
f1 (ppm)

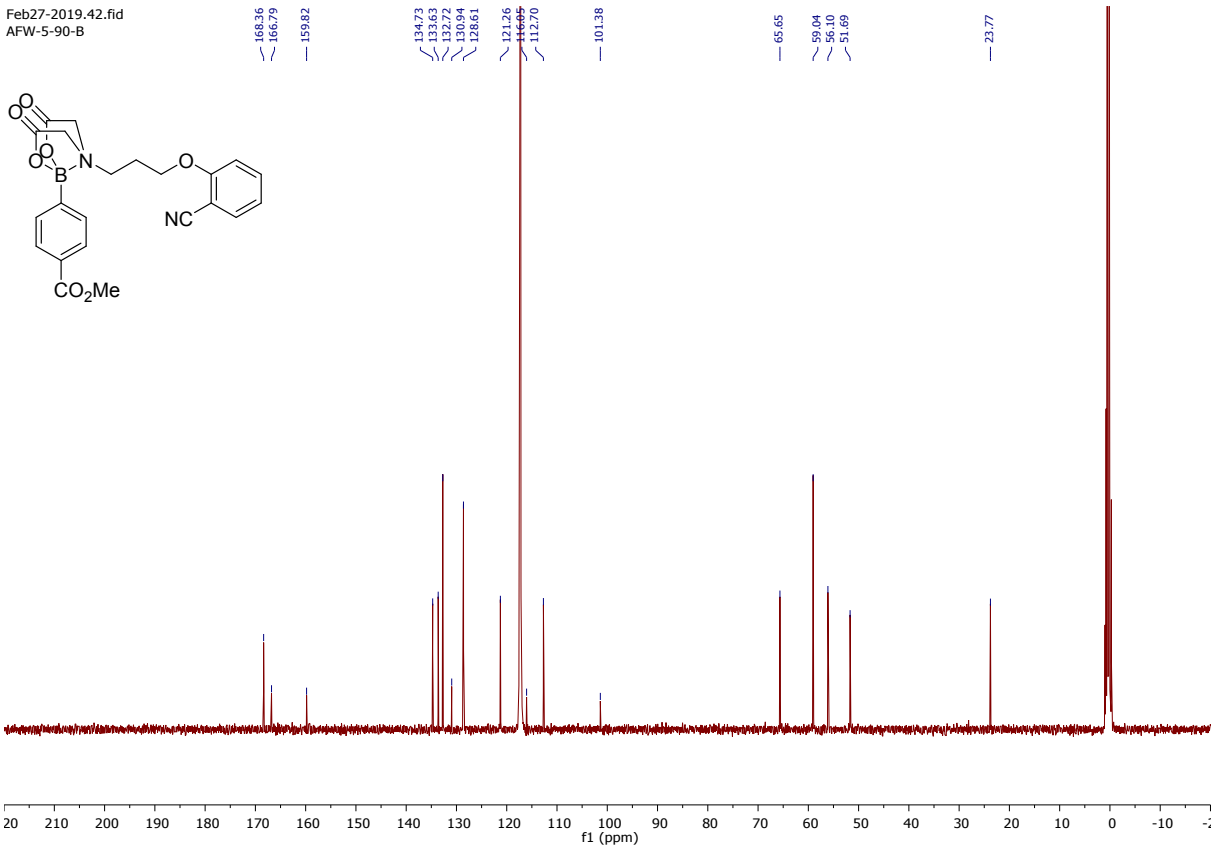

Feb27-2019.22.fid
AFW-5-90-A1
168.40
166.92
159.83
137.17
134.72
133.63
133.24
130.19
129.84
128.29
121.27
116.62
112.70
101.39
65.69
59.06
56.16
51.66
23.81
f1 (ppm)

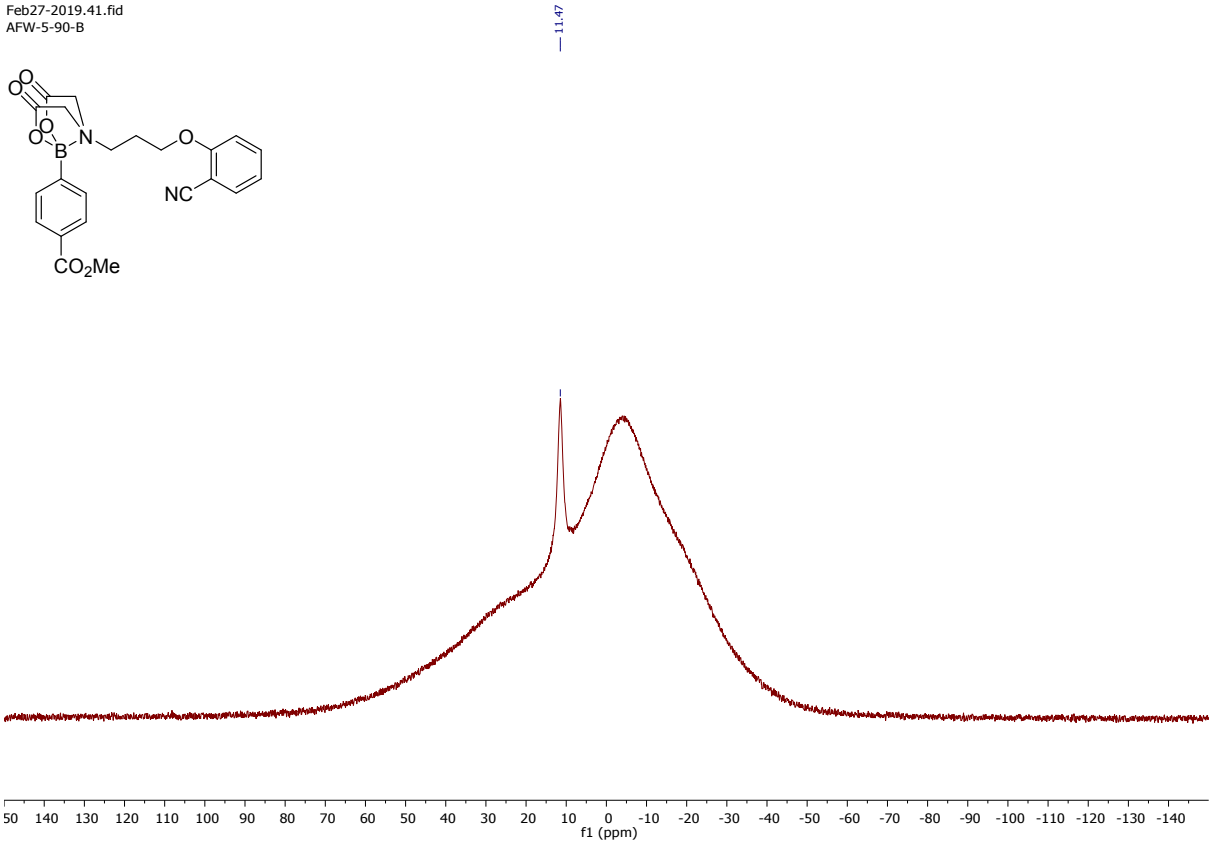
Feb27-2019.21.fid
AFW-5-90-A1

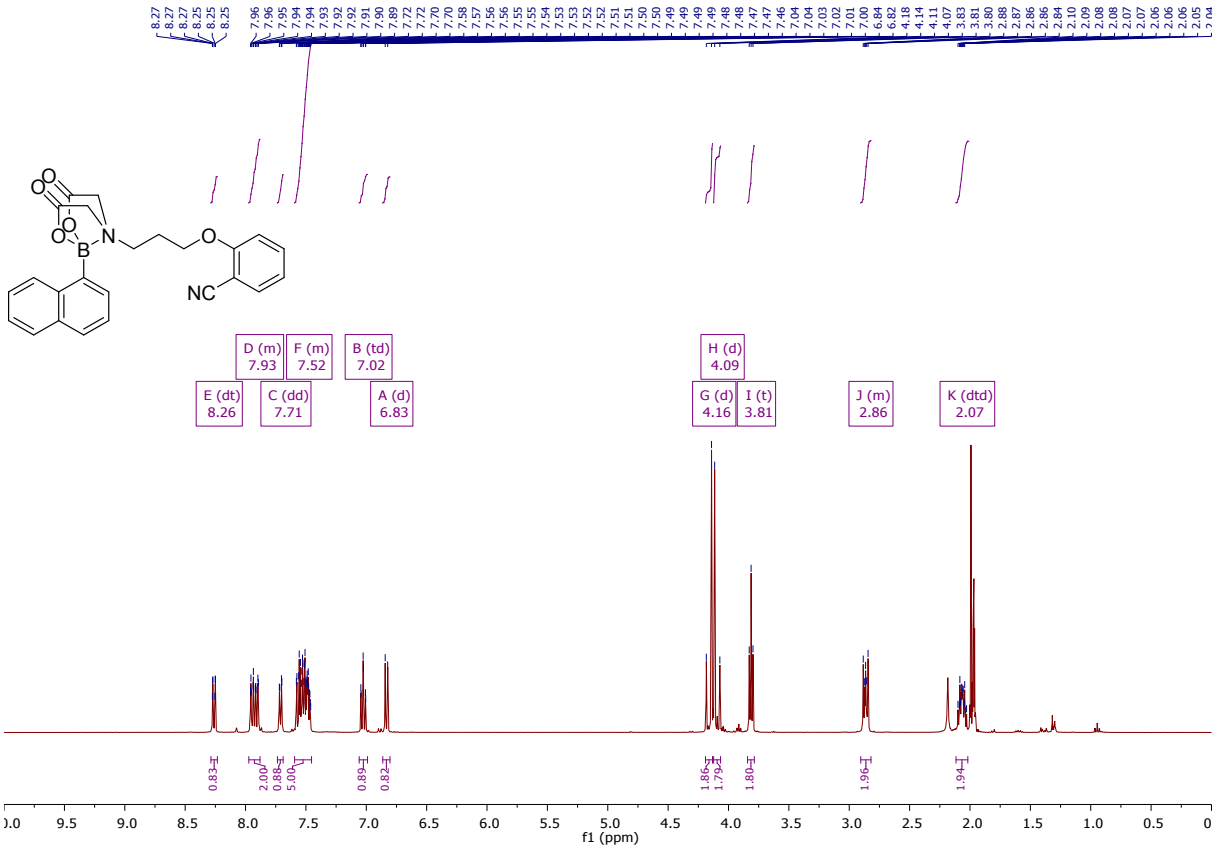


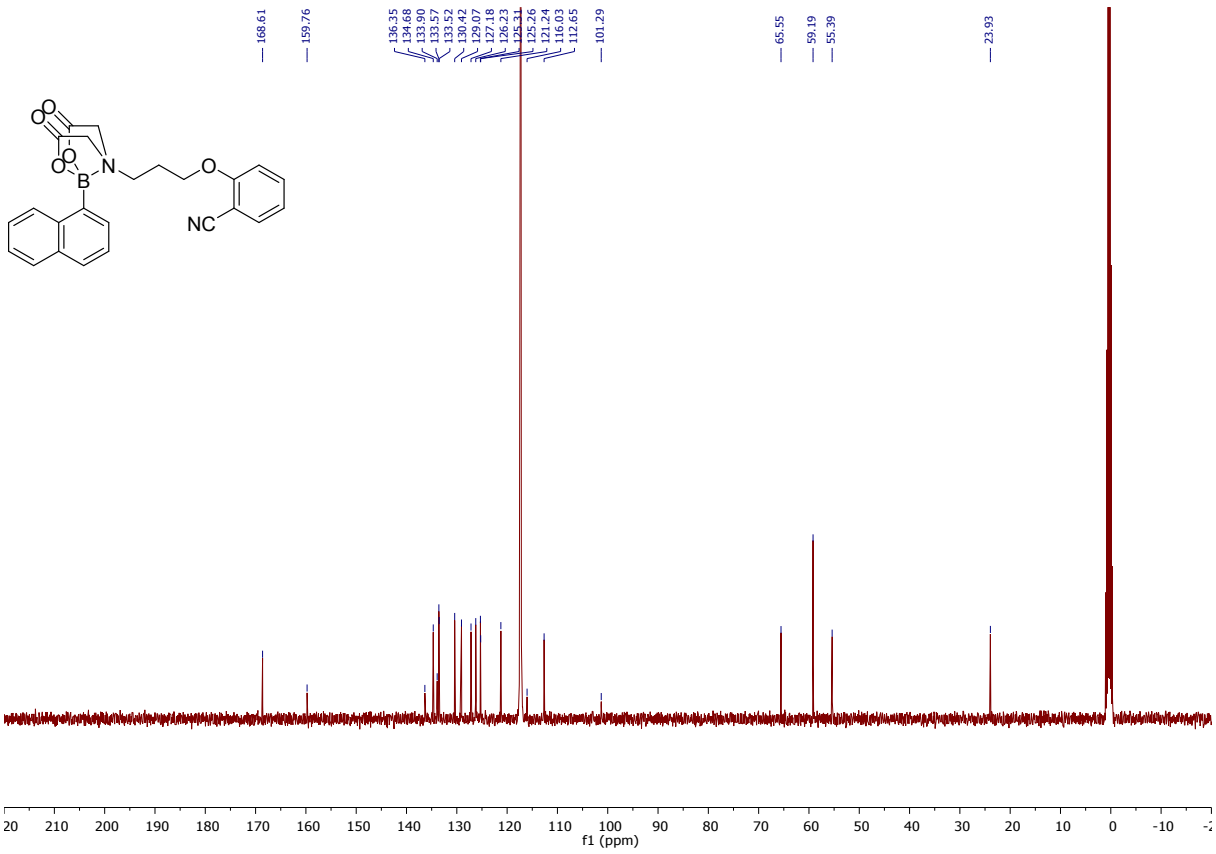
Feb27-2019.40.fid
AFW-5-90-B

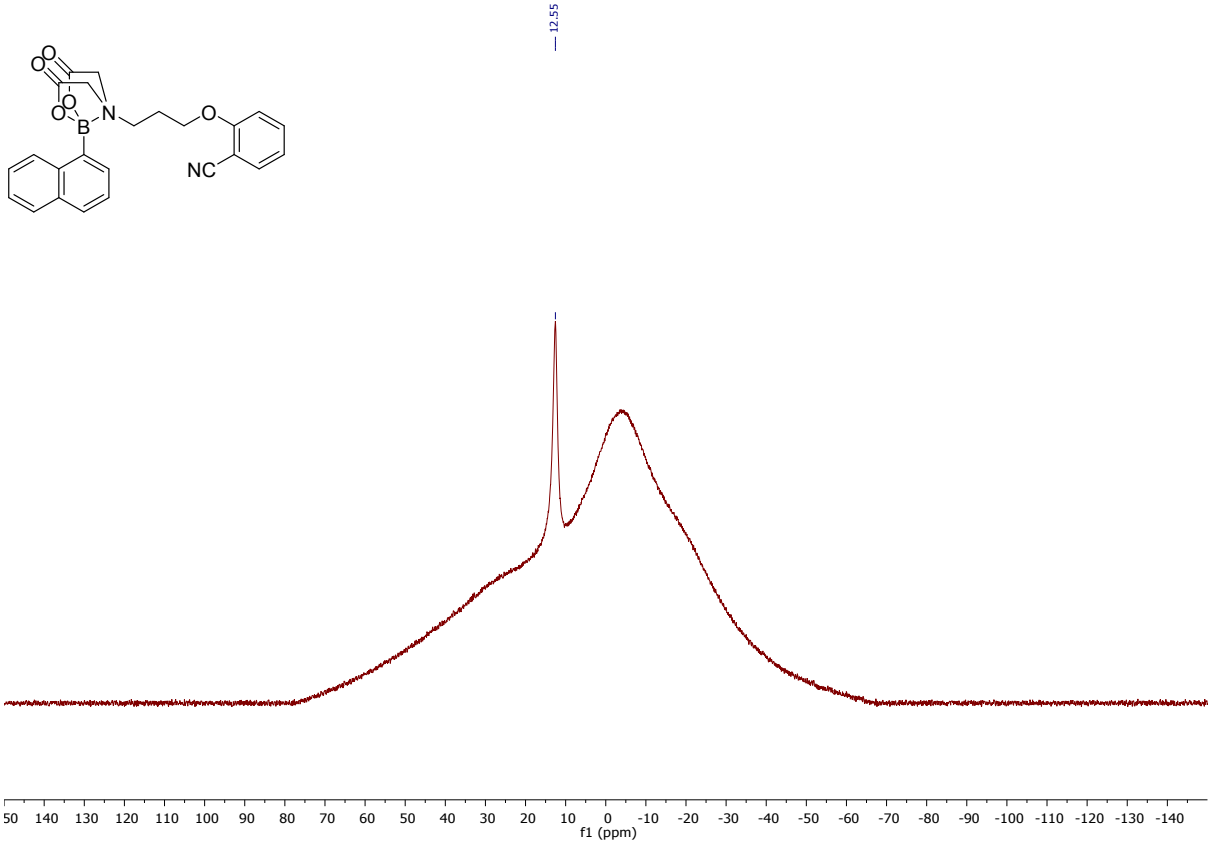


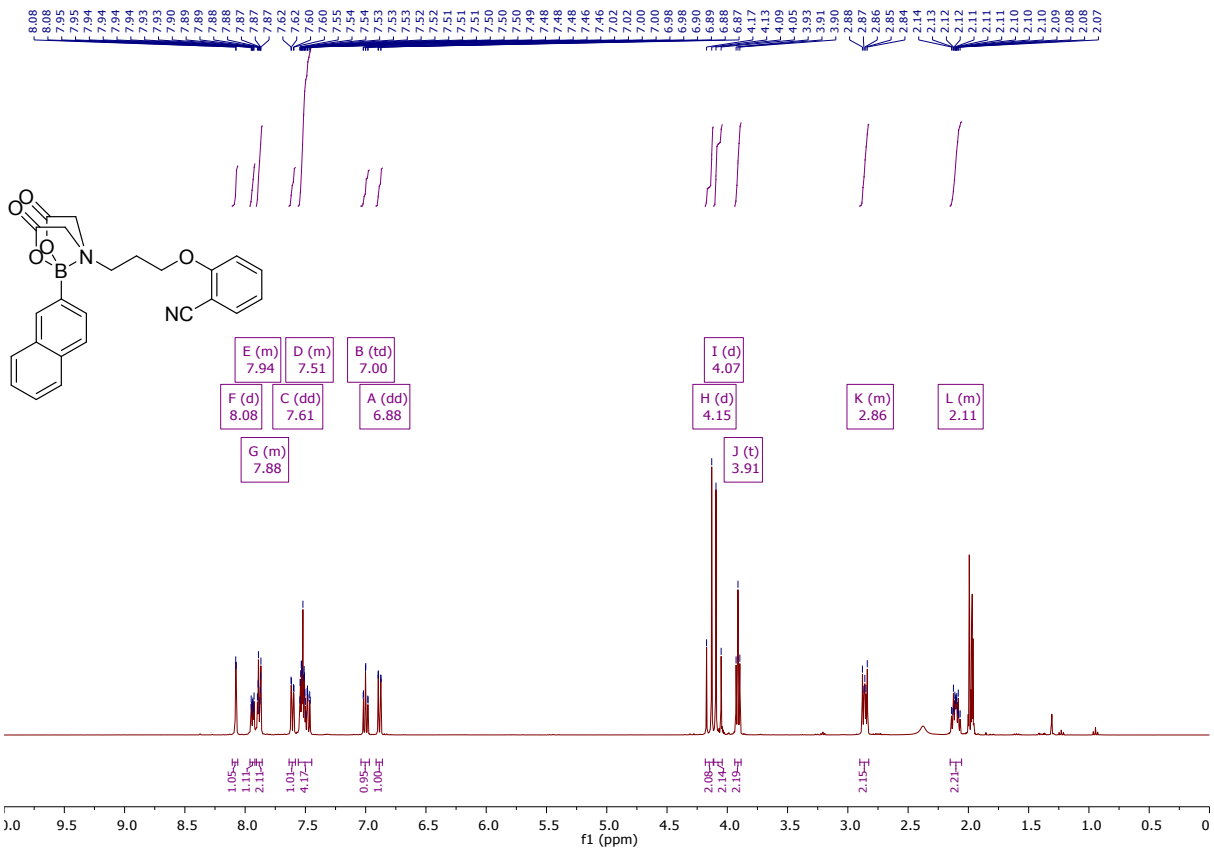

Feb27-2019.42.fid
AFW-5-90-B
168.36
166.79
159.82
134.73
133.63
132.72
130.94
128.61
121.26
116.05
112.70
101.38
65.65
59.04
56.10
51.69
23.77
NC
CO2Me
f1 (ppm)

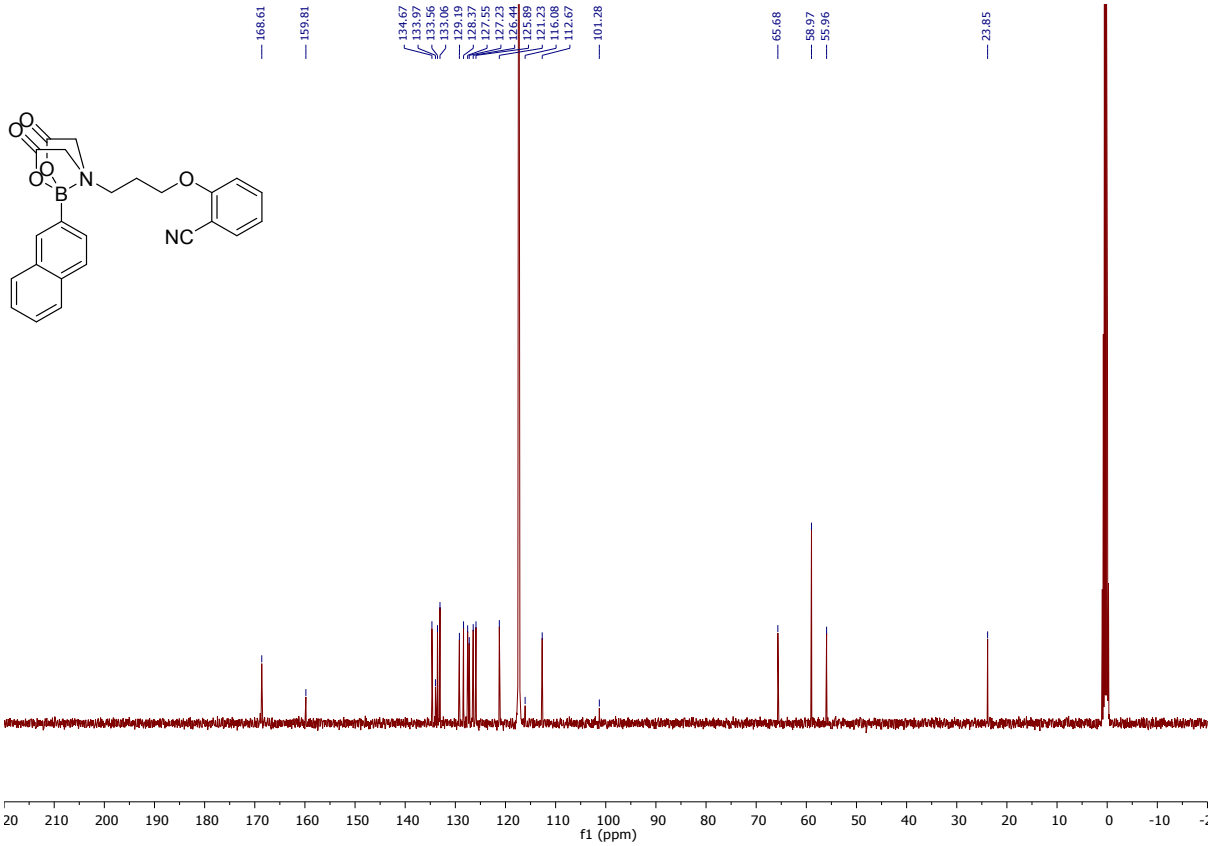

Feb27-2019.41.fid
AFW-5-90-B
11.47
NC
CO2Me
f1 (ppm)

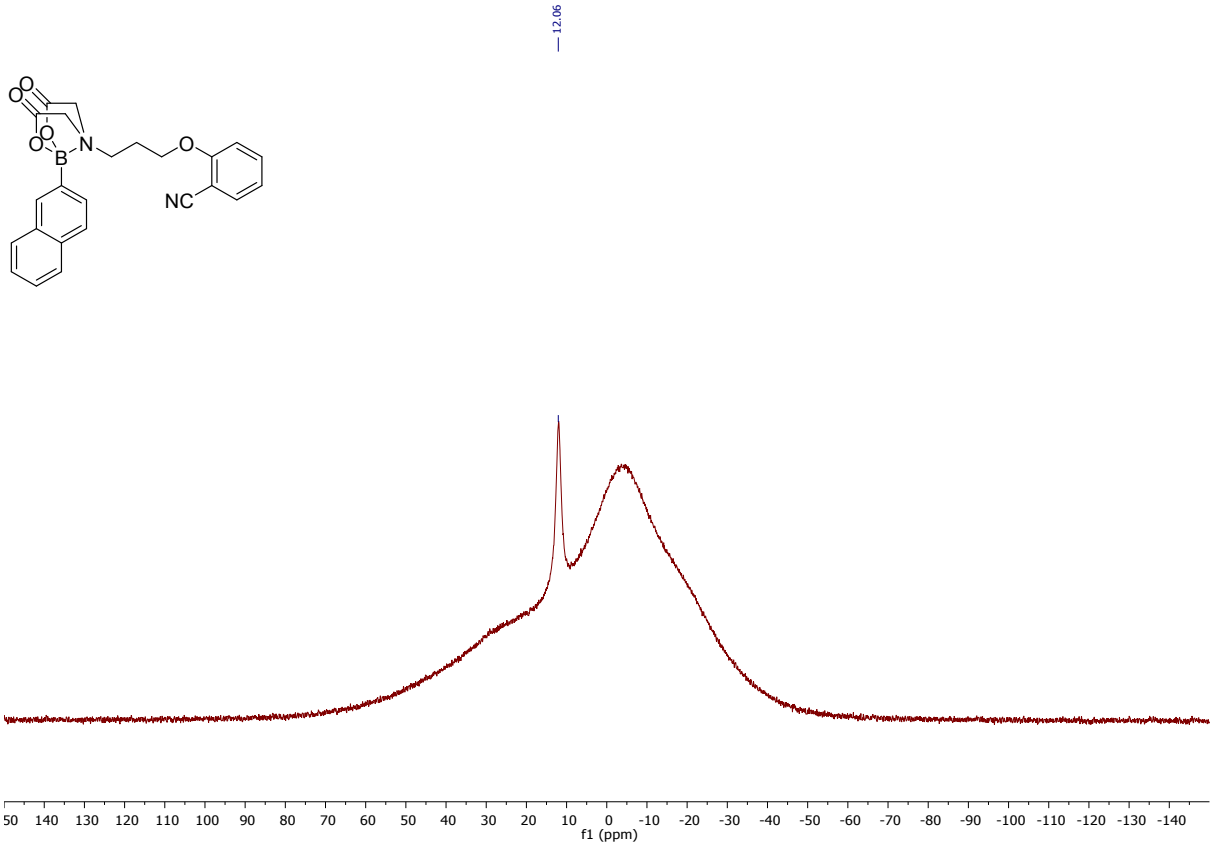

D (m) 7.93
F (m) 7.52
B (td) 7.02
H (d) 4.09
E (dt) 8.26
C (dd) 7.71
A (d) 6.83
G (d) 4.16
I (t) 3.81
J (m) 2.86
K (dtd) 2.07
f1 (ppm)

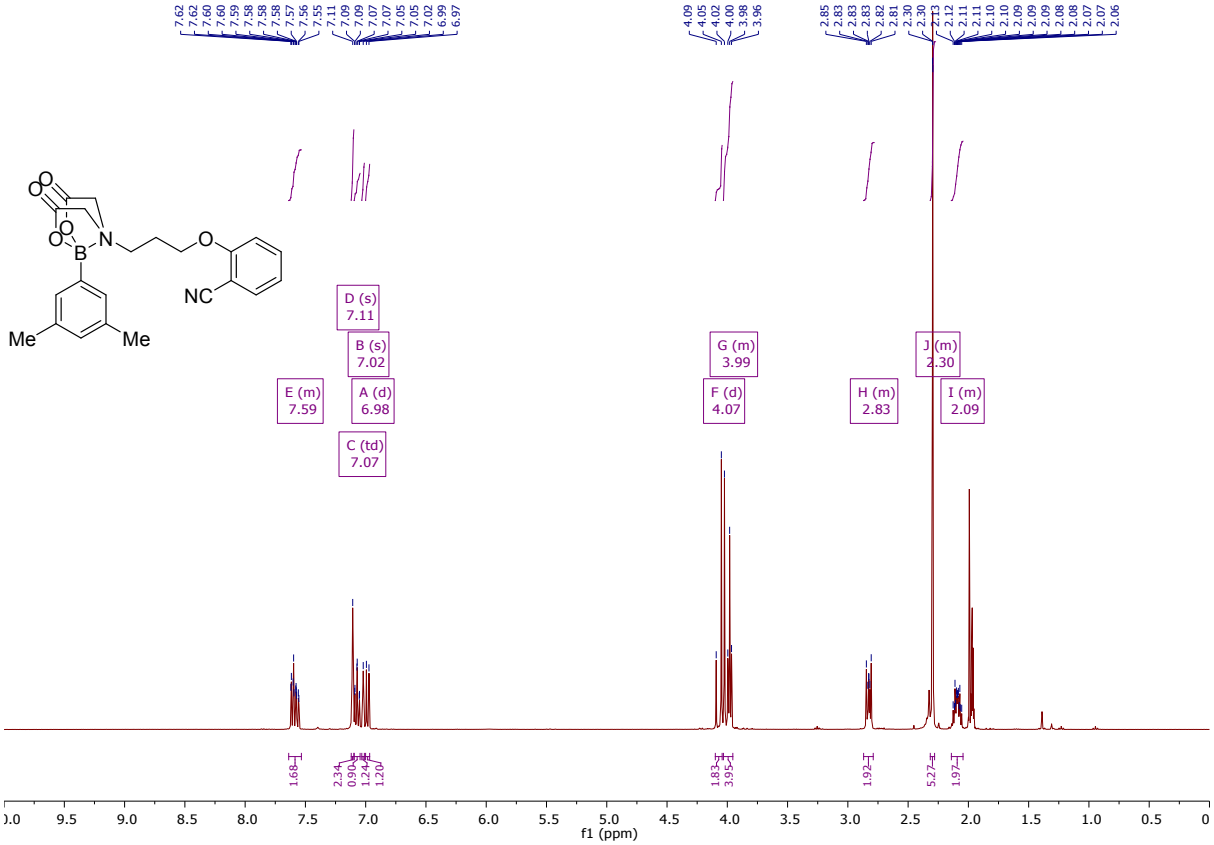

168.61
159.76
136.35
134.68
133.90
133.57
133.52
130.42
129.07
127.18
126.23
125.31
125.26
121.24
116.03
112.65
101.29
65.55
59.19
55.39
23.93
f1 (ppm)

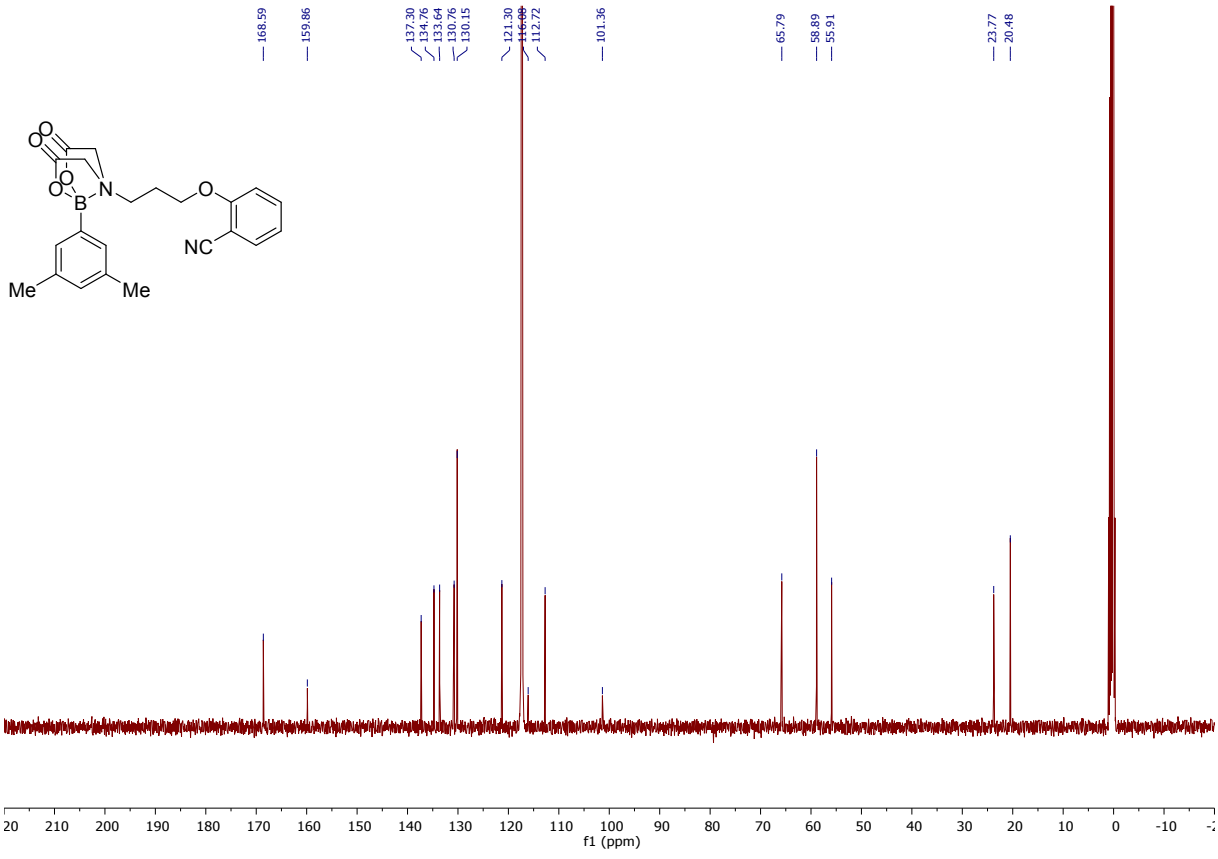

12.55
f1 (ppm)

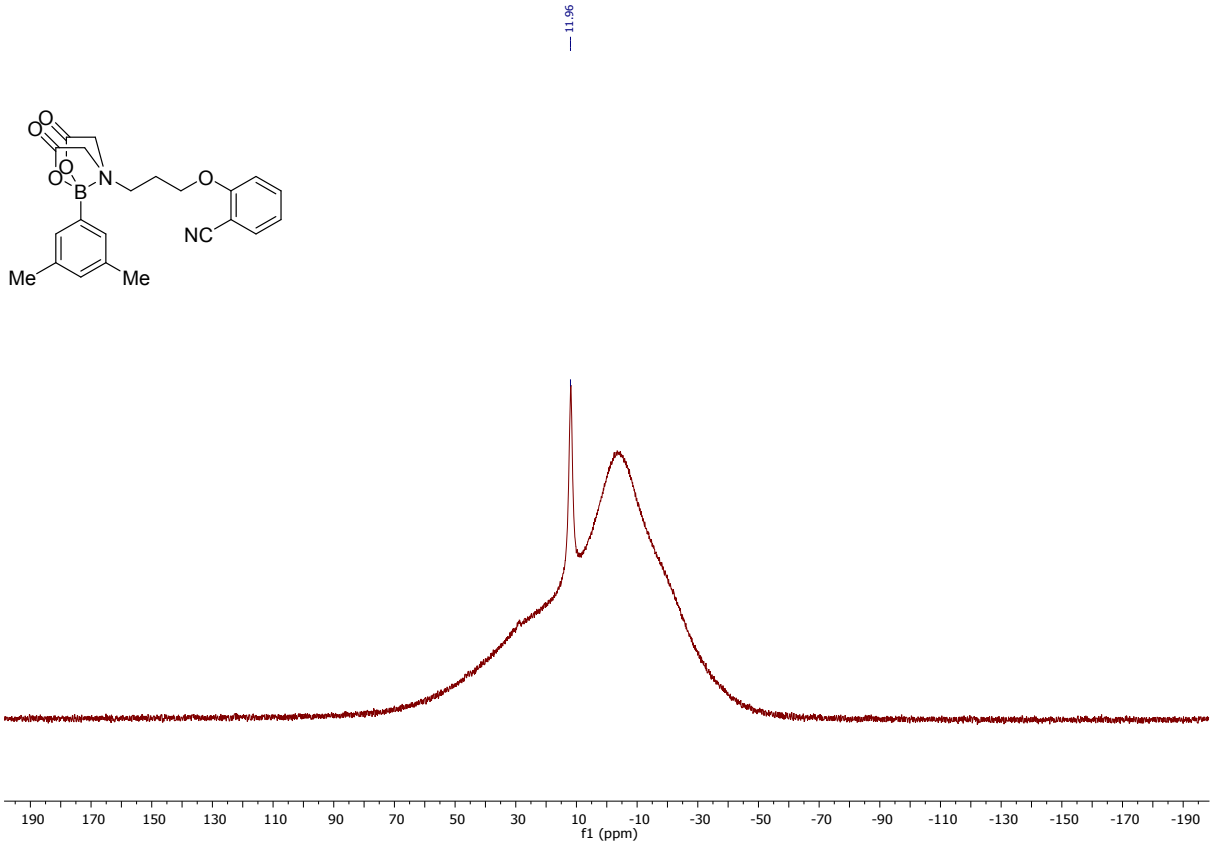

E (m) 7.94
D (m) 7.51
B (td) 7.00
I (d) 4.07
F (d) 8.08
C (dd) 7.61
A (dd) 6.88
H (d) 4.15
K (m) 2.86
L (m) 2.11
G (m) 7.88
J (t) 3.91
f1 (ppm)

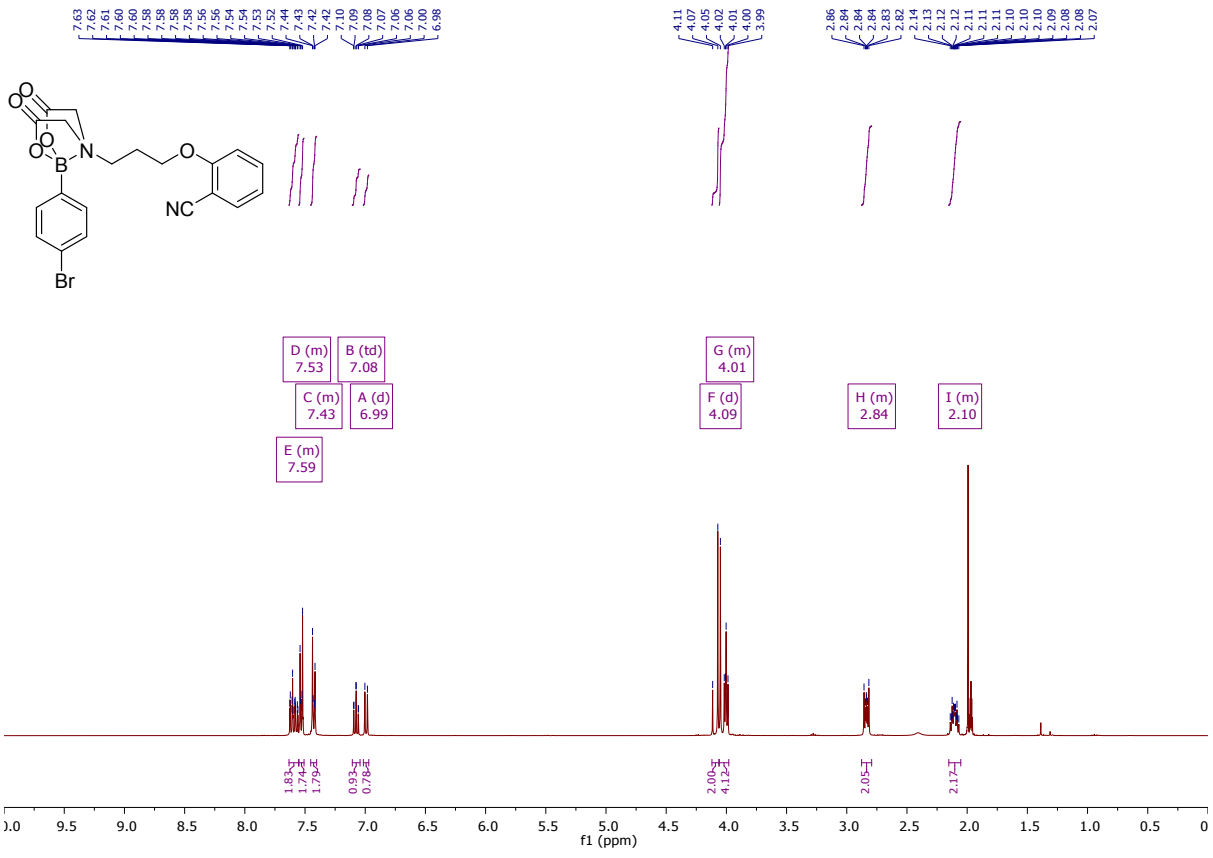

168.61
159.81
134.67
133.97
133.56
133.06
129.19
128.37
127.55
127.23
126.44
125.89
121.23
116.08
112.67
101.28
65.68
58.97
55.96
23.85
O
O
O
B
N
O
NC
f1 (ppm)

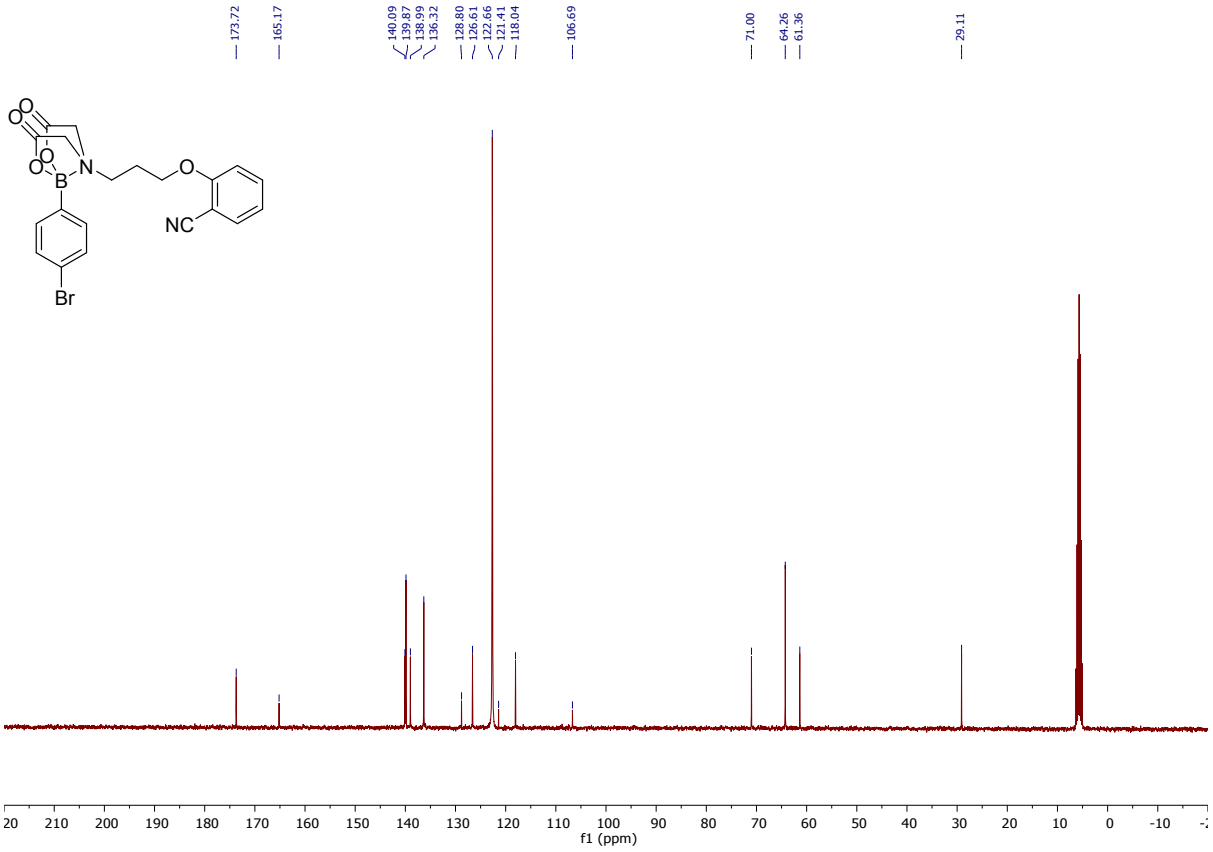

12.06
O
O
O
B
N
O
NC
f1 (ppm)

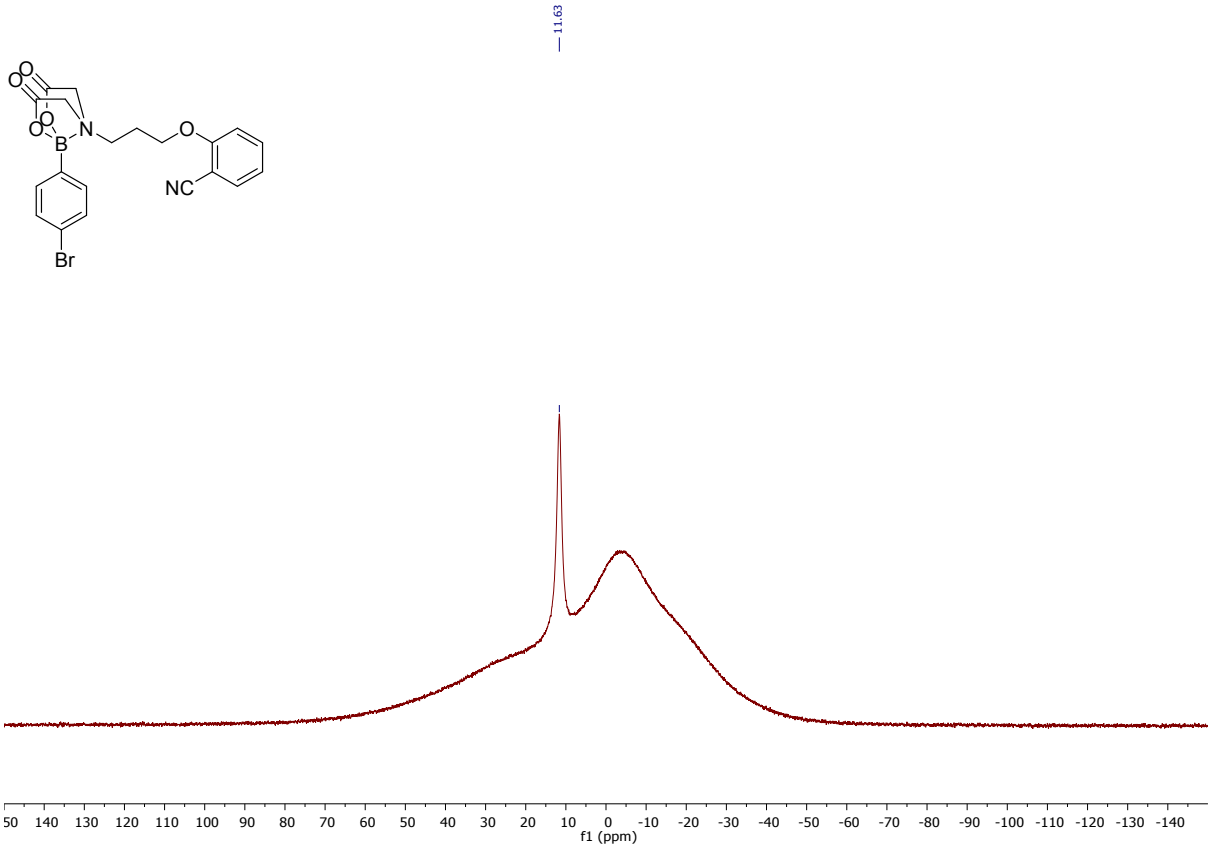

D (s)
7.11
B (s)
7.02
E (m)
7.59
A (d)
6.98
C (td)
7.07
G (m)
3.99
F (d)
4.07
H (m)
2.83
J (m)
2.30
I (m)
2.09
f1 (ppm)

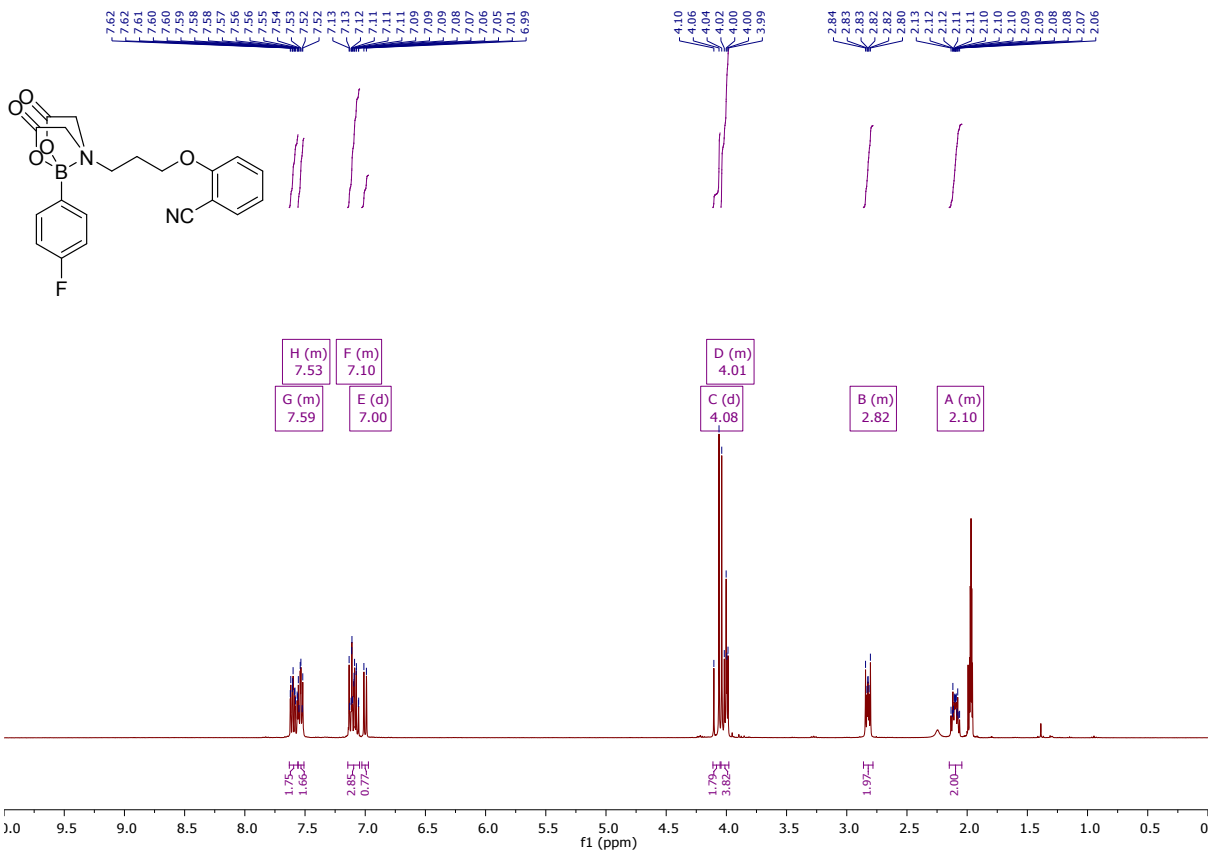

f1 (ppm)

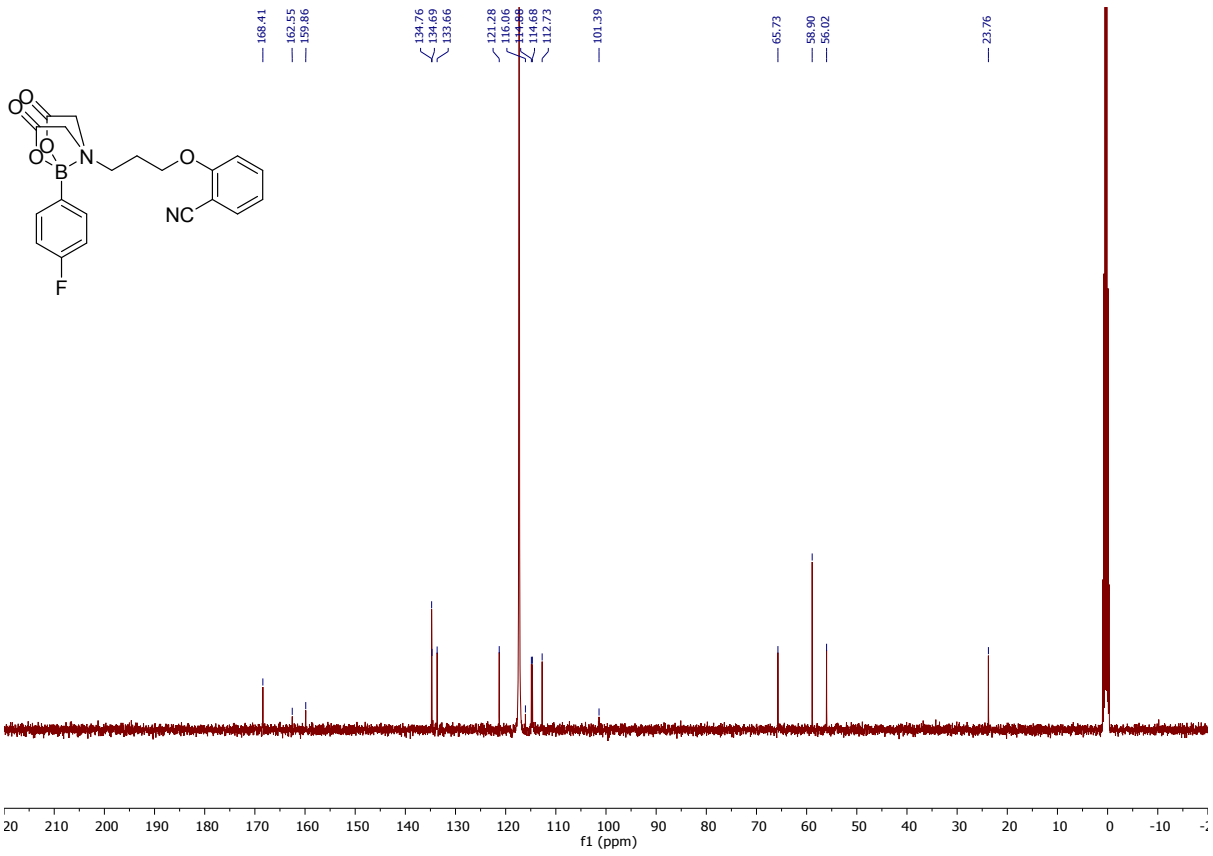

11.96
Me
Me
NC
f1 (ppm)

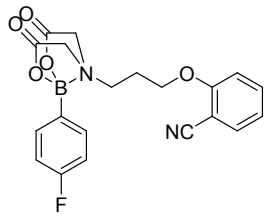

Br
NC
D (m) 7.53
B (td) 7.08
C (m) 7.43
A (d) 6.99
E (m) 7.59
G (m) 4.01
F (d) 4.09
H (m) 2.84
I (m) 2.10
f1 (ppm)


173.72
165.17
140.09
139.87
138.99
136.32
128.80
126.61
122.66
121.41
118.04
106.69
71.00
64.26
61.36
29.11
O
O
O
B
N
O
NC
Br
f1 (ppm)

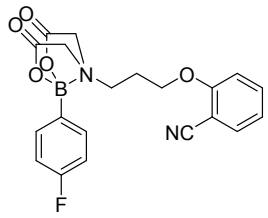

11.63
O
O
O
B
N
O
NC
Br
f1 (ppm)


7.62 7.62 7.61 7.60 7.60 7.59 7.58 7.58 7.57 7.56 7.56 7.55 7.54 7.53 7.52 7.52 7.13 7.12 7.11 7.11 7.11 7.09 7.09 7.09 7.08 7.07 7.06 7.05 7.01 6.99
4.10 4.06 4.04 4.02 4.00 4.00 3.99
2.84 2.83 2.83 2.82 2.82 2.80 2.13 2.12 2.12 2.11 2.11 2.10 2.10 2.10 2.09 2.09 2.08 2.08 2.07 2.06
O
O
O
B
N
O
NC
F
H (m) 7.53
F (m) 7.10
G (m) 7.59
E (d) 7.00
D (m) 4.01
C (d) 4.08
B (m) 2.82
A (m) 2.10
1.75
1.66
2.85
0.77
1.79
3.82
1.97
2.00
f1 (ppm)

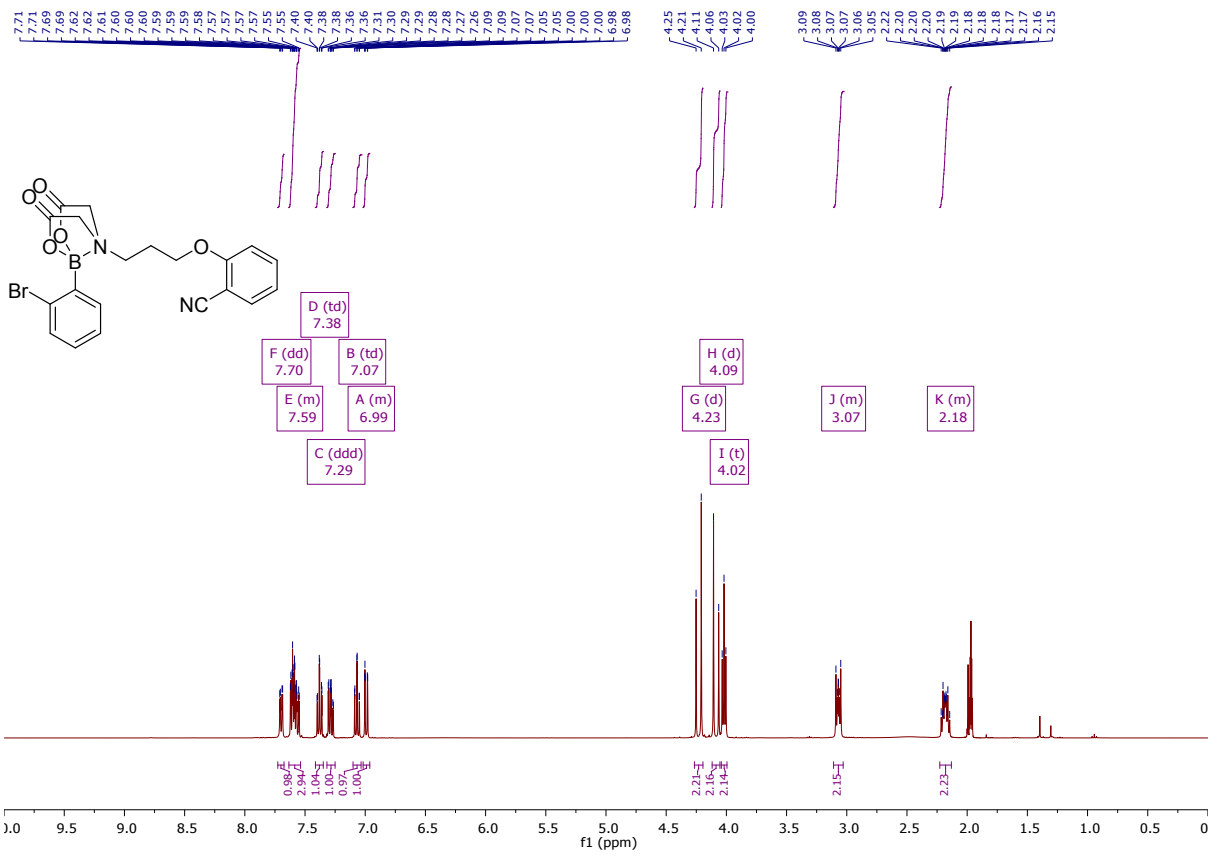

168.41
162.55
159.86
134.76
134.69
133.66
121.28
116.06
114.68
112.73
101.39
65.73
58.90
56.02
23.76
O
O
O
B
N
O
NC
F
f1 (ppm)

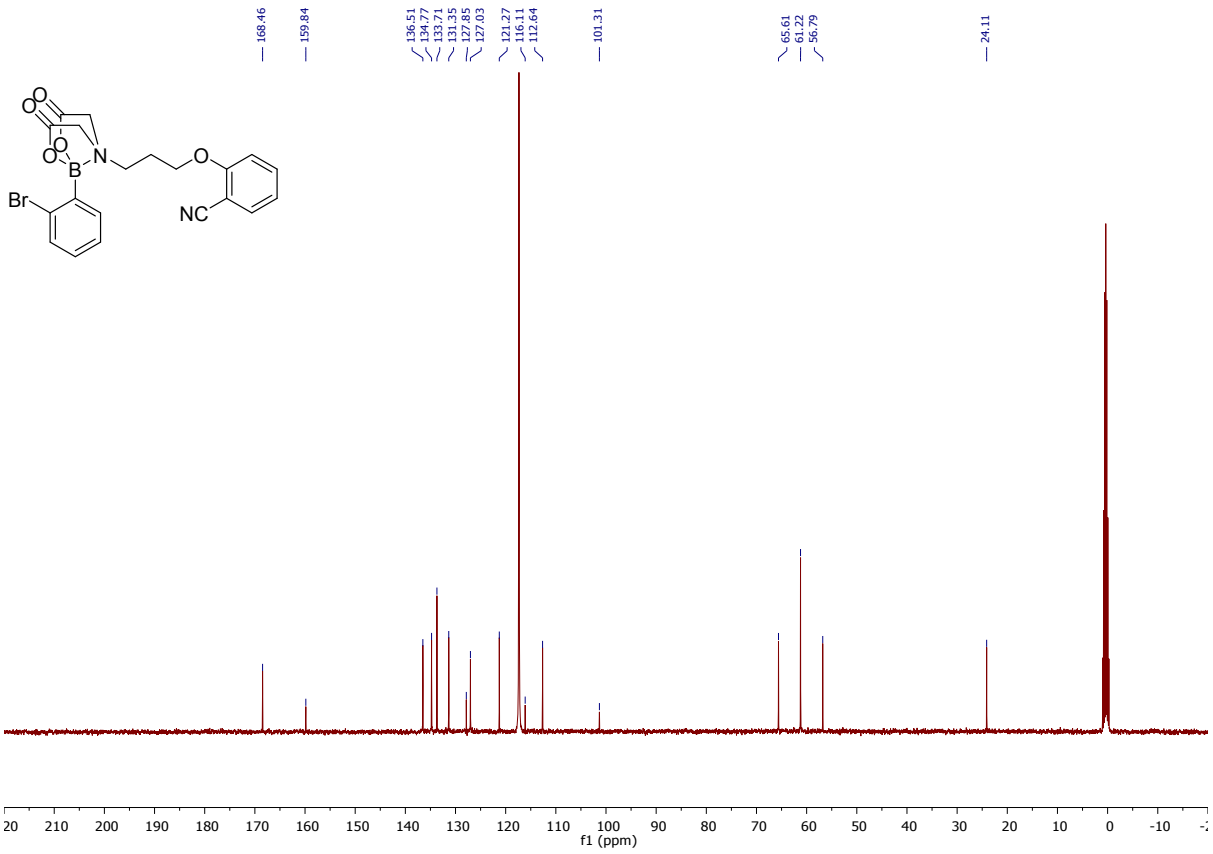

O
O
O
B
N
O
NC
F

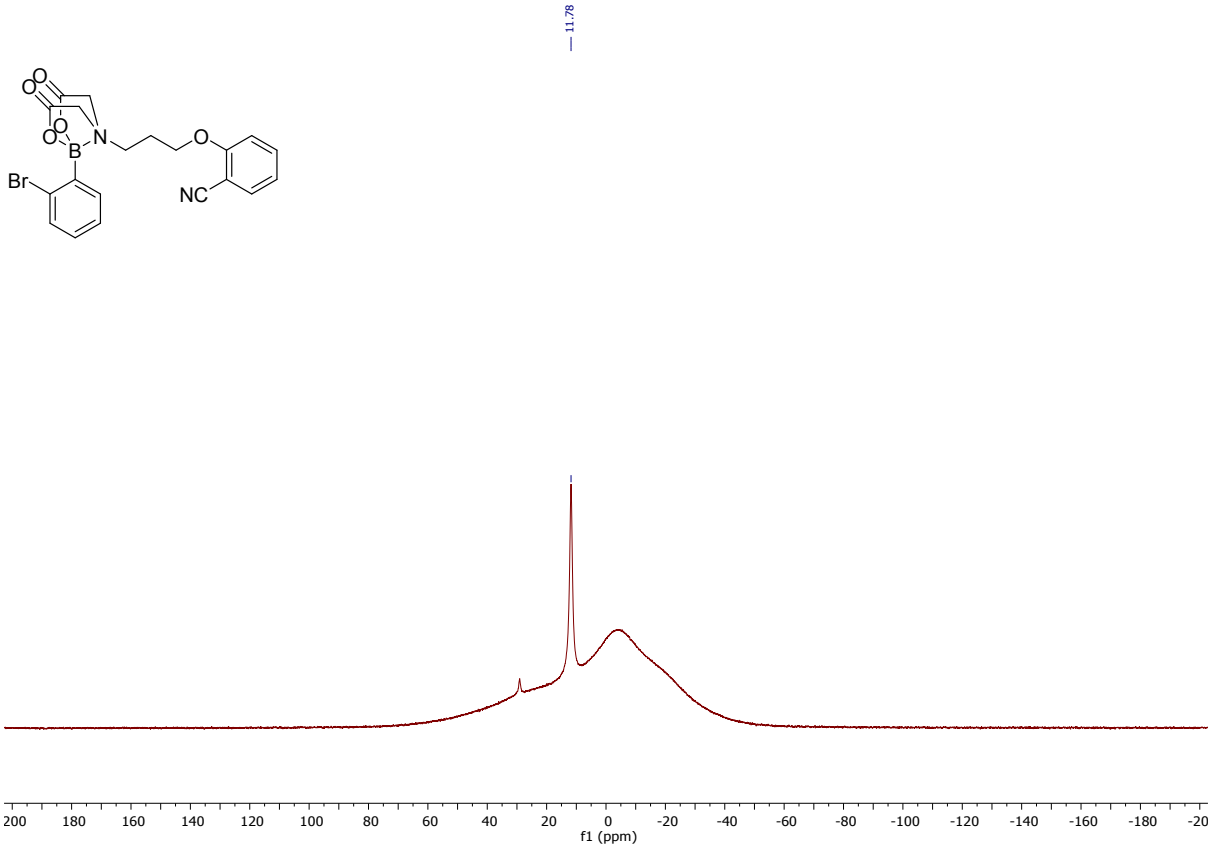
11.58
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)


O
O
O
B
N
O
NC
F

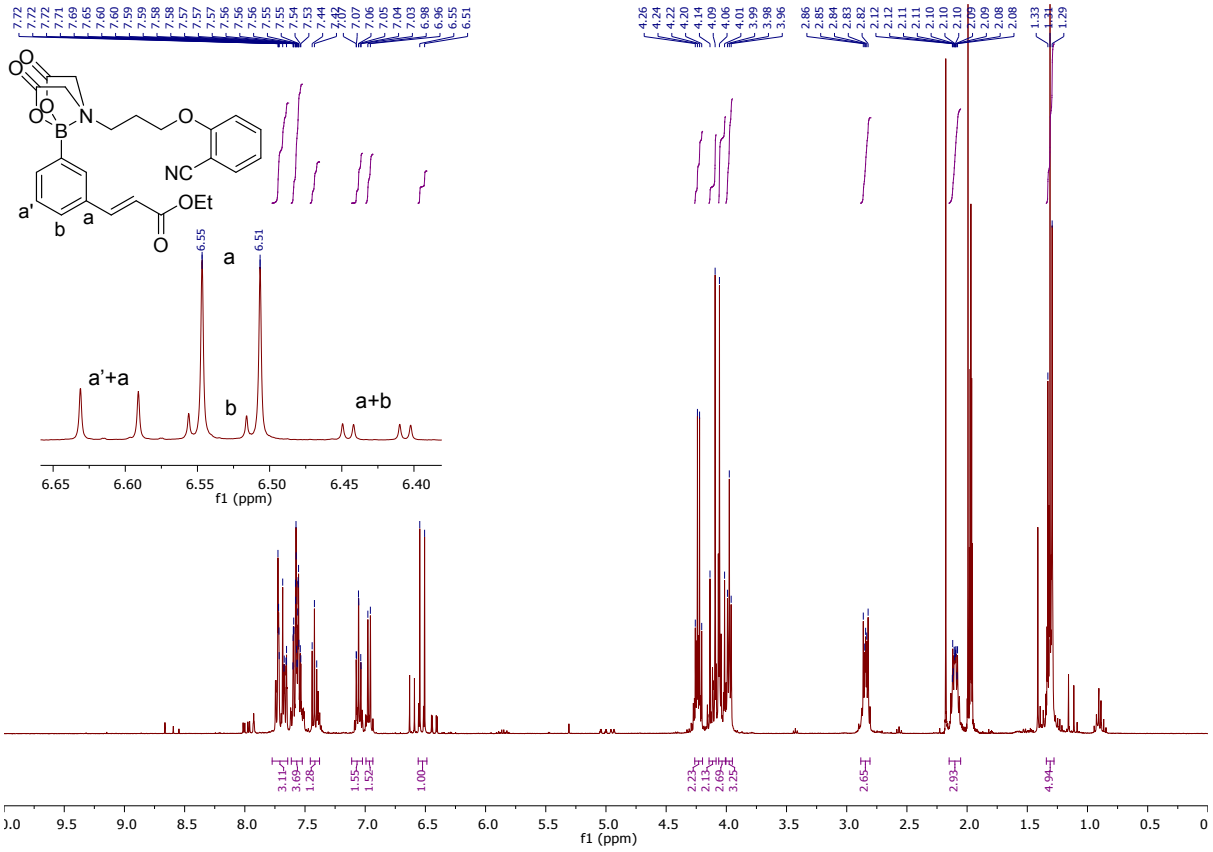
-76.50
-114.01
-114.03
-114.05
-114.07
B (s)
-76.50
A (q)
-114.04
0.40
1.00
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

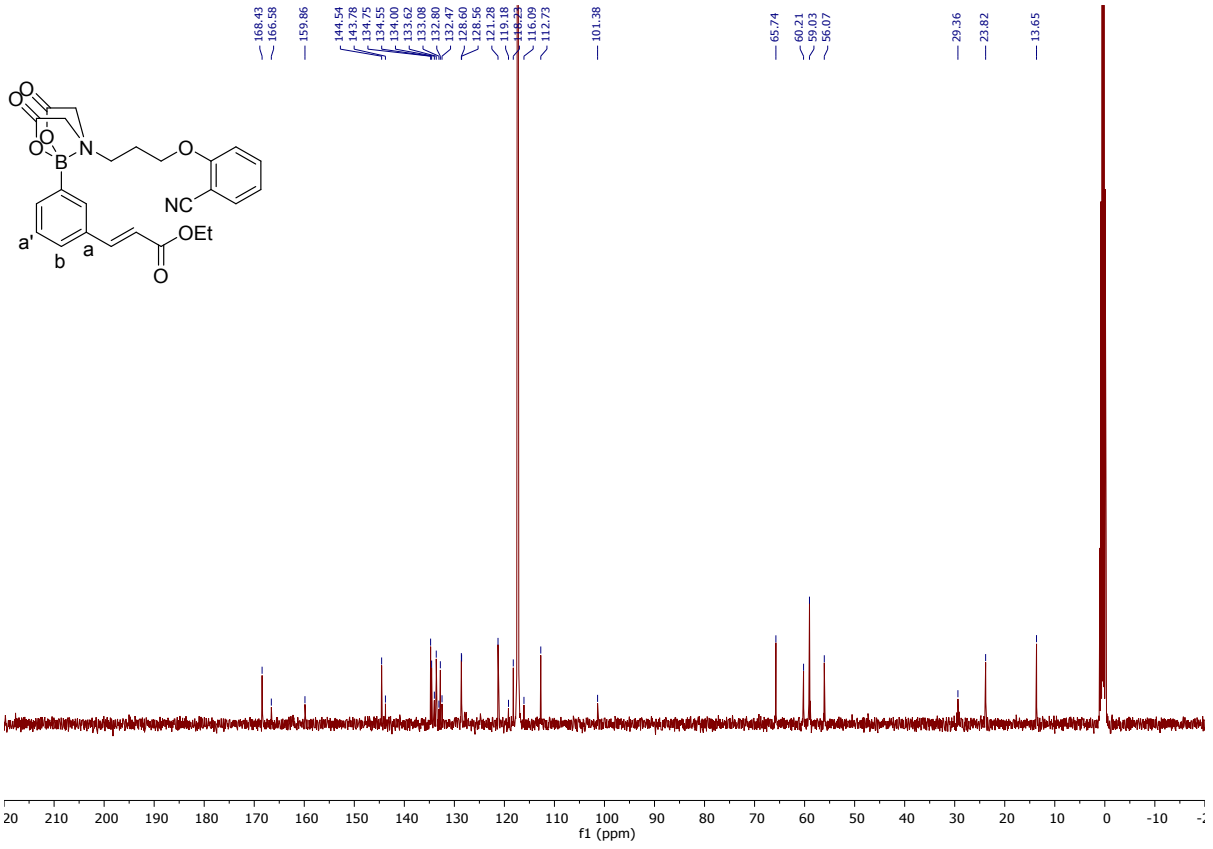

D (td)
7.38
F (dd)
7.70
B (td)
7.07
H (d)
4.09
E (m)
7.59
A (m)
6.99
G (d)
4.23
J (m)
3.07
K (m)
2.18
C (ddd)
7.29
I (t)
4.02
f1 (ppm)

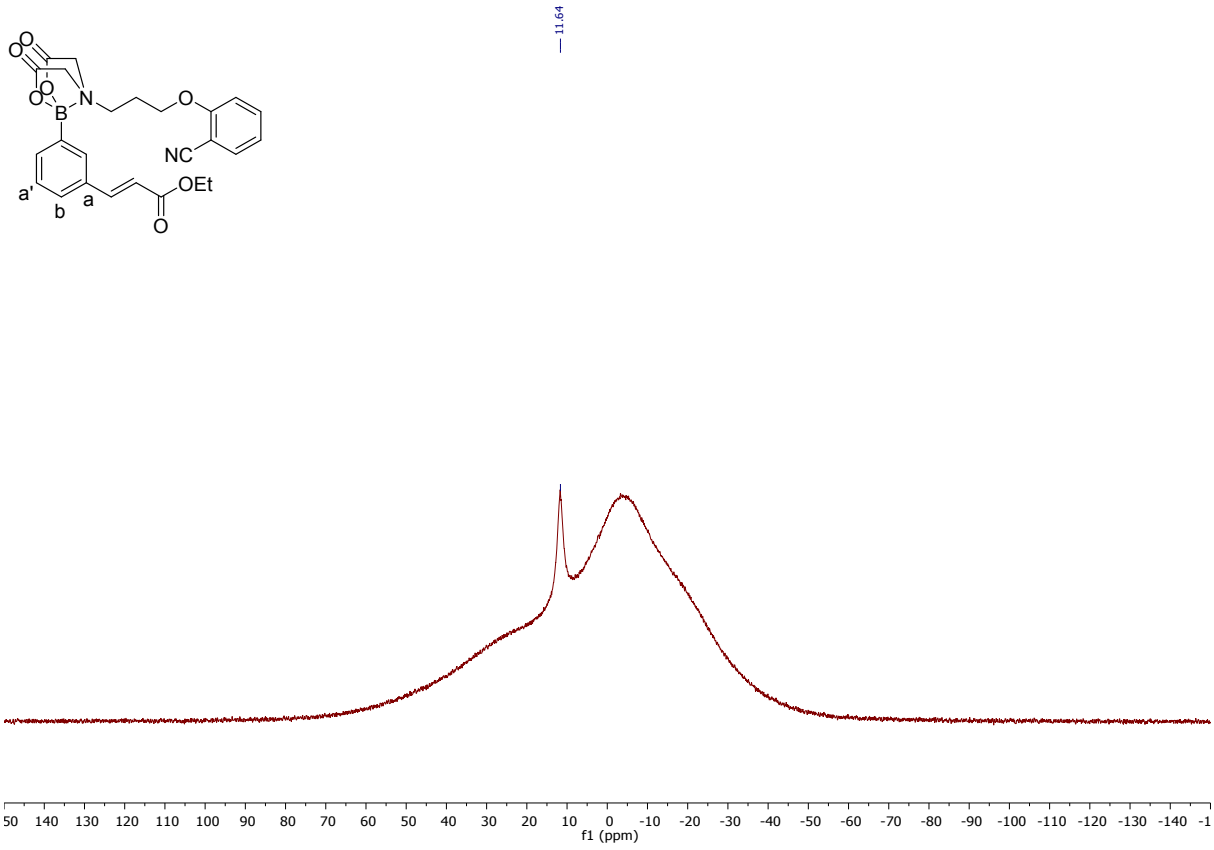

168.46
159.84
136.51
134.77
133.71
131.35
127.85
127.03
121.27
116.11
112.64
101.31
65.61
61.22
56.79
24.11
f1 (ppm)

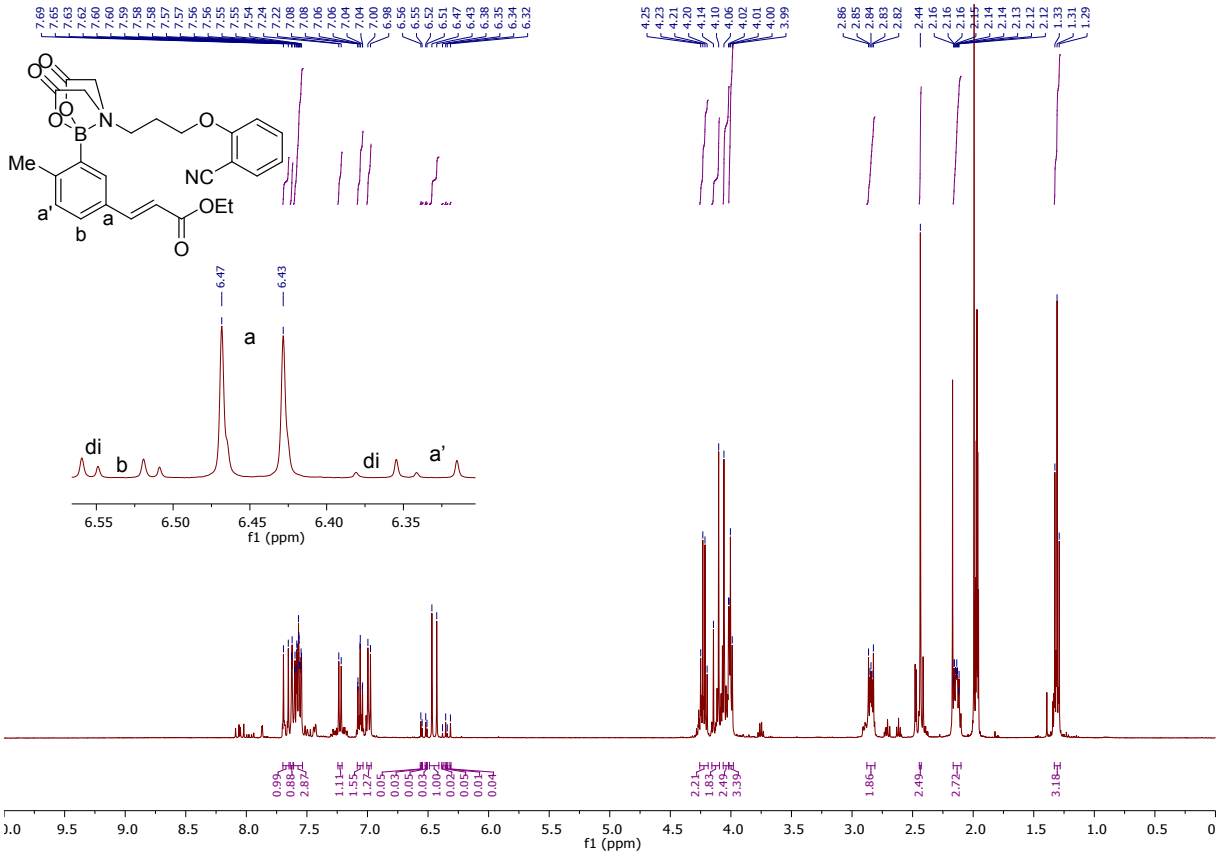


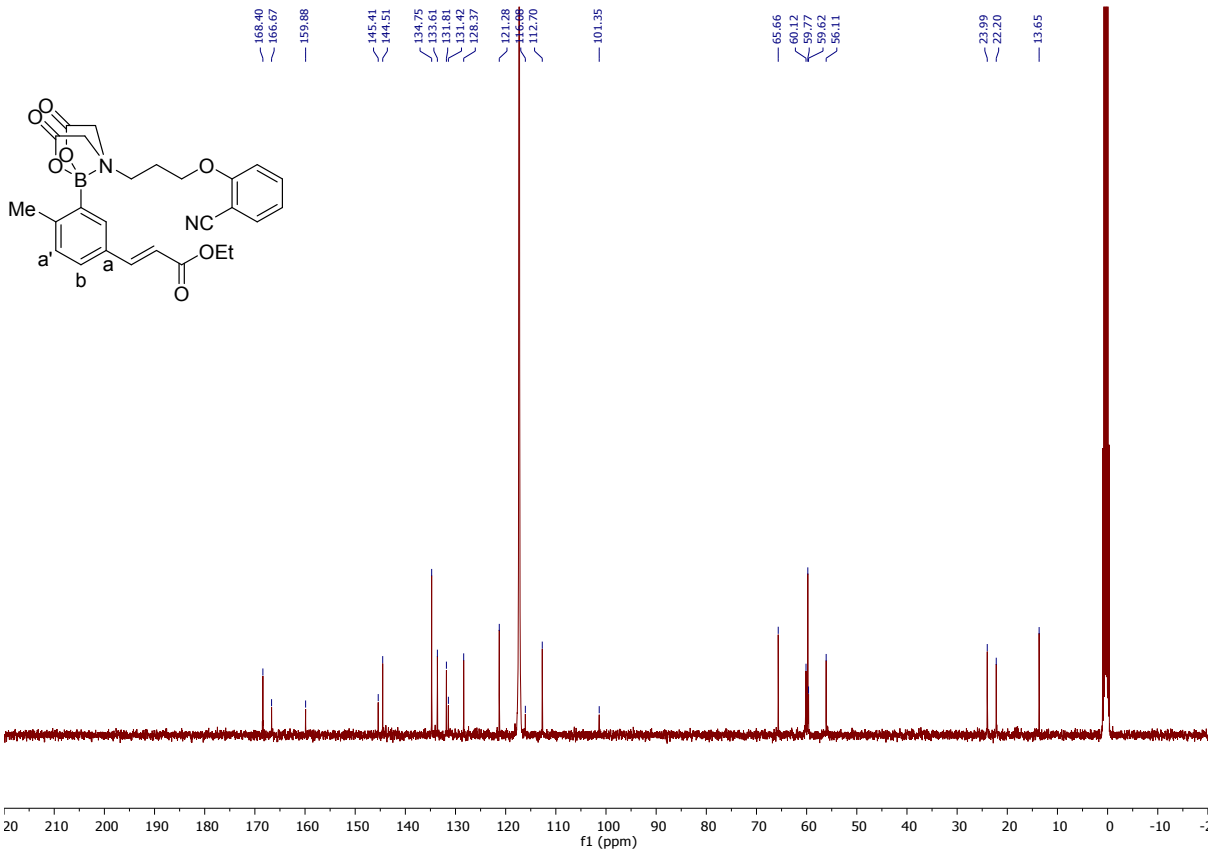
Alkenylated Aryl Boronic Acid MIDA-DG Ester NMR Spectra

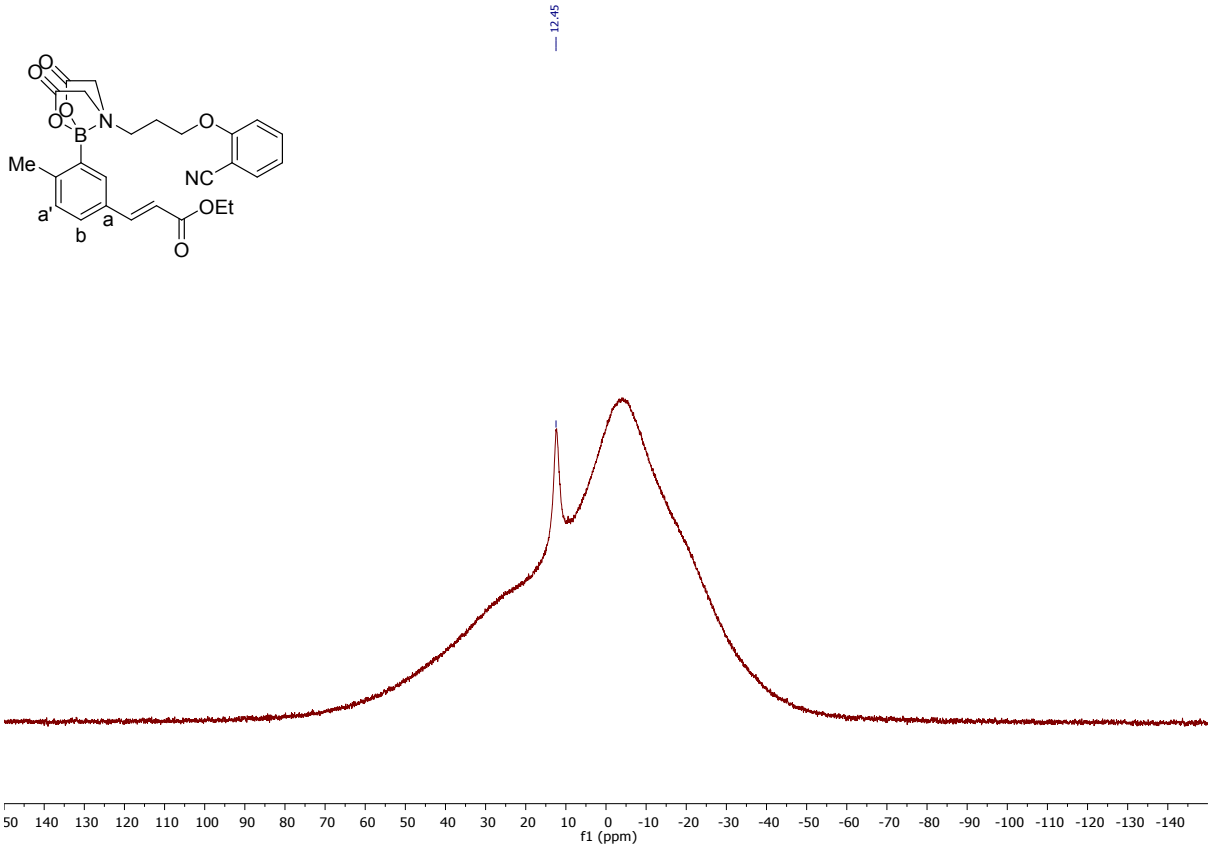


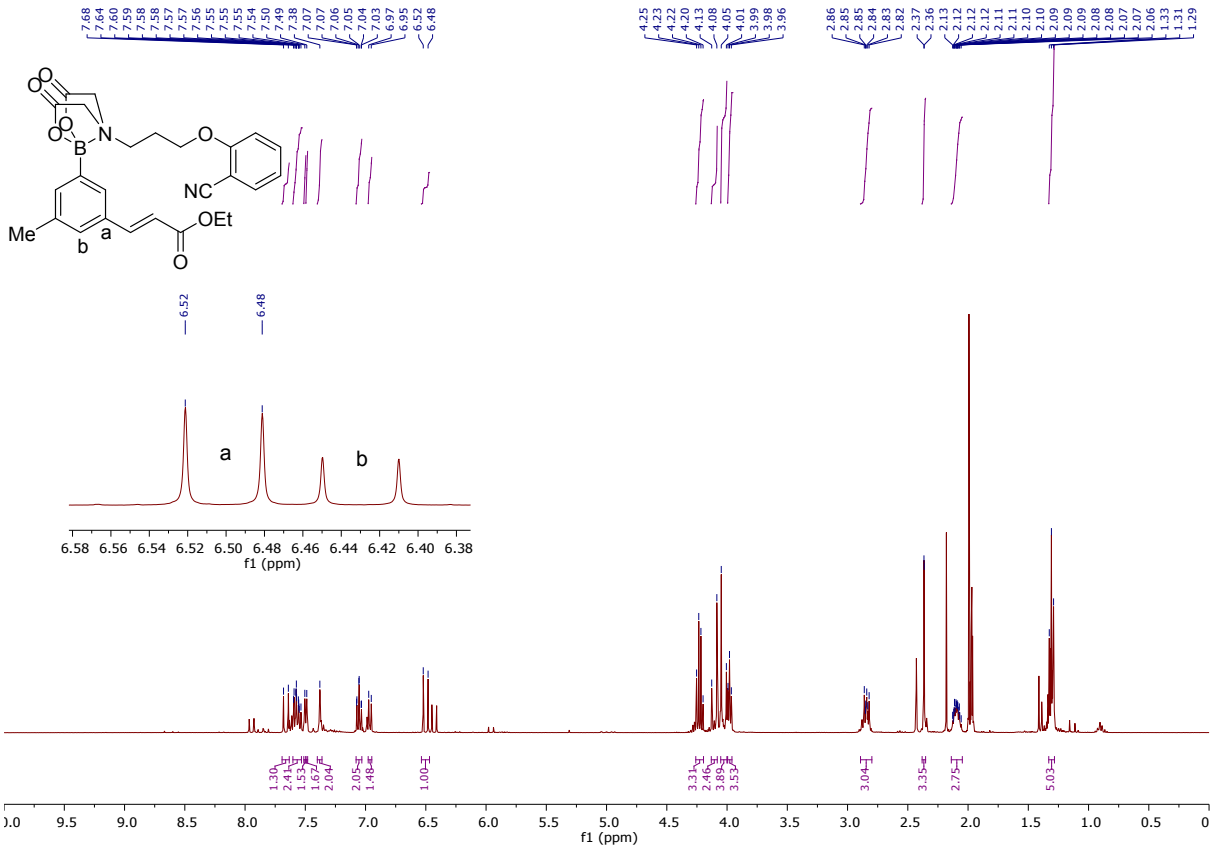

168.43
166.58
159.86
144.54
143.78
134.75
134.55
134.00
133.62
133.08
132.80
132.47
128.60
128.56
121.28
119.18
118.23
116.09
112.73
101.38
65.74
60.21
59.03
56.07
29.36
23.82
13.65
O
O
O
B
N
O
NC
OEt
O
a'
a
b
f1 (ppm)

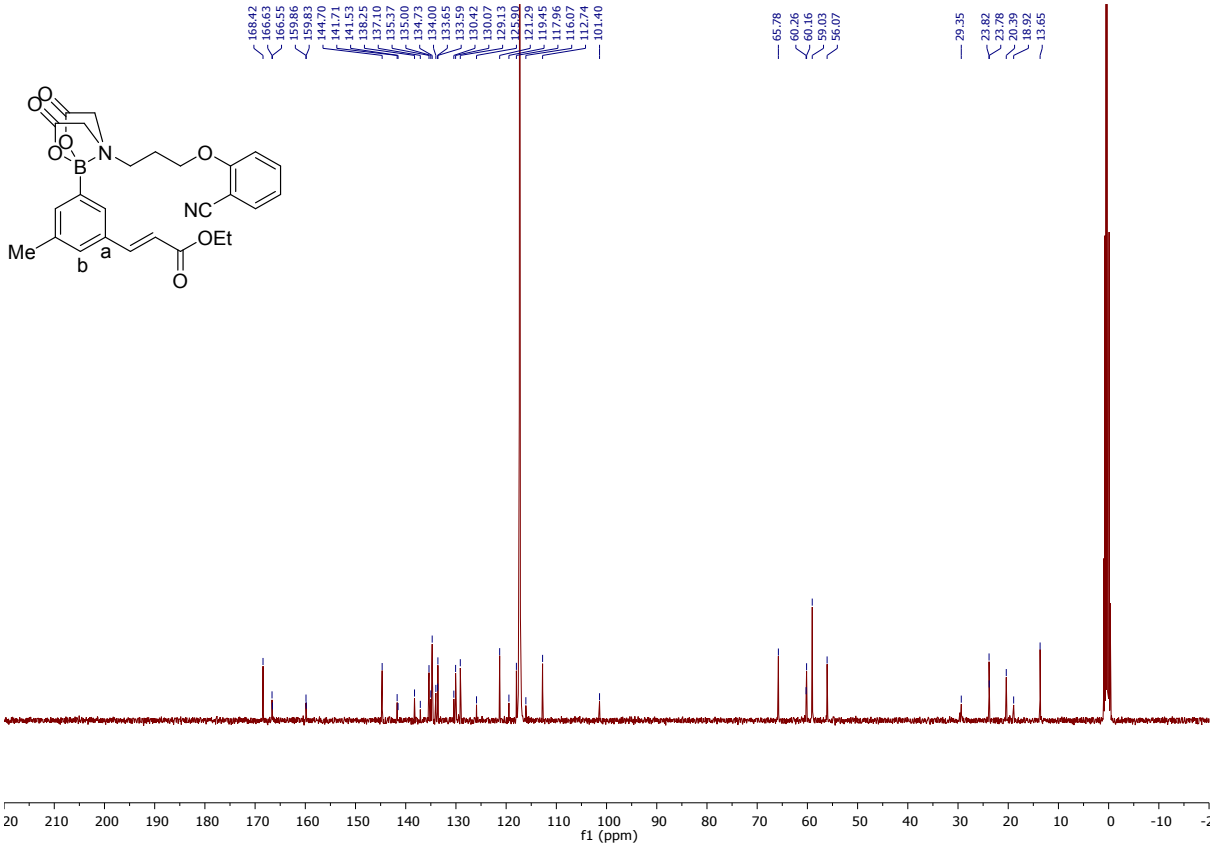

11.64
O
O
O
B
N
O
NC
OEt
O
a'
a
b
f1 (ppm)


Me
NC
OEt
a'
a
b
di
f1 (ppm)


Me
NC
OEt
a'
a
b
f1 (ppm)


12.45
f1 (ppm)


6.52
6.48
a
b
f1 (ppm)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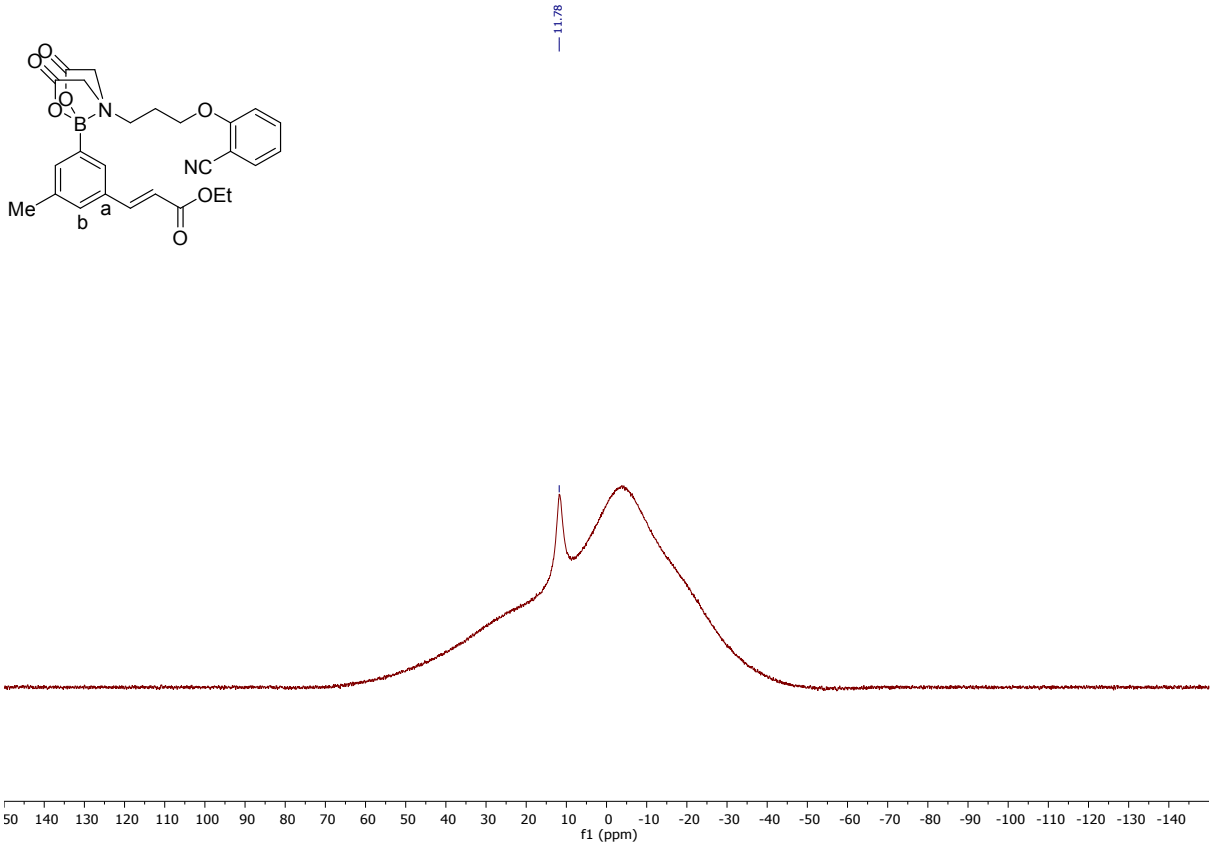
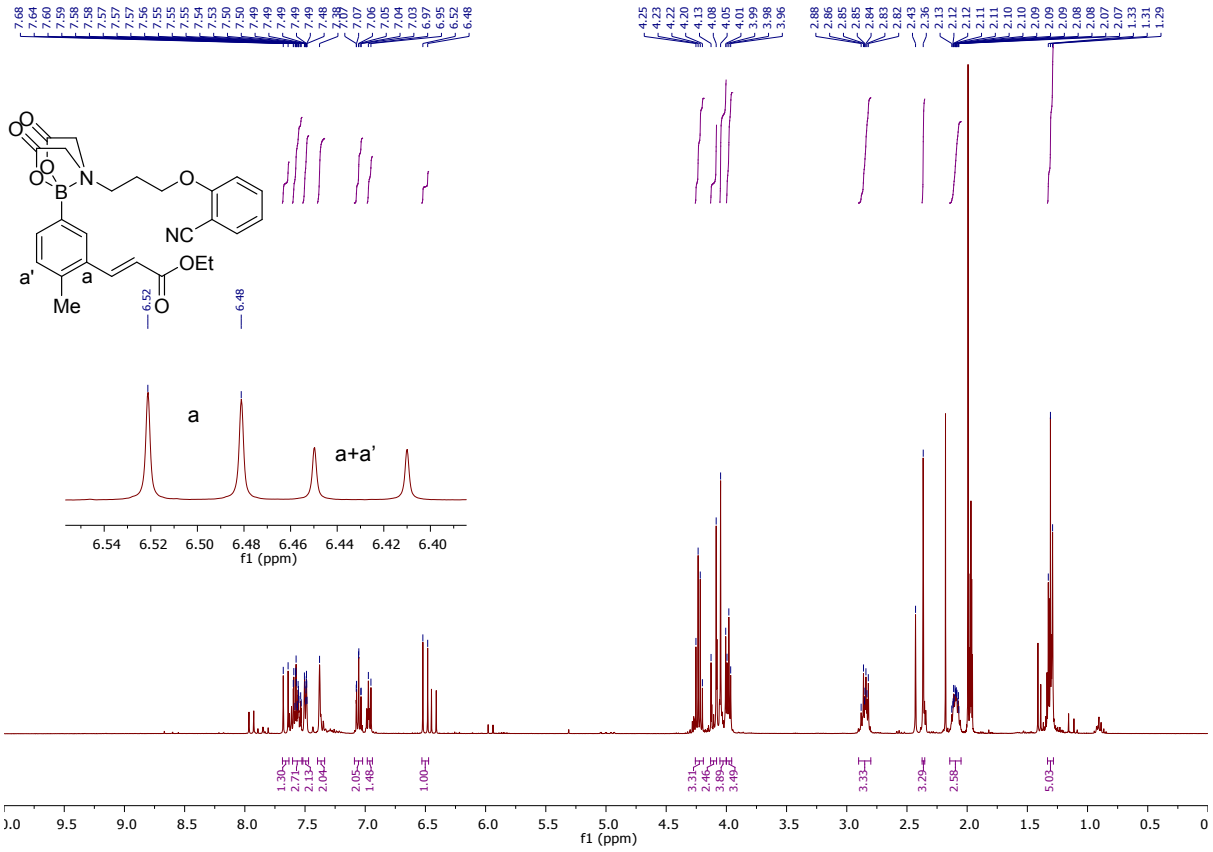
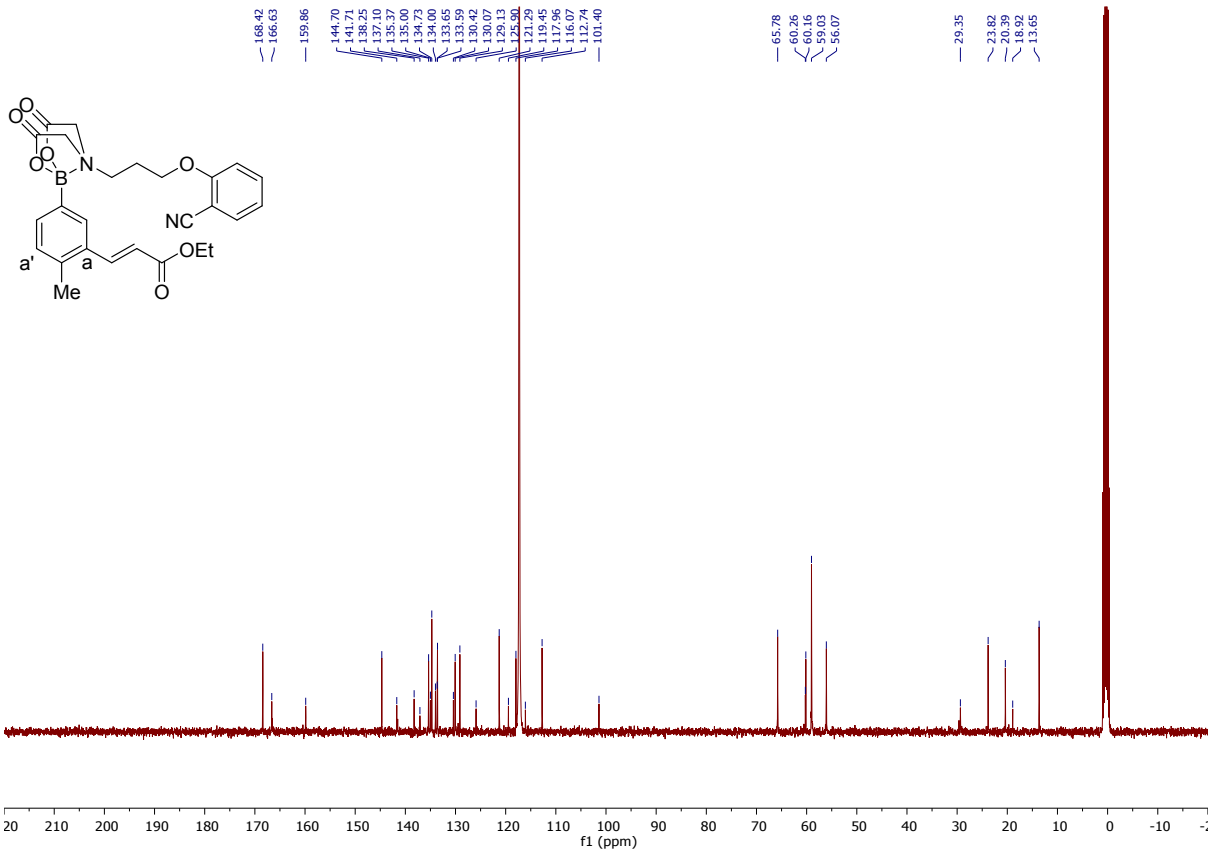
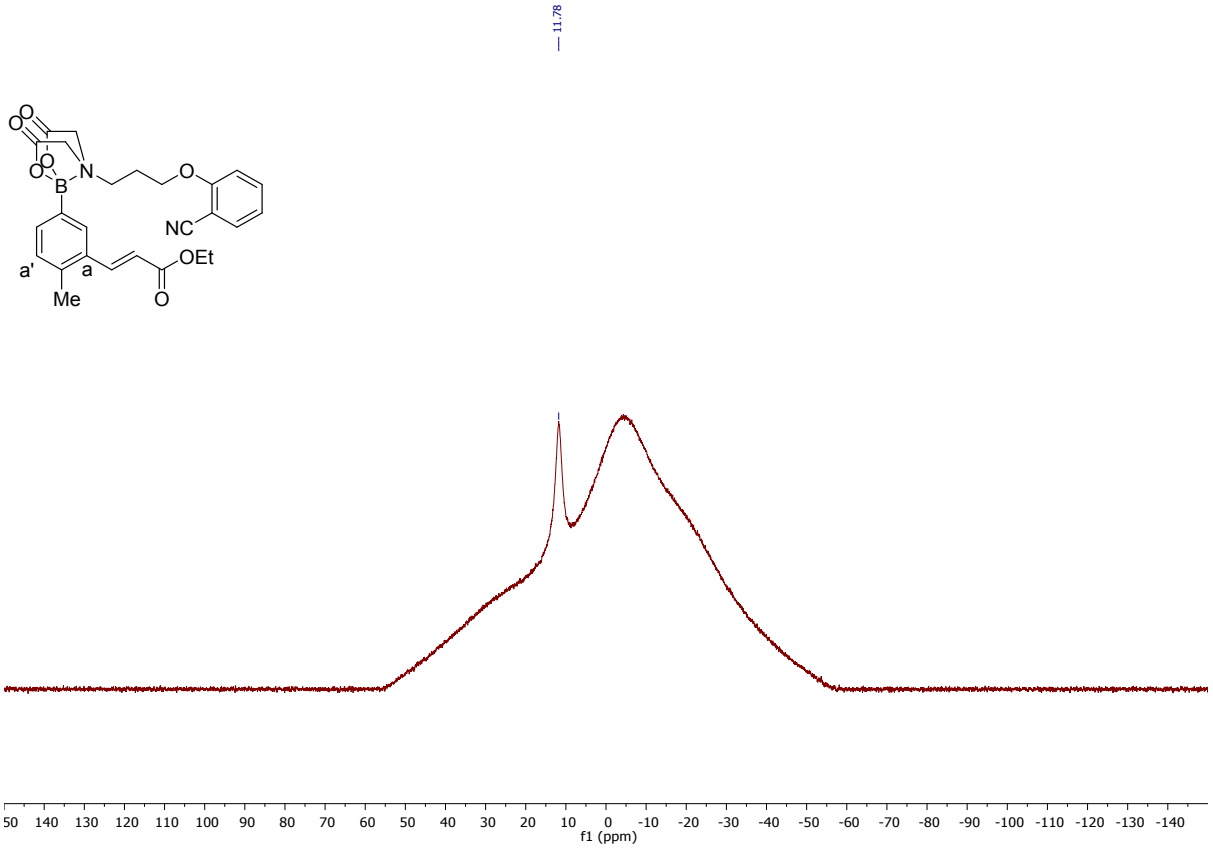
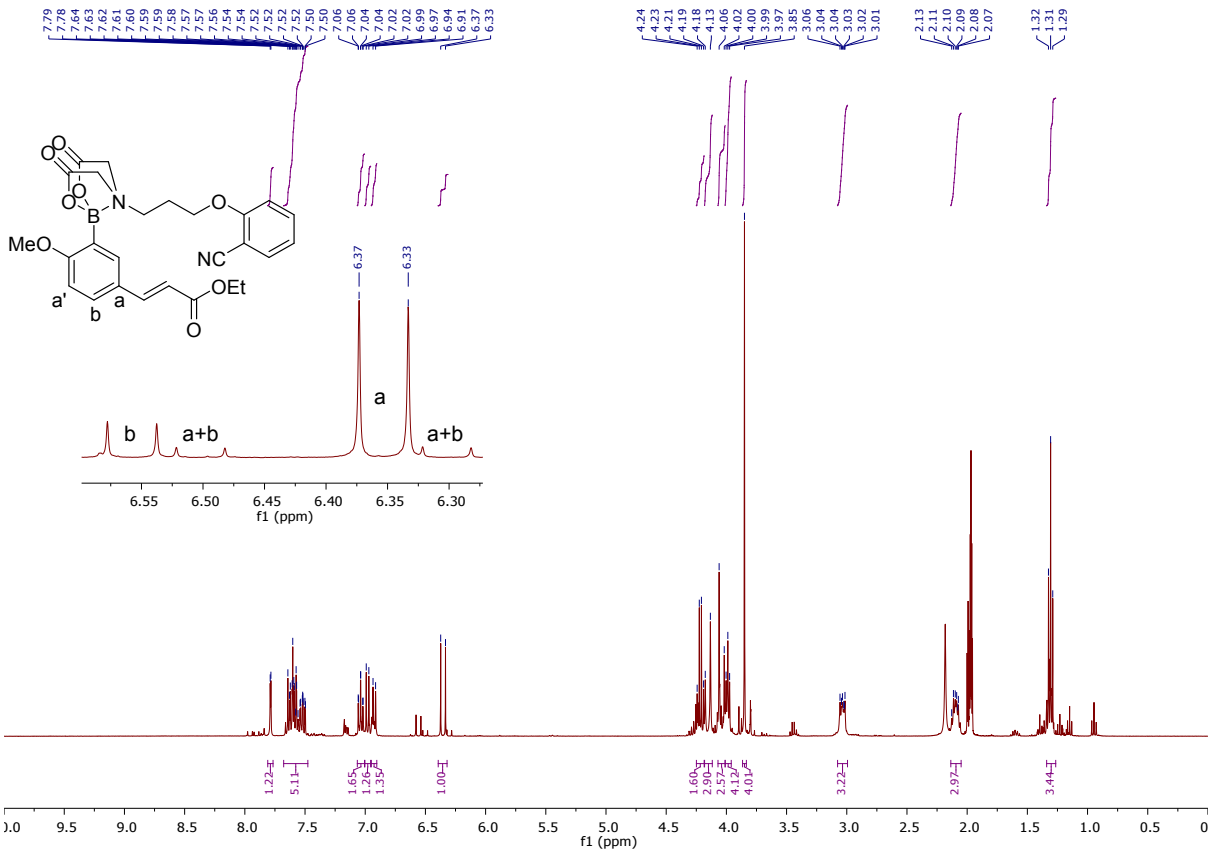
166.63
166.55
159.86
159.83
144.70
141.71
141.53
138.25
137.10
135.37
135.00
134.73
134.00
133.65
133.59
130.42
130.07
129.13
125.90
121.29
119.45
117.96
116.07
112.74
101.40
65.78
60.26
60.16
59.03
56.07
29.35
23.82
23.78
20.39
18.92
13.65
O
O
O
O
B
N
O
NC
OEt
Me
a
b
O
f1 (ppm)

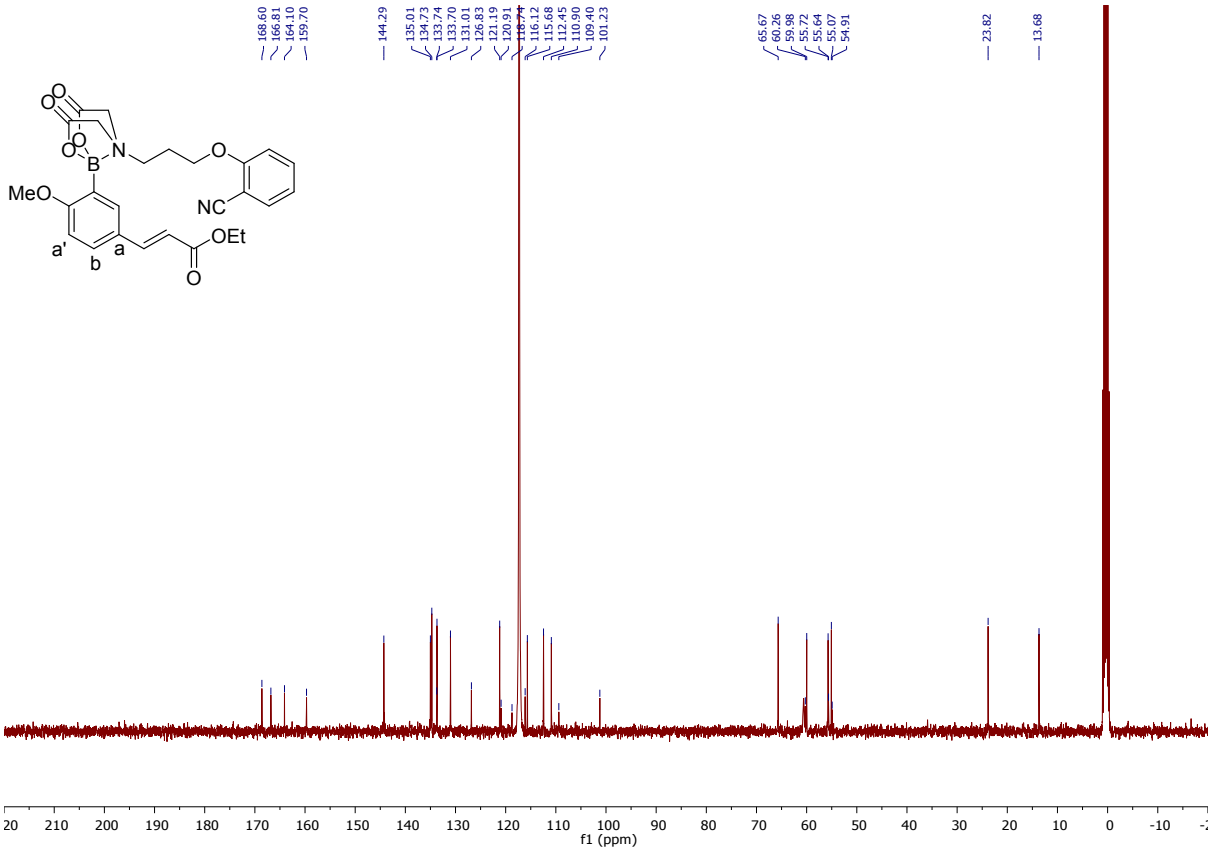

11.78
O
O
O
O
B
N
O
NC
OEt
Me
a
b
O
f1 (ppm)

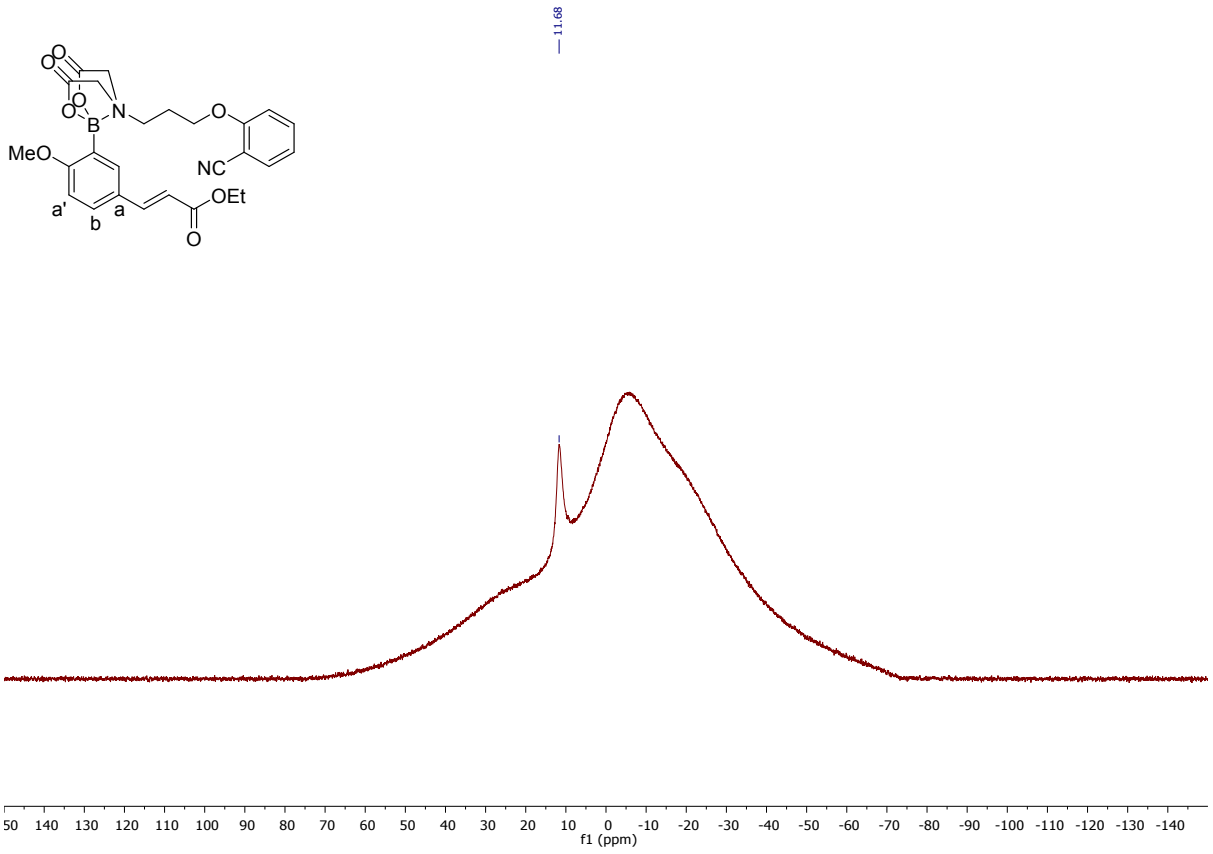

a
a+a'
6.54 6.52 6.50 6.48 6.46 6.44 6.42 6.40
f1 (ppm)
NC
OEt
Me
a'
a
f1 (ppm)

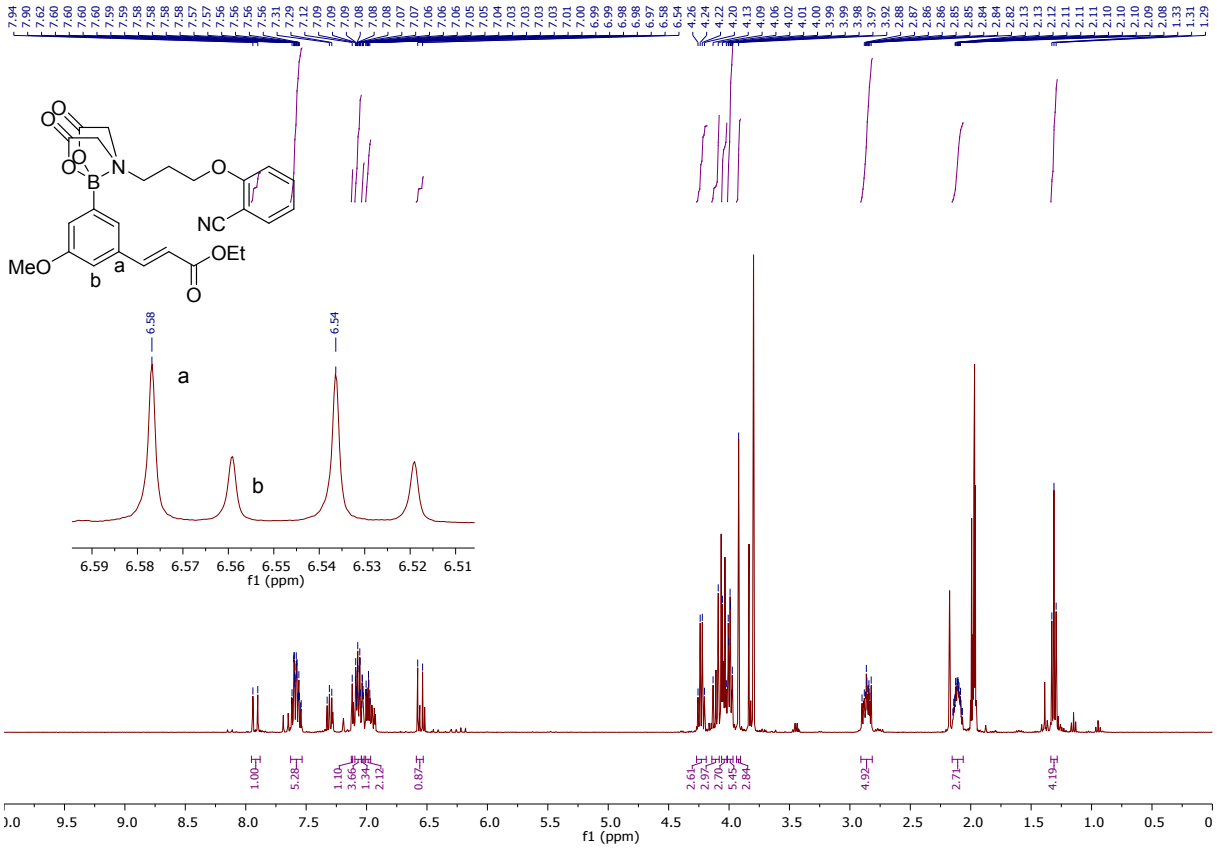

NC
OEt
Me
a'
a
f1 (ppm)

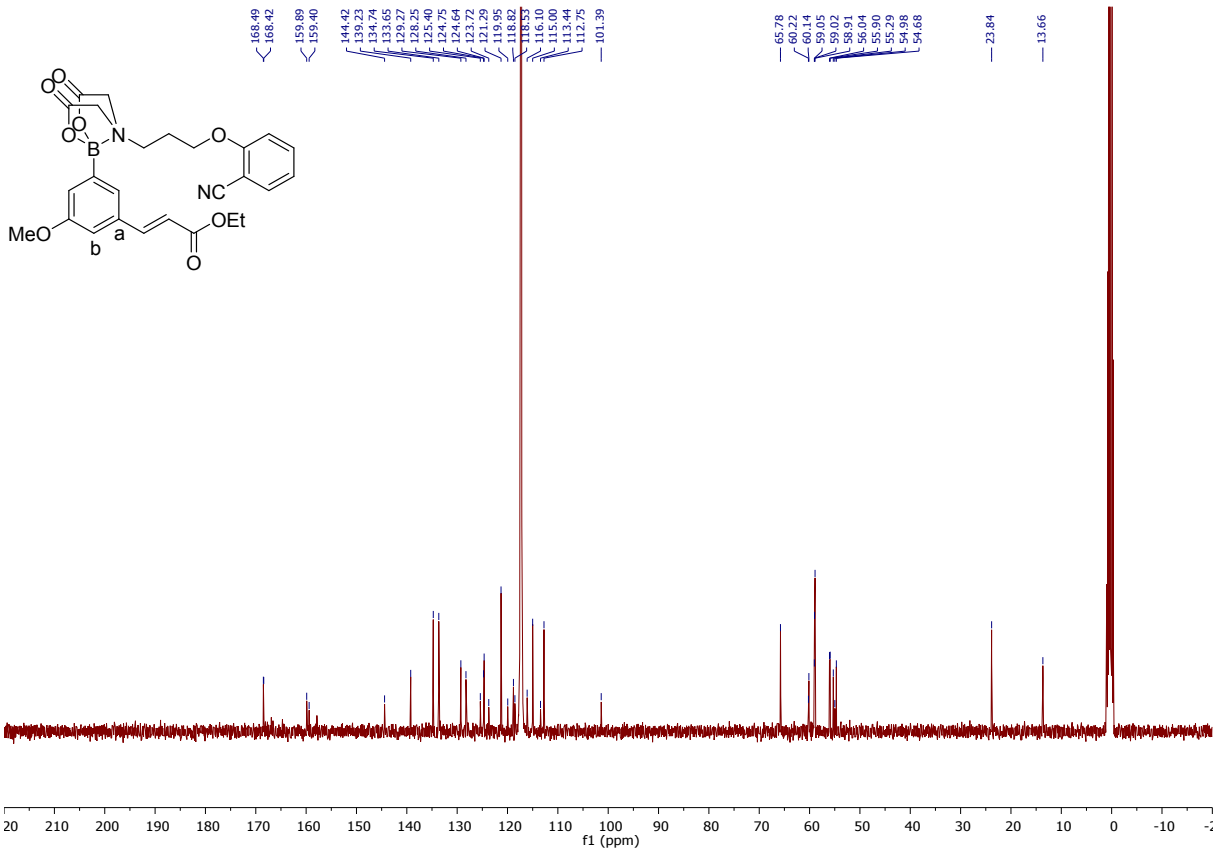

11.78
O
O
O
B
N
O
NC
OEt
a'
a
Me
O
50 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)

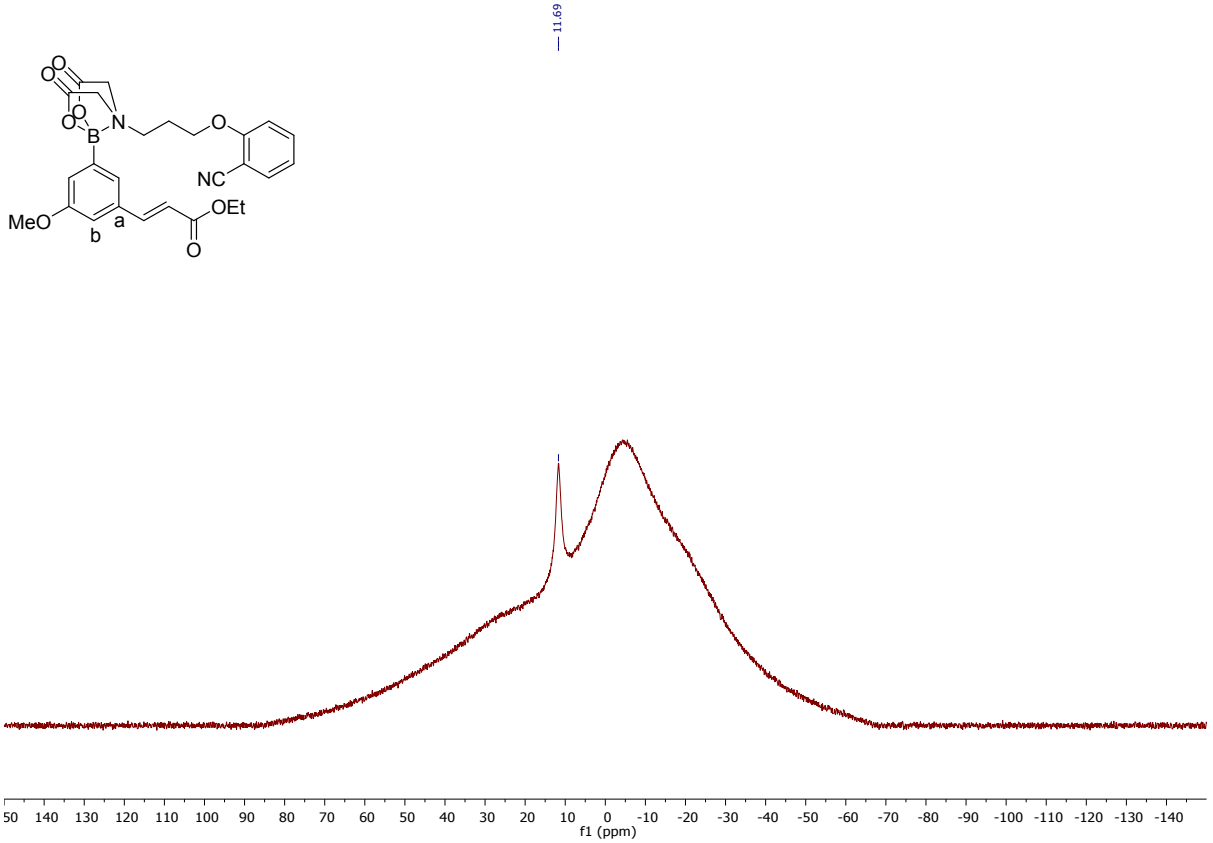

7.79 7.78 7.64 7.63 7.62 7.61 7.60 7.59 7.59 7.58 7.57 7.57 7.56 7.54 7.54 7.52 7.52 7.52 7.52 7.50 7.50 7.06 7.06 7.04 7.04 7.02 7.02 6.99 6.97 6.94 6.91 6.37 6.33
4.24 4.23 4.21 4.19 4.18 4.13 4.06 4.02 4.00 3.99 3.97 3.85 3.06 3.04 3.04 3.03 3.02 3.01
2.13 2.11 2.10 2.09 2.08 2.07
1.32 1.31 1.29
MeO
O
O
O
B
N
O
NC
OEt
a'
b
a
6.37
6.33
a
b
a+b
a+b
6.55 6.50 6.45 6.40 6.35 6.30
f1 (ppm)
1.22 5.11 1.65 1.26 1.35 1.00 1.60 2.90 2.57 4.12 4.01 3.22 2.97 3.44
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

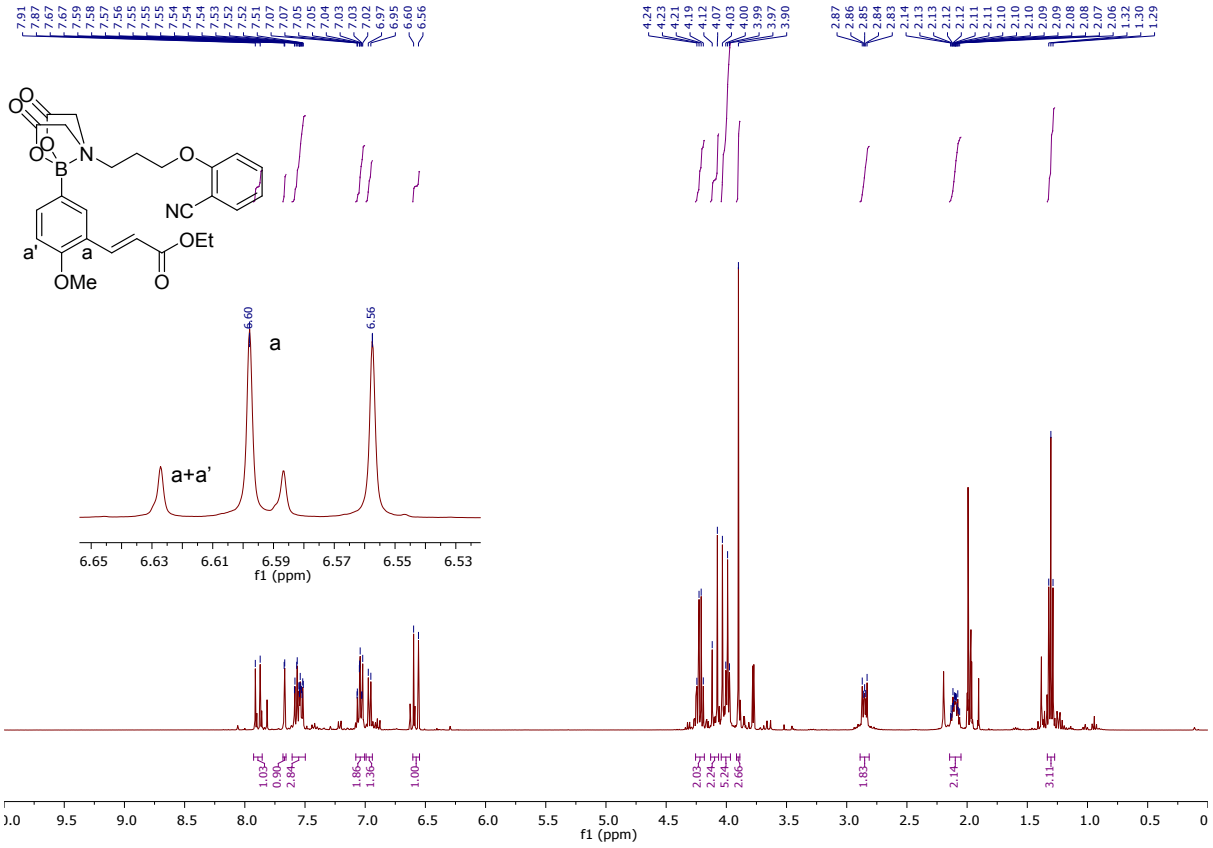

168.60
166.81
164.10
159.70
144.29
135.01
134.73
133.74
133.70
131.01
126.83
121.19
120.91
118.74
116.12
115.68
112.45
110.90
109.40
101.23
65.67
60.26
59.98
55.72
55.64
55.07
54.91
23.82
13.68
MeO
NC
OEt
a'
a
b
f1 (ppm)

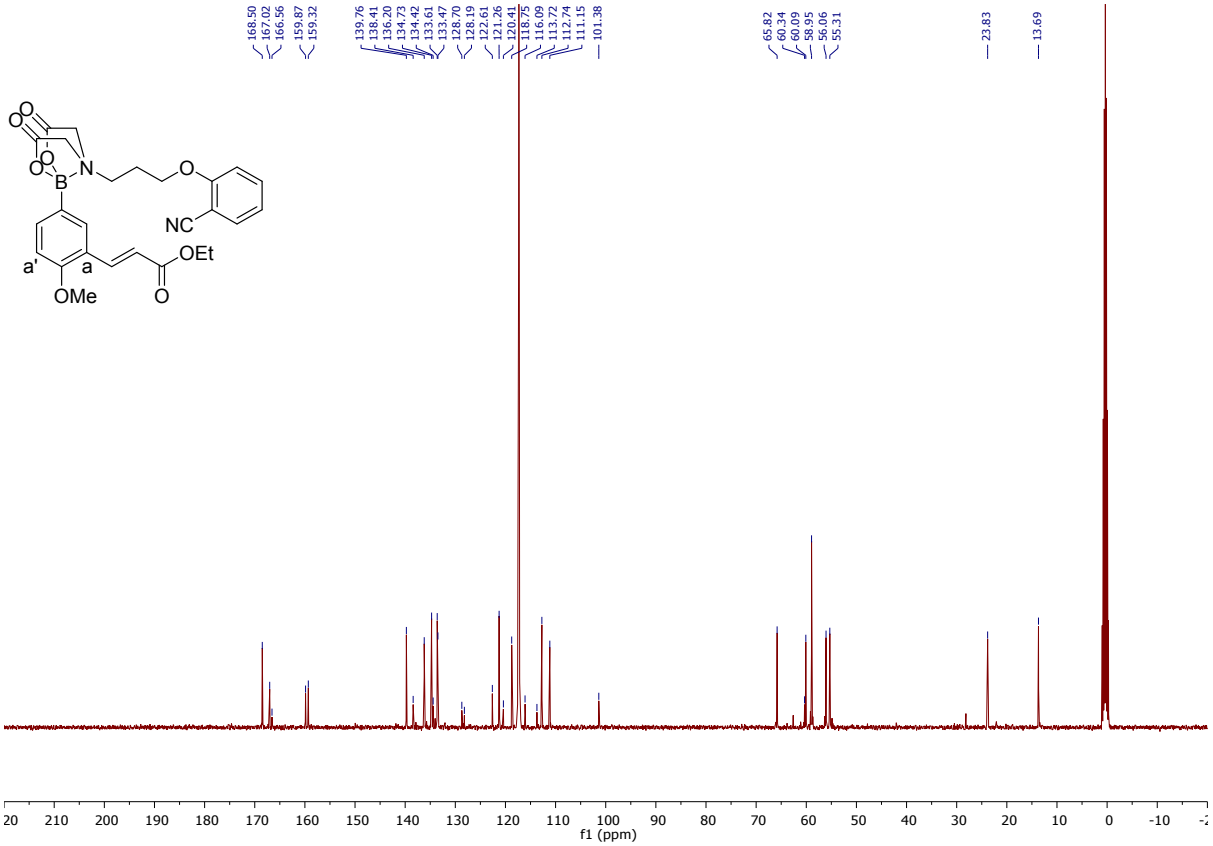

11.68
MeO
NC
OEt
a'
a
b
f1 (ppm)


MeO
OEt
NC
a
b
f1 (ppm)


MeO
OEt
NC
a
b
f1 (ppm)


11.69
MeO
a
b
NC
OEt
O
f1 (ppm)


a
a+a'
a'
OMe
NC
OEt
6.60
6.56
f1 (ppm)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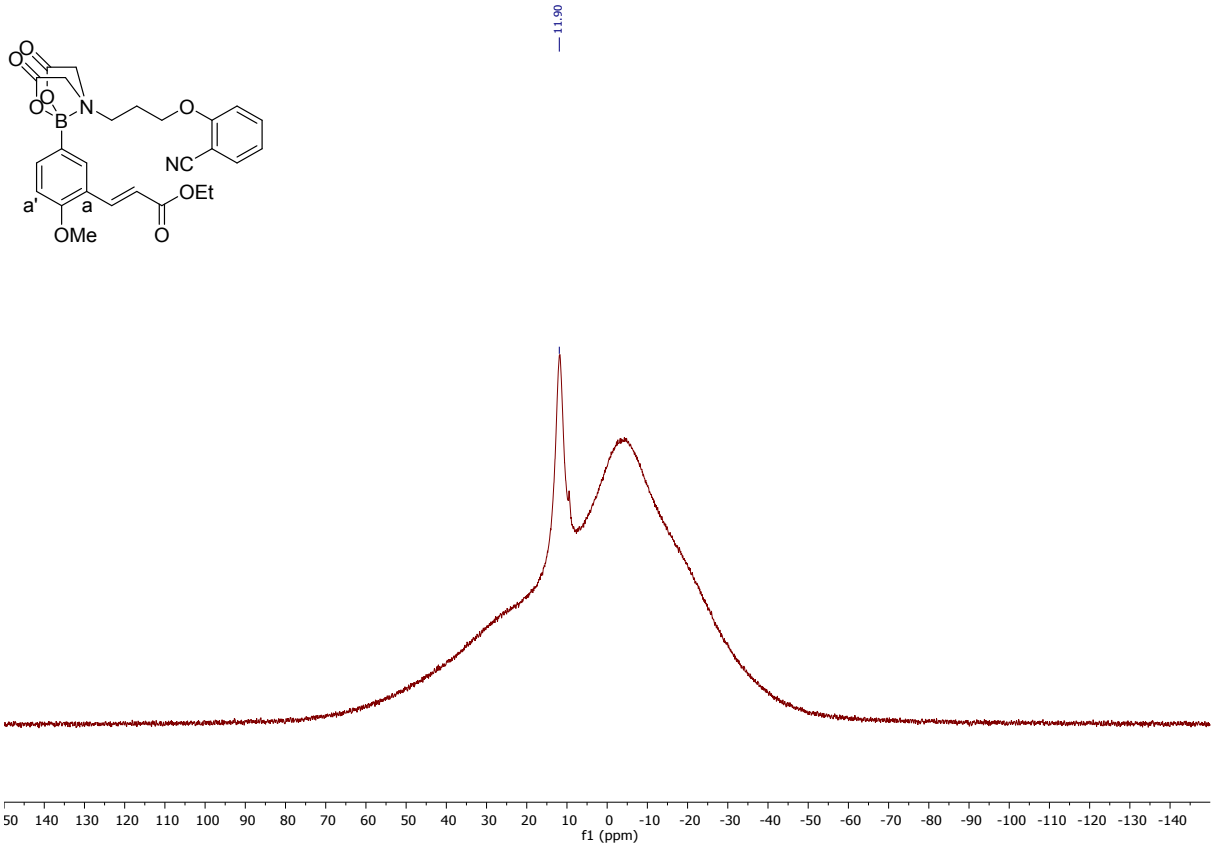
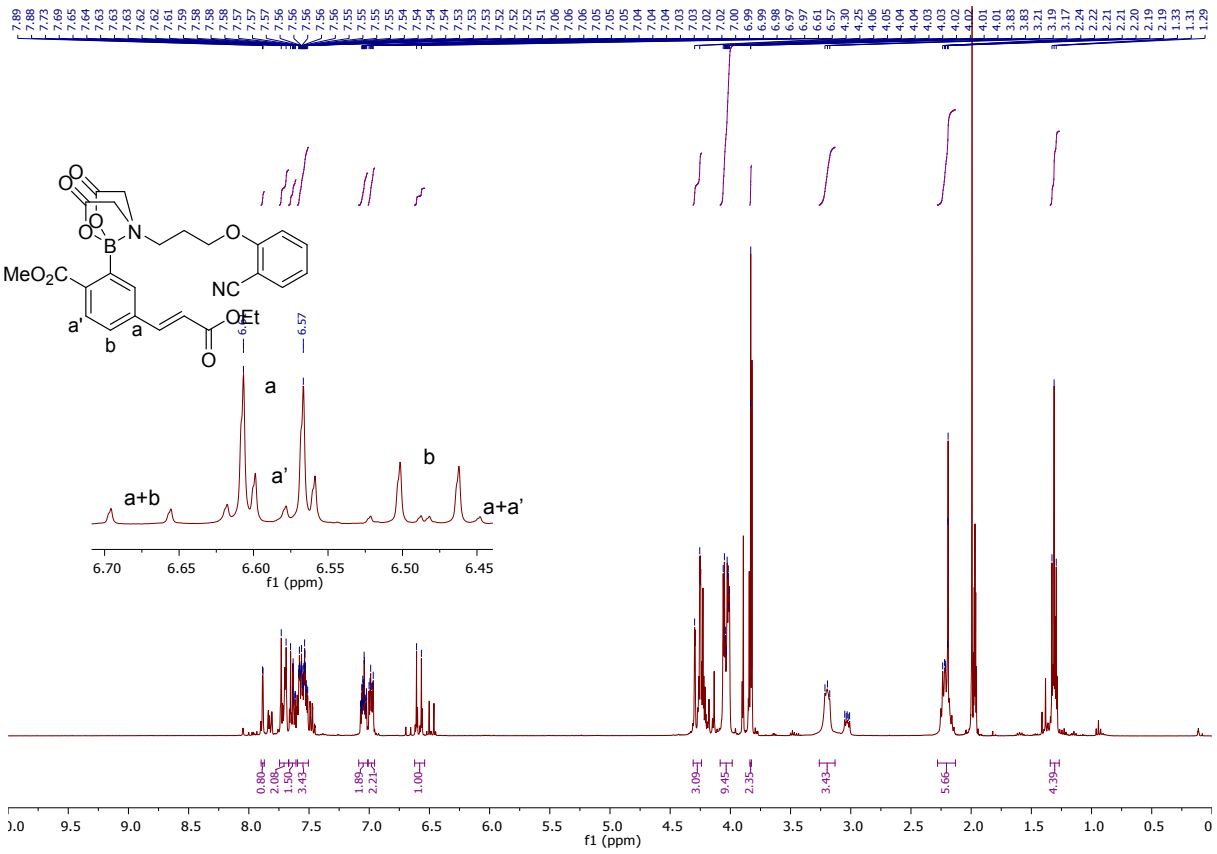
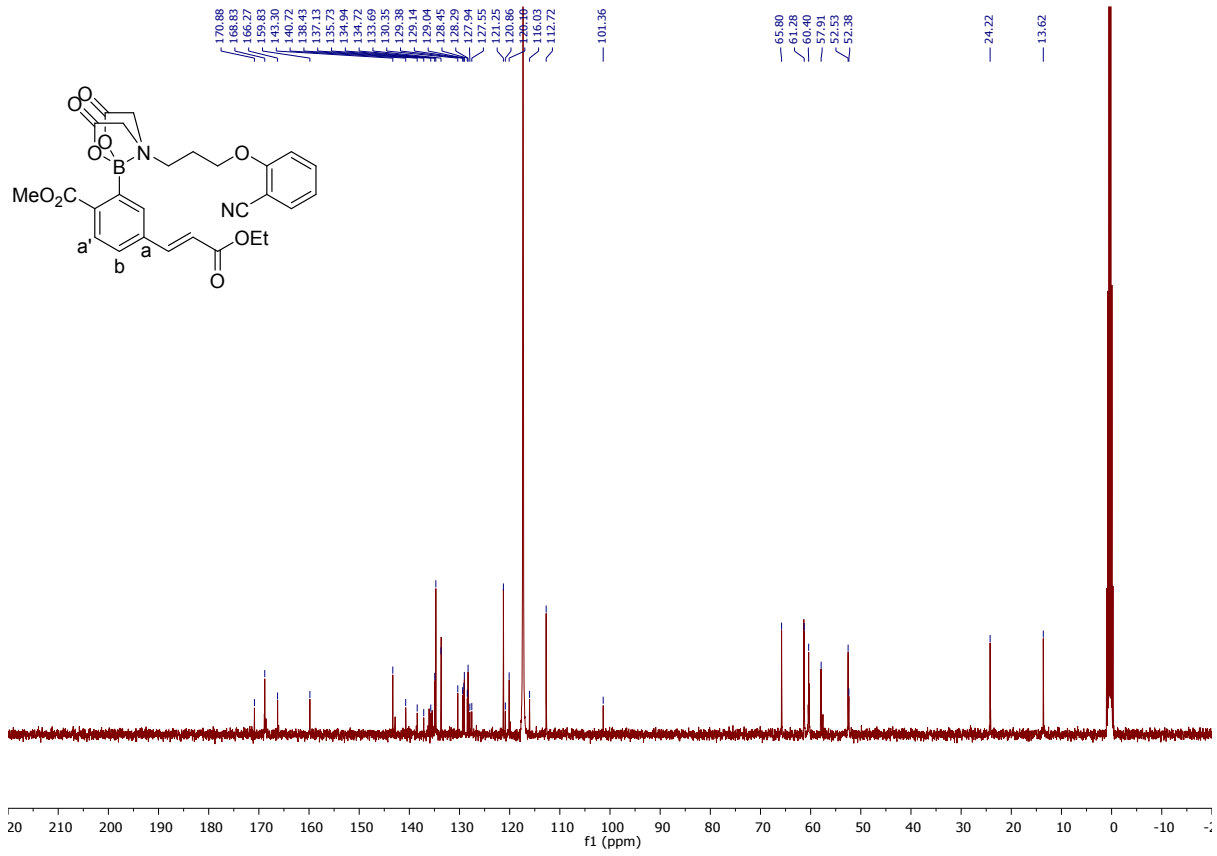
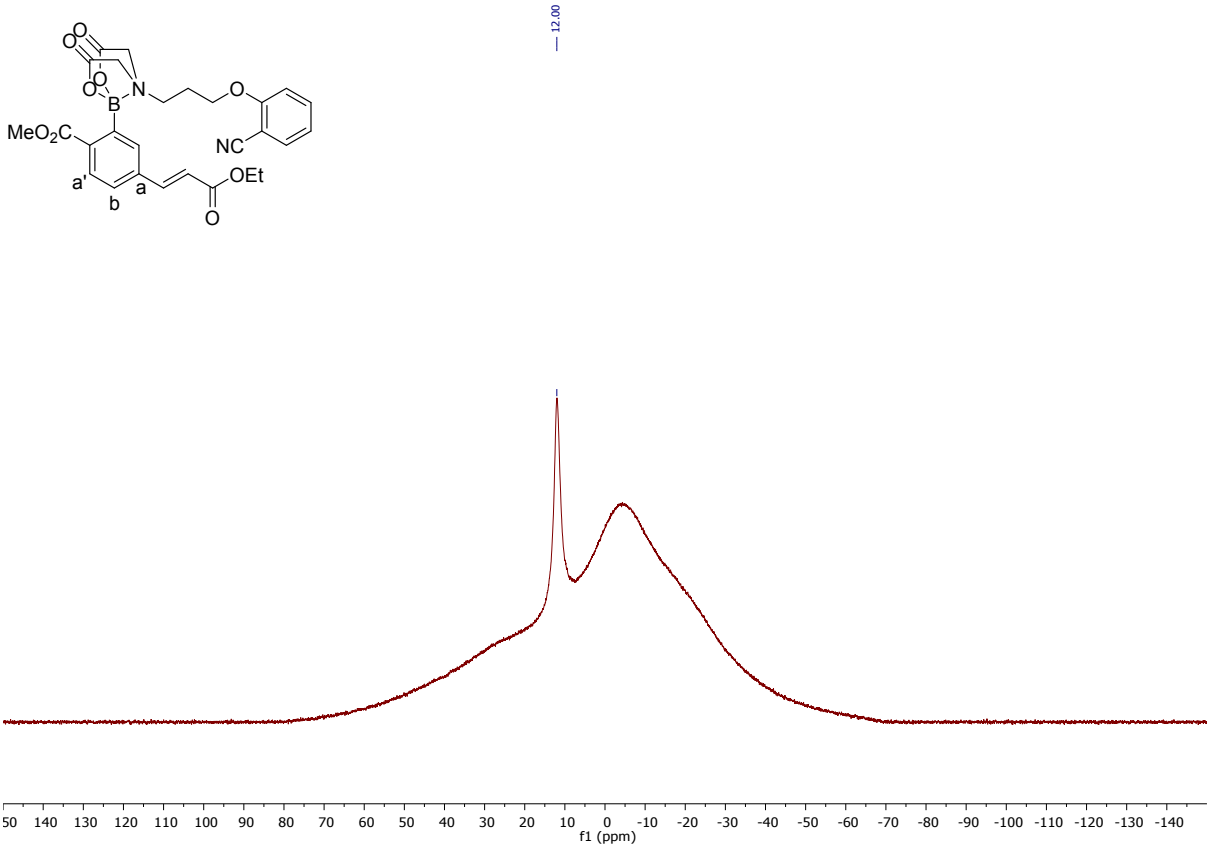
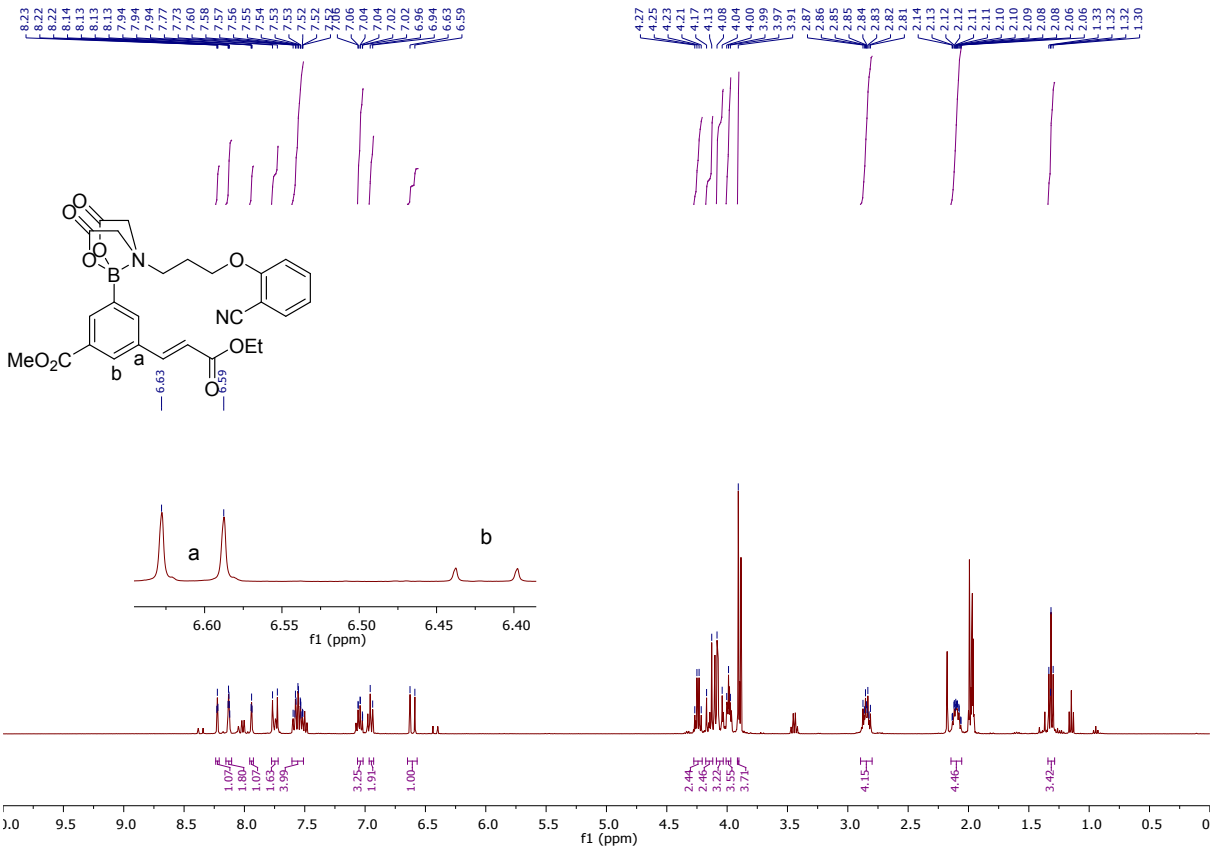
167.02
166.56
159.87
159.32
139.76
138.41
136.20
134.73
134.42
133.61
133.47
128.70
128.19
122.61
122.26
120.41
118.75
116.09
113.72
112.74
111.15
101.38
65.82
60.34
60.09
58.95
56.06
55.31
23.83
13.69
NC
OEt
a'
a
OMe
O
f1 (ppm)

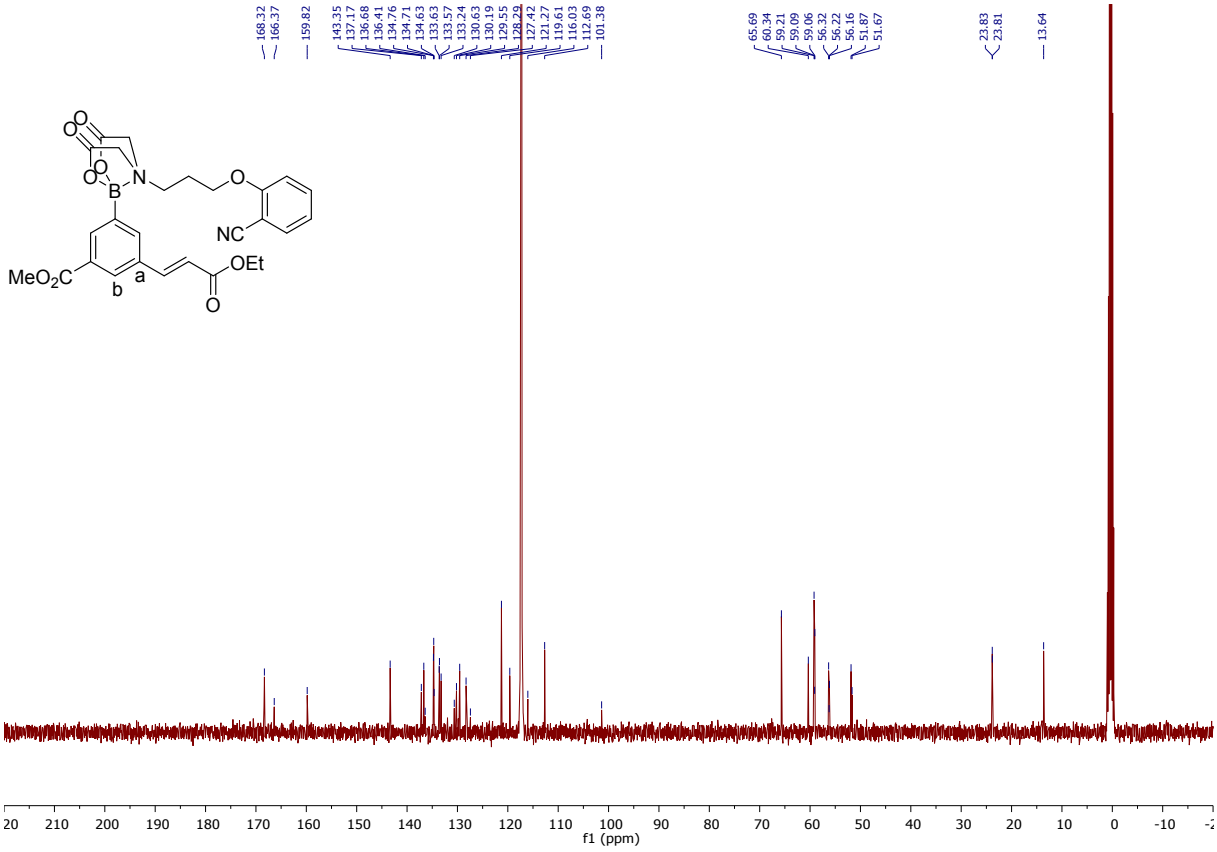

11.90
NC
OEt
a'
a
OMe
O
f1 (ppm)

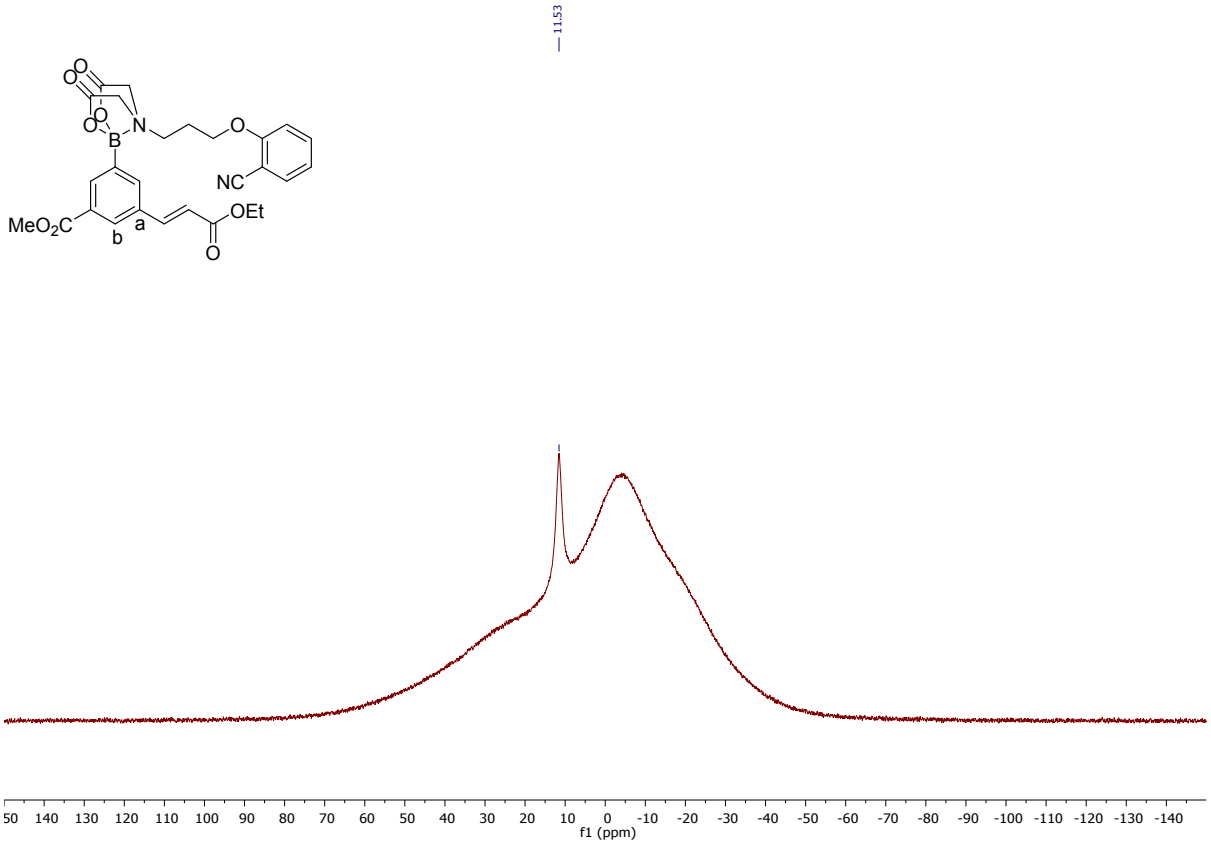

MeO2C
NC
OEt
a
a'
b
a+b
a+a'
f1 (ppm)

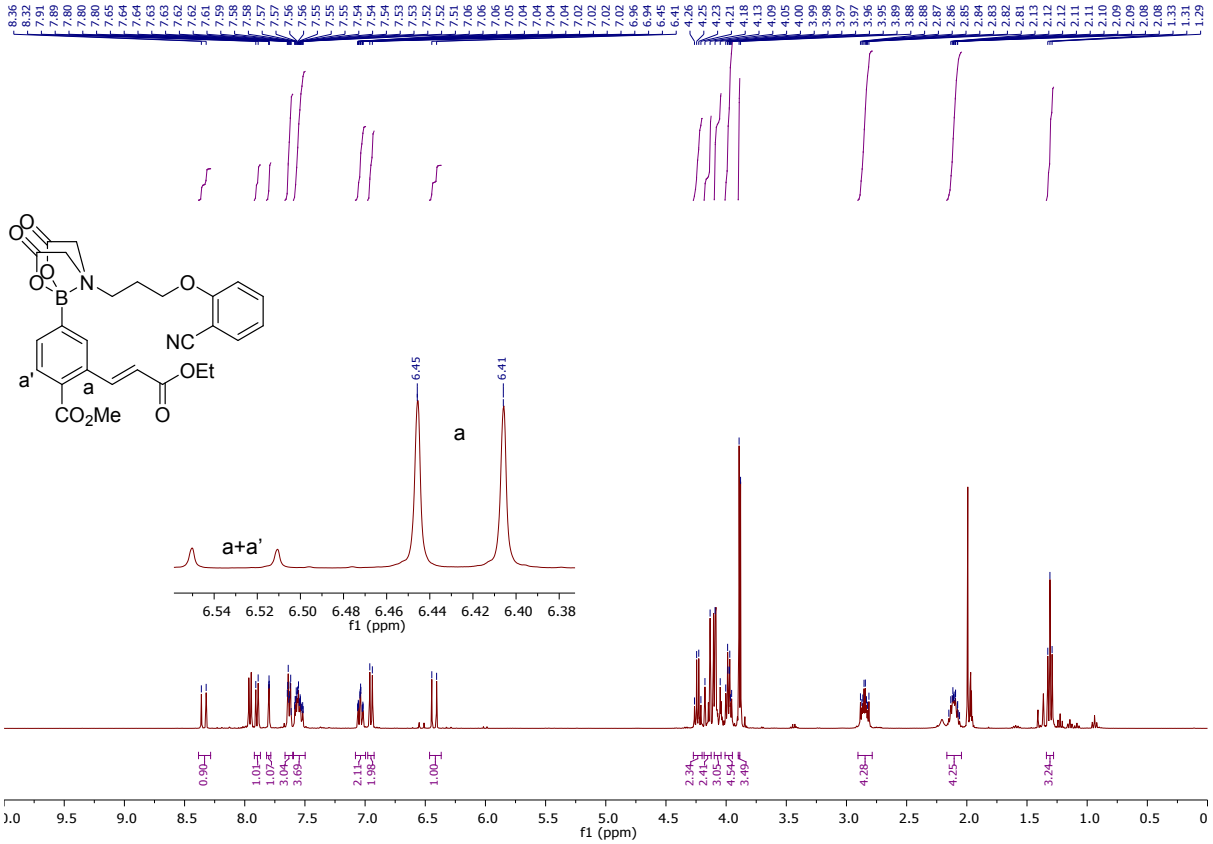

MeO2C
NC
OEt
a
a'
b
f1 (ppm)

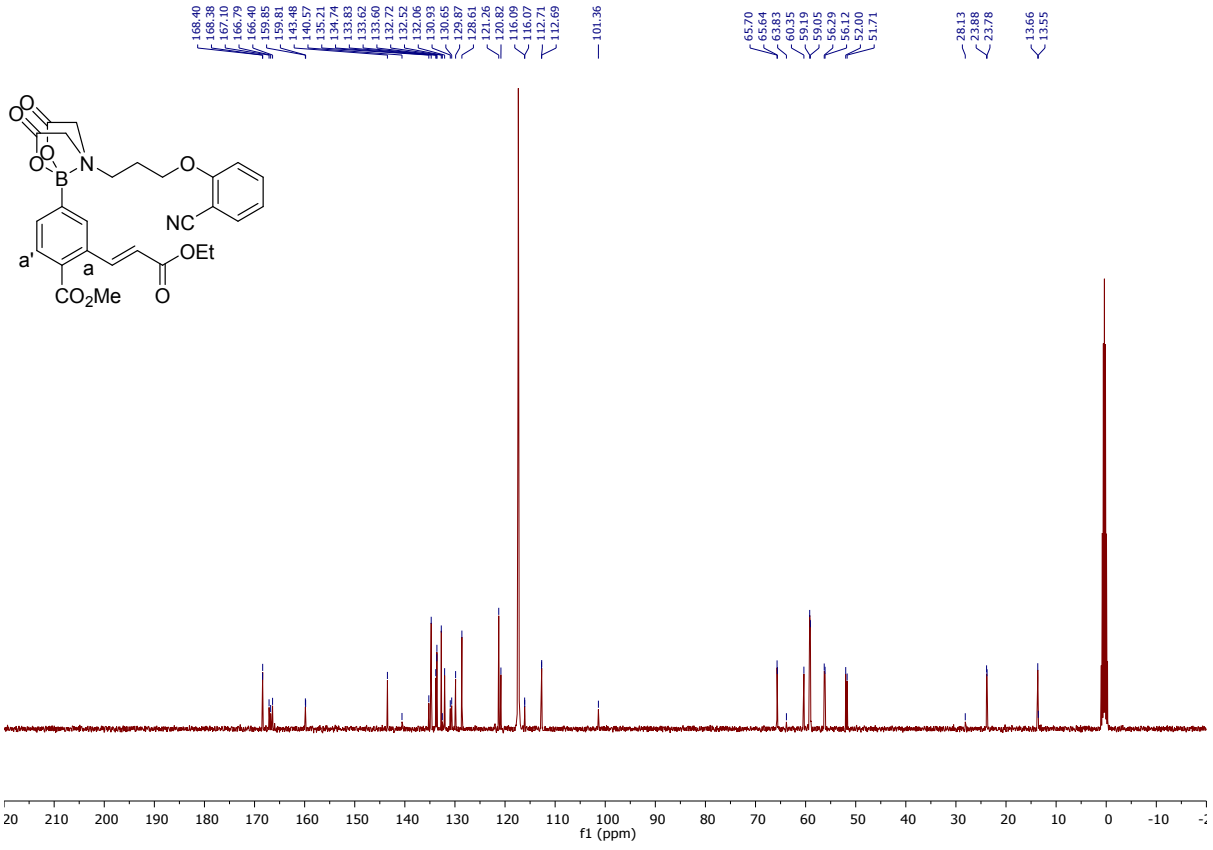

MeO2C
NC
OEt
a'
a
b
12.00
f1 (ppm)

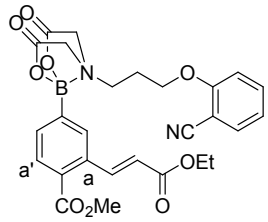

MeO2C
NC
OEt
a
b
6.63
6.59
a
b
f1 (ppm)


168.32
166.37
159.82
143.35
137.17
136.68
136.41
134.76
134.71
134.63
133.63
133.57
133.24
130.63
130.19
129.55
128.29
127.42
121.27
119.61
116.03
112.69
101.38
65.69
60.34
59.21
59.09
59.06
56.32
56.22
56.16
51.87
51.67
23.83
23.81
13.64
O
O
O
B
N
O
NC
MeO2C
a
b
OEt
O
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


11.53
O
O
O
B
N
O
NC
MeO2C
a
b
OEt
O
50 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)


a'
a
CO2Me
OEt
NC
a+a'
6.45
6.41
f1 (ppm)


a'
a
CO2Me
OEt
NC
f1 (ppm)


O
O
O
B
N
O
NC
a'
a
OEt
CO2Me
O

11.38
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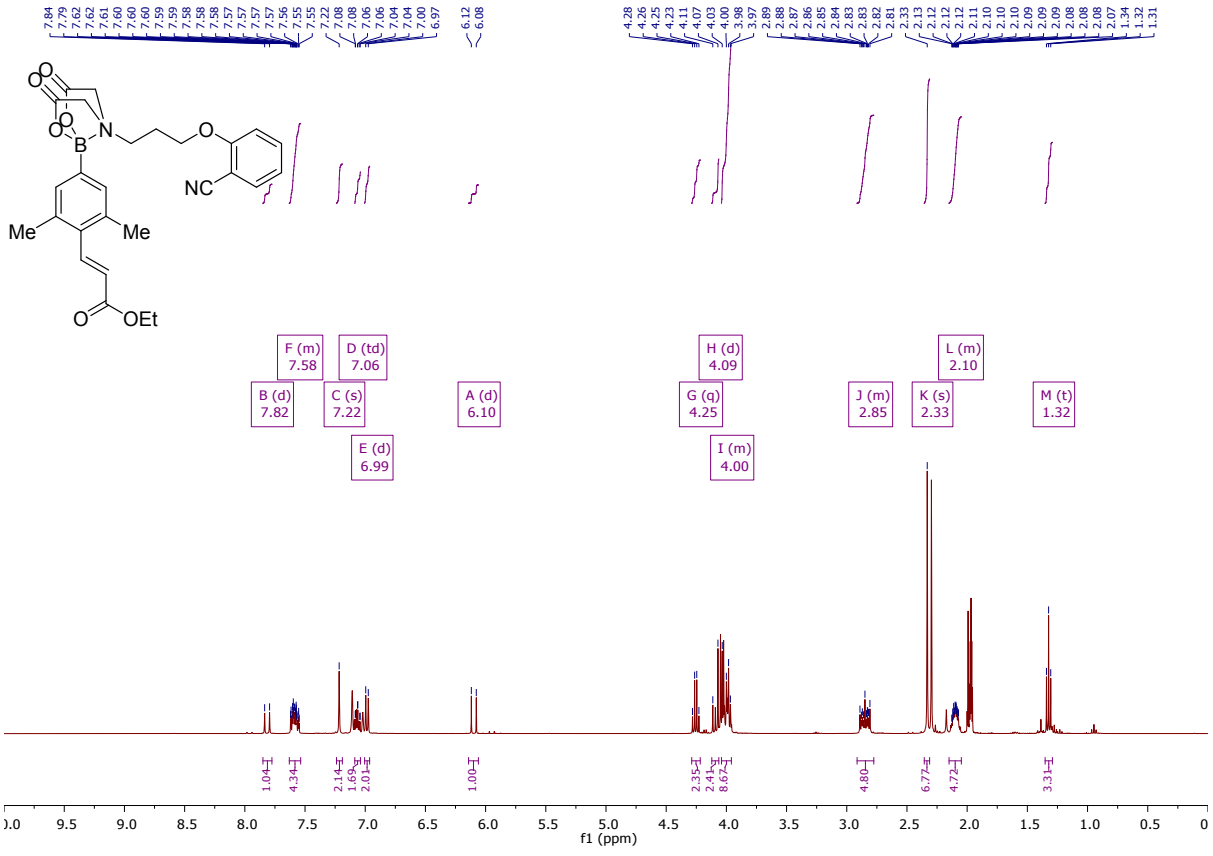
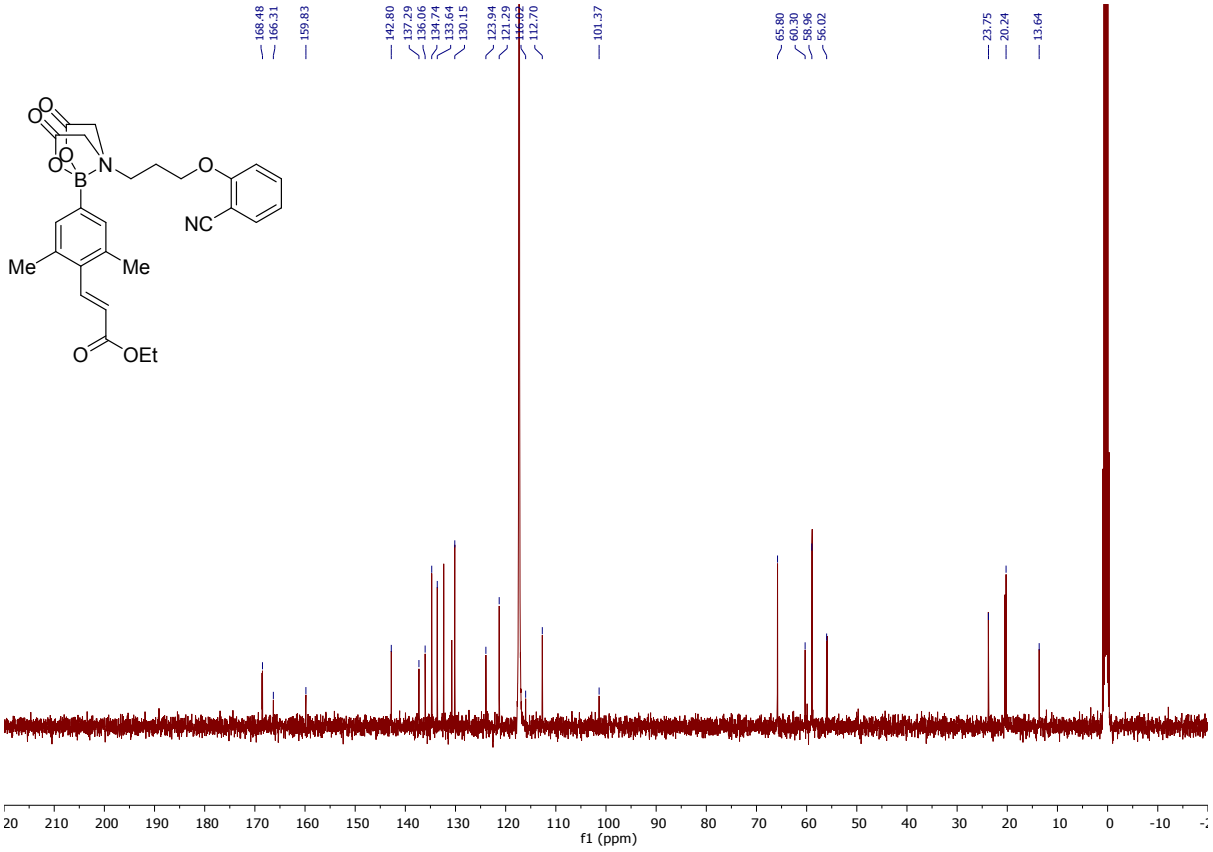
f1 (ppm)


7.84 7.79 7.62 7.62 7.61 7.60 7.60 7.60 7.59 7.59 7.58 7.58 7.57 7.57 7.57 7.57 7.56 7.55 7.55 7.22 7.08 7.08 7.06 7.06 7.04 7.04 7.00 6.97 6.12 6.08
4.28 4.26 4.25 4.23 4.11 4.07 4.03 4.00 3.98 3.97 2.89 2.88 2.87 2.86 2.85 2.84 2.83 2.83 2.82 2.81 2.33 2.13 2.12 2.12 2.11 2.10 2.10 2.09 2.09 2.09 2.08 2.08 2.08 2.07 1.34 1.32 1.31
O
O
O
B
N
O
NC
Me
Me
O
OEt
F (m) 7.58
D (td) 7.06
H (d) 4.09
L (m) 2.10
B (d) 7.82
C (s) 7.22
A (d) 6.10
G (q) 4.25
J (m) 2.85
K (s) 2.33
M (t) 1.32
E (d) 6.99
I (m) 4.00
1.04 4.34 2.14 1.69 2.01 1.00 2.35 2.41 8.67 4.80 6.77 4.72 3.31
0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)


168.48
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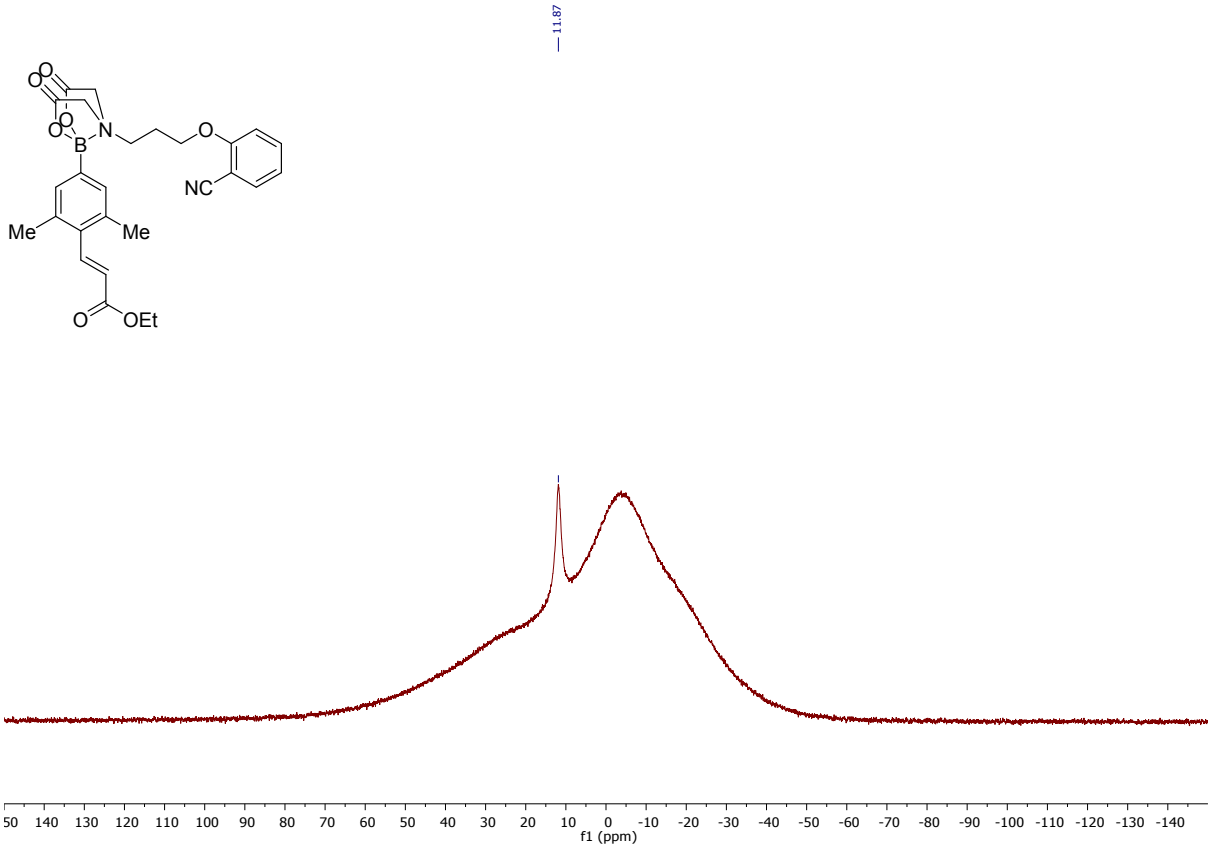
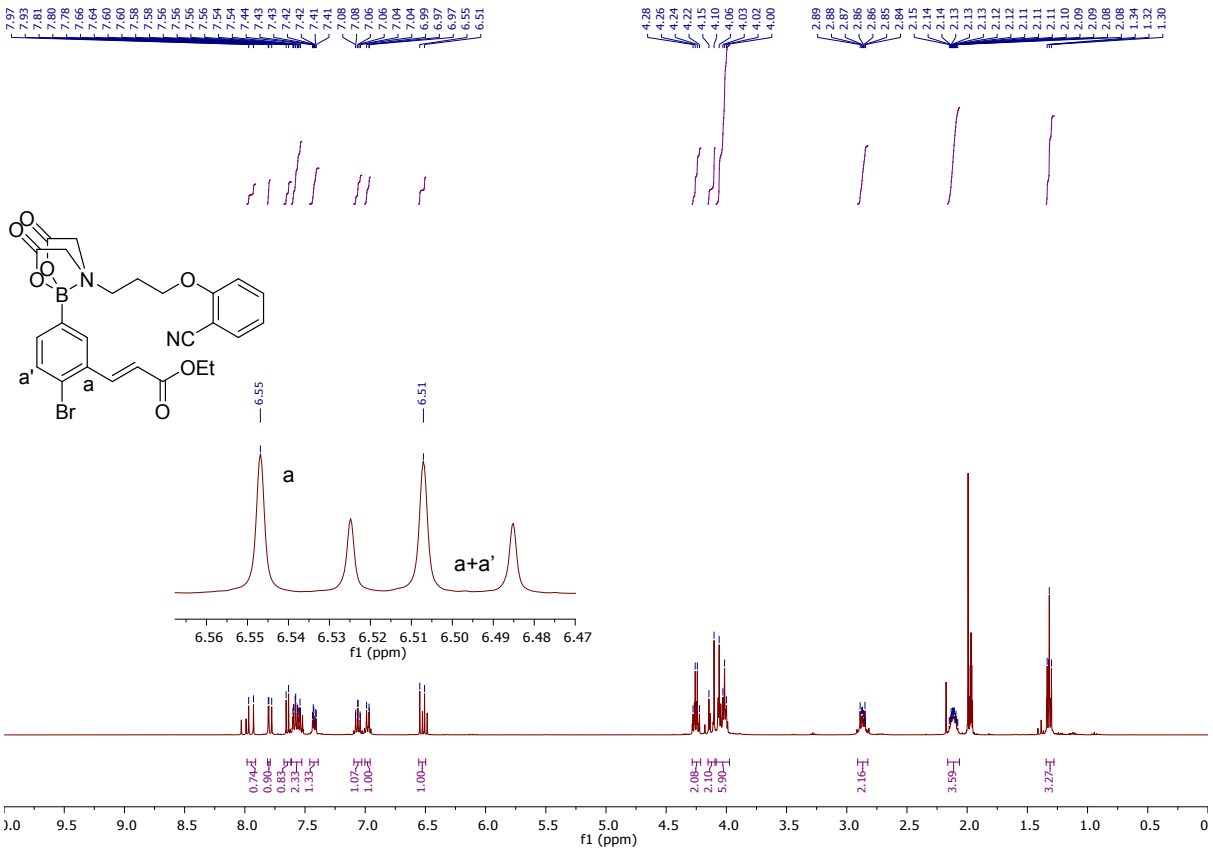
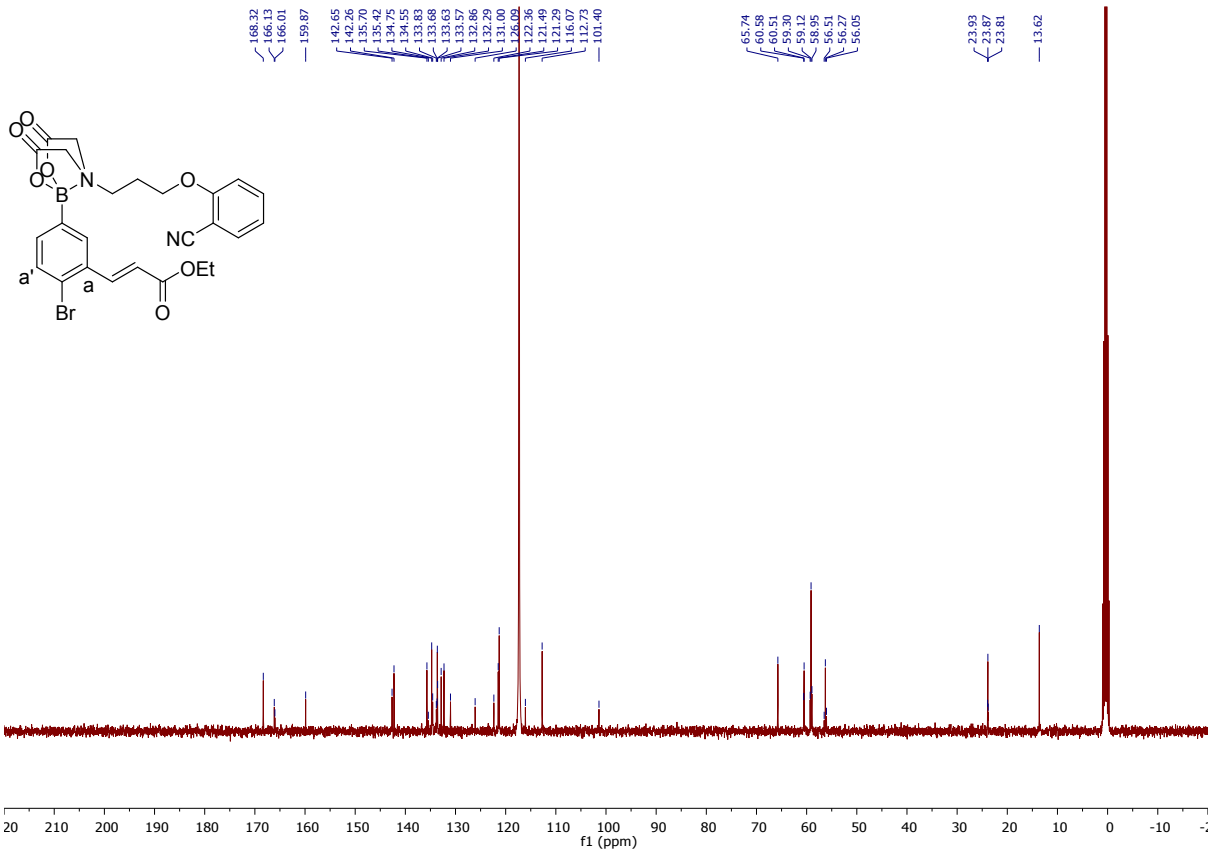
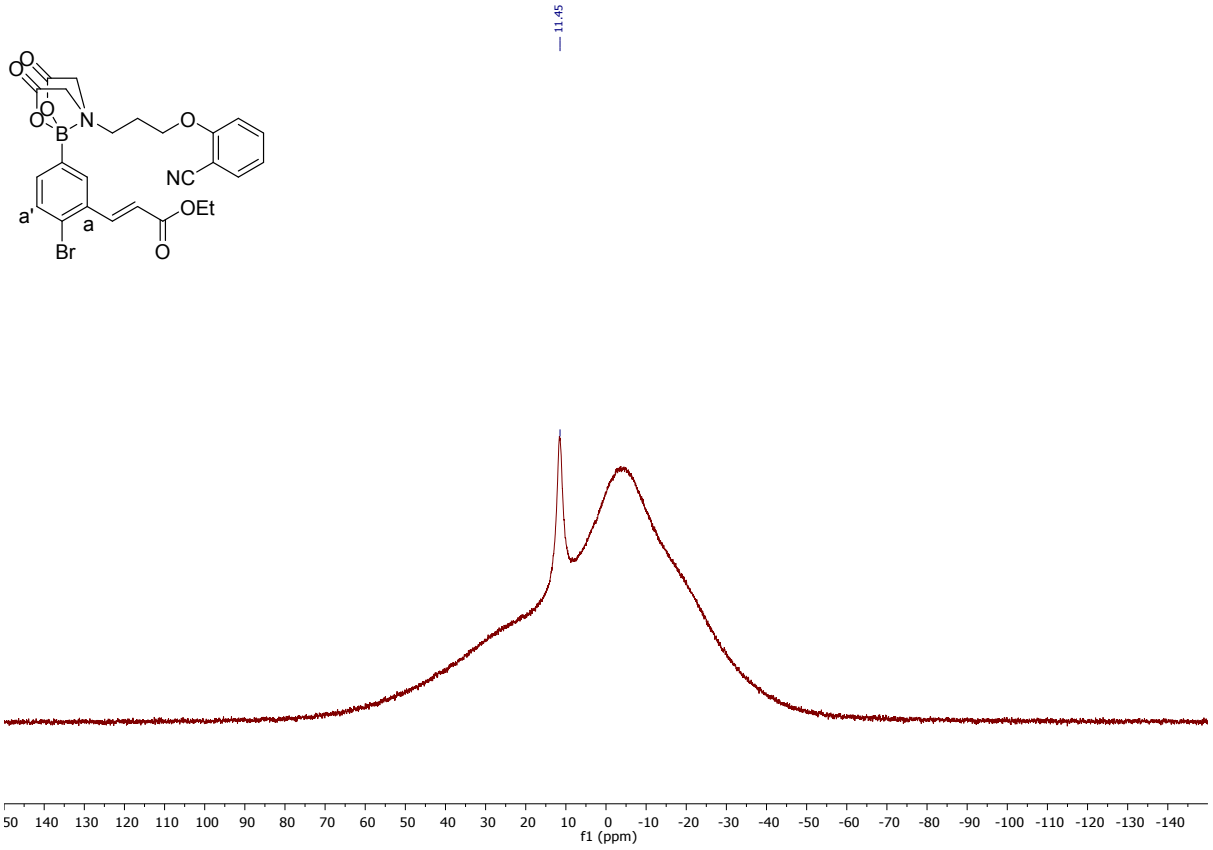
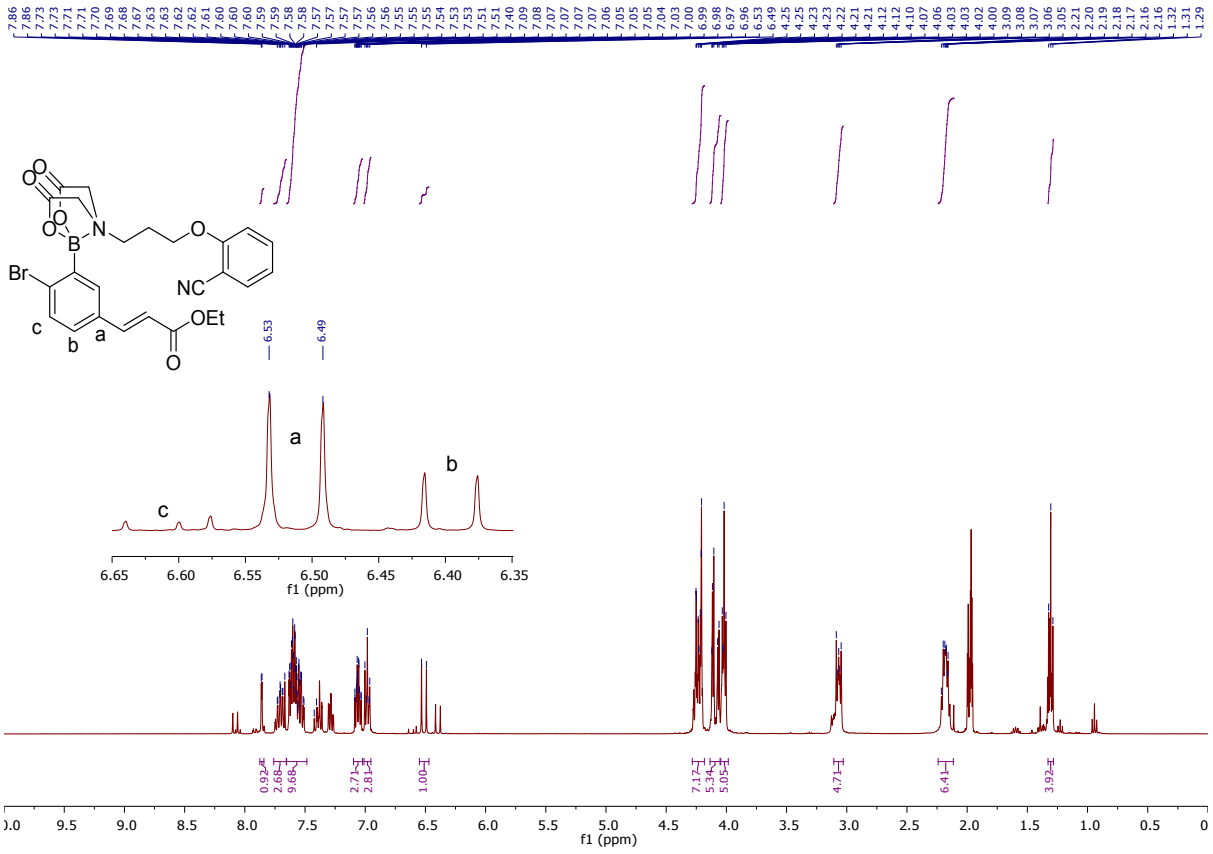
142.80
137.29
136.06
134.74
133.64
130.15
123.94
121.29
116.02
112.70
101.37
65.80
60.30
58.96
56.02
23.75
20.24
13.64
O
O
O
B
N
O
NC
Me
Me
O
OEt
f1 (ppm)

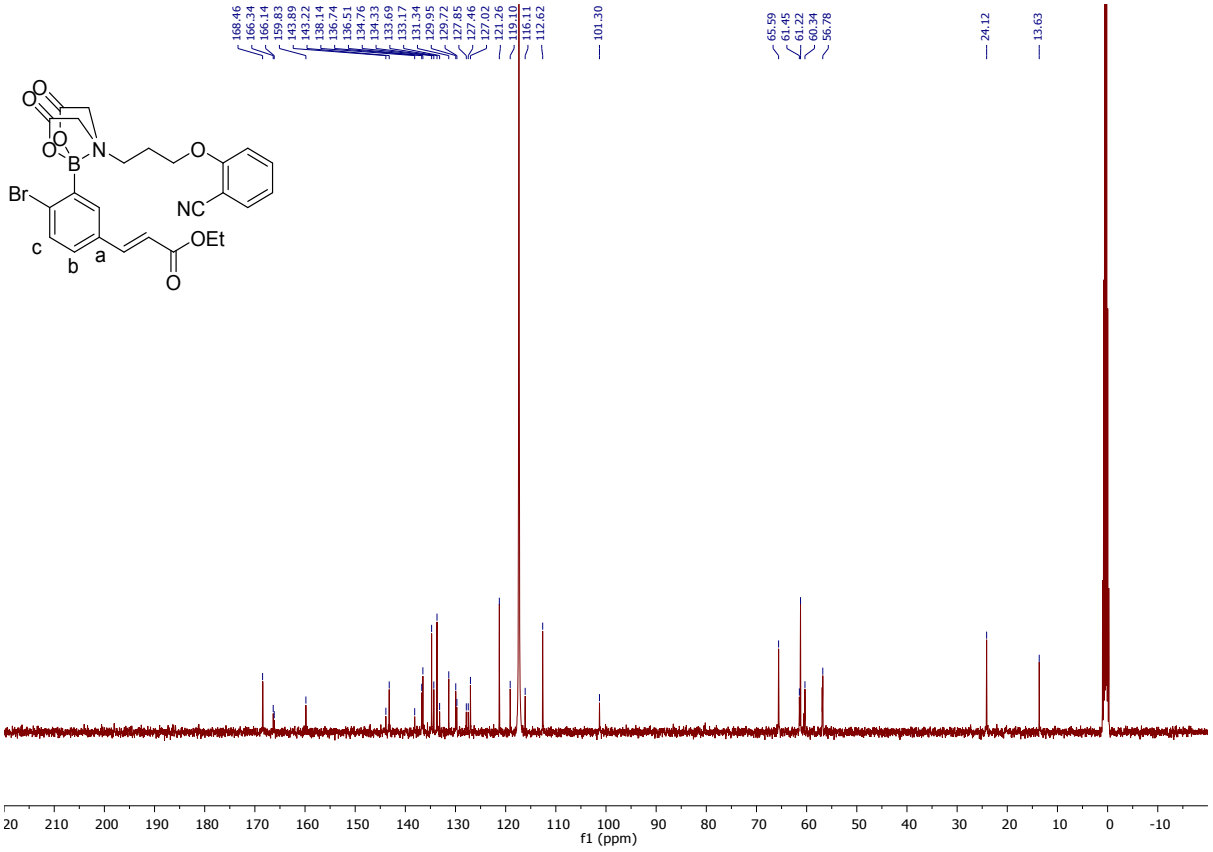

11.87
O
O
O
B
N
O
NC
Me
Me
O
OEt
f1 (ppm)


a
a+a'
f1 (ppm)


f1 (ppm)


11.45
f1 (ppm)


6.53
6.49
a
b
c
f1 (ppm)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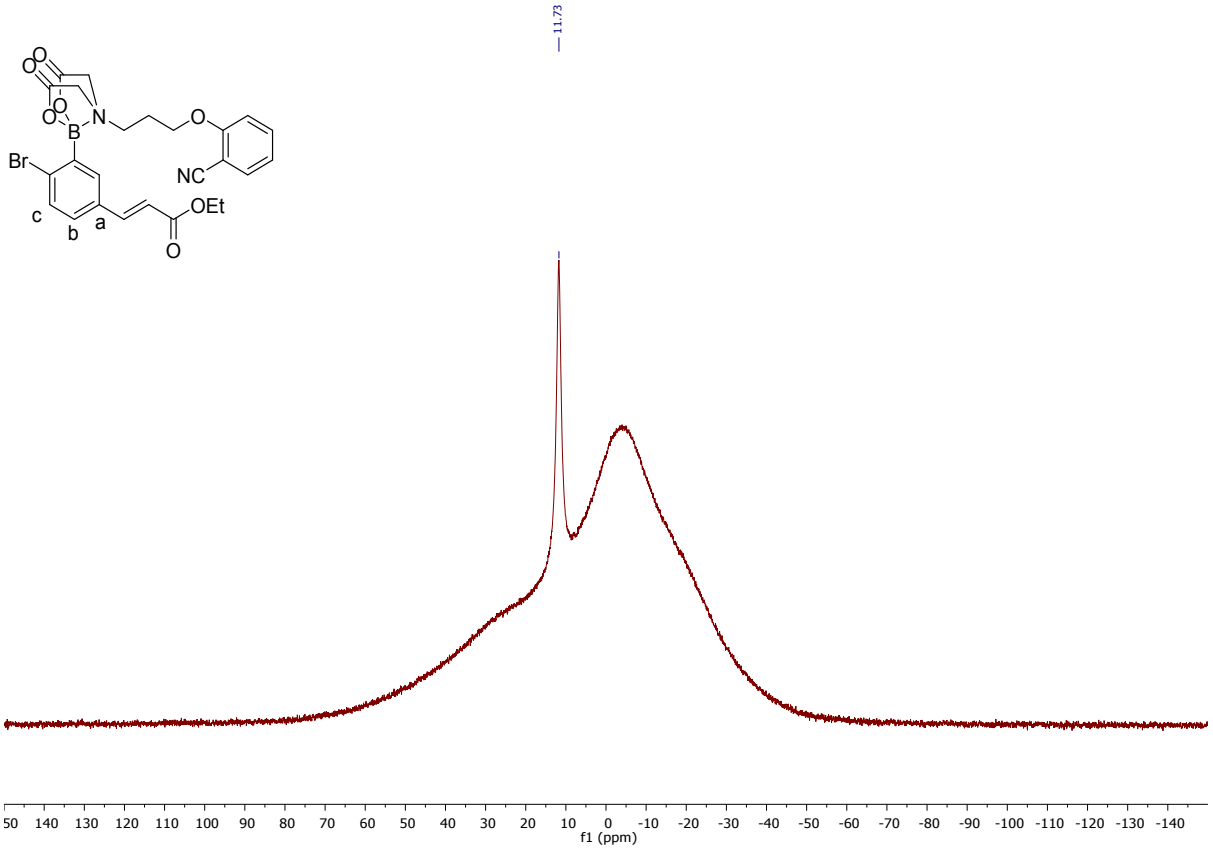
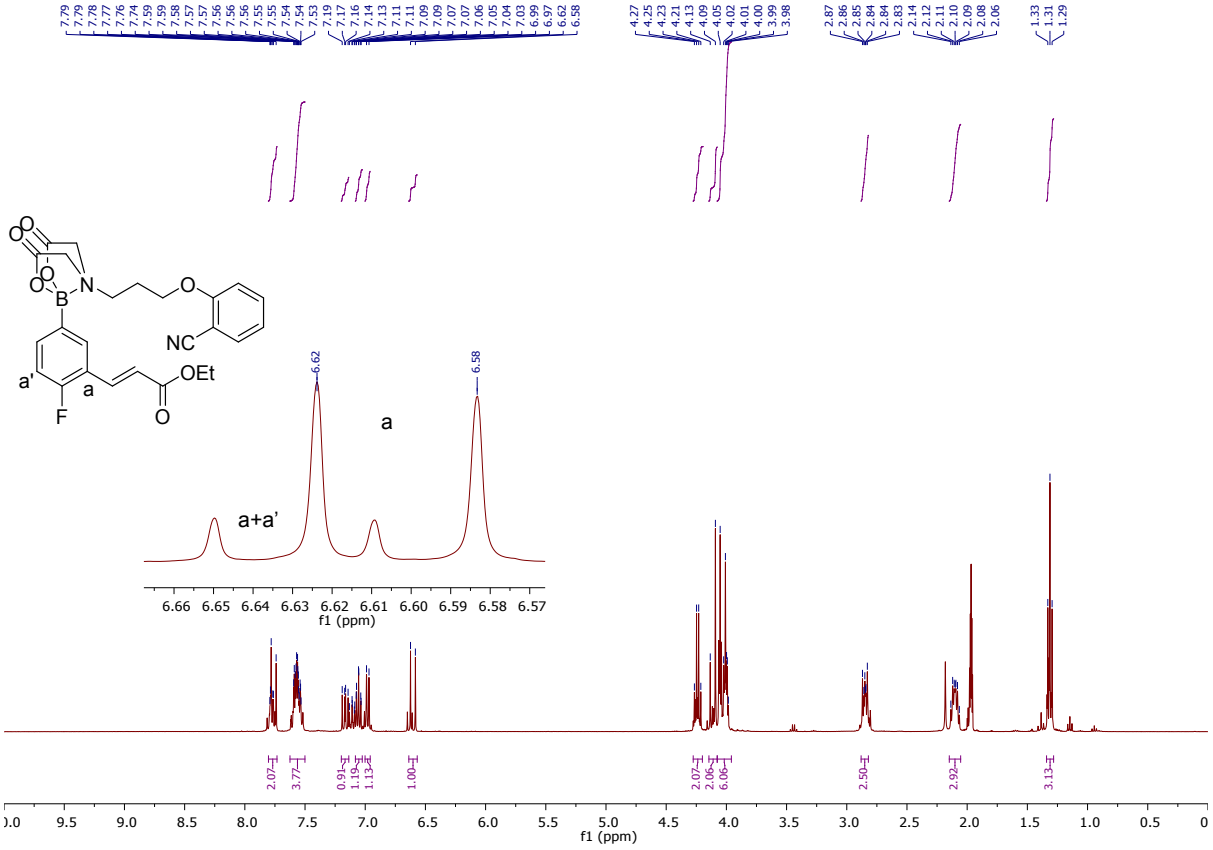
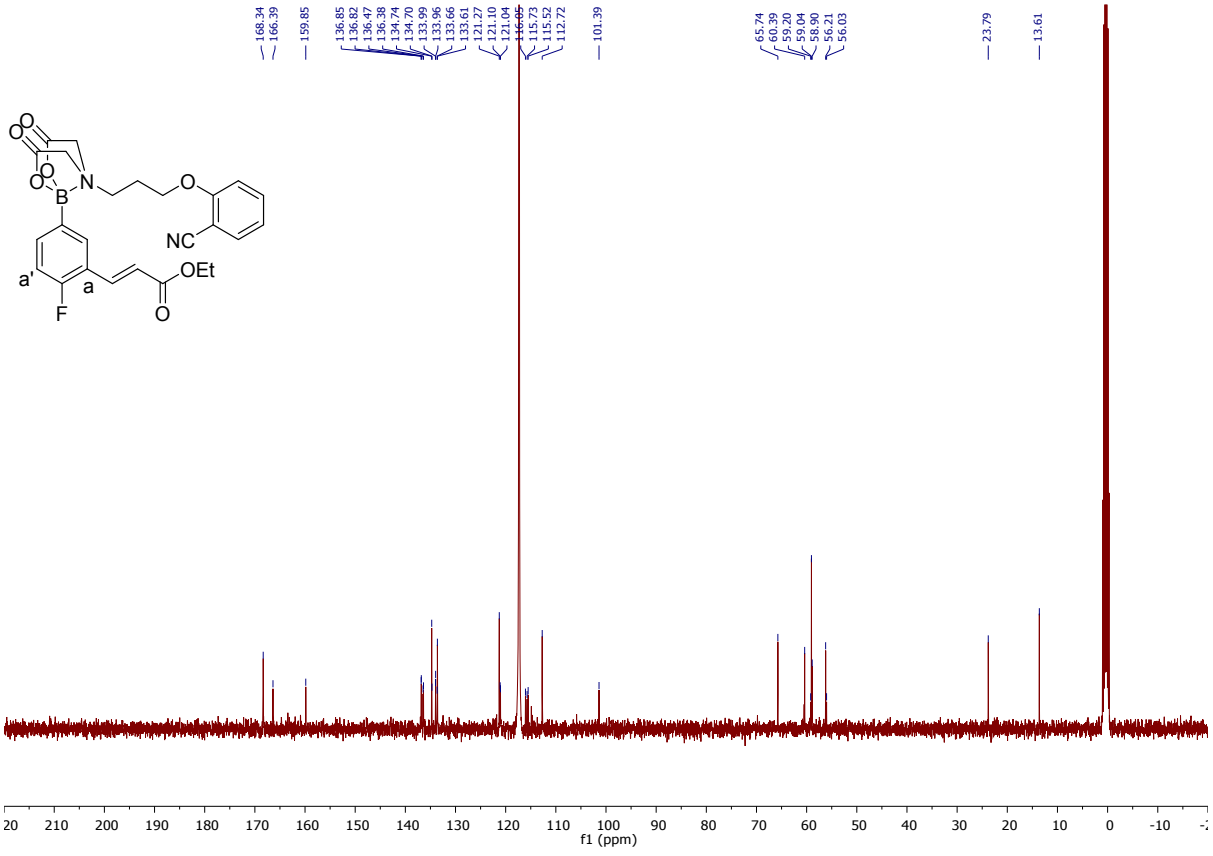
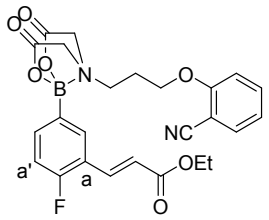
166.14
159.83
143.89
143.22
138.14
136.74
136.51
134.76
134.33
133.69
133.17
131.34
129.95
129.72
127.85
127.46
127.02
121.26
119.10
116.11
112.62
101.30
65.59
61.45
61.22
60.34
56.78
24.12
13.63
O
O
O
B
N
O
Br
NC
OEt
O
c
b
a
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

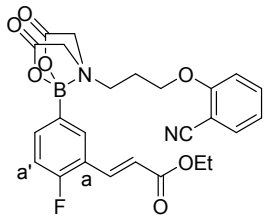

11.73
O
O
O
B
N
O
Br
NC
OEt
O
c
b
a
50 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)


a
a+a'
f1 (ppm)
f1 (ppm)

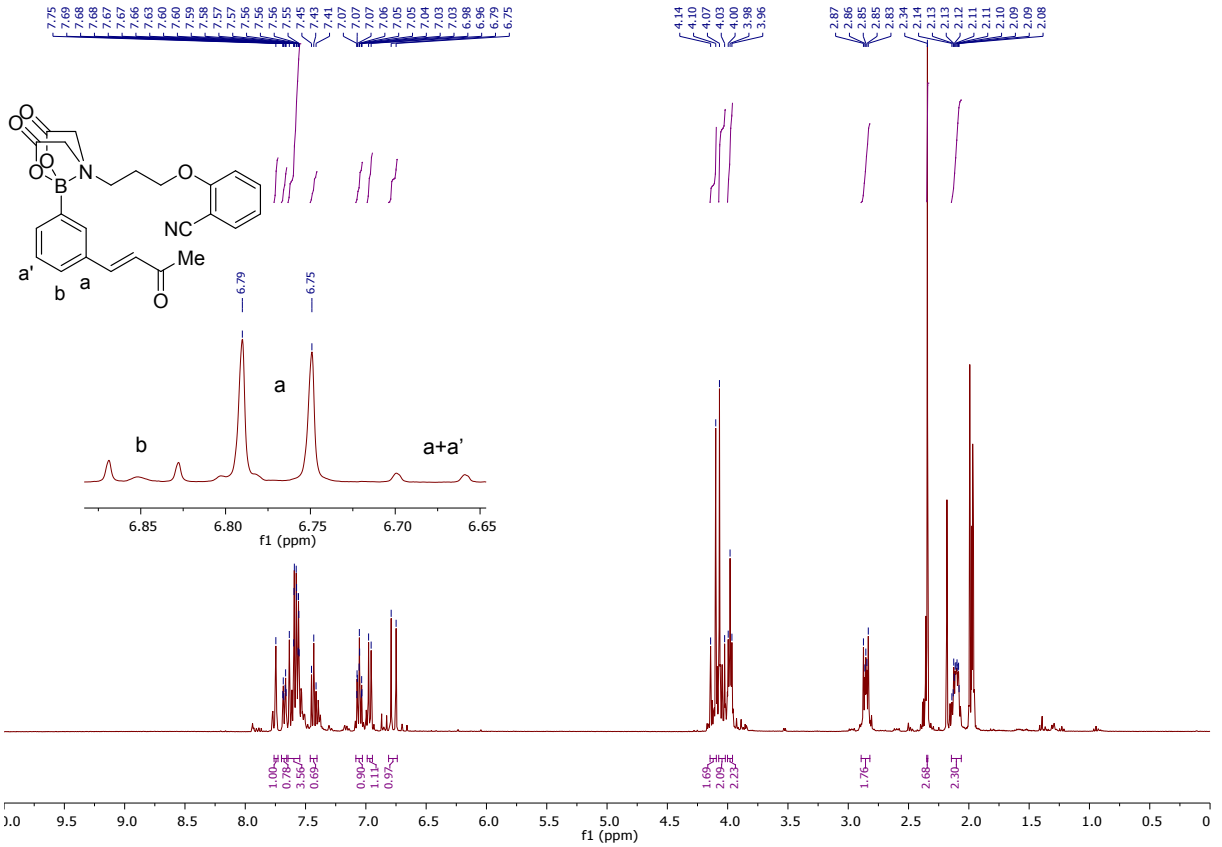

f1 (ppm)
f1 (ppm)

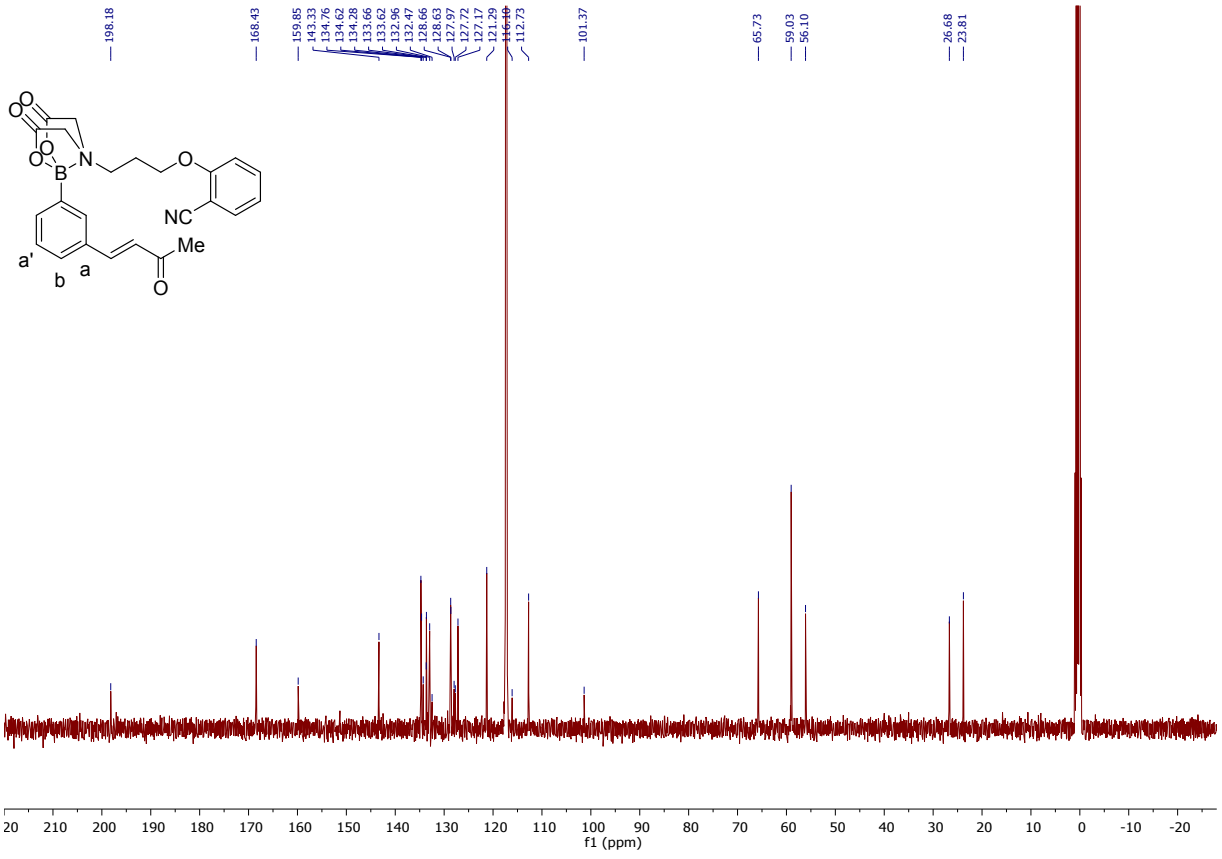

O
O
O
B
N
O
NC
OEt
a'
a
F
O

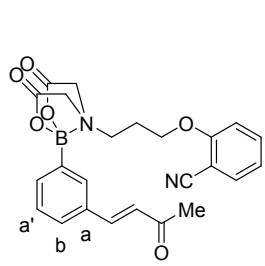
11.52
50 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)


O
O
O
B
N
O
NC
OEt
a'
a
F
O

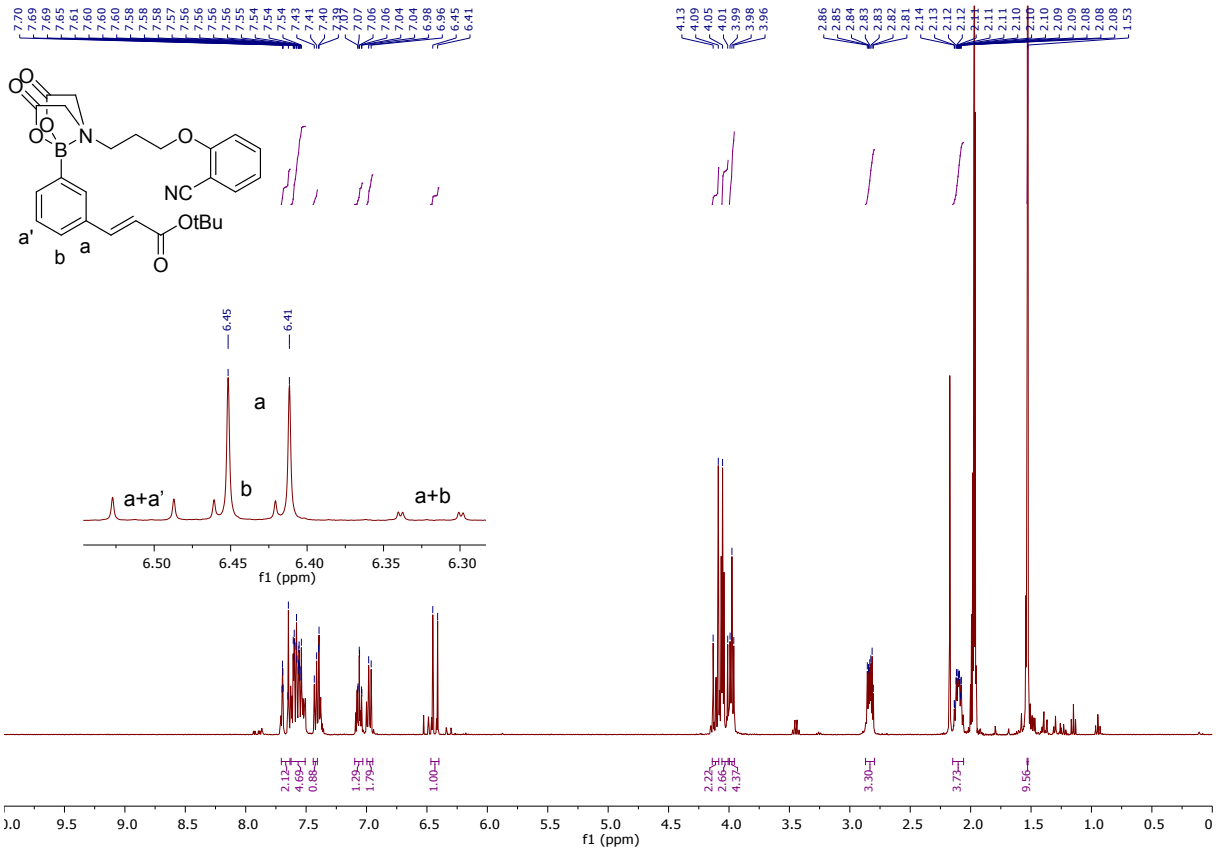
-115.89
-115.91
-115.93
-115.94
-115.96
A (dt)
-115.93
1.00
0 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

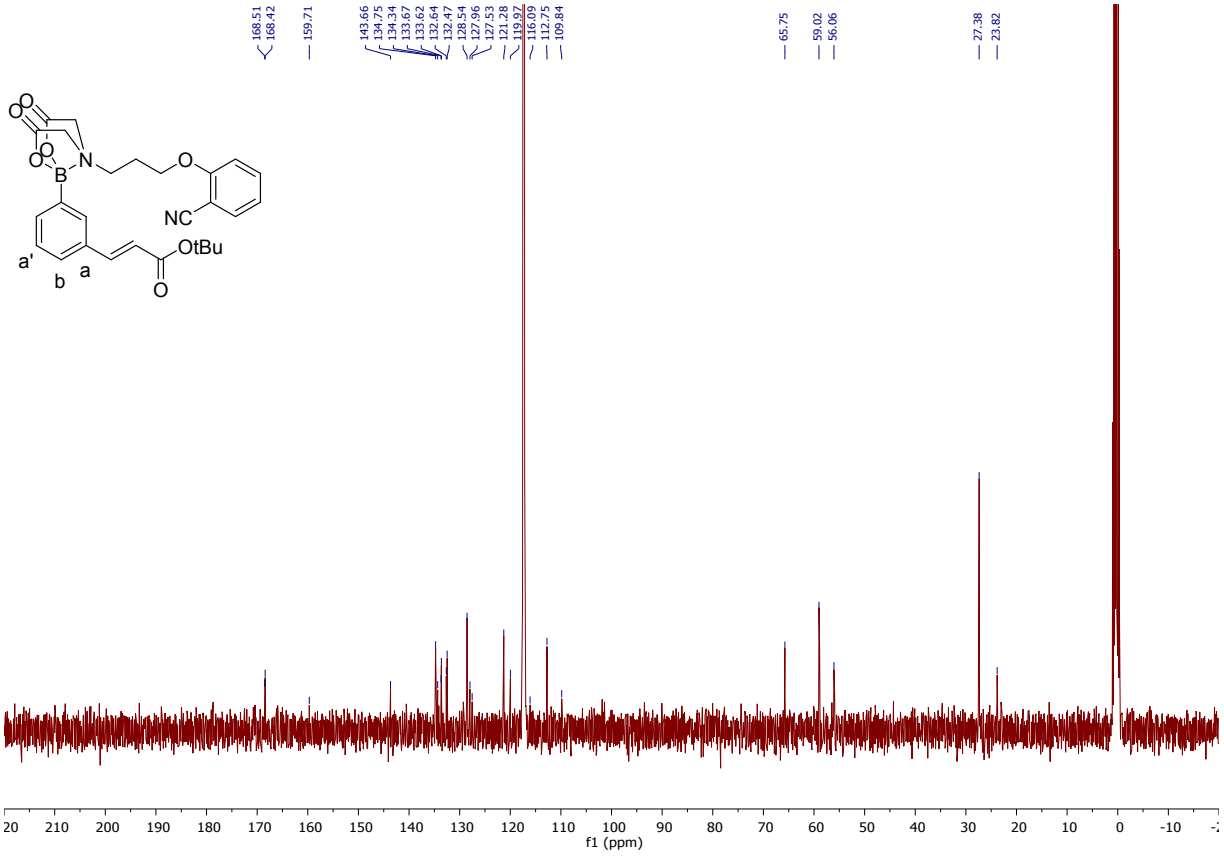

7.75 7.69 7.68 7.68 7.67 7.67 7.66 7.63 7.60 7.60 7.59 7.58 7.57 7.57 7.56 7.56 7.56 7.55 7.45 7.43 7.41 7.07 7.07 7.07 7.06 7.05 7.04 7.03 7.03 6.98 6.96 6.79 6.75
4.14 4.10 4.07 4.03 4.00 3.98 3.96
2.87 2.86 2.85 2.85 2.83 2.34 2.14 2.13 2.13 2.12 2.11 2.11 2.10 2.09 2.09 2.08
O
O
O
B
N
O
NC
Me
O
a'
b
a
6.79
6.75
a
b
a+a'
6.85 6.80 6.75 6.70 6.65
f1 (ppm)
1.00 0.78 3.56 0.69 0.90 1.11 0.97 1.69 2.09 2.23 1.76 2.68 2.30
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

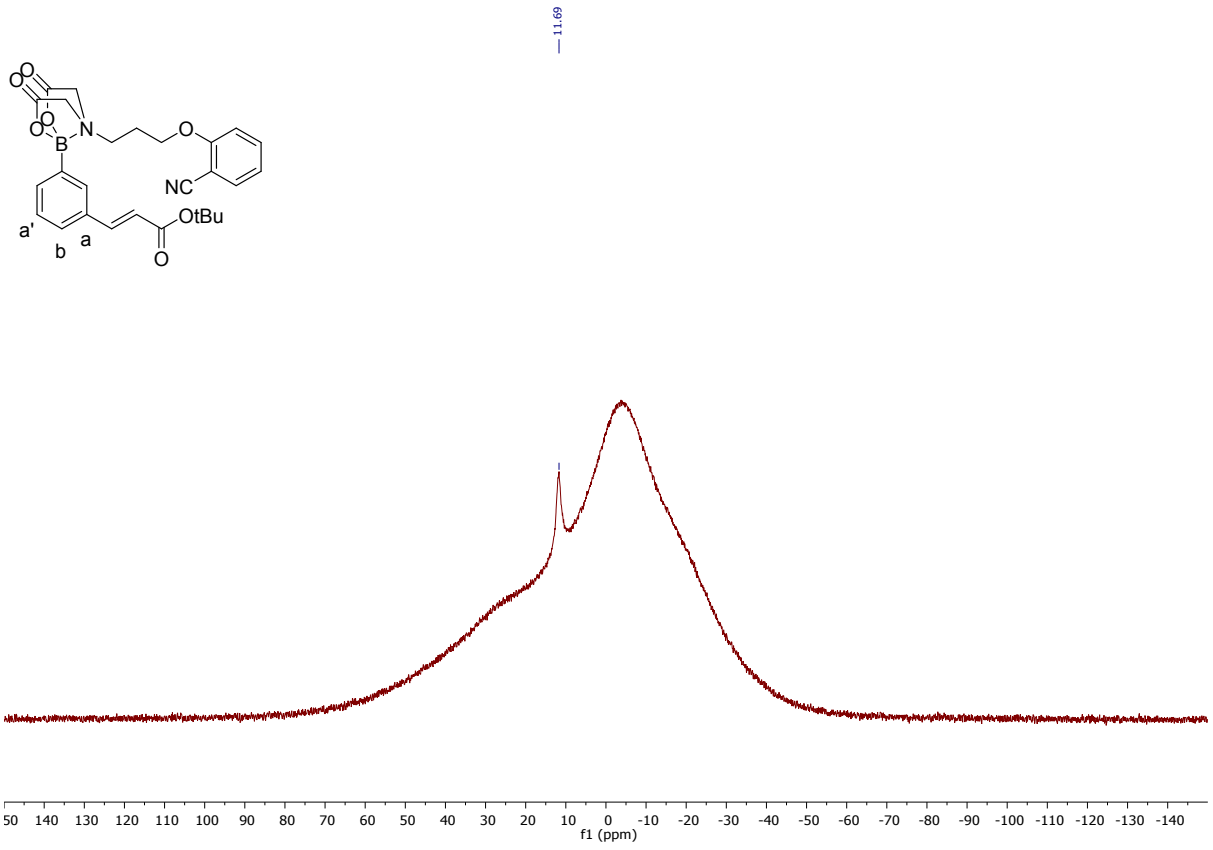

198.18
168.43
159.85 143.33 134.76 134.62 134.28 133.66 133.62 132.96 132.47 128.66 128.63 127.97 127.72 127.17 121.29 116.10 112.73
101.37
65.73
59.03
56.10
26.68
23.81
O
O
O
B
N
O
NC
Me
O
a'
b
a
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

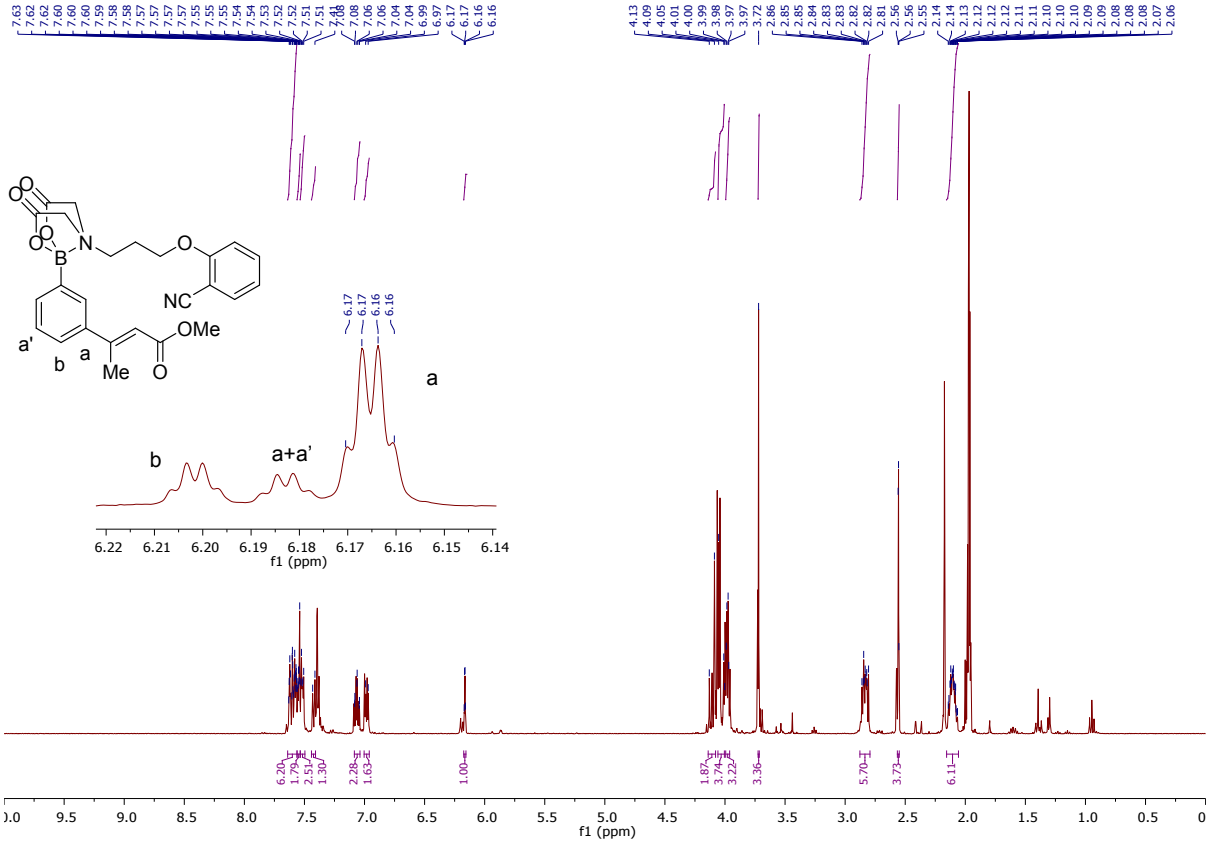

O
O
O
B
N
O
NC
Me
a'
b
a
O

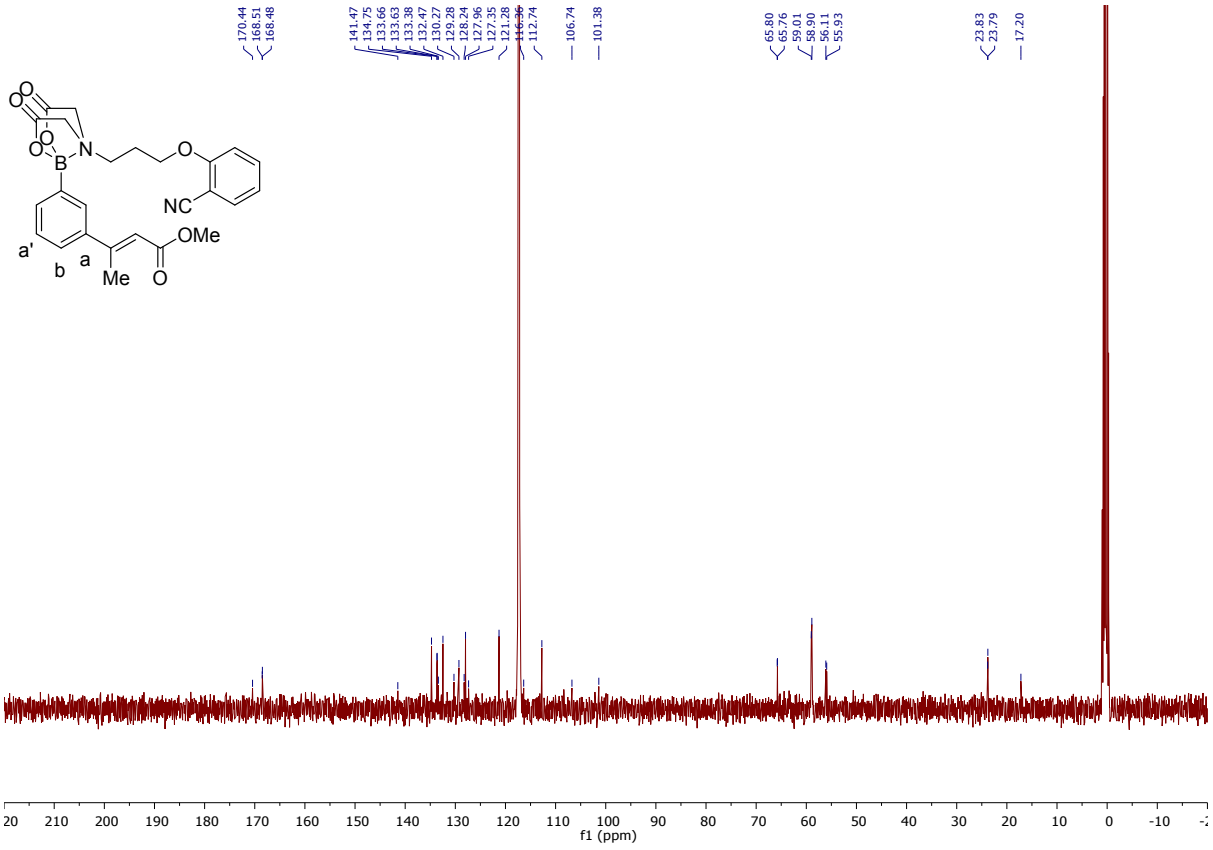
11.59
50 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)

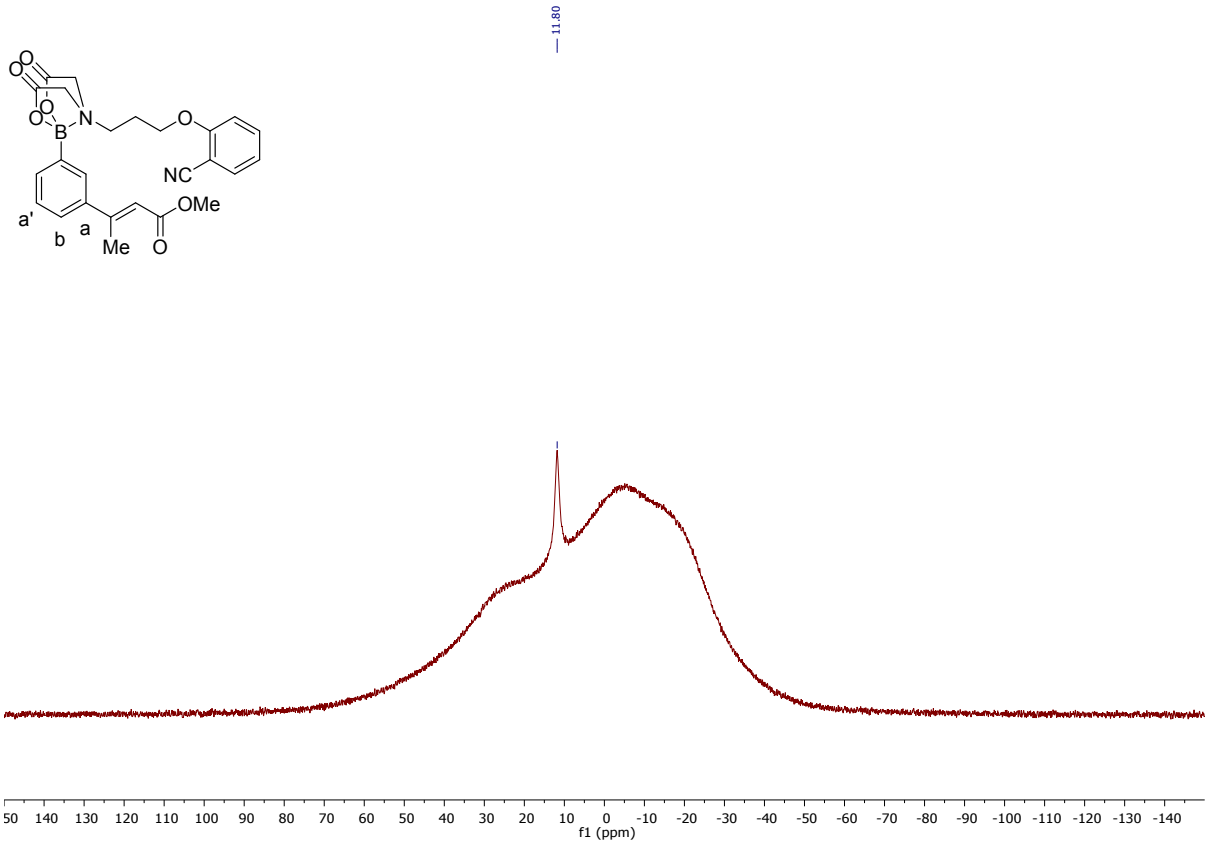

7.70 7.69 7.69 7.65 7.61 7.60 7.60 7.60 7.58 7.58 7.58 7.57 7.56 7.56 7.56 7.56 7.55 7.54 7.54 7.54 7.43 7.41 7.40 7.39 7.37 7.07 7.06 7.06 7.04 7.04 6.98 6.96 6.45 6.41
4.13 4.09 4.05 4.01 3.99 3.98 3.96
2.86 2.85 2.84 2.83 2.83 2.82 2.81 2.14 2.13 2.12 2.12 2.11 2.11 2.11 2.10 2.10 2.09 2.09 2.08 2.08 2.08 1.53
O
O
O
B
N
O
NC
OtBu
a'
b
a
O
6.45
6.41
a
b
a+a'
a+b
6.50 6.45 6.40 6.35 6.30
f1 (ppm)
2.12 4.69 0.88 1.29 1.79 1.00 2.22 2.66 4.37 3.30 3.73 9.56
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

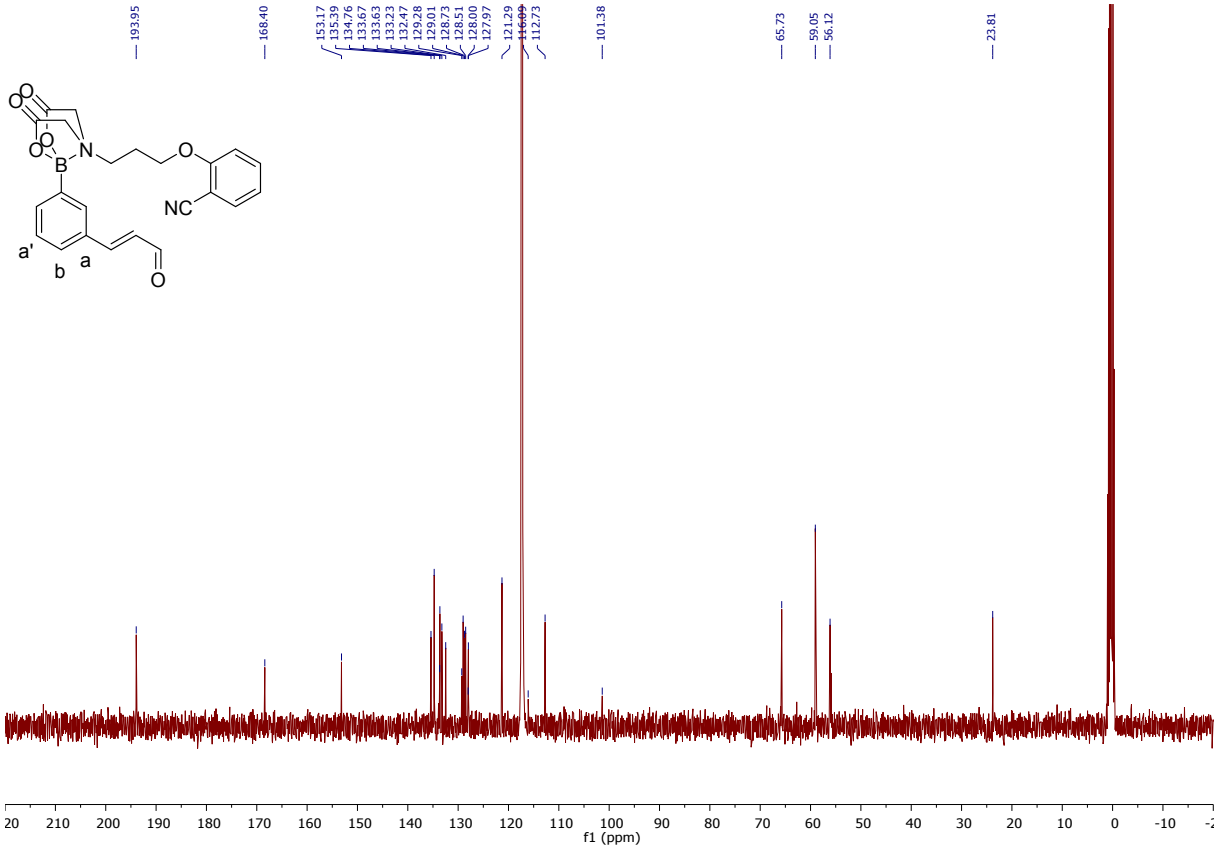

168.51
168.42
159.71
143.66
134.75
134.34
133.67
133.62
132.64
132.47
128.54
127.96
127.53
121.28
119.97
116.09
112.75
109.84
65.75
59.02
56.06
27.38
23.82
O
O
O
B
N
O
NC
OtBu
a'
b
a
O
f1 (ppm)

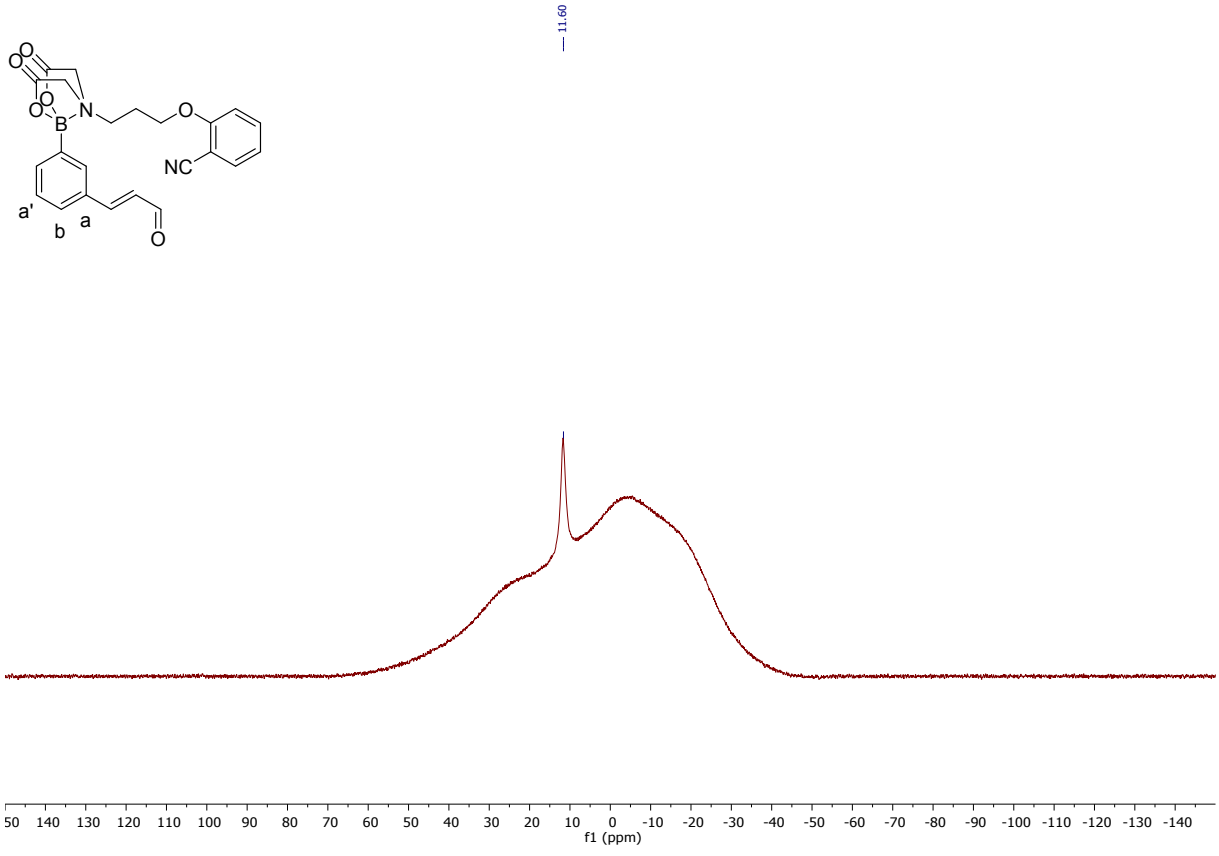

11.69
O
O
O
B
N
O
NC
OtBu
a'
b
a
O
f1 (ppm)

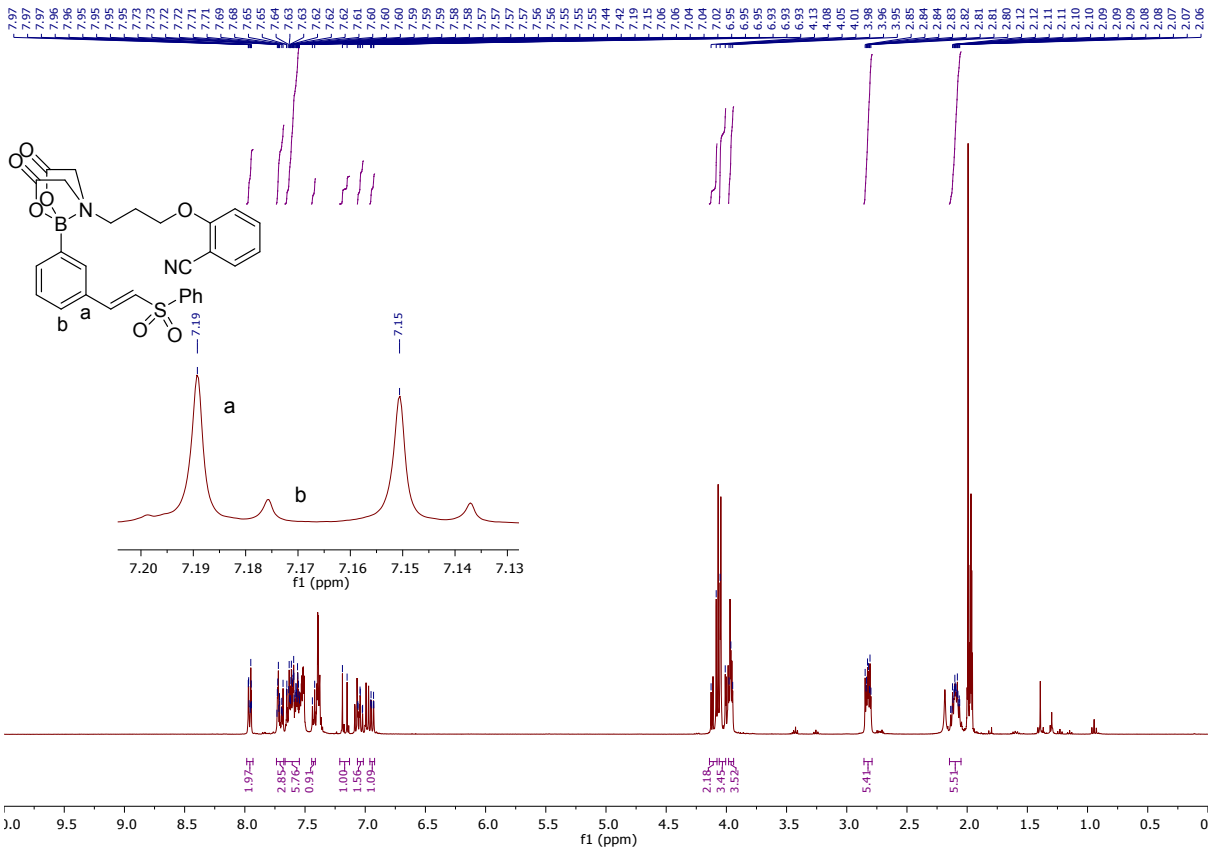

NC
OMe
Me
a'
b
a
a+a'
f1 (ppm)

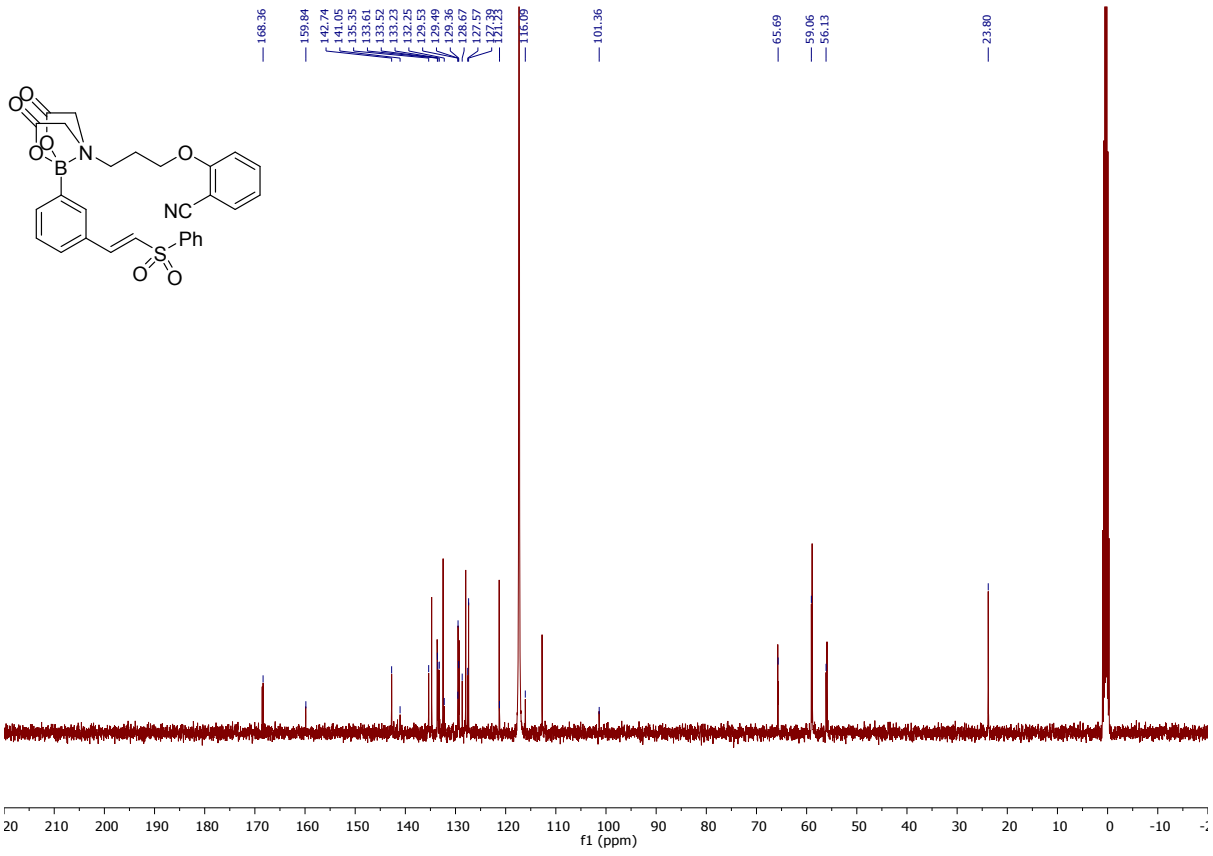

NC
OMe
Me
a'
b
a
f1 (ppm)

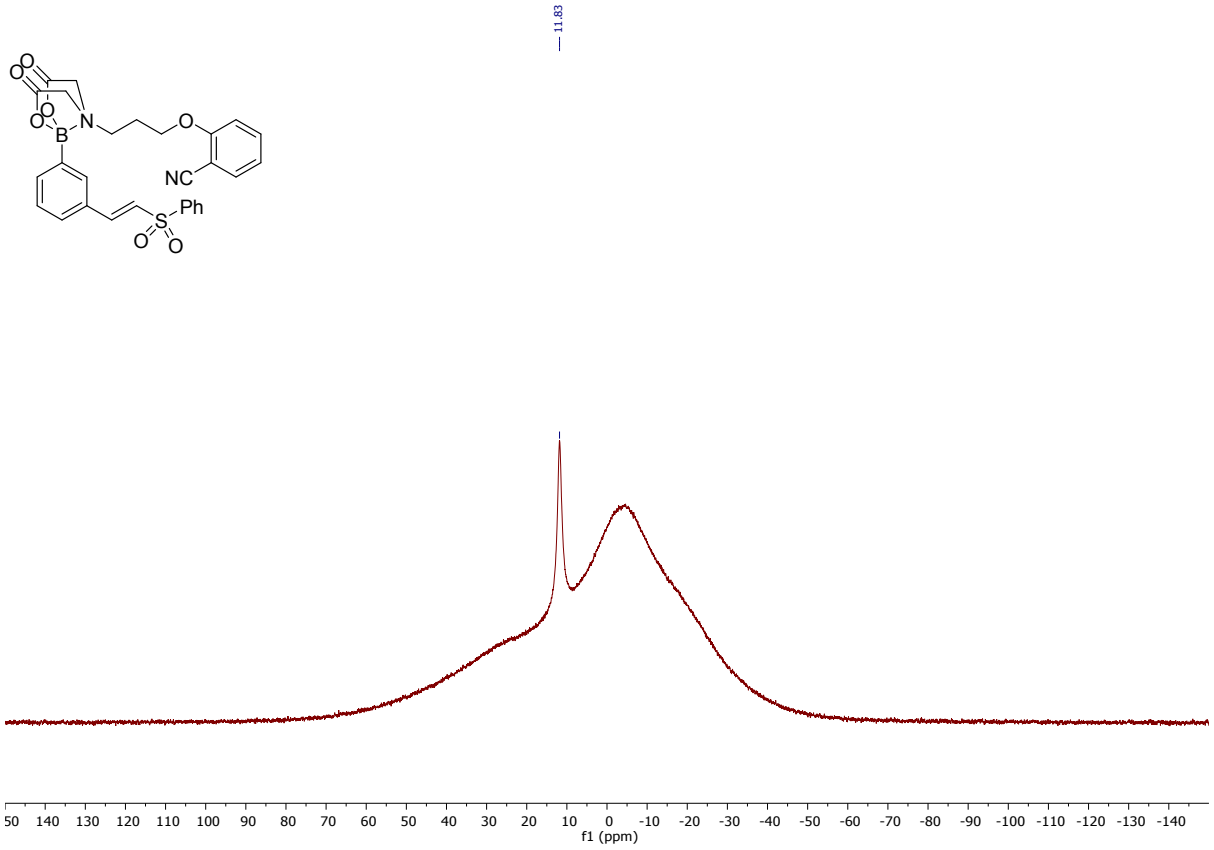

11.80
f1 (ppm)
9.70
9.68
7.78
7.77
7.77
7.72
7.71
7.70
7.70
7.69
7.68
7.64
7.61
7.60
7.59
7.58
7.58
7.57
7.56
7.56
7.55
7.55
7.49
7.47
7.45
7.08
7.07
7.07
7.06
7.05
7.05
7.04
7.04
7.03
6.98
6.96
6.80
6.78
6.76
6.74
4.14
4.10
4.07
4.03
4.00
3.99
3.97
2.88
2.87
2.86
2.85
2.84
2.84
2.13
2.12
2.11
2.11
2.10
2.09
2.09
2.09
2.08
6.80
6.78
6.76
6.74
a
b
6.88 6.86 6.84 6.82 6.80 6.78 6.76 6.74 6.72
f1 (ppm)
0.94
0.77
0.75
1.02
1.75
0.70
1.07
1.25
1.00
1.83
3.03
2.90
1.83
2.66
f1 (ppm)

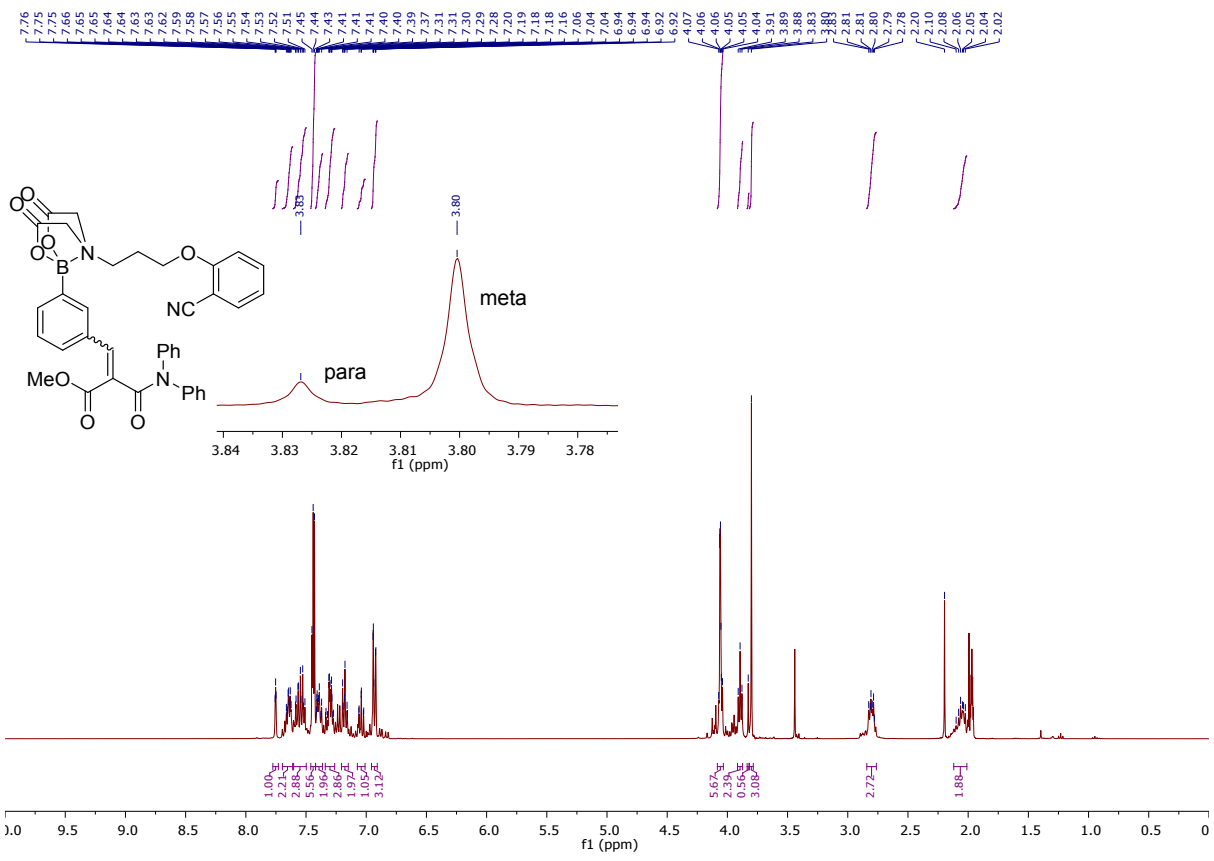

193.95
168.40
153.17
135.39
134.76
133.67
133.63
133.23
132.47
129.28
129.01
128.73
128.51
128.00
127.97
121.29
116.69
112.73
101.38
65.73
59.05
56.12
23.81
O
O
O
B
N
O
NC
a'
b
a
O
f1 (ppm)

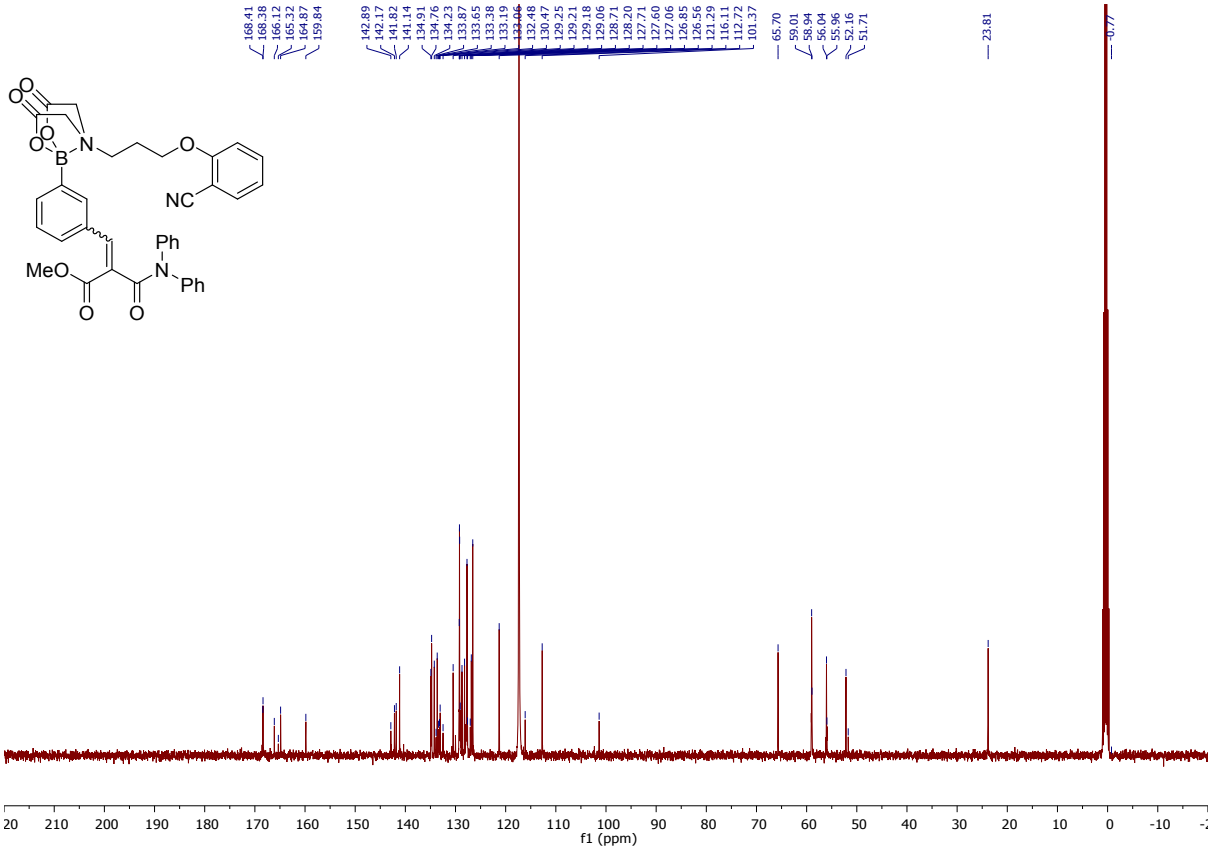

11.60
O
O
O
B
N
O
NC
a'
b
a
O
f1 (ppm)

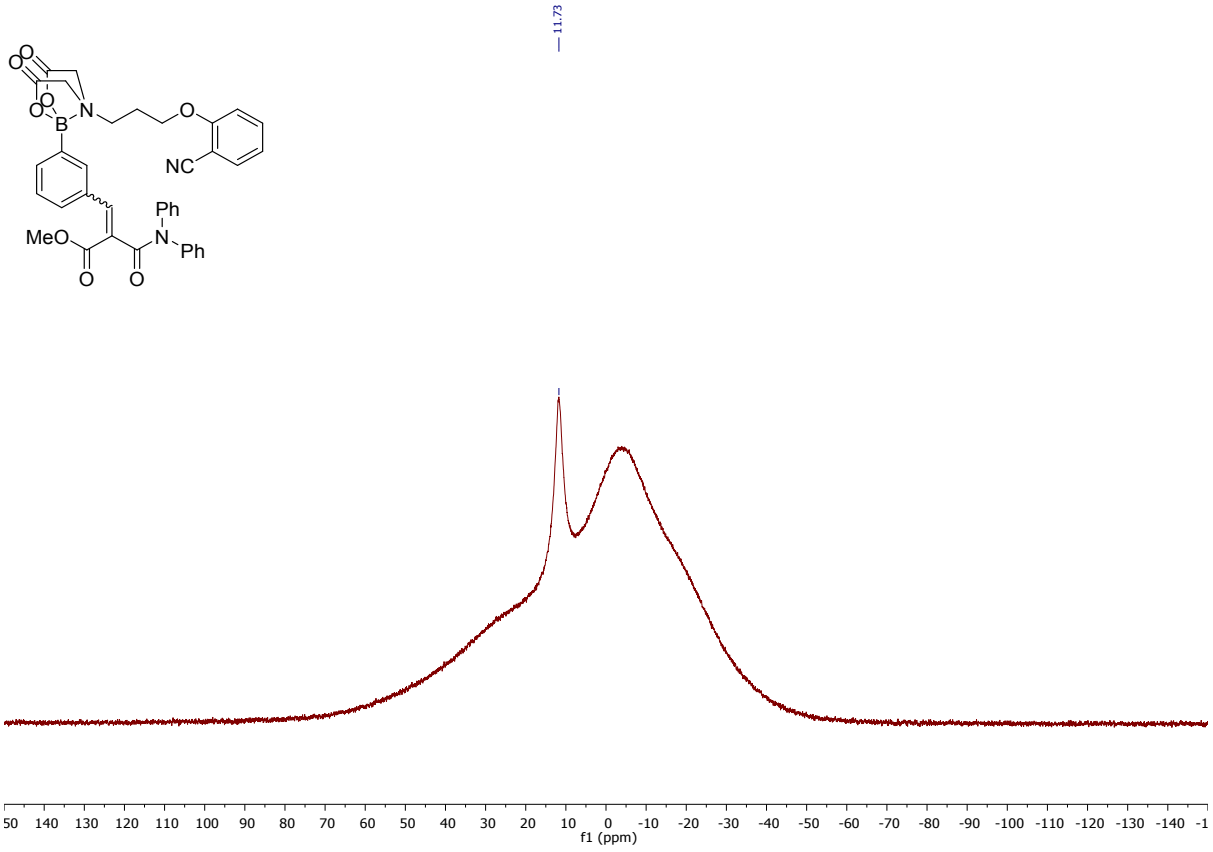

NC
Ph
a
b
7.19
7.15
f1 (ppm)

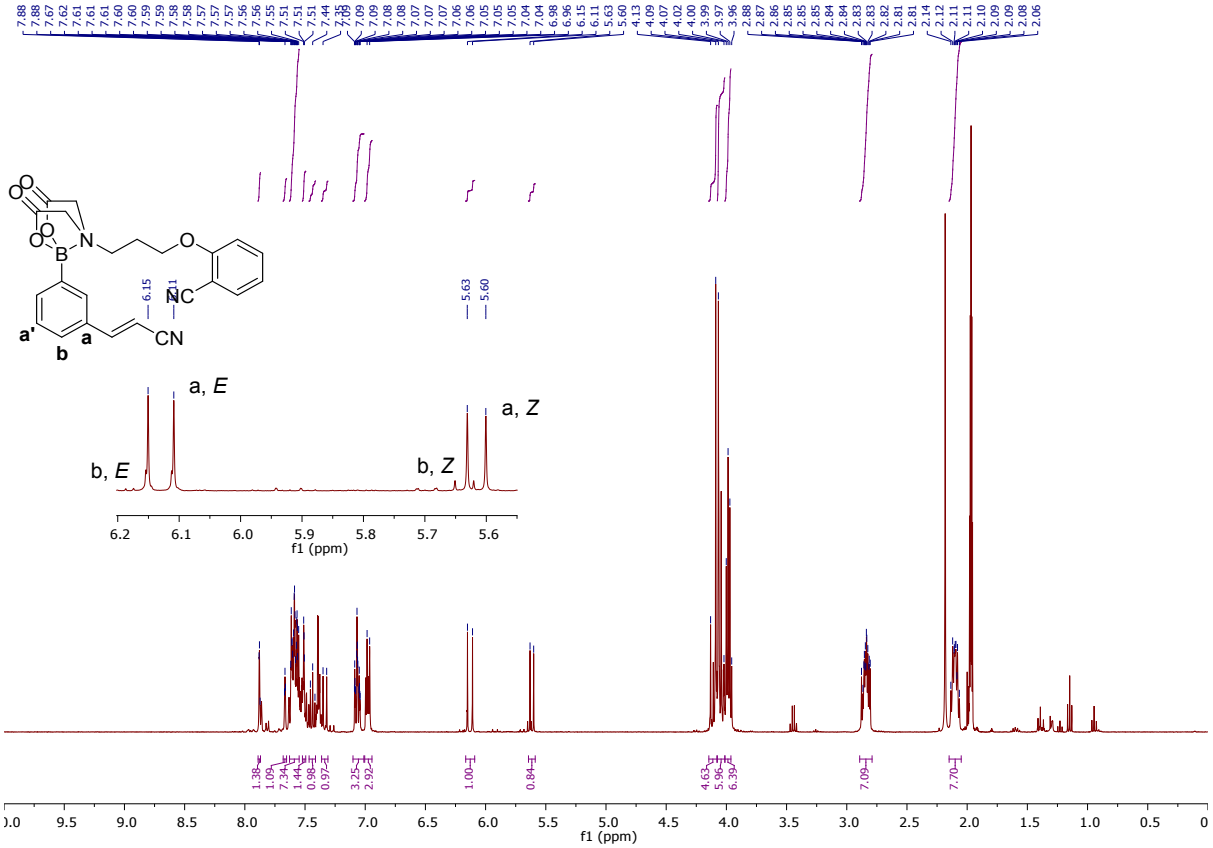

168.36
159.84
142.74
141.05
135.35
133.61
133.52
133.23
132.25
129.53
129.49
129.36
128.67
127.57
116.09
101.36
65.69
59.06
56.13
23.80
NC
Ph
f1 (ppm)

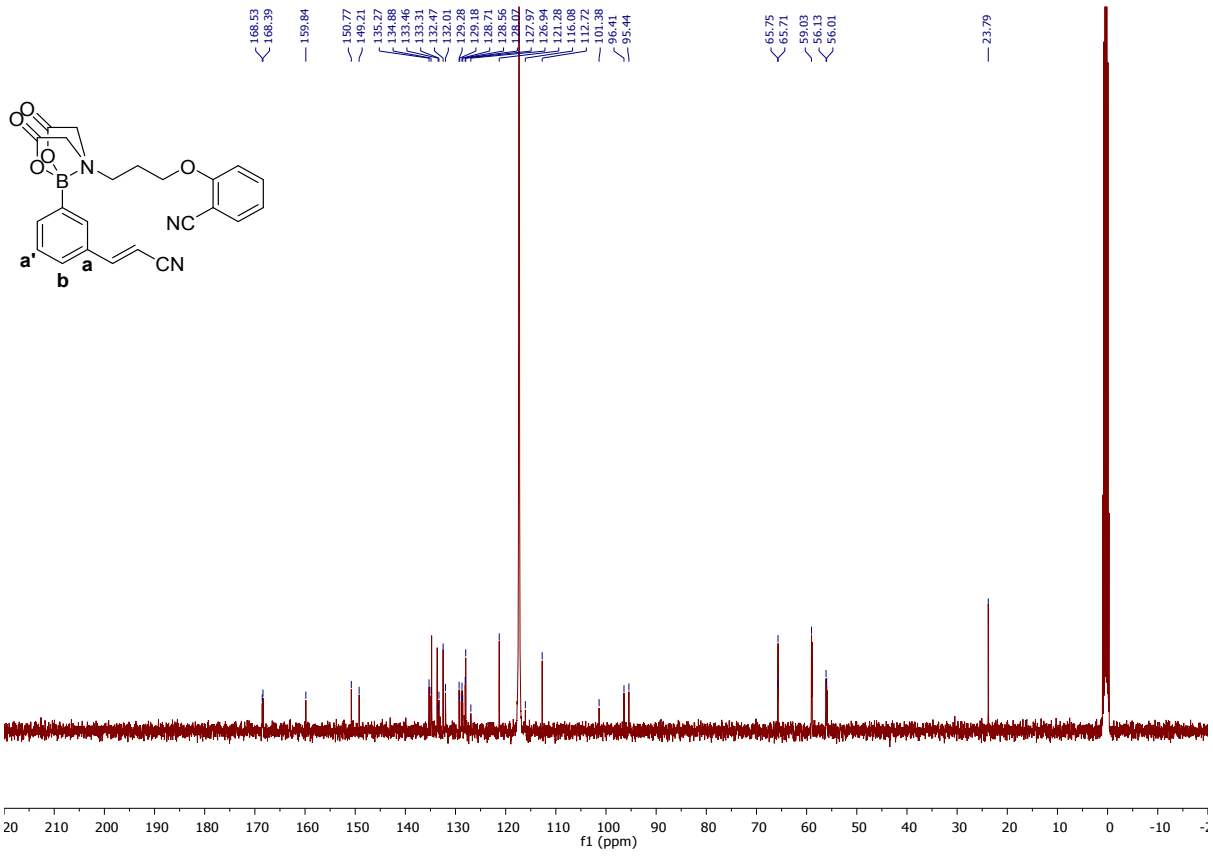

11.83
f1 (ppm)

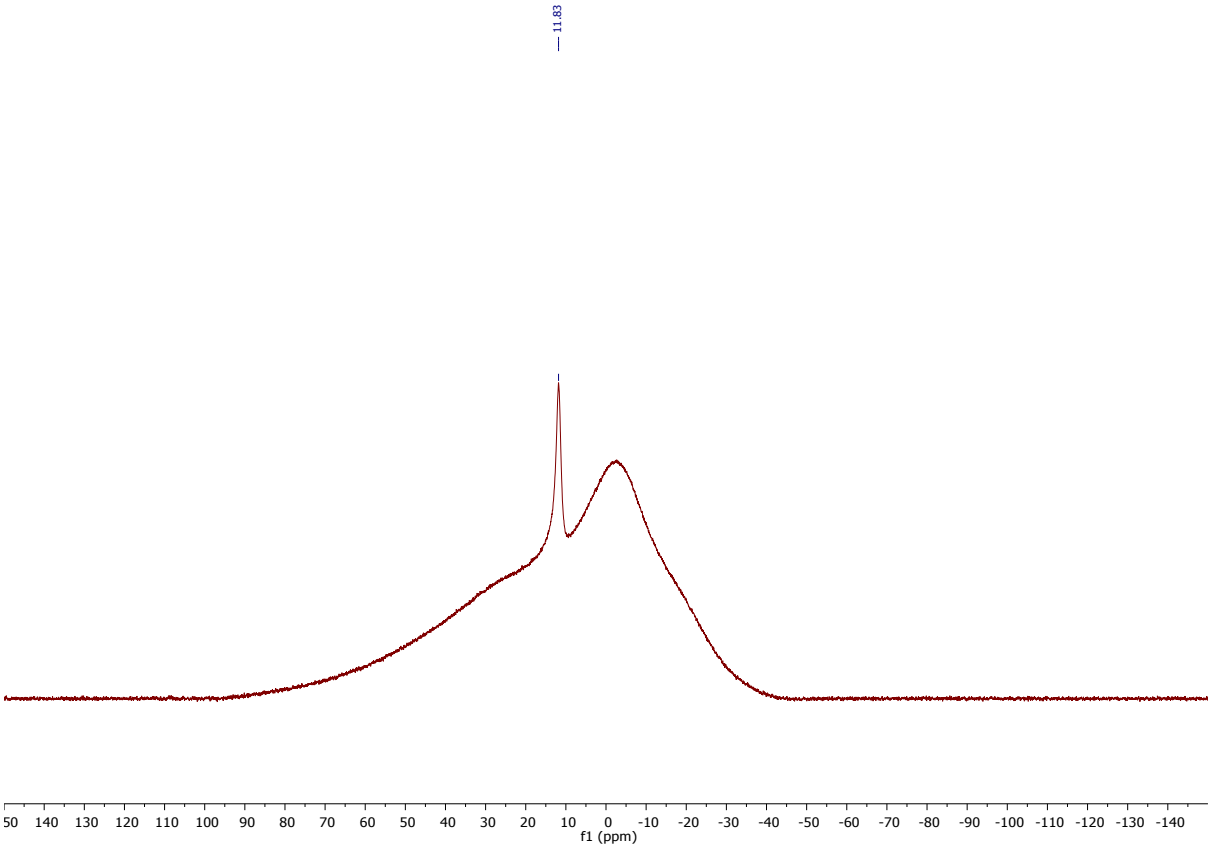

meta
para
3.80
3.33
f1 (ppm)


168.41
168.38
166.12
165.32
164.87
159.84
142.89
142.17
141.82
141.14
134.91
134.76
134.23
133.87
133.65
133.38
133.19
132.48
130.47
129.25
129.21
129.18
129.06
128.71
128.20
127.71
127.60
127.06
126.85
126.56
121.29
116.11
112.72
101.37
65.70
59.01
58.94
56.04
55.96
52.16
51.71
23.81
10.77
O
O
O
B
N
O
NC
Ph
MeO
N
Ph
O
O
f1 (ppm)

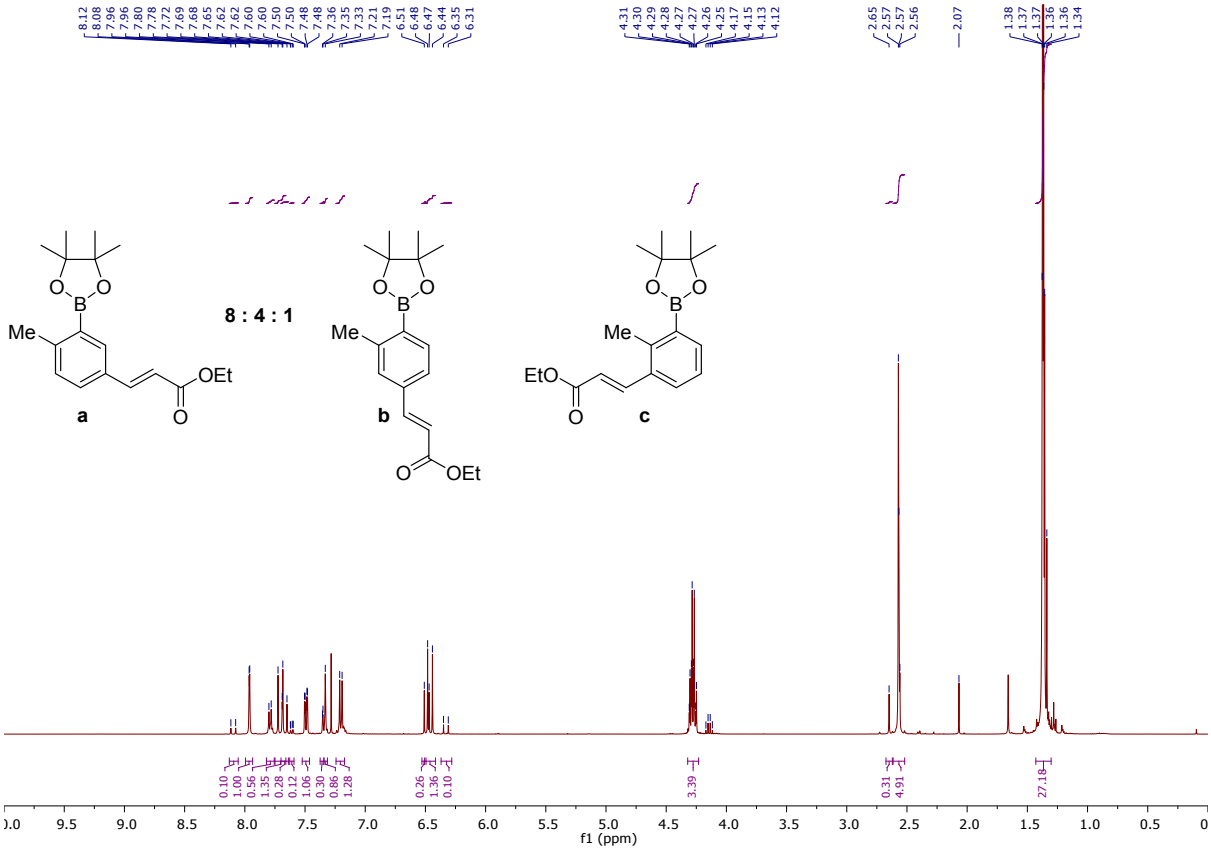

11.73
O
O
O
B
N
O
NC
Ph
MeO
N
Ph
O
O
f1 (ppm)

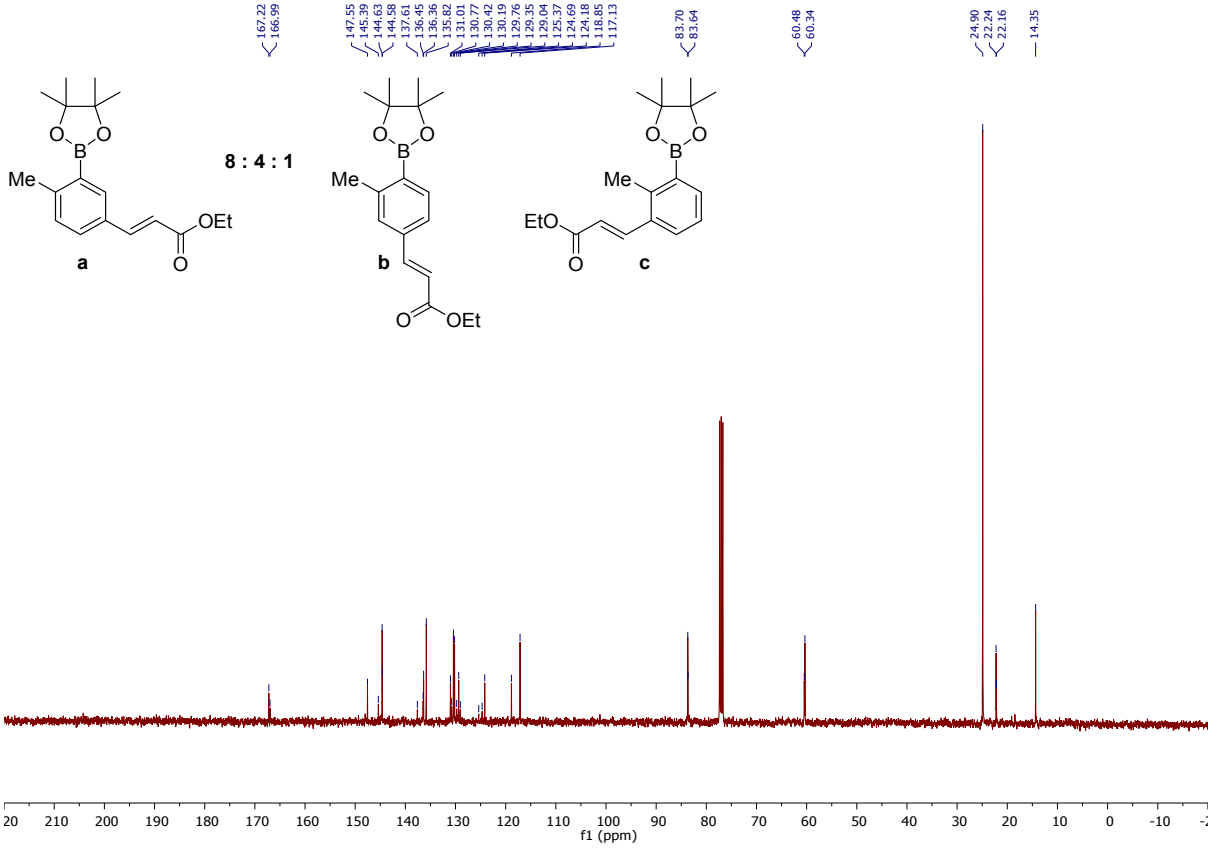

a, E
a, Z
b, E
b, Z
f1 (ppm)

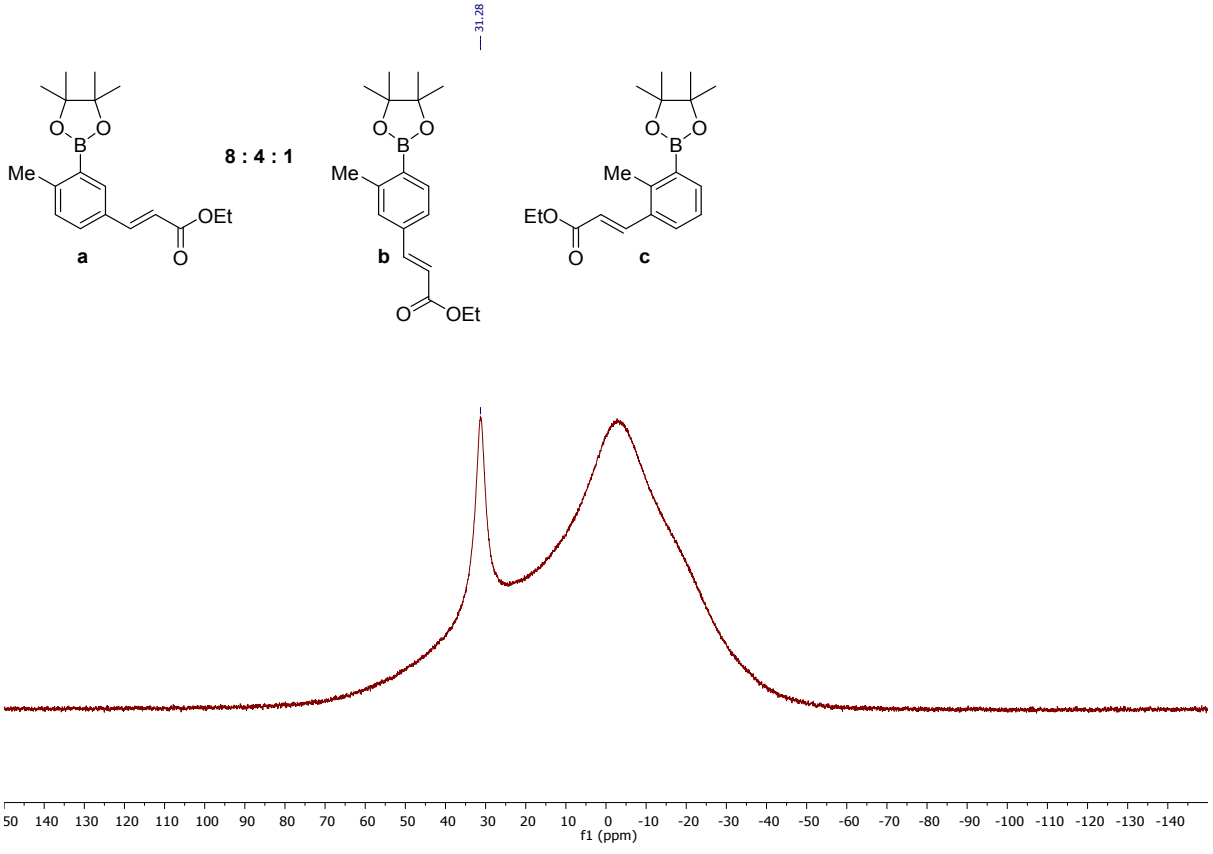

f1 (ppm)

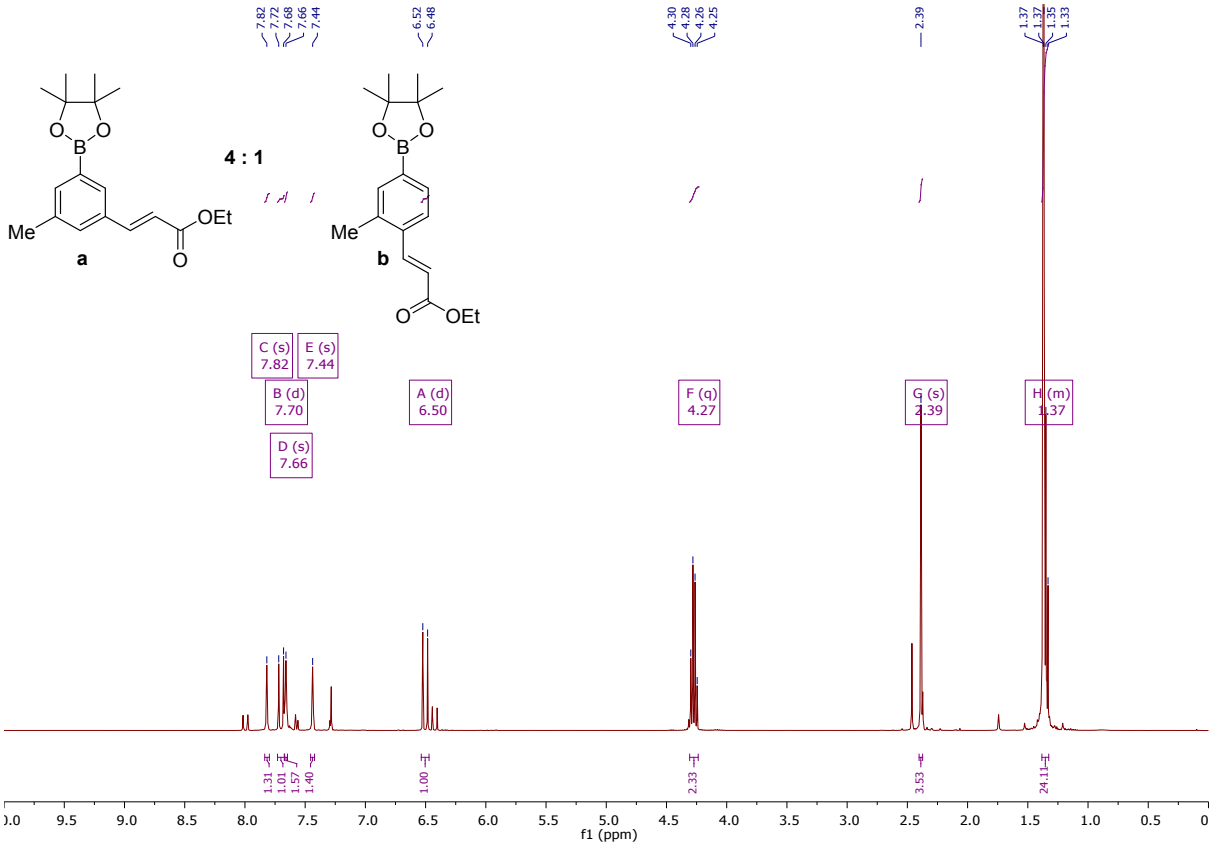


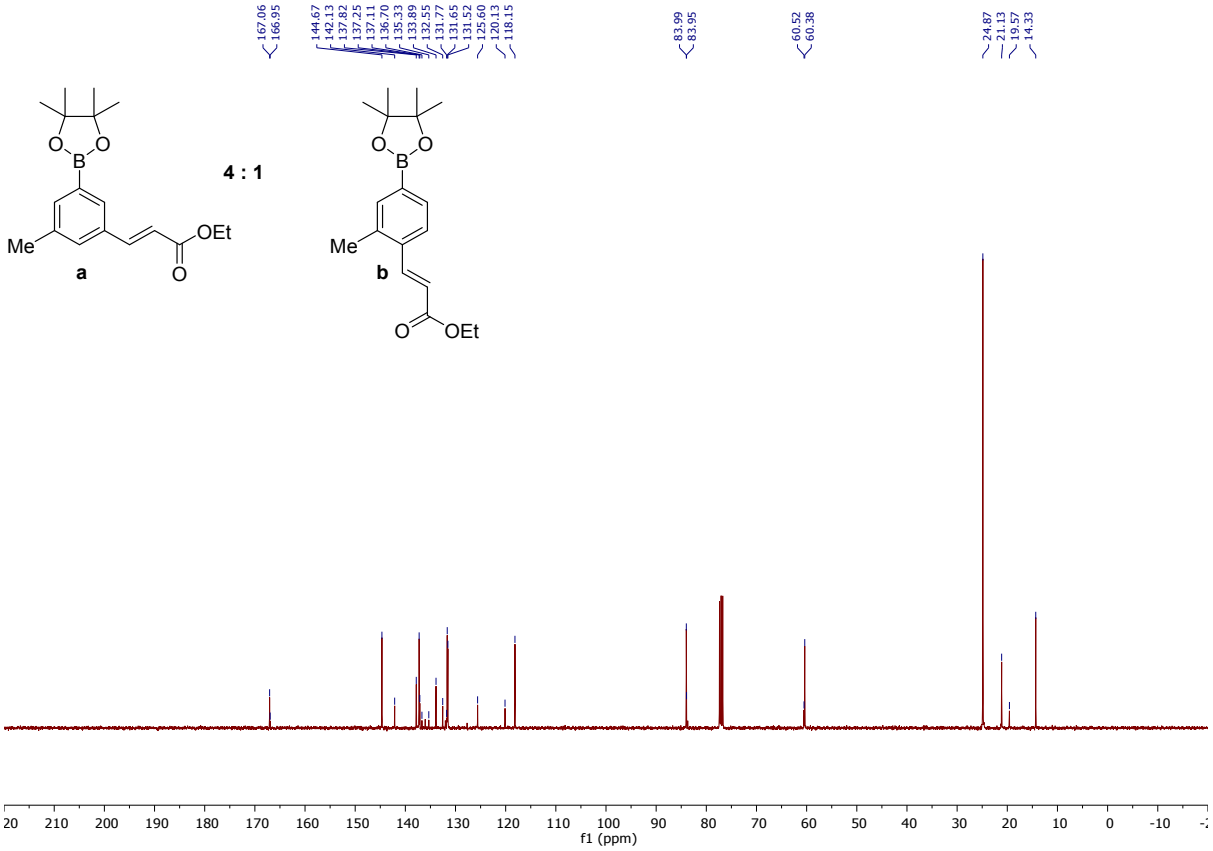
Alkenylated Aryl Boronic acid Pinacol Ester NMR Spectra

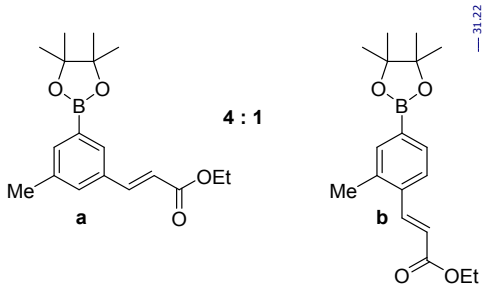


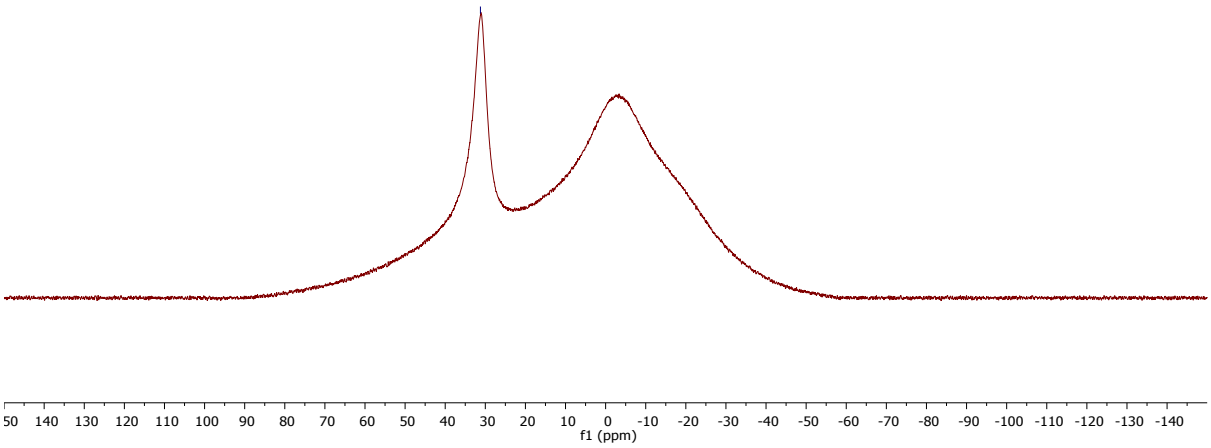

167.22
166.99
147.55
145.39
144.63
144.58
137.61
136.45
136.36
135.82
131.01
130.77
130.42
130.19
129.76
129.35
129.04
125.37
124.69
124.18
118.85
117.13
83.70
83.64
60.48
60.34
24.90
22.24
22.16
14.35
8 : 4 : 1
Me
OEt
O
a
b
c
EtO
f1 (ppm)

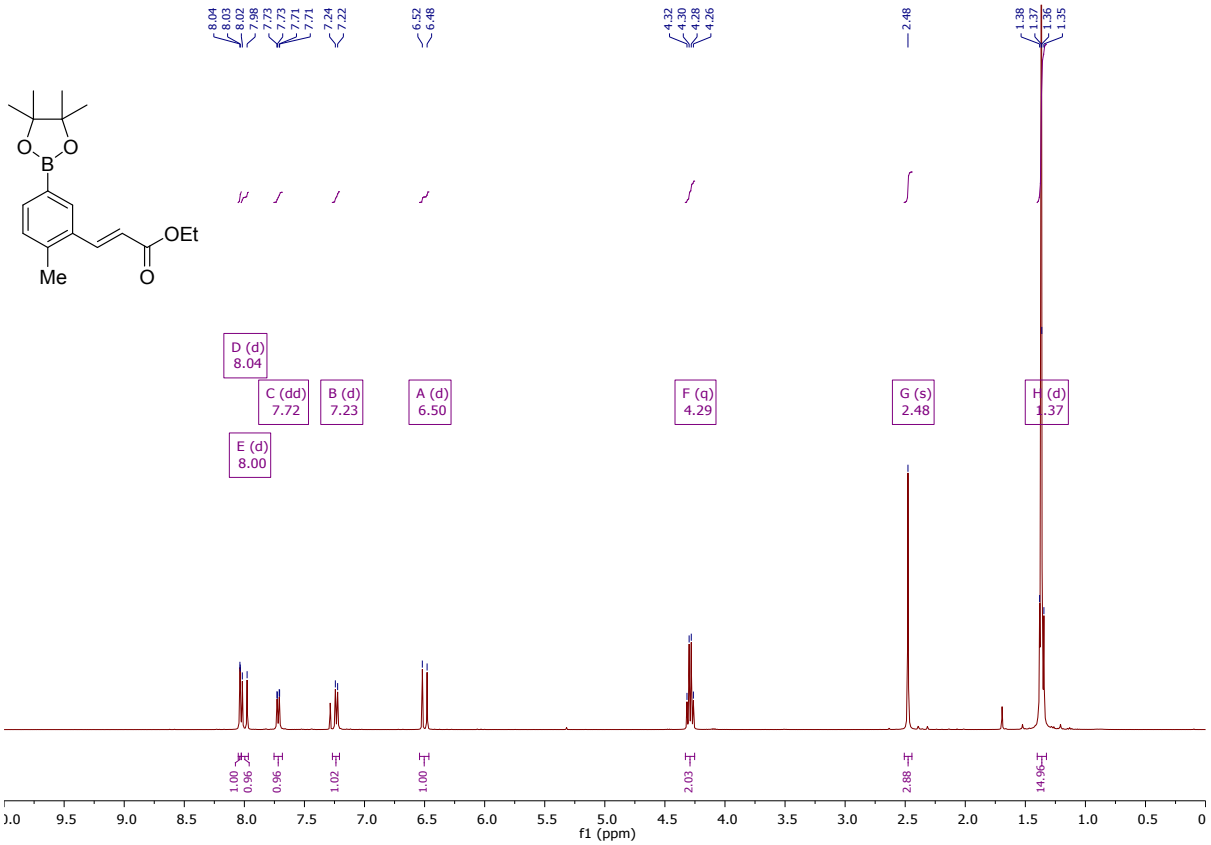

31.28
8 : 4 : 1
Me
OEt
O
a
b
c
EtO
f1 (ppm)

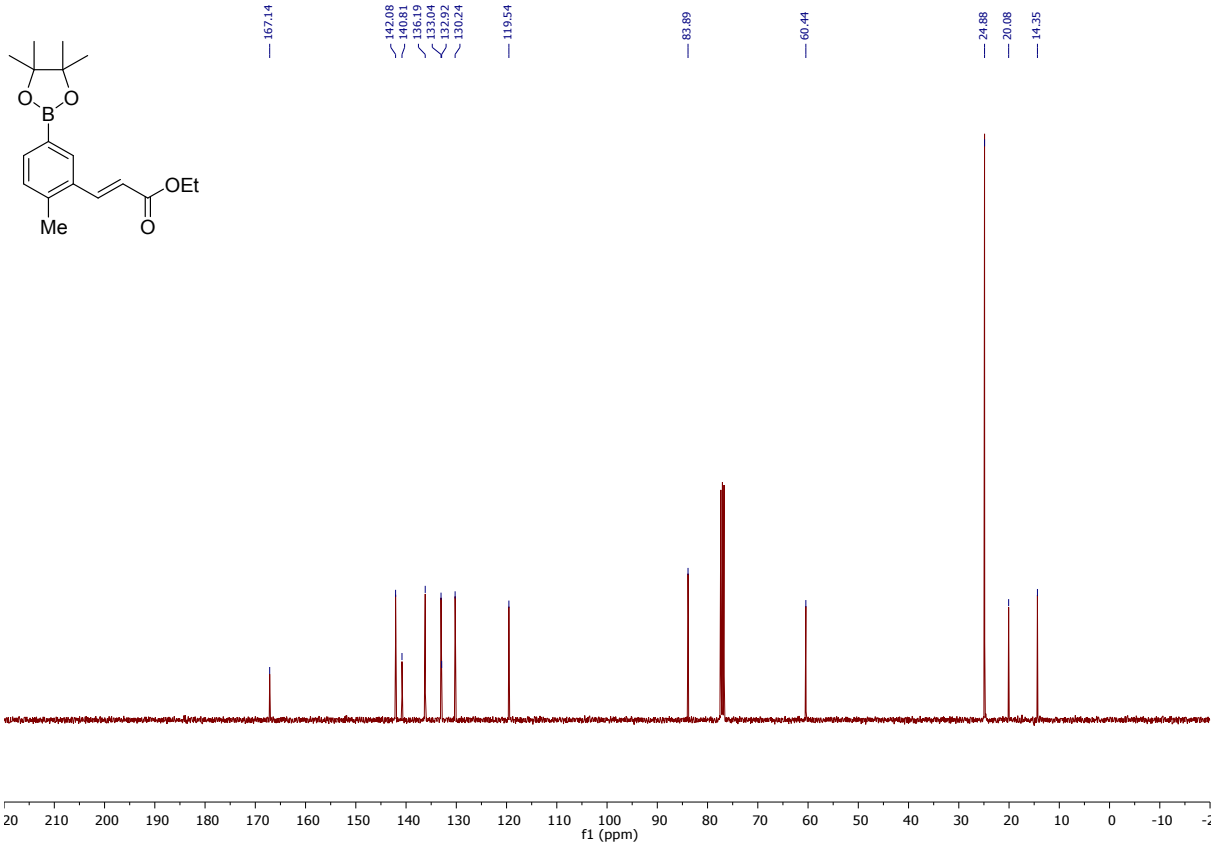

4 : 1
Me
OEt
a
b
C (s) 7.82
E (s) 7.44
B (d) 7.70
D (s) 7.66
A (d) 6.50
F (q) 4.27
G (s) 2.39
H (m) 1.37
f1 (ppm)

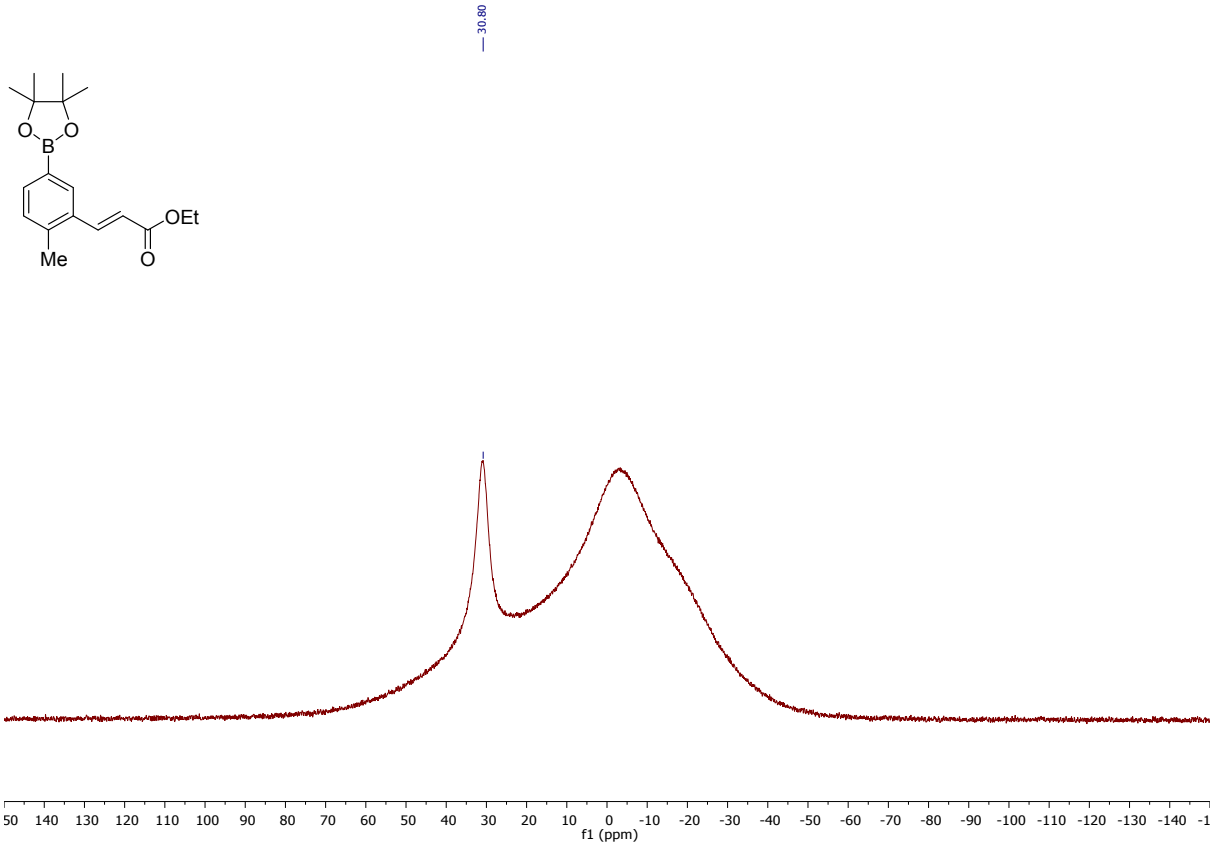

4 : 1
Me
OEt
a
b
f1 (ppm)

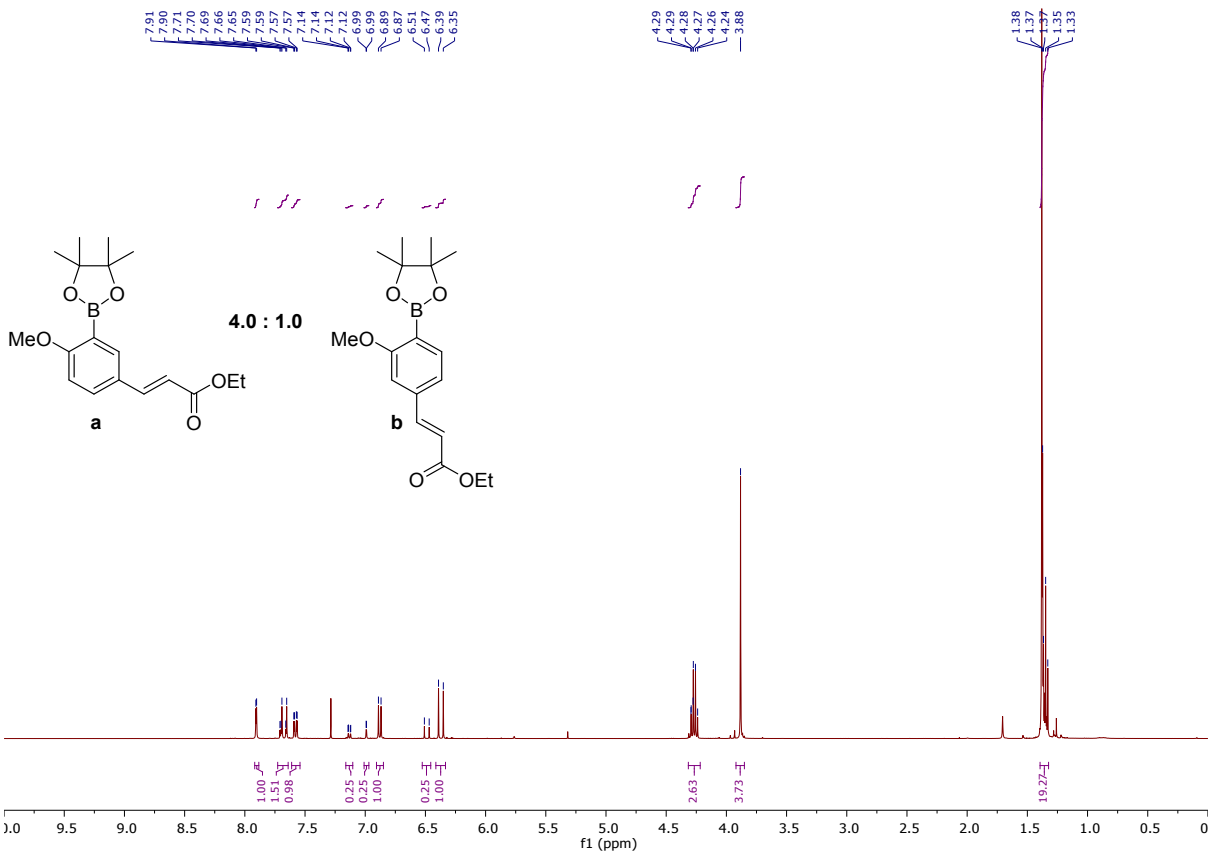

4 : 1
Me
OEt
O
a
Me
OEt
O
b
31.22

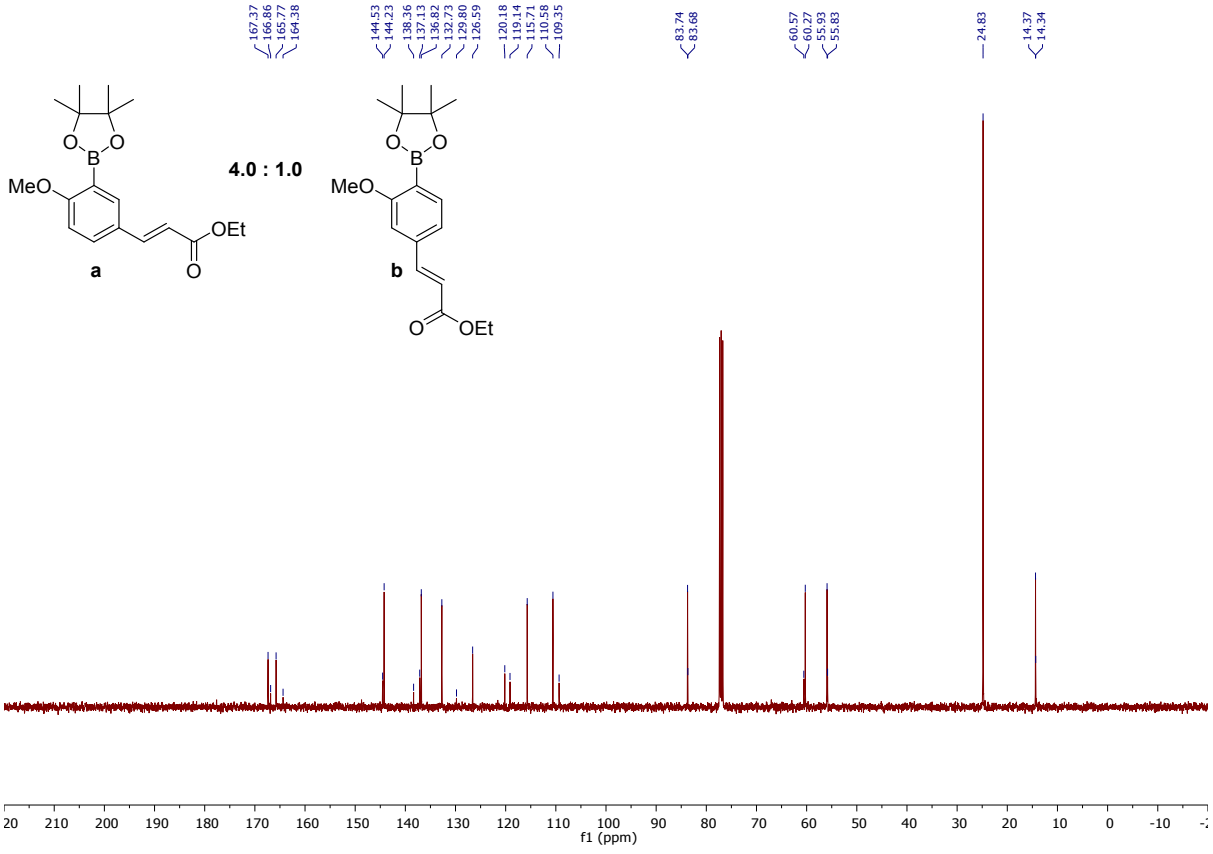

f1 (ppm)

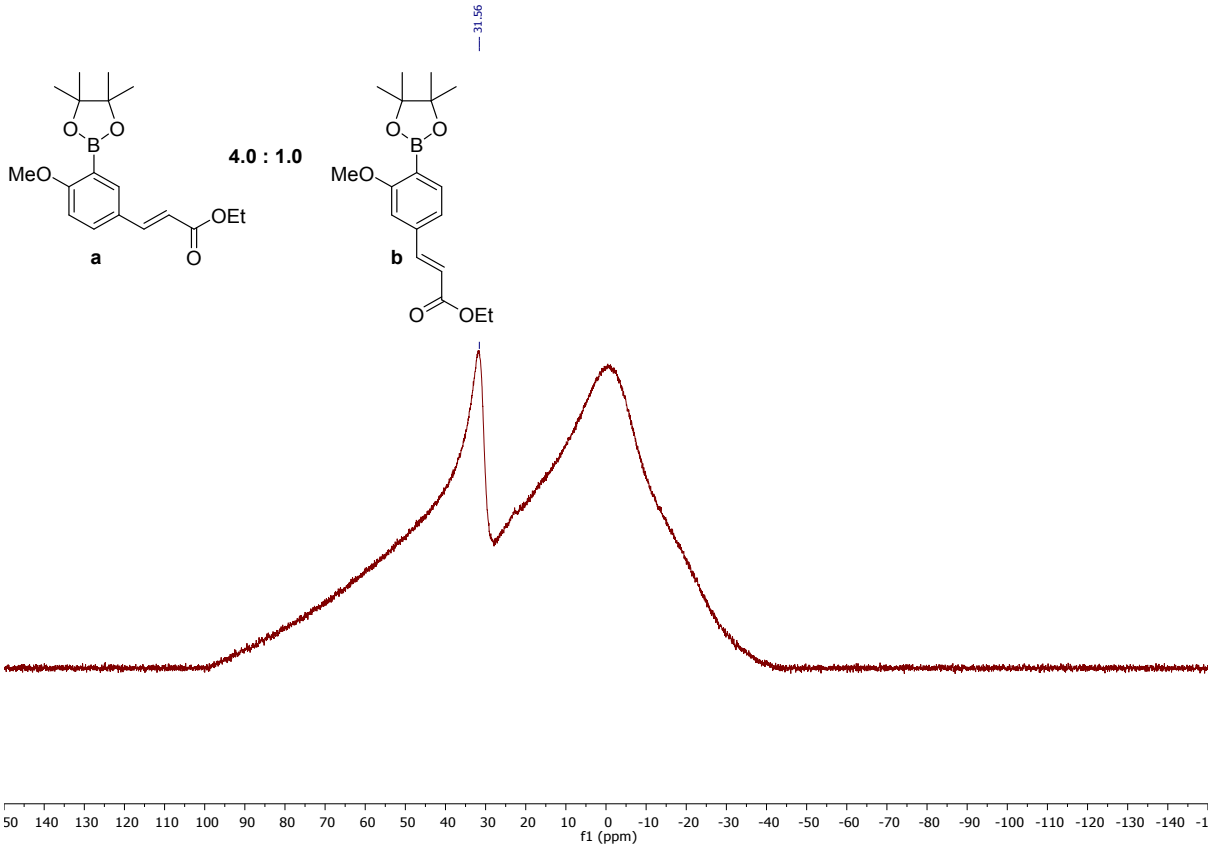

8.04
8.03
8.02
7.98
7.73
7.73
7.71
7.71
7.24
7.22
6.52
6.48
4.32
4.30
4.28
4.26
2.48
1.38
1.37
1.36
1.35
Me
OEt
O
D (d) 8.04
C (dd) 7.72
B (d) 7.23
A (d) 6.50
F (q) 4.29
G (s) 2.48
H (d) 1.37
E (d) 8.00
1.00
0.96
0.96
1.02
1.00
2.03
2.88
14.96
f1 (ppm)

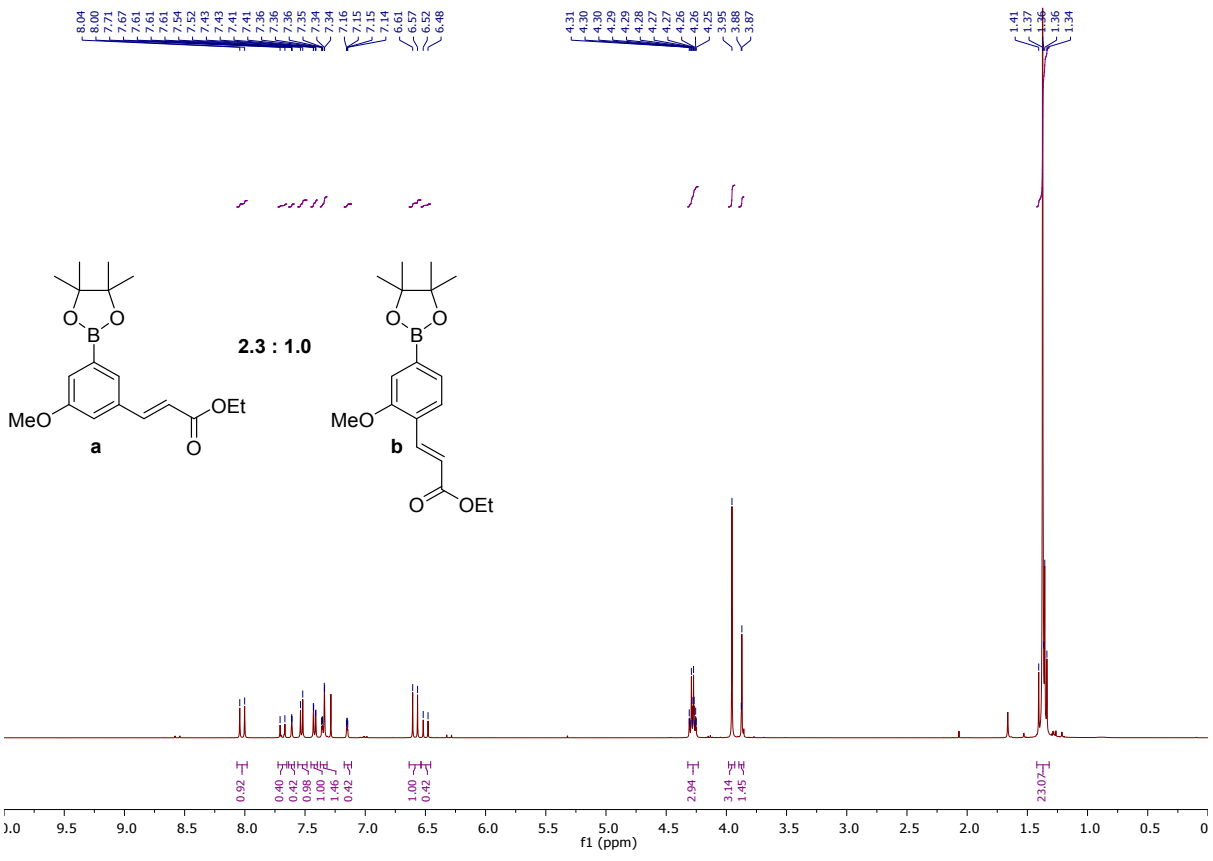

167.14
142.08
140.81
136.19
133.04
132.92
130.24
119.54
83.89
60.44
24.88
20.08
14.35
O
B
O
OEt
Me
O
f1 (ppm)

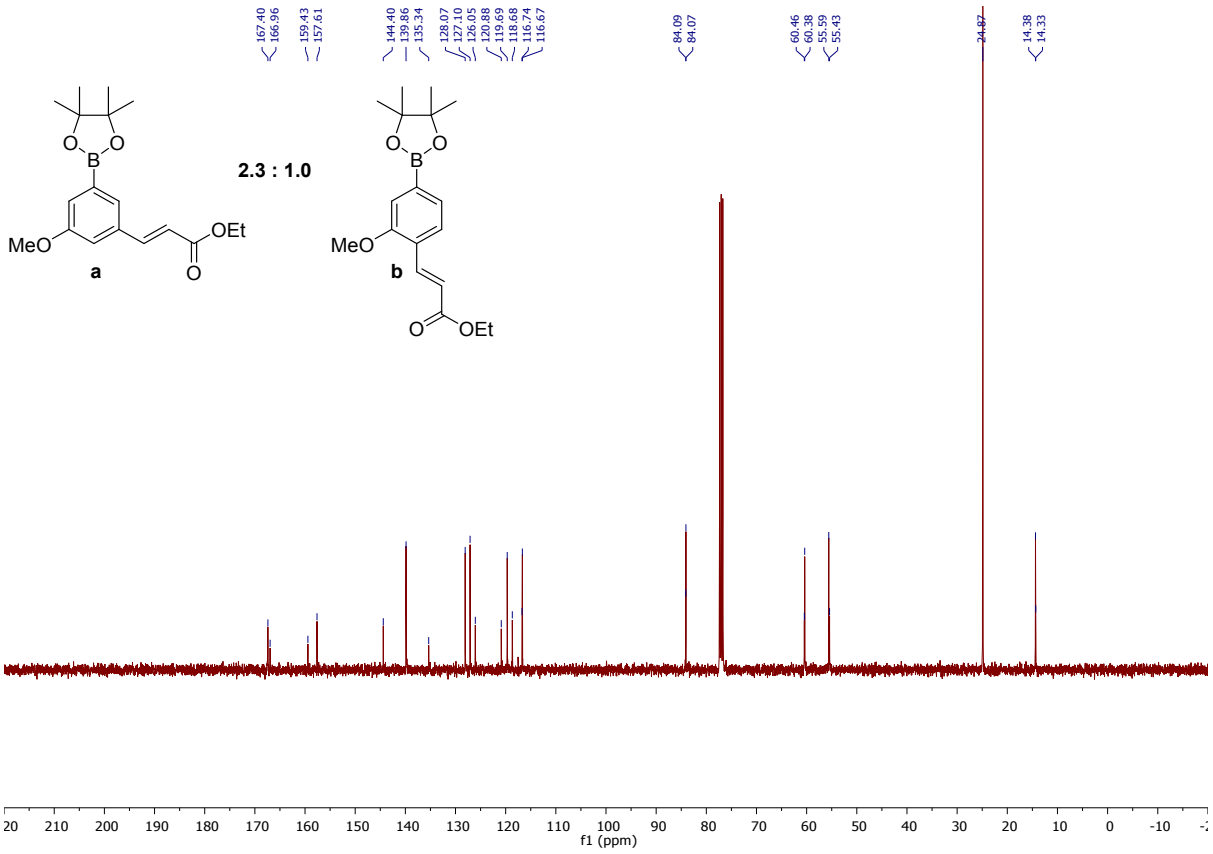

30.80
O
B
O
OEt
Me
O
f1 (ppm)

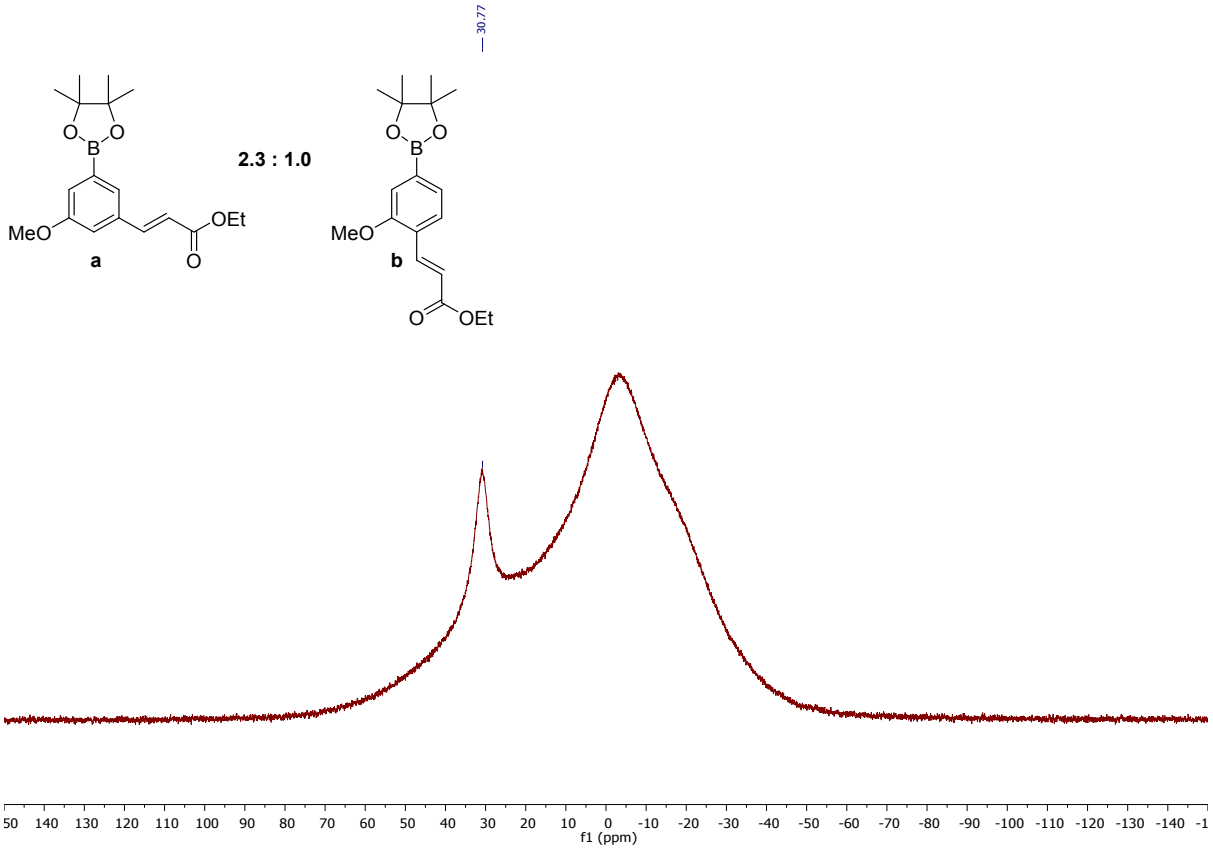

4.0 : 1.0
MeO
OEt
a
b
f1 (ppm)

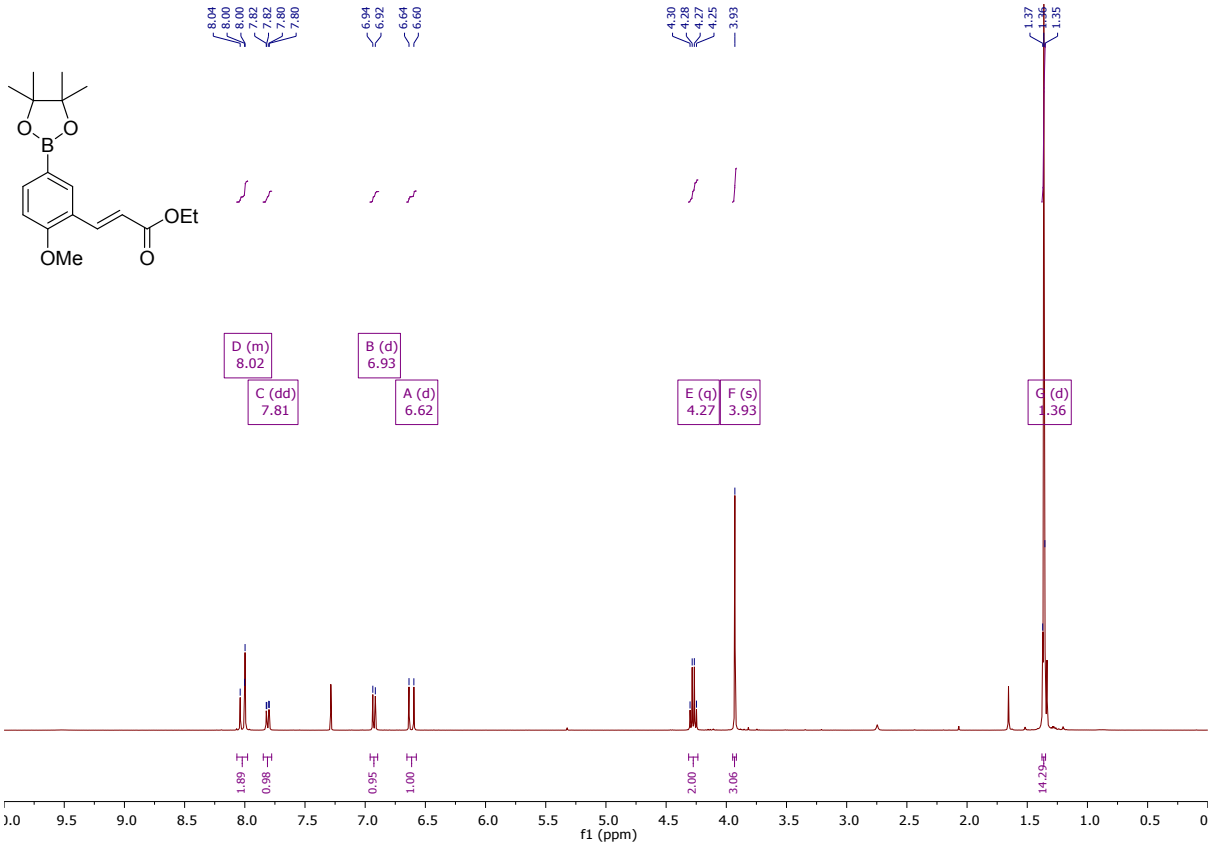

4.0 : 1.0
MeO
OEt
a
b
f1 (ppm)

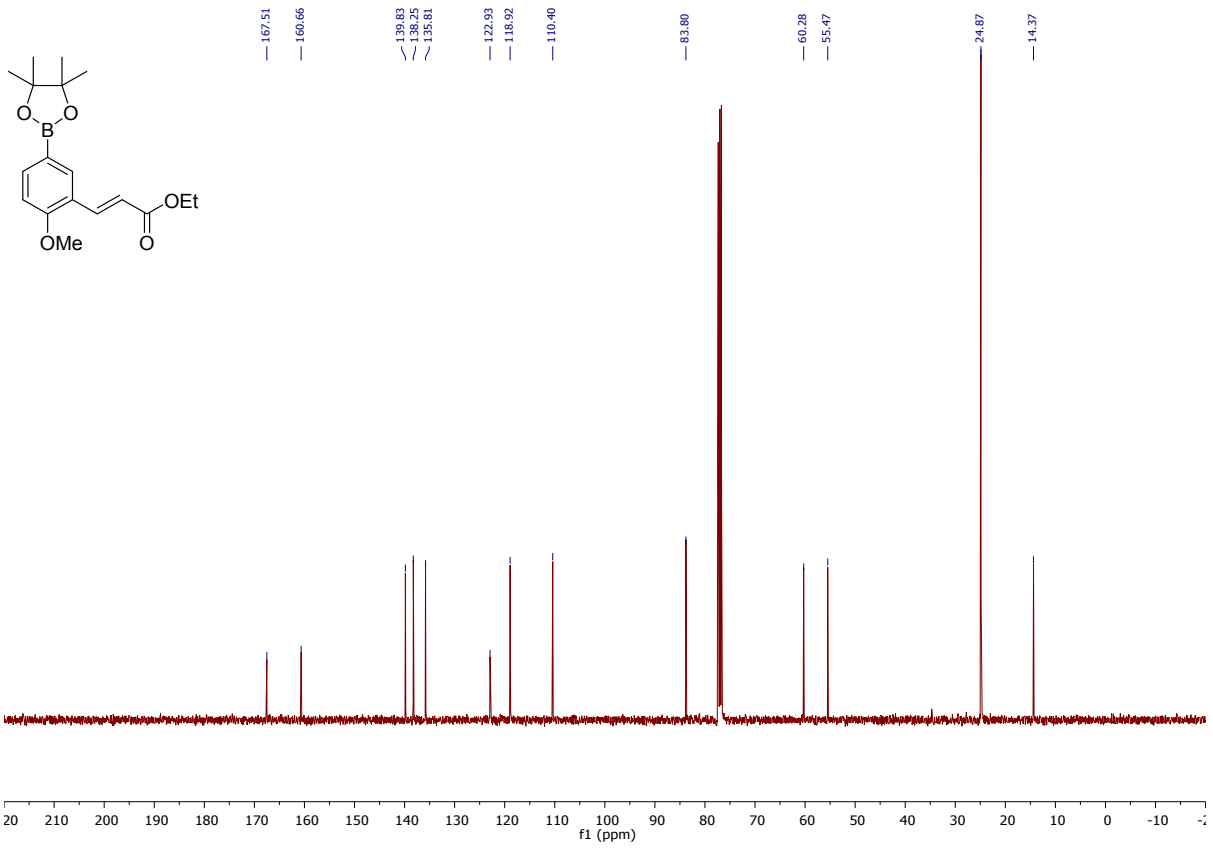

31.56
4.0 : 1.0
MeO
OEt
O
a
b
f1 (ppm)

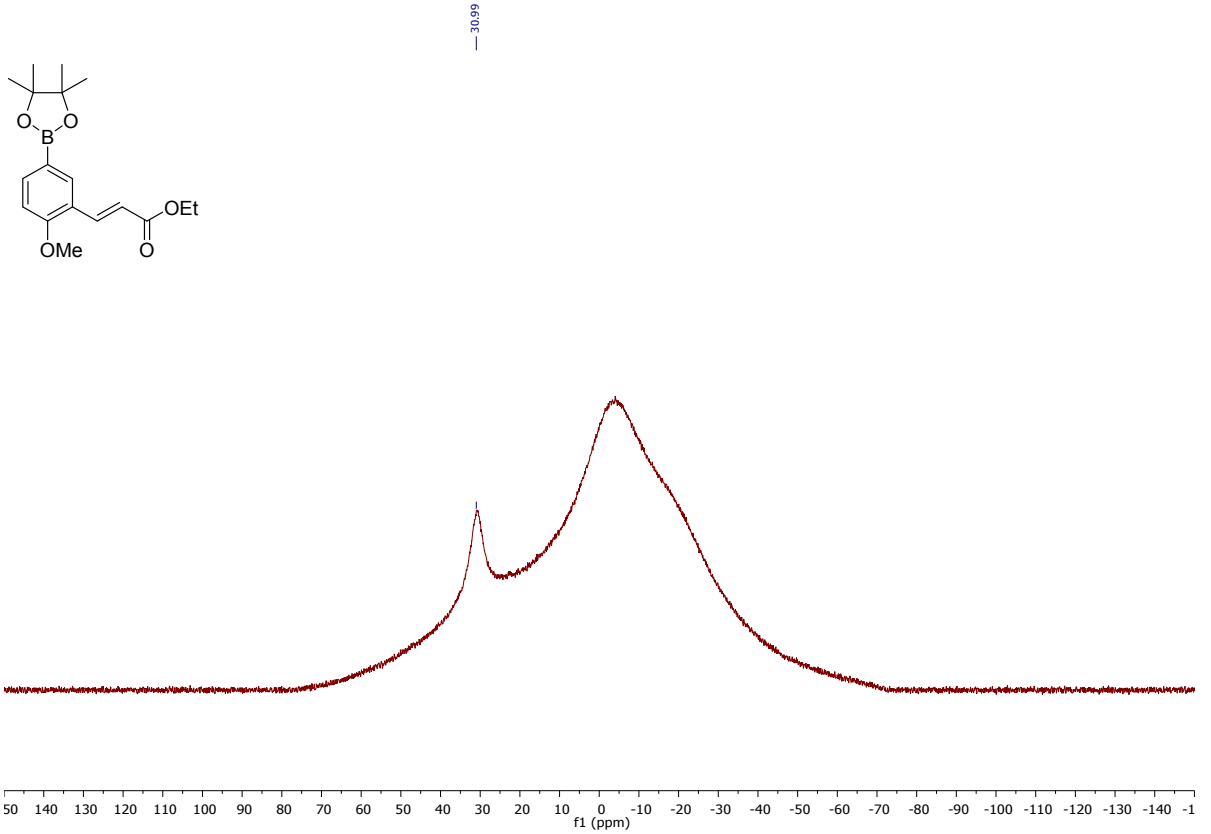

8.04
8.00
7.71
7.67
7.61
7.61
7.61
7.54
7.52
7.43
7.43
7.41
7.41
7.36
7.36
7.35
7.34
7.34
7.16
7.15
7.15
7.14
6.61
6.57
6.52
6.48
4.31
4.30
4.30
4.29
4.29
4.28
4.27
4.27
4.26
4.26
4.25
3.95
3.88
3.87
1.41
1.37
1.36
1.36
1.34
2.3 : 1.0
MeO
OEt
O
a
b
0.92
0.40
0.42
0.98
1.00
1.46
0.42
1.00
0.42
2.94
3.14
1.45
23.07
f1 (ppm)

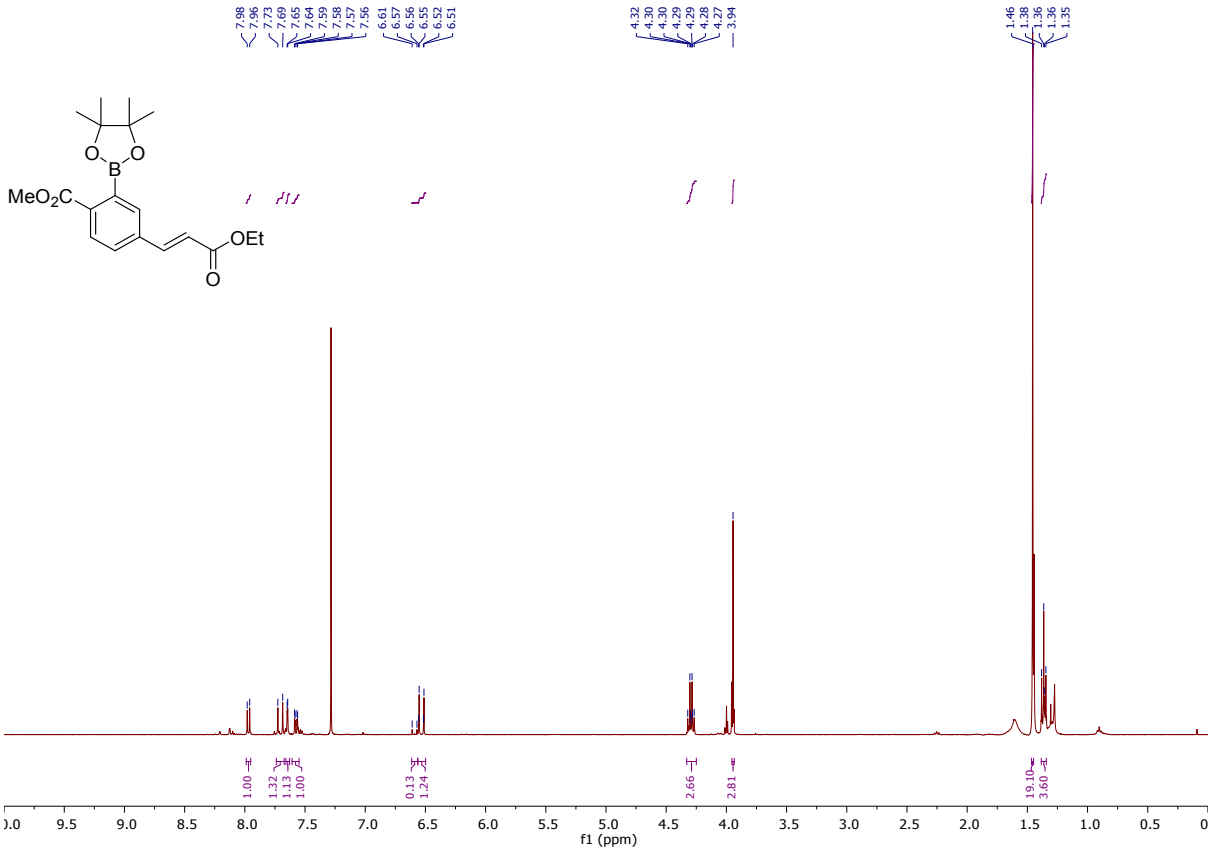

167.40
166.96
159.43
157.61
144.40
139.86
135.34
128.07
127.10
126.05
120.88
119.69
118.68
116.74
116.67
84.09
84.07
60.46
60.38
55.59
55.43
24.87
14.38
14.33
2.3 : 1.0
MeO
OEt
O
a
b
f1 (ppm)

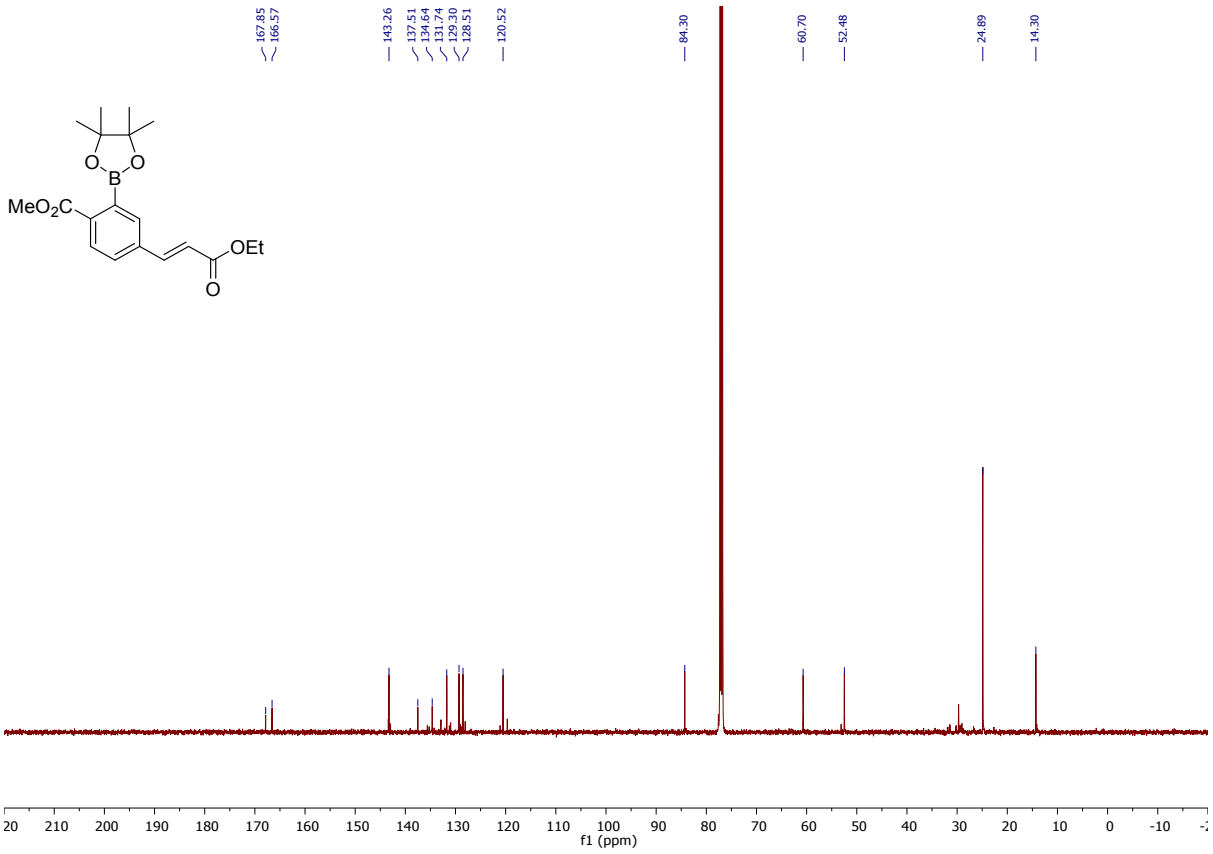

30.77
2.3 : 1.0
MeO
OEt
O
a
b
f1 (ppm)

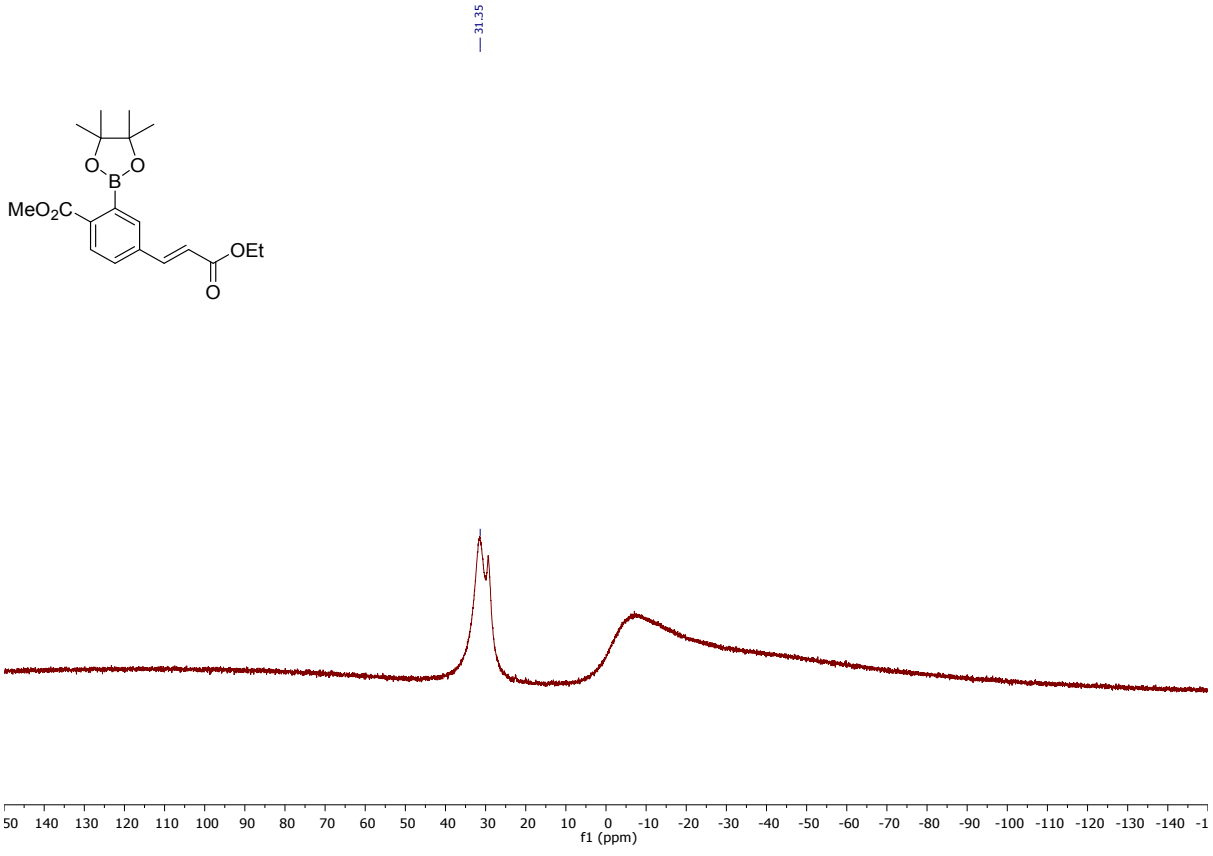

8.04
8.00
8.00
7.82
7.82
7.80
7.80
6.94
6.92
6.64
6.60
4.30
4.28
4.27
4.25
3.93
1.37
1.36
1.35
O
B
O
OEt
OMe
O
D (m)
8.02
C (dd)
7.81
B (d)
6.93
A (d)
6.62
E (q)
4.27
F (s)
3.93
G (d)
1.36
1.89
0.98
0.95
1.00
2.00
3.06
14.29
f1 (ppm)

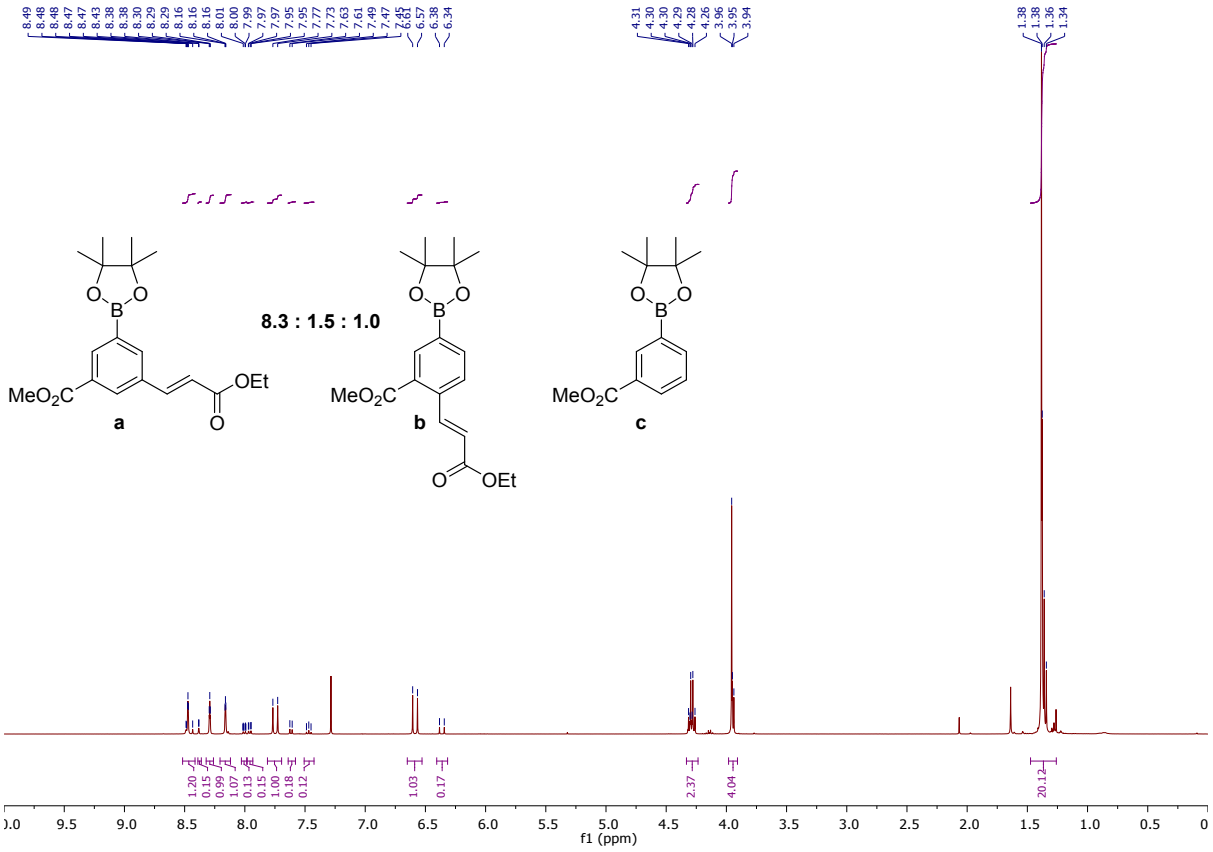

167.51
160.66
139.83
138.25
135.81
122.93
118.92
110.40
83.80
60.28
55.47
24.87
14.37
O
B
O
OEt
OMe
O
f1 (ppm)

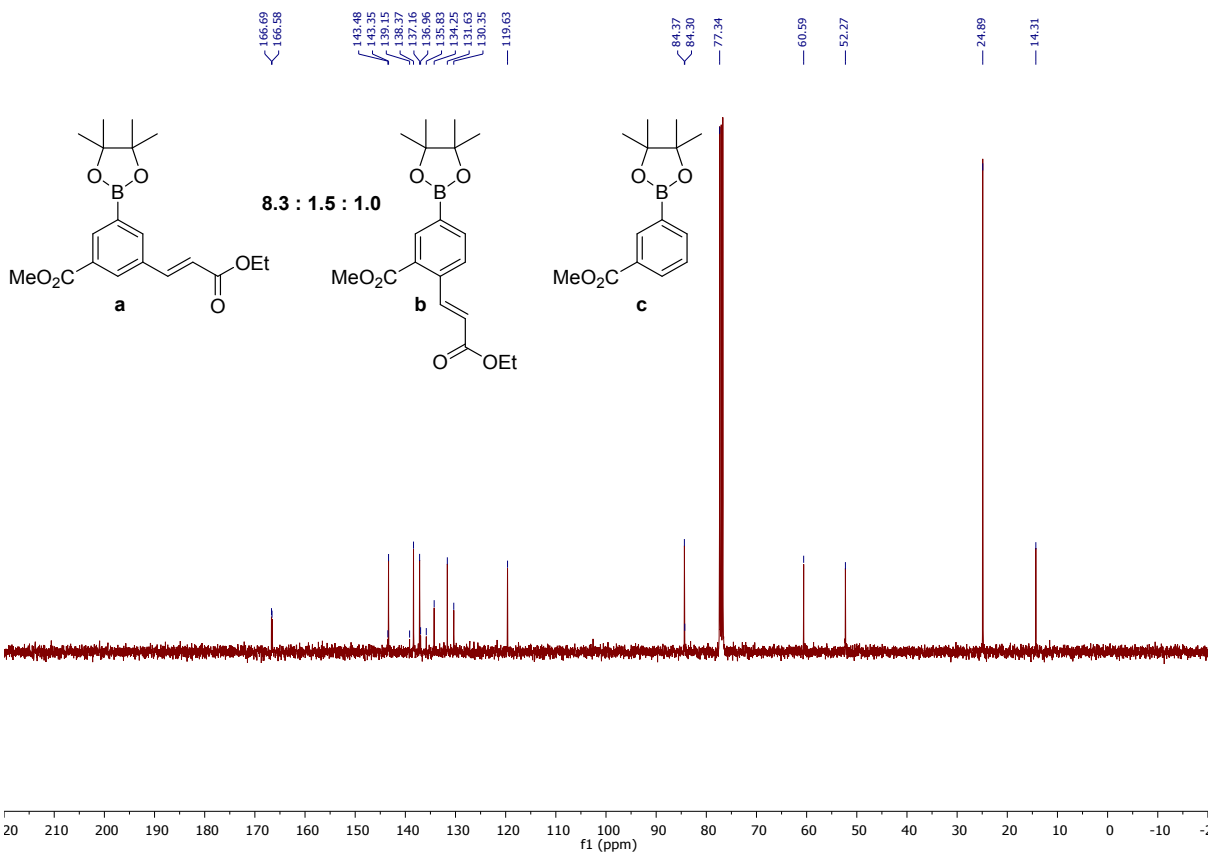

30.99
OEt
OMe
O
f1 (ppm)

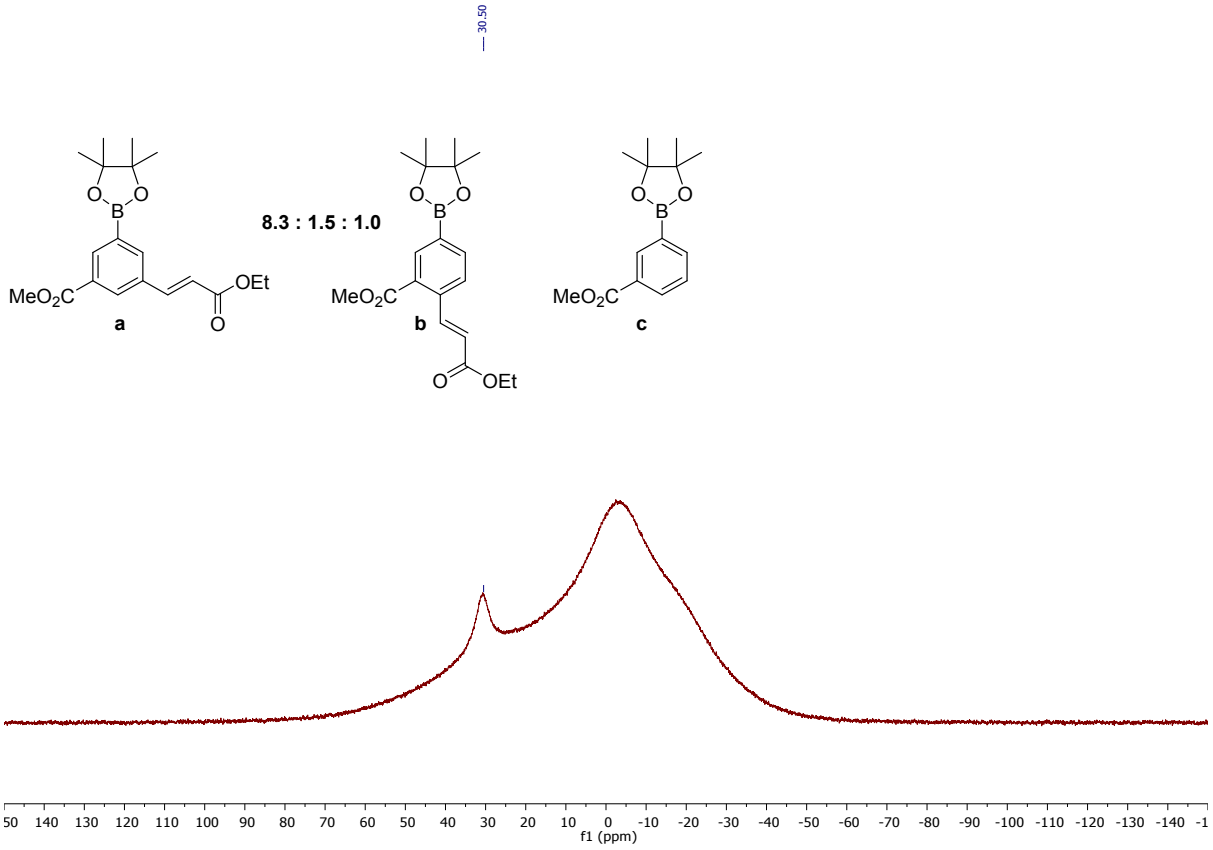

7.98
7.96
7.73
7.69
7.65
7.64
7.59
7.58
7.57
7.56
6.61
6.57
6.56
6.55
6.52
6.51
4.32
4.30
4.30
4.29
4.29
4.28
4.27
3.94
1.46
1.38
1.36
1.36
1.35
MeO2C
OEt
O
1.00
1.32
1.13
1.00
0.13
1.24
2.66
2.81
19.10
3.60
f1 (ppm)

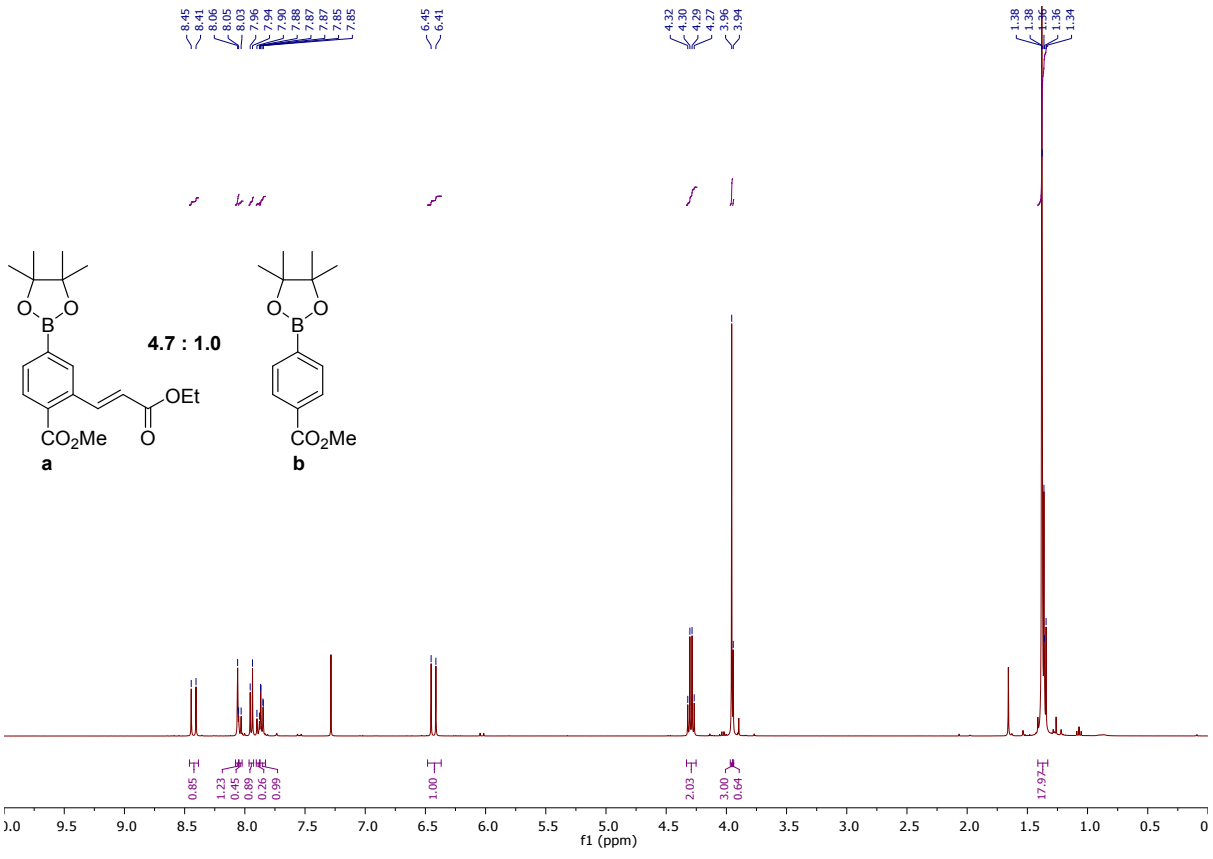

167.85
166.57
143.26
137.51
134.64
131.74
129.30
128.51
120.52
84.30
60.70
52.48
24.89
14.30
MeO2C
OEt
O
B
O
O
f1 (ppm)

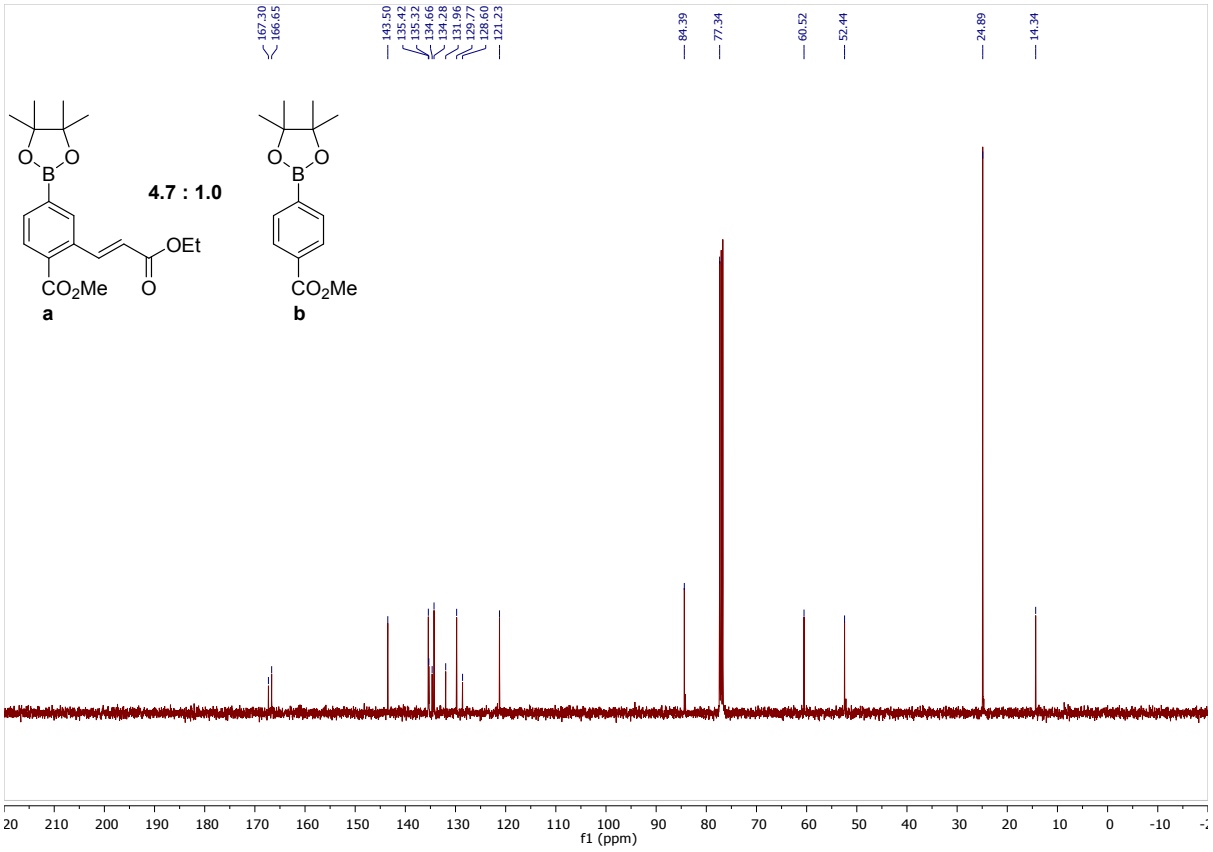

31.35
MeO2C
OEt
O
B
O
O
f1 (ppm)


8.3 : 1.5 : 1.0
a
b
c
f1 (ppm)


8.3 : 1.5 : 1.0
a
b
c
f1 (ppm)


30.50
8.3 : 1.5 : 1.0
MeO2C
OEt
O
a
b
c
f1 (ppm)


8.45
8.41
8.06
8.05
8.03
7.96
7.94
7.90
7.88
7.87
7.87
7.85
7.85
6.45
6.41
4.32
4.30
4.29
4.27
3.96
3.94
1.38
1.38
1.36
1.36
1.34
4.7 : 1.0
CO2Me
OEt
O
a
b
0.85
1.23
0.45
0.89
0.26
0.99
1.00
2.03
3.00
0.64
17.97
f1 (ppm)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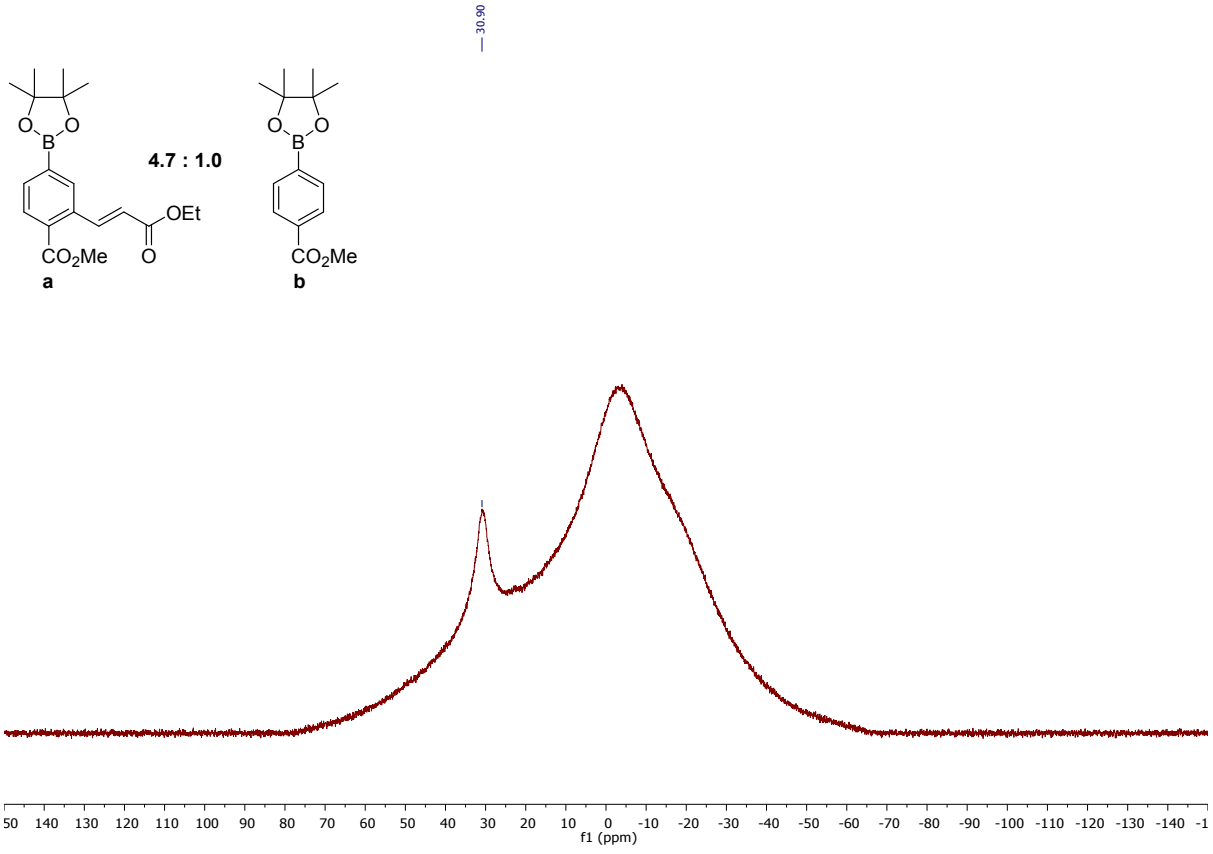
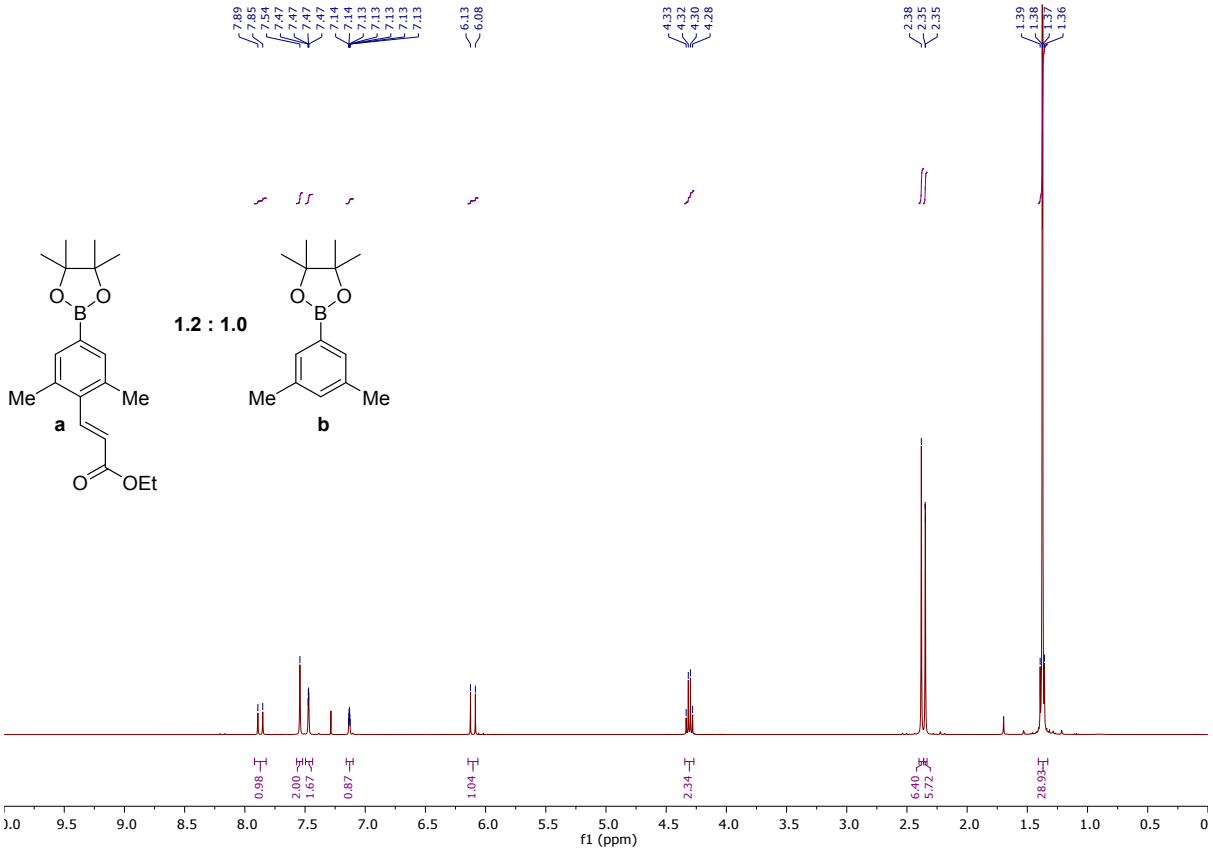
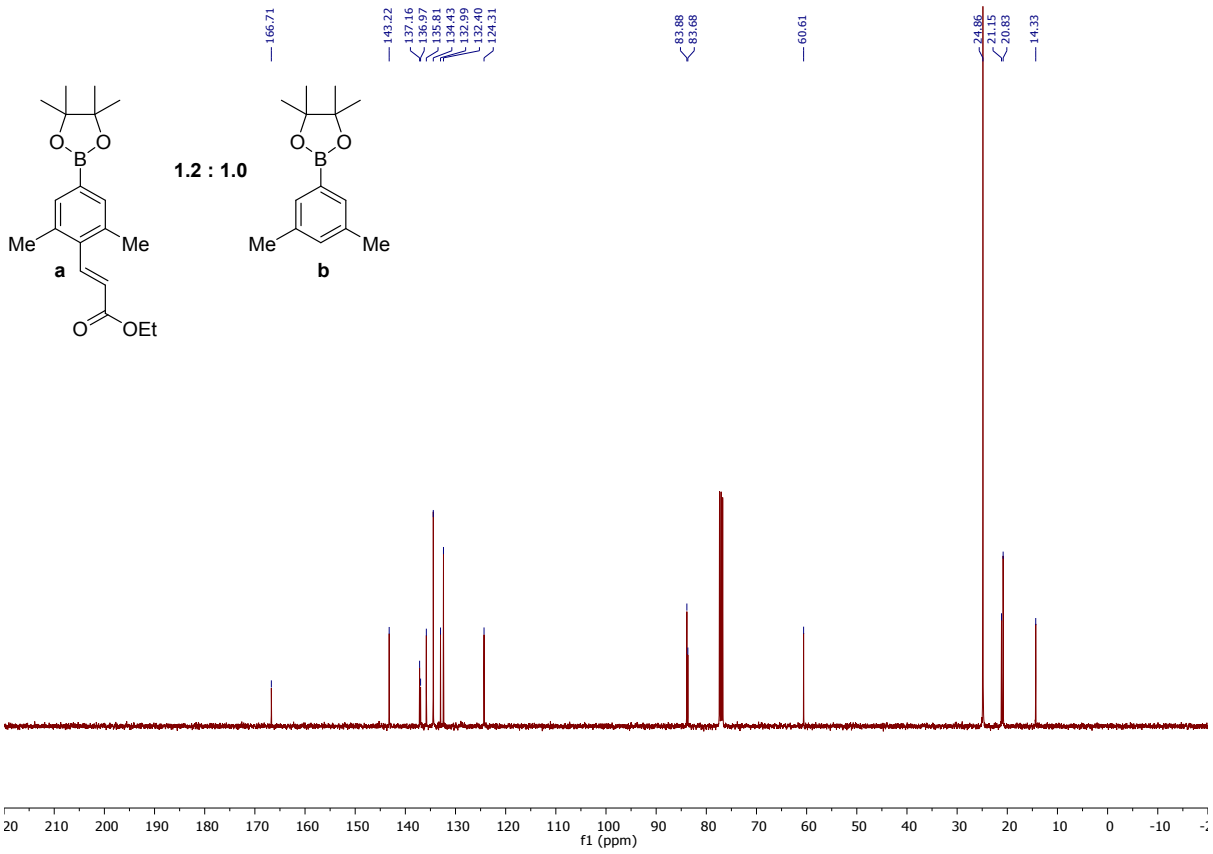
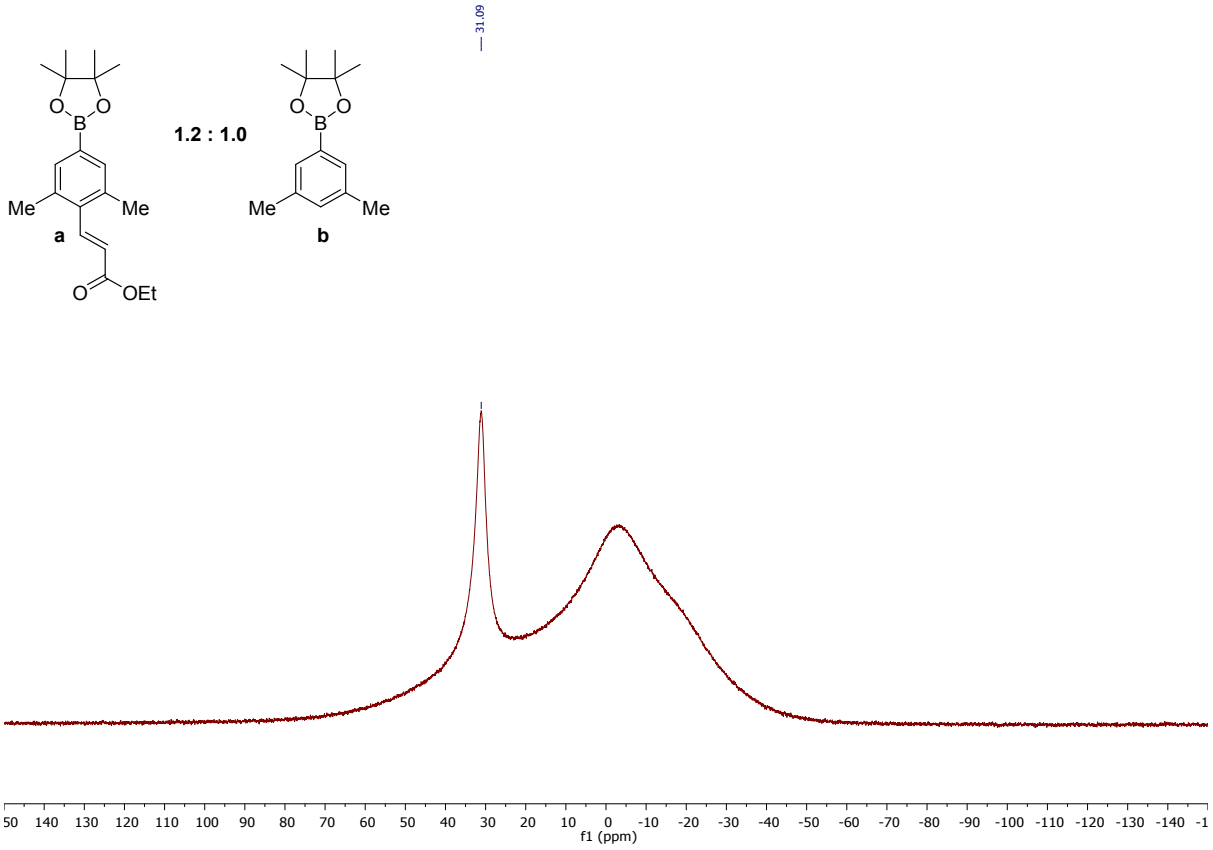
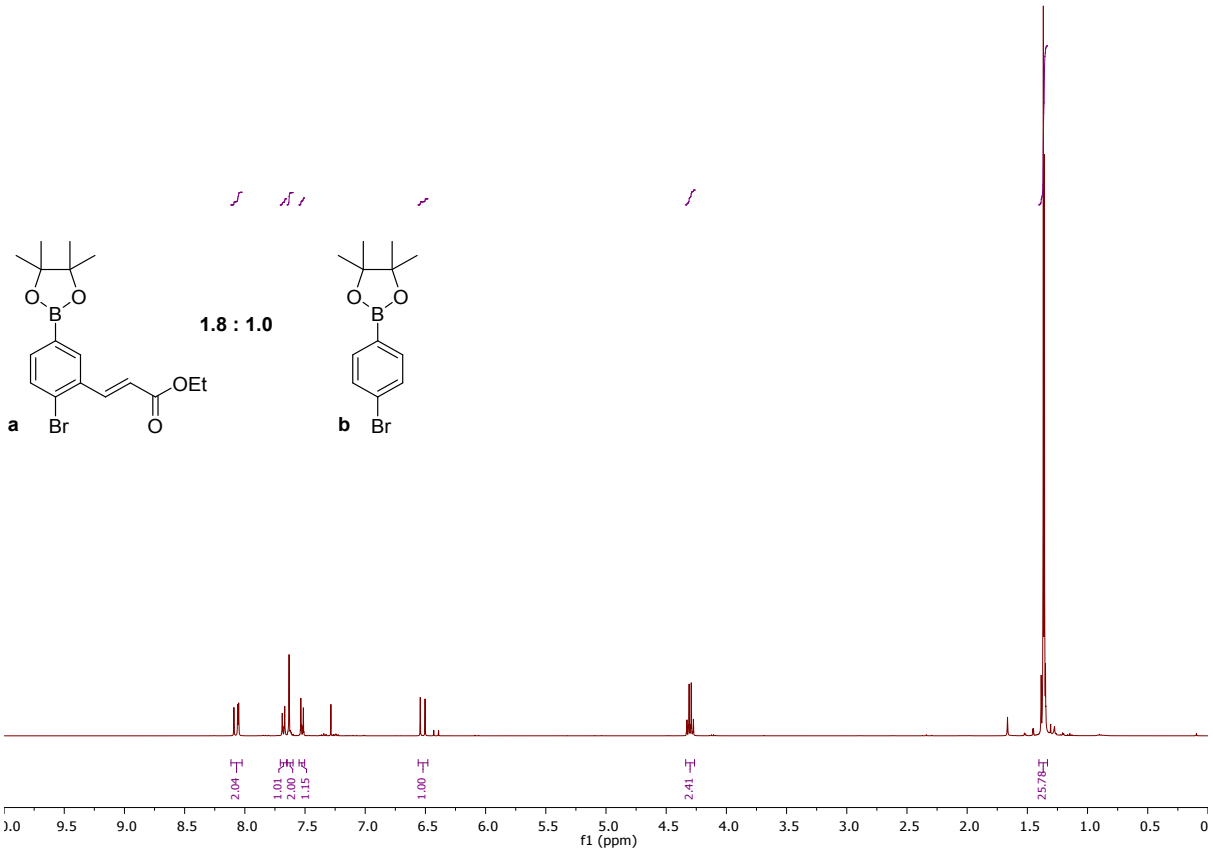
166.65
143.50
135.42
135.32
134.66
134.28
131.96
129.77
128.60
121.23
84.39
77.34
60.52
52.44
24.89
14.34
4.7 : 1.0
OEt
O
CO2Me
a
CO2Me
b
f1 (ppm)

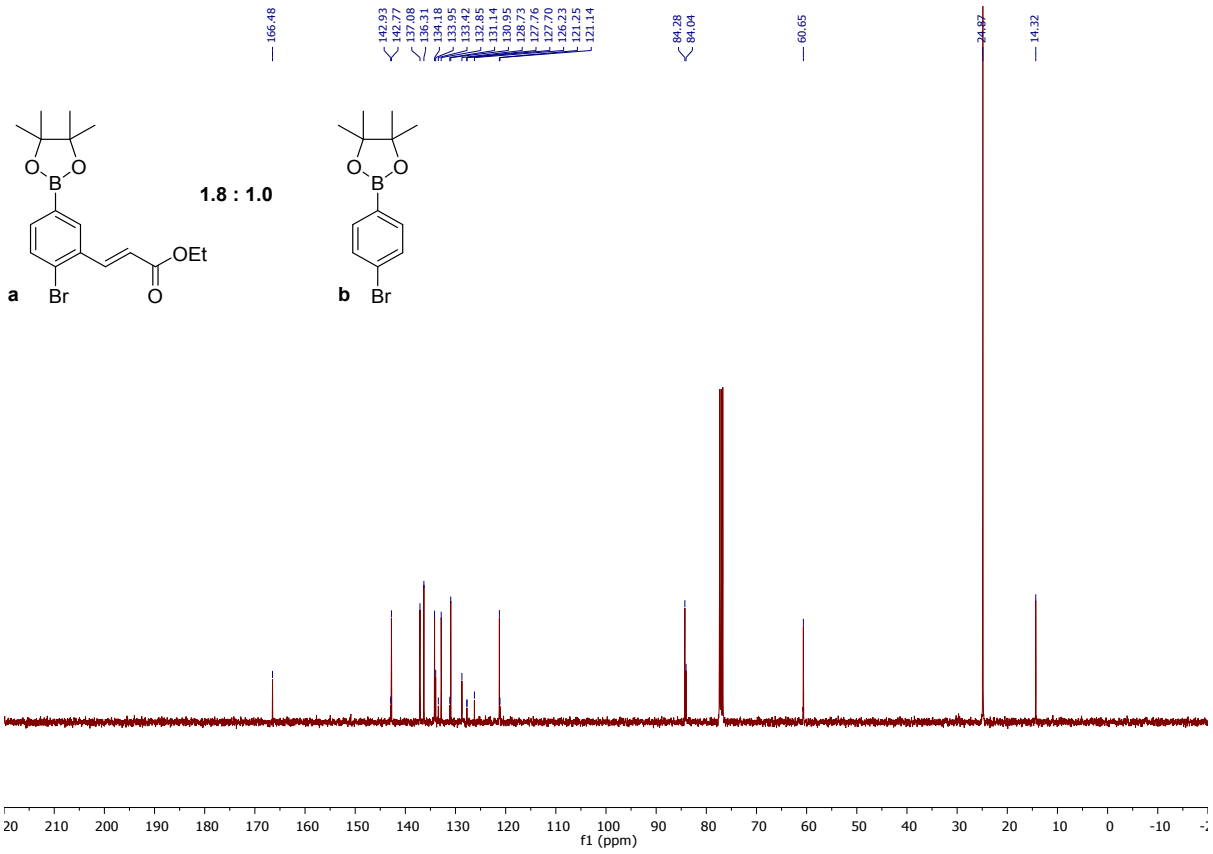

30.90
4.7 : 1.0
OEt
O
CO2Me
a
CO2Me
b
f1 (ppm)

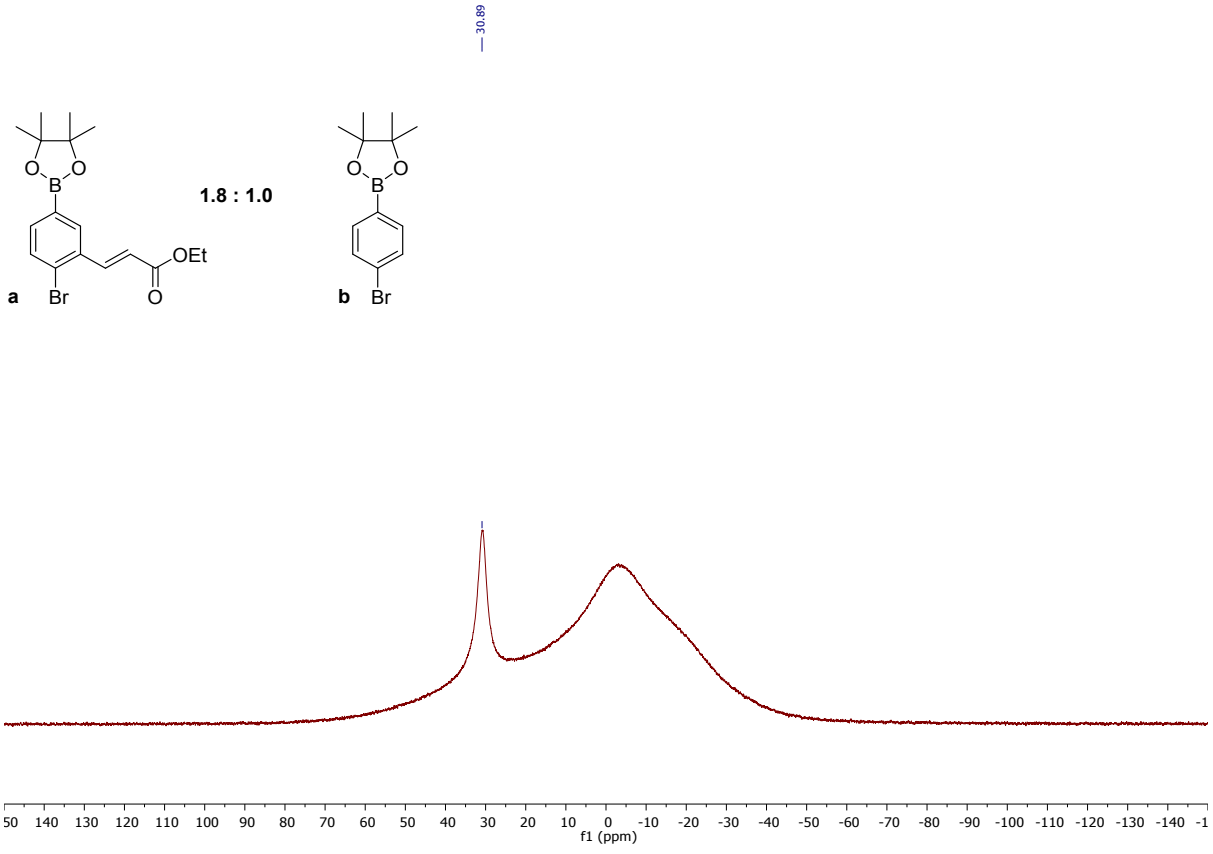

7.89
7.85
7.54
7.47
7.47
7.47
7.47
7.14
7.14
7.13
7.13
7.13
7.13
7.13
6.13
6.08
4.33
4.32
4.30
4.28
2.38
2.35
2.35
1.39
1.38
1.37
1.36
1.2 : 1.0
Me
Me
a
O
OEt
Me
Me
b
0.98
2.00
1.67
0.87
1.04
2.34
6.40
5.72
28.93
f1 (ppm)

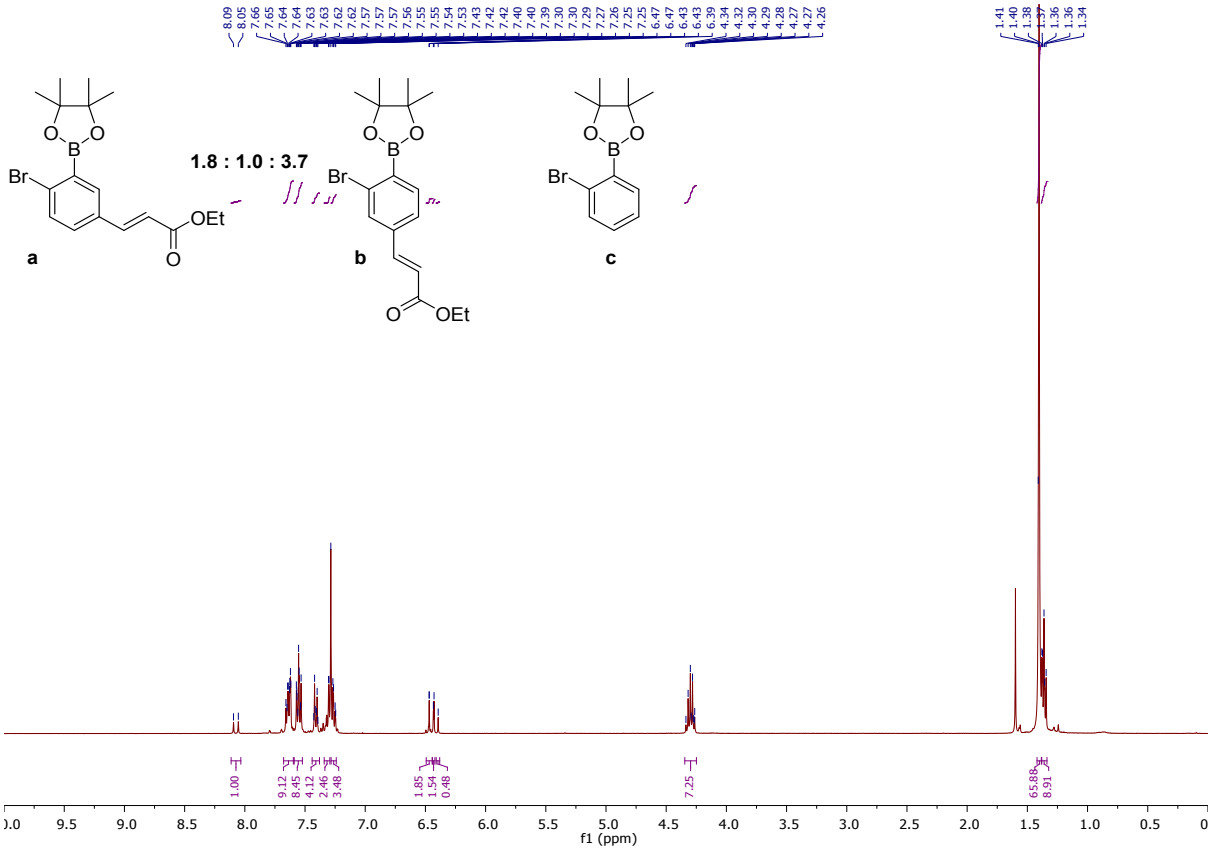

166.71
143.22
137.16
136.97
135.81
134.43
132.99
132.40
124.31
83.88
83.68
60.61
24.86
21.15
20.83
14.33
1.2 : 1.0
Me
Me
a
O
OEt
Me
Me
b
f1 (ppm)

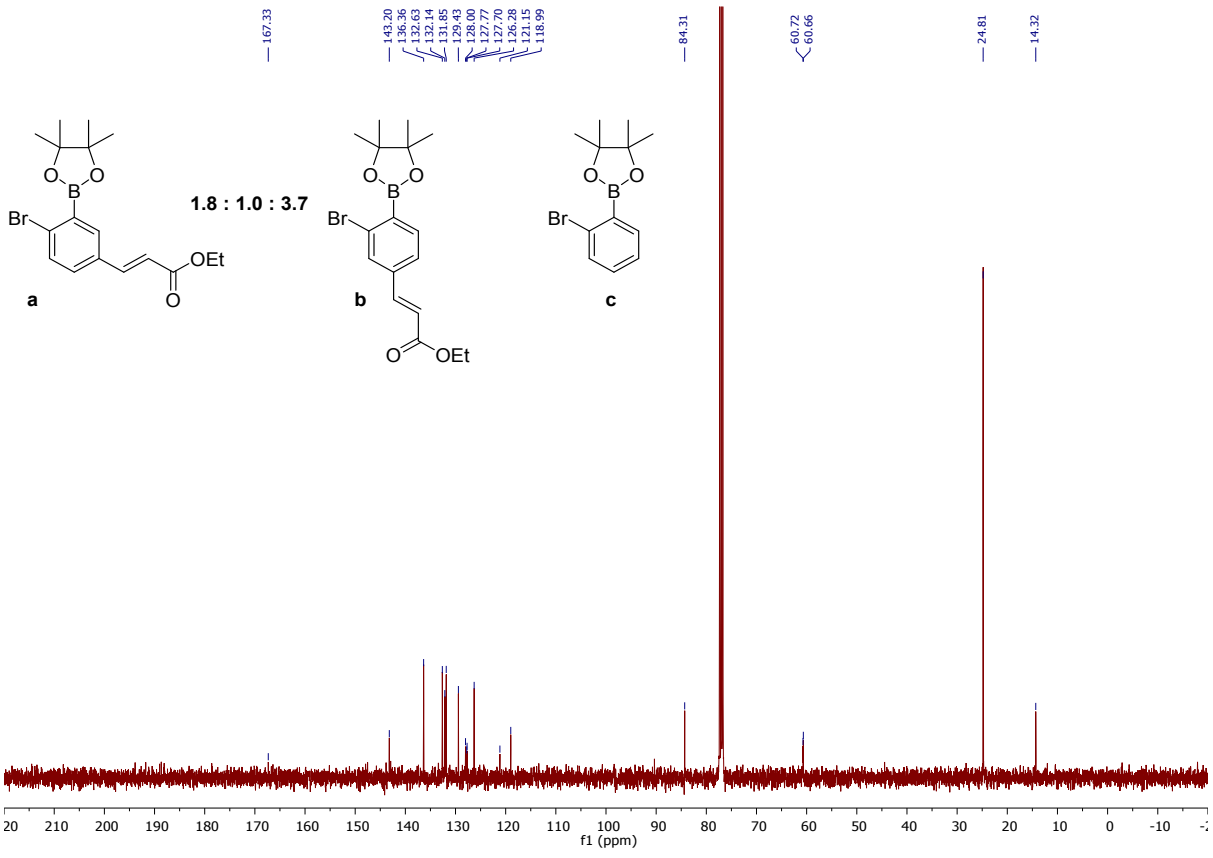

31.09
1.2 : 1.0
Me
Me
a
Me
Me
b
O
B
O
OEt
f1 (ppm)

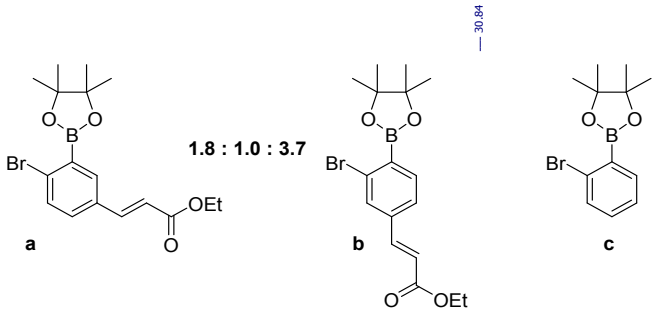

1.8 : 1.0
a
Br
OEt
O
b
Br
2.04
1.01
2.00
1.15
1.00
2.41
25.78
f1 (ppm)

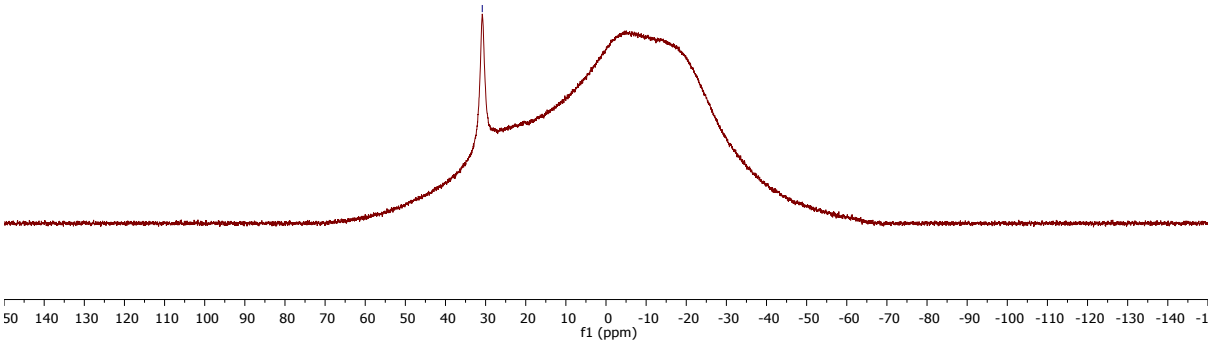

166.48
142.93
142.77
137.08
136.31
134.18
133.95
133.42
132.85
131.14
130.95
128.73
127.76
127.70
126.23
121.25
121.14
84.28
84.04
60.65
24.87
14.32
1.8 : 1.0
OEt
a
Br
O
b
Br
f1 (ppm)

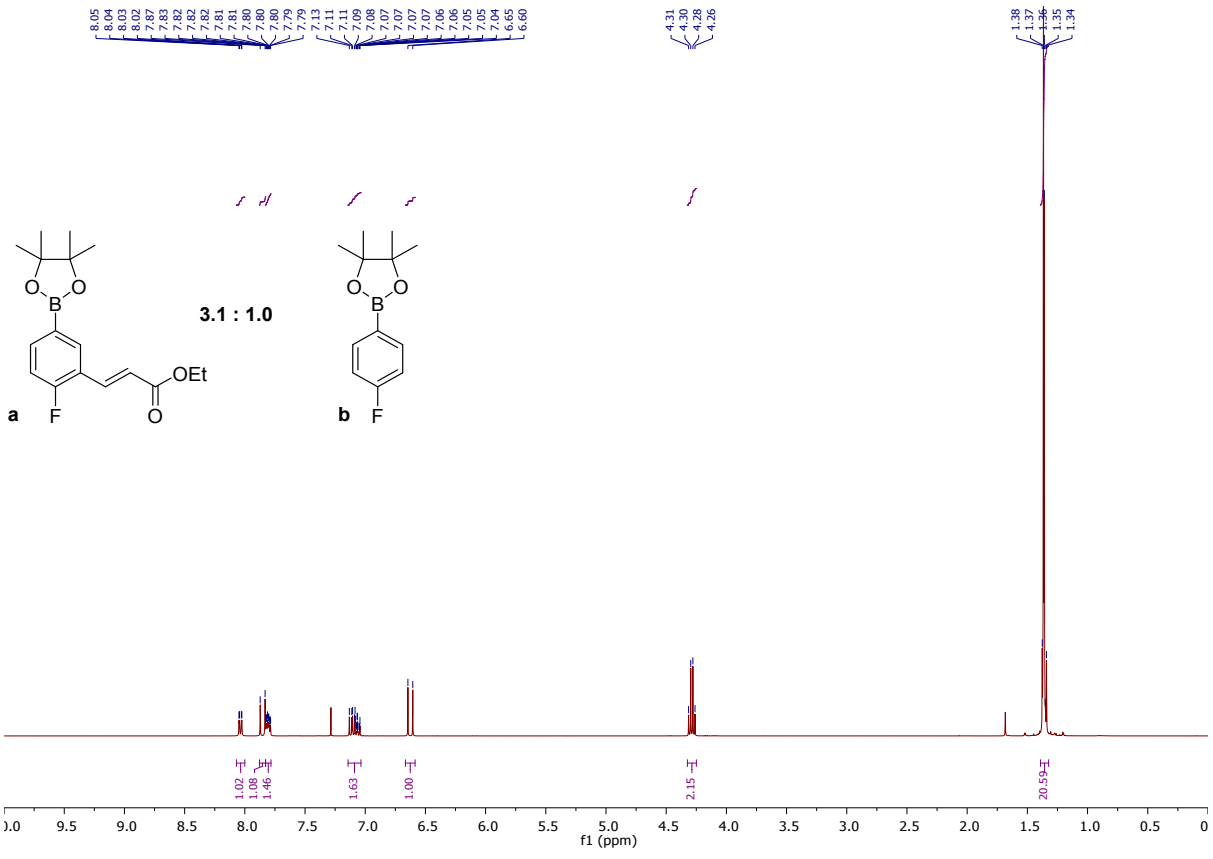

30.89
1.8 : 1.0
OEt
a
Br
O
b
Br
f1 (ppm)

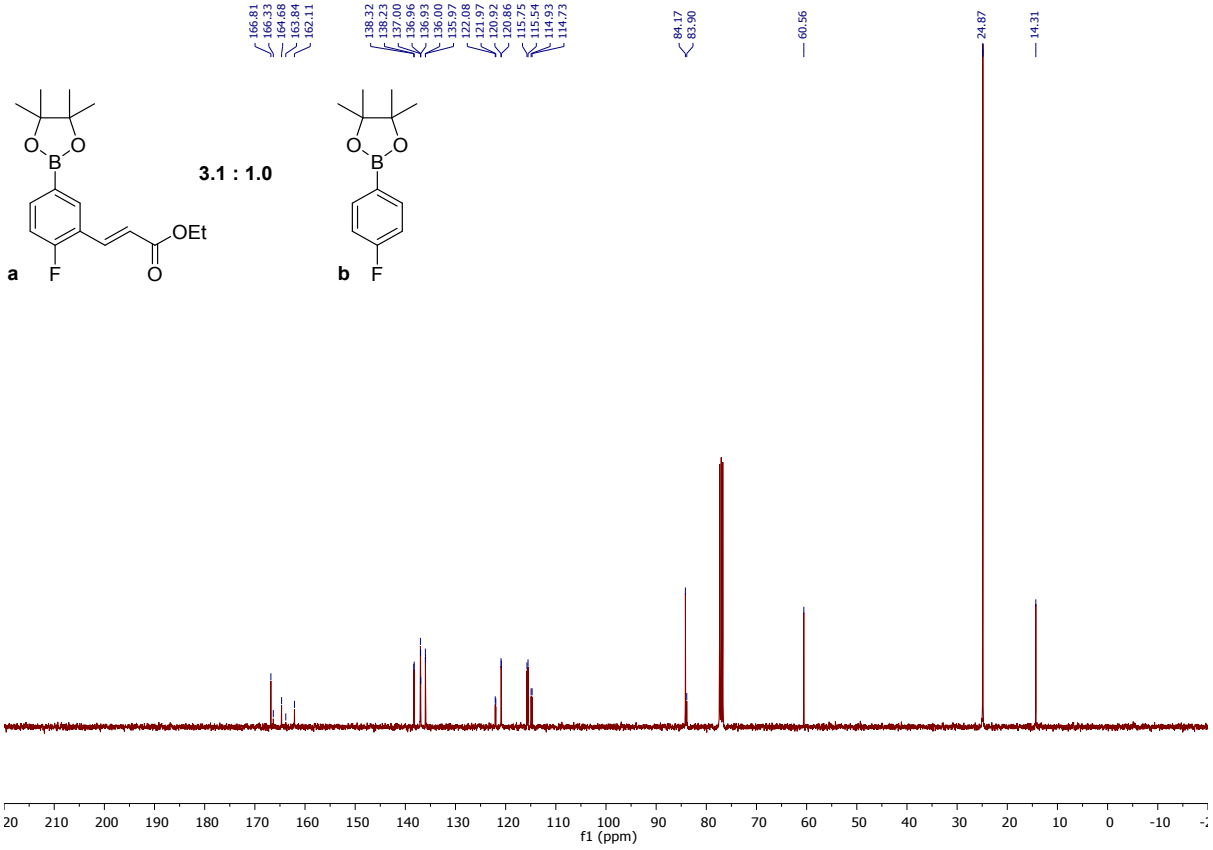

1.8 : 1.0 : 3.7
a
b
c
f1 (ppm)

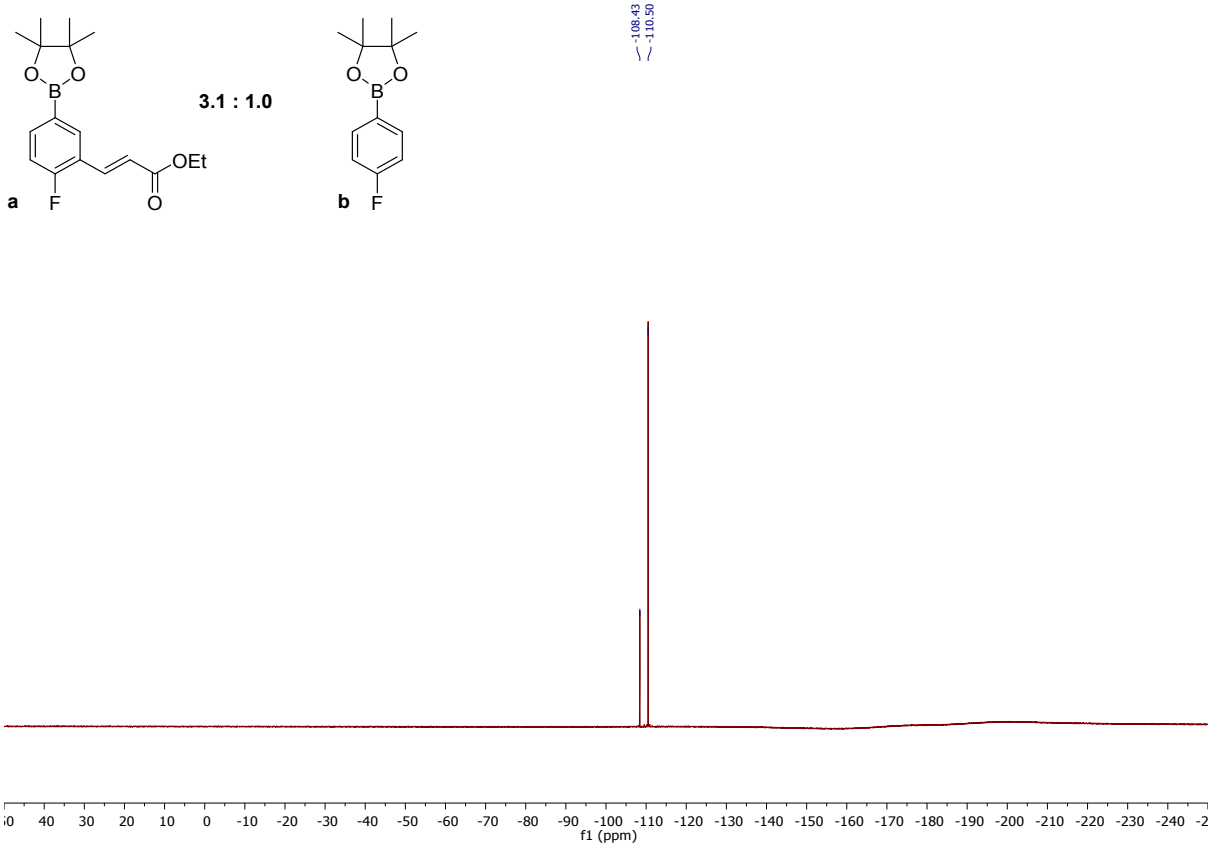

1.8 : 1.0 : 3.7
a
b
c
f1 (ppm)

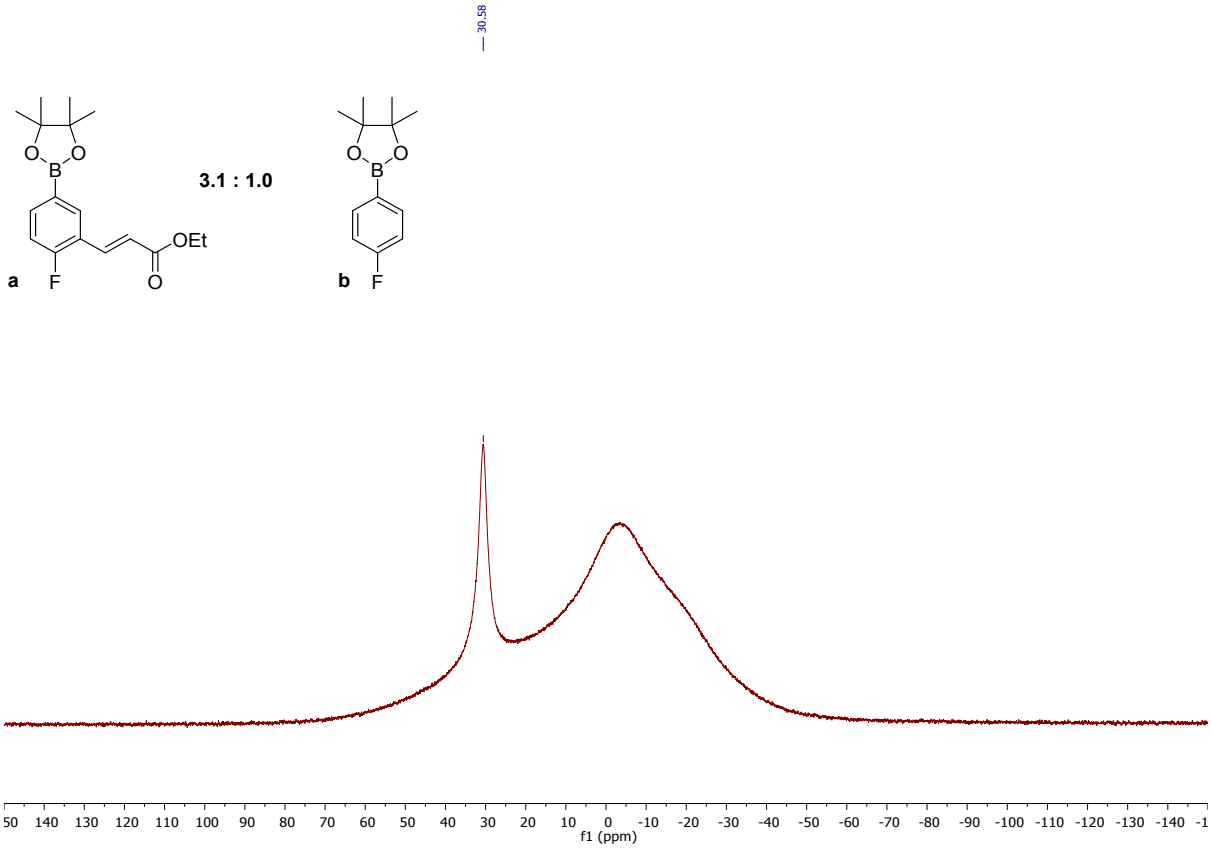

30.84
1.8 : 1.0 : 3.7
Br
OEt
O
a
b
c

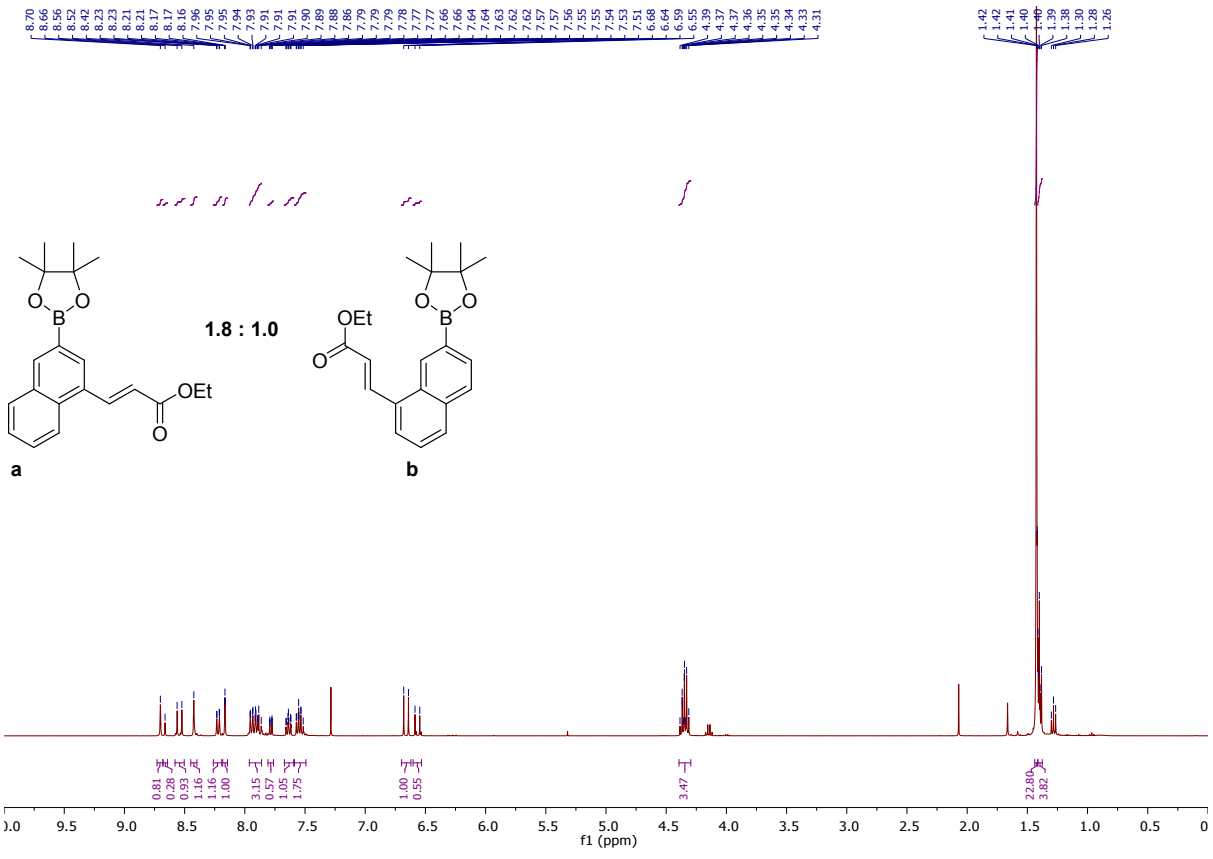

f1 (ppm)

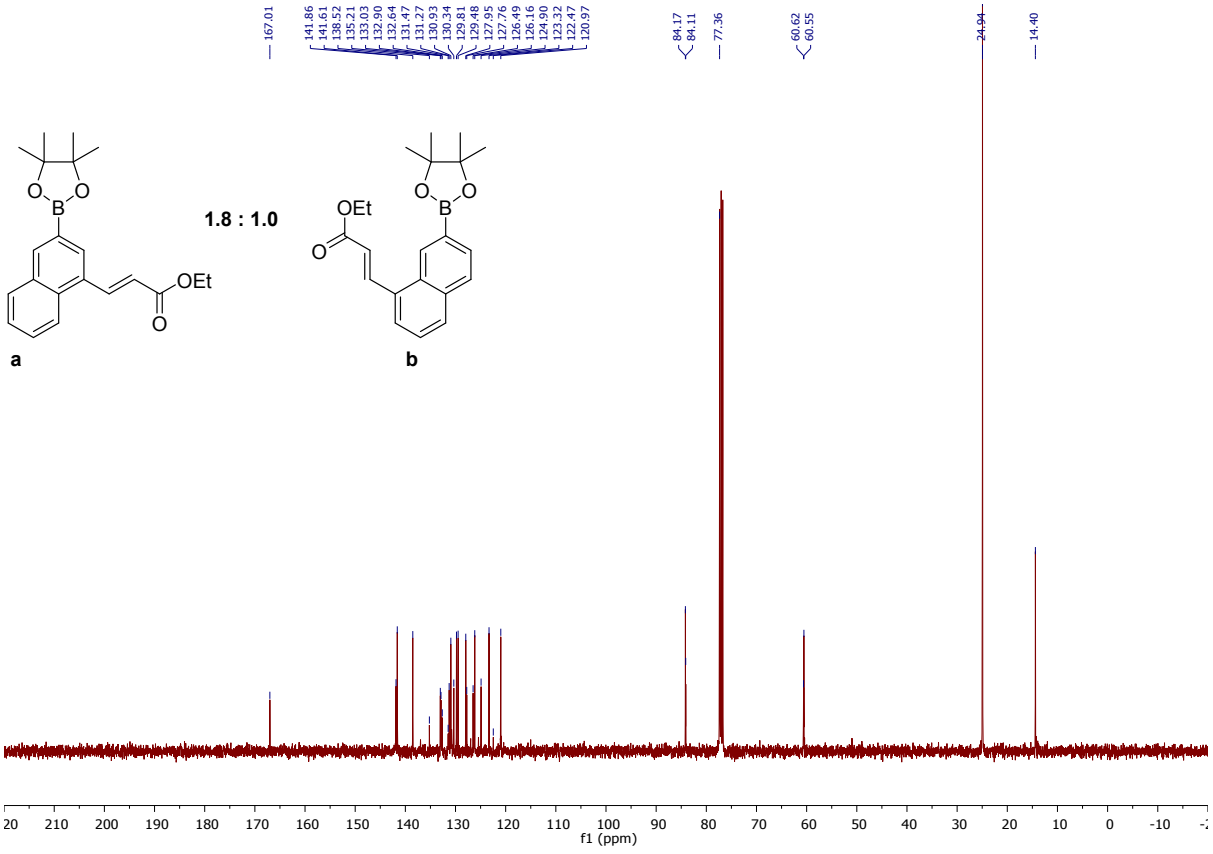

3.1 : 1.0
OEt
F
O
a
b
f1 (ppm)


166.81
166.33
164.68
163.84
162.11
138.32
138.23
137.00
136.96
136.93
136.00
135.97
122.08
121.97
120.92
120.86
115.75
115.54
114.93
114.73
84.17
83.90
60.56
24.87
14.31
3.1 : 1.0
a
b
F
O
OEt
f1 (ppm)


-108.43
-110.50
3.1 : 1.0
a
b
F
O
OEt
f1 (ppm)


30.58
3.1 : 1.0
a
b
OEt
F
O
B
f1 (ppm)


1.8 : 1.0
a
b
OEt
O
B
f1 (ppm)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141.86
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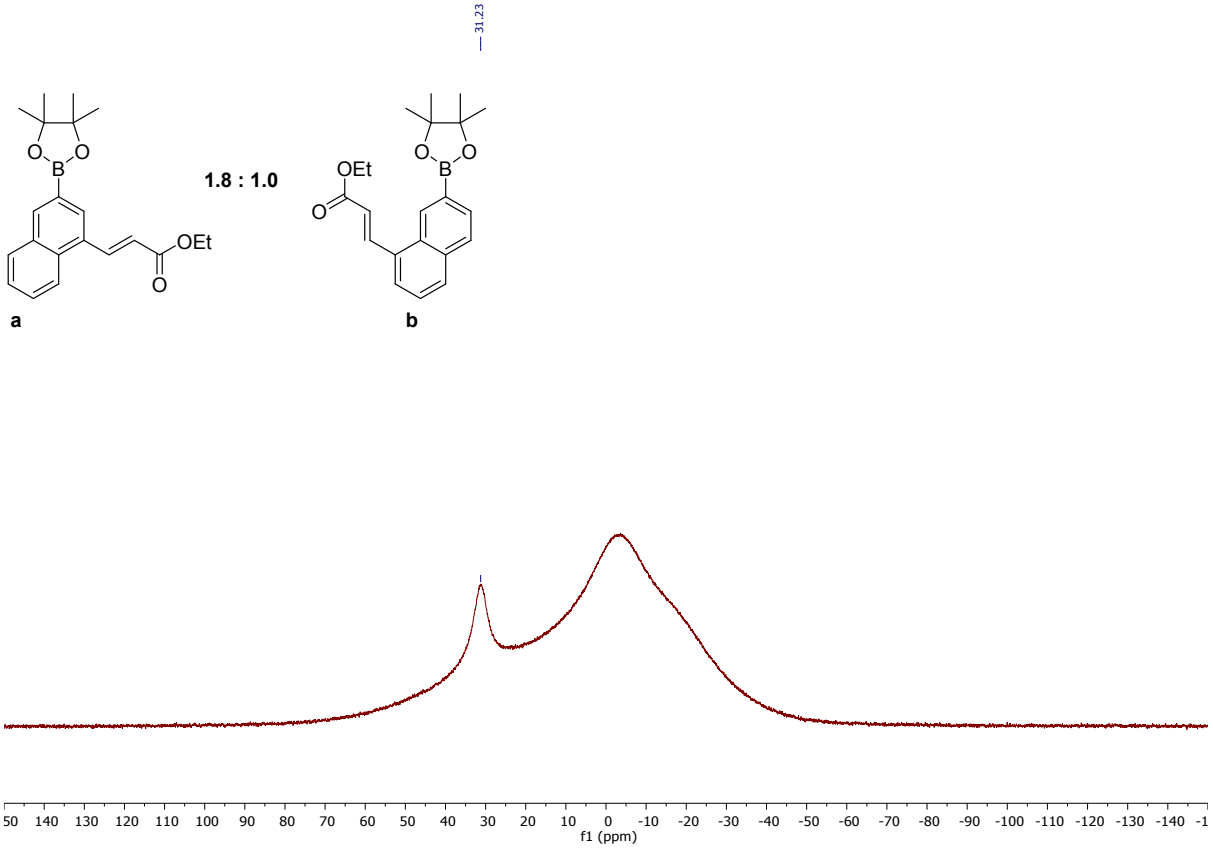
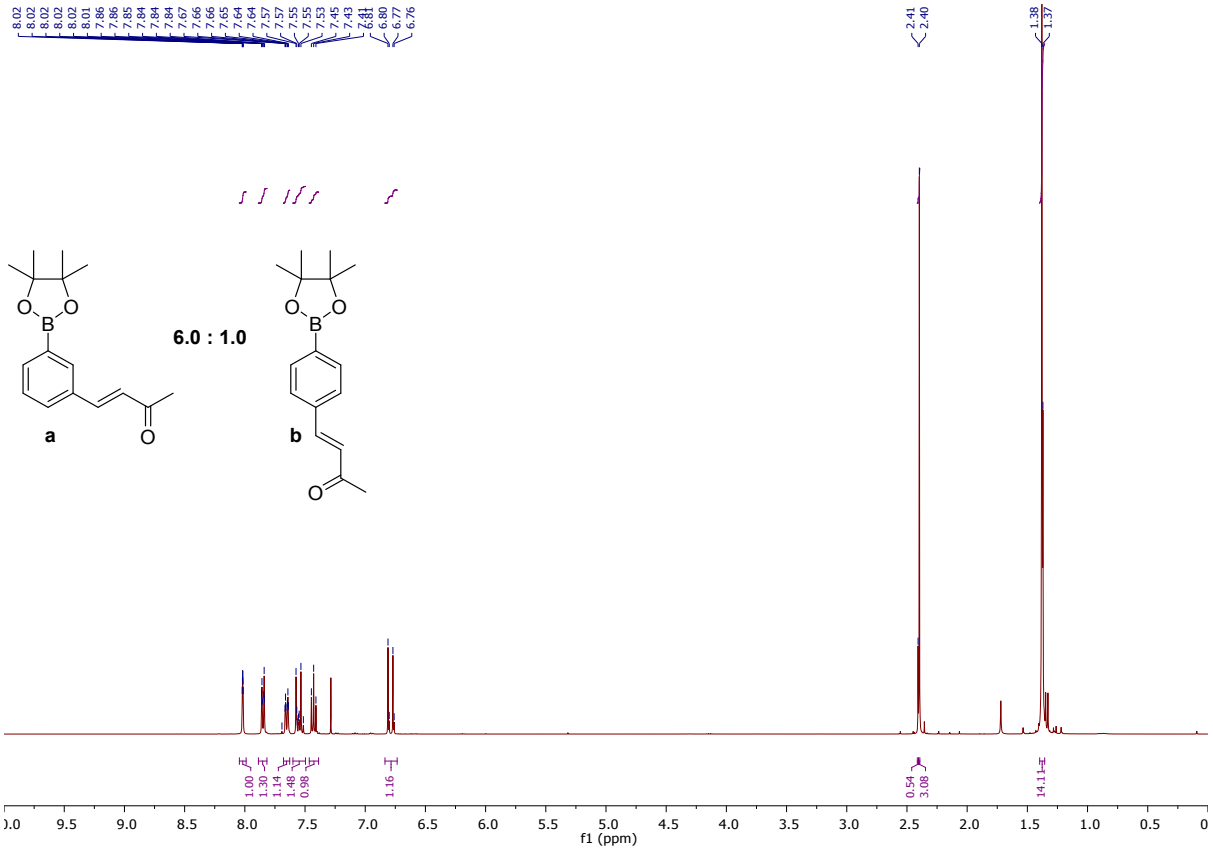
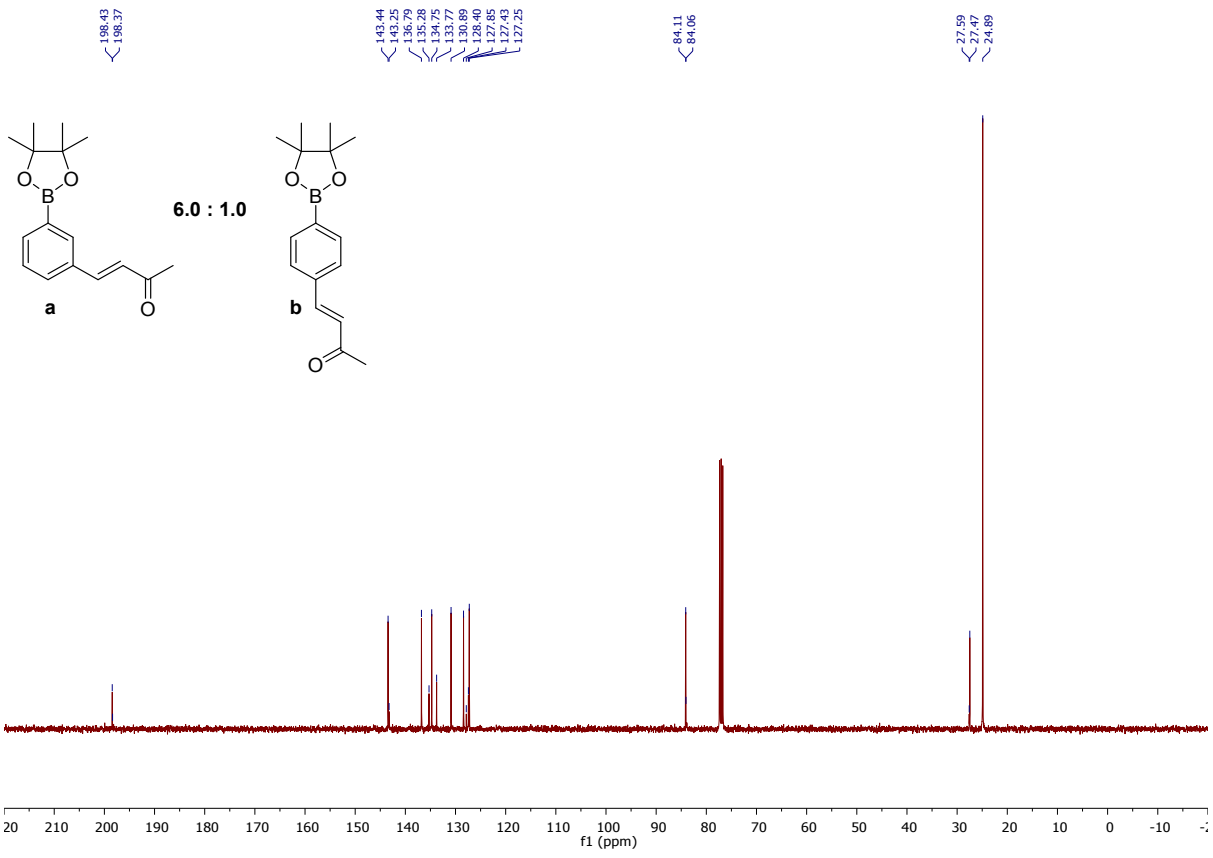
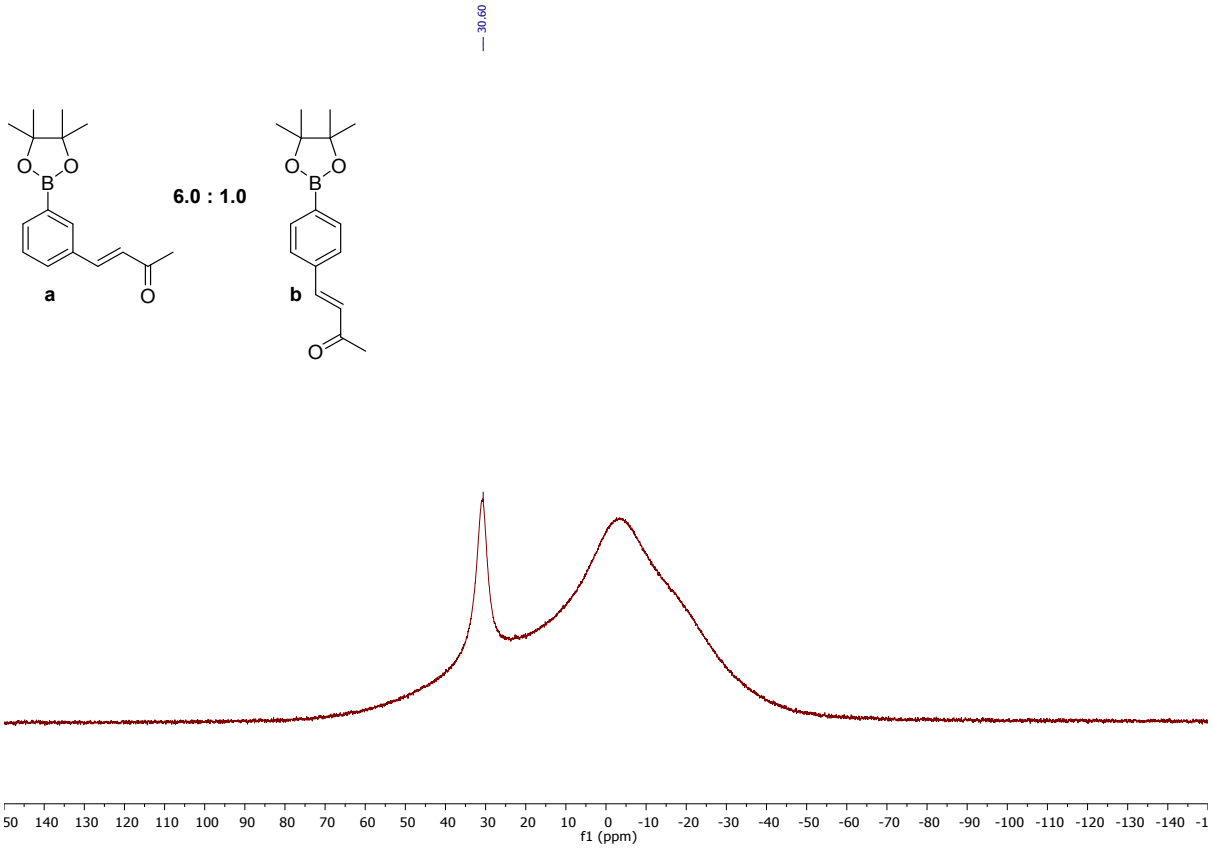
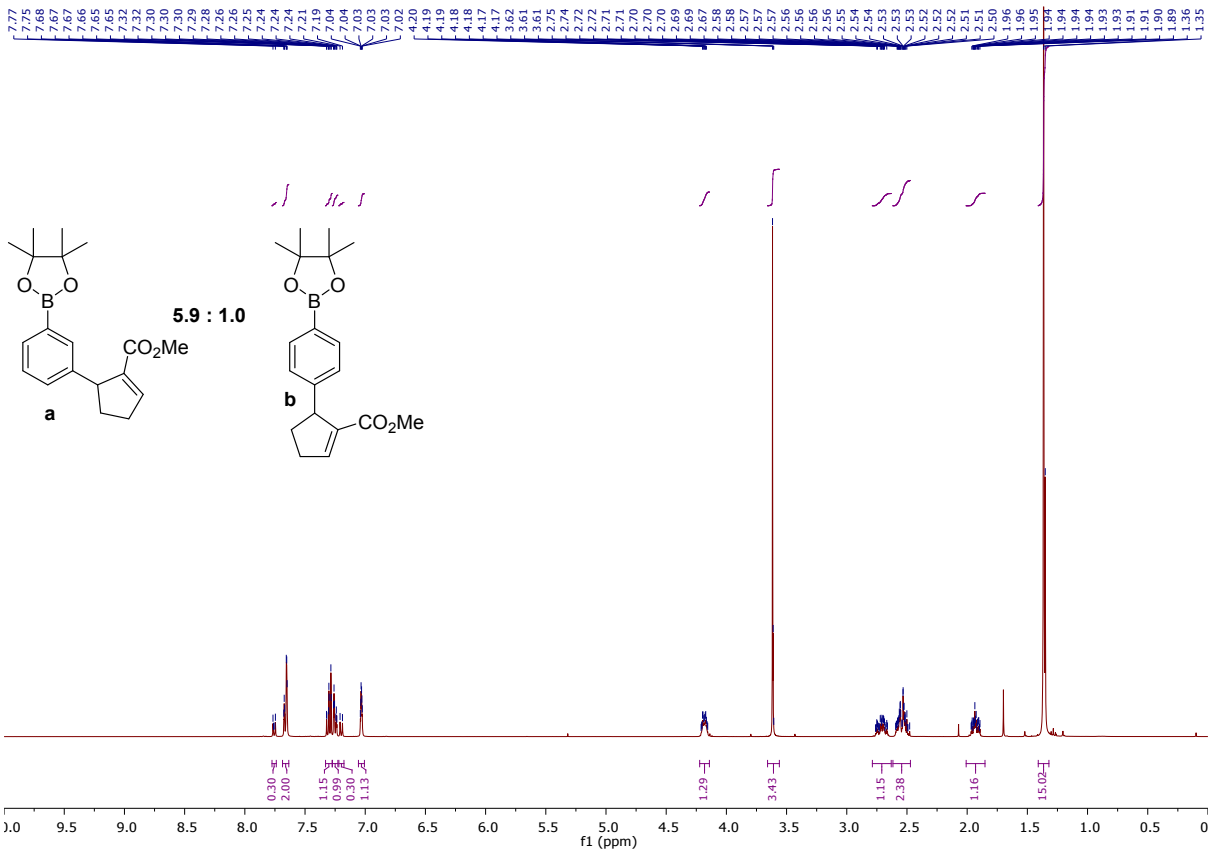
138.52
135.21
133.03
132.90
132.64
131.47
131.27
130.93
130.34
129.81
129.48
127.95
127.76
126.49
126.16
124.90
123.32
122.47
120.97
84.17
84.11
77.36
60.62
60.55
24.94
14.40
1.8 : 1.0
OEt
O
B
O
O
OEt
a
b
f1 (ppm)

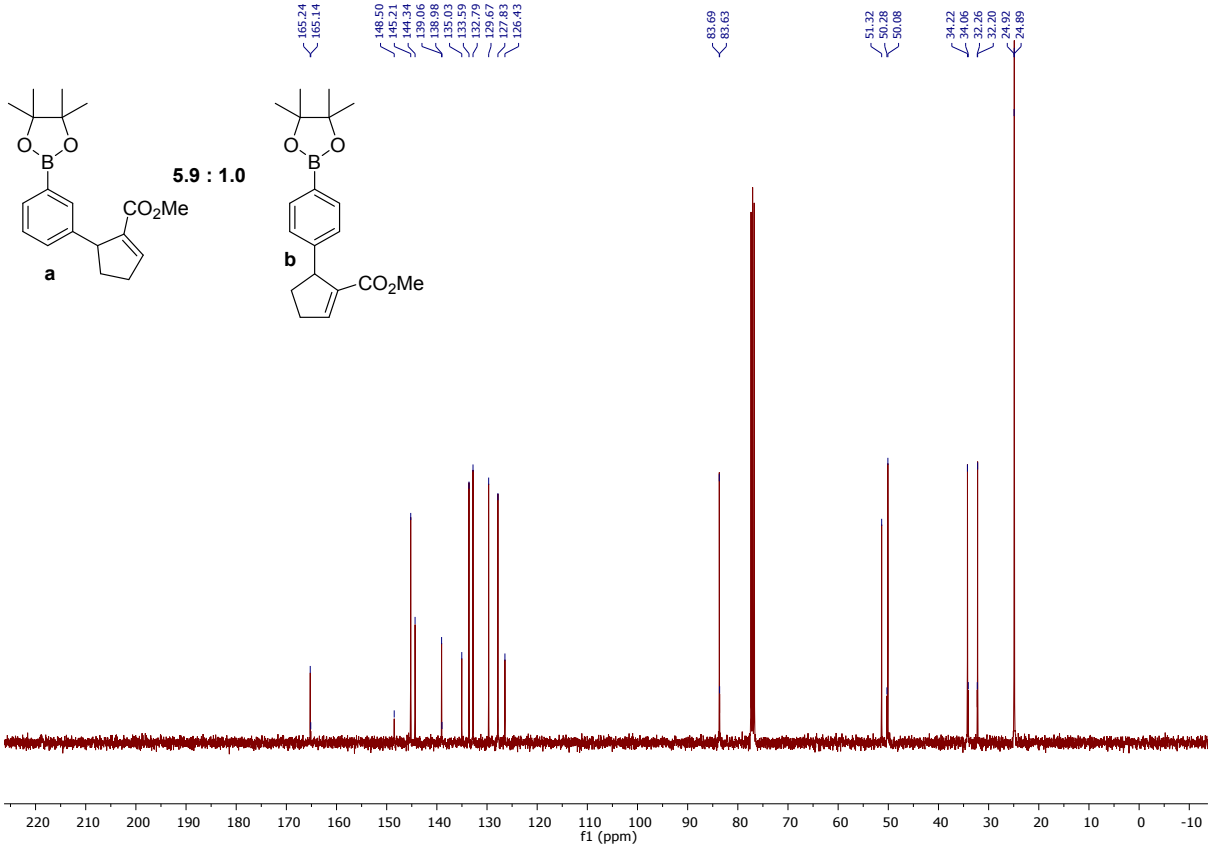

31.23
1.8 : 1.0
OEt
O
B
O
O
OEt
a
b
f1 (ppm)

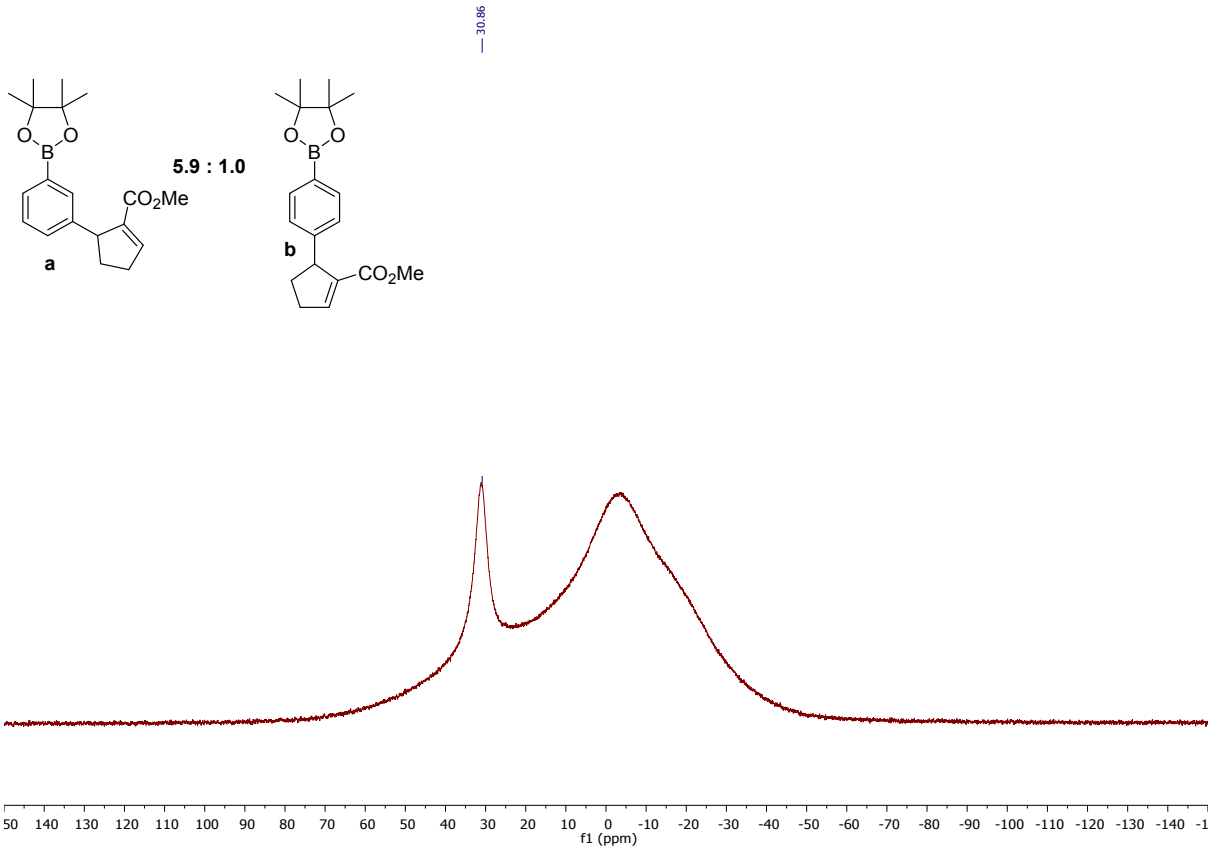

6.0 : 1.0
a
b
f1 (ppm)

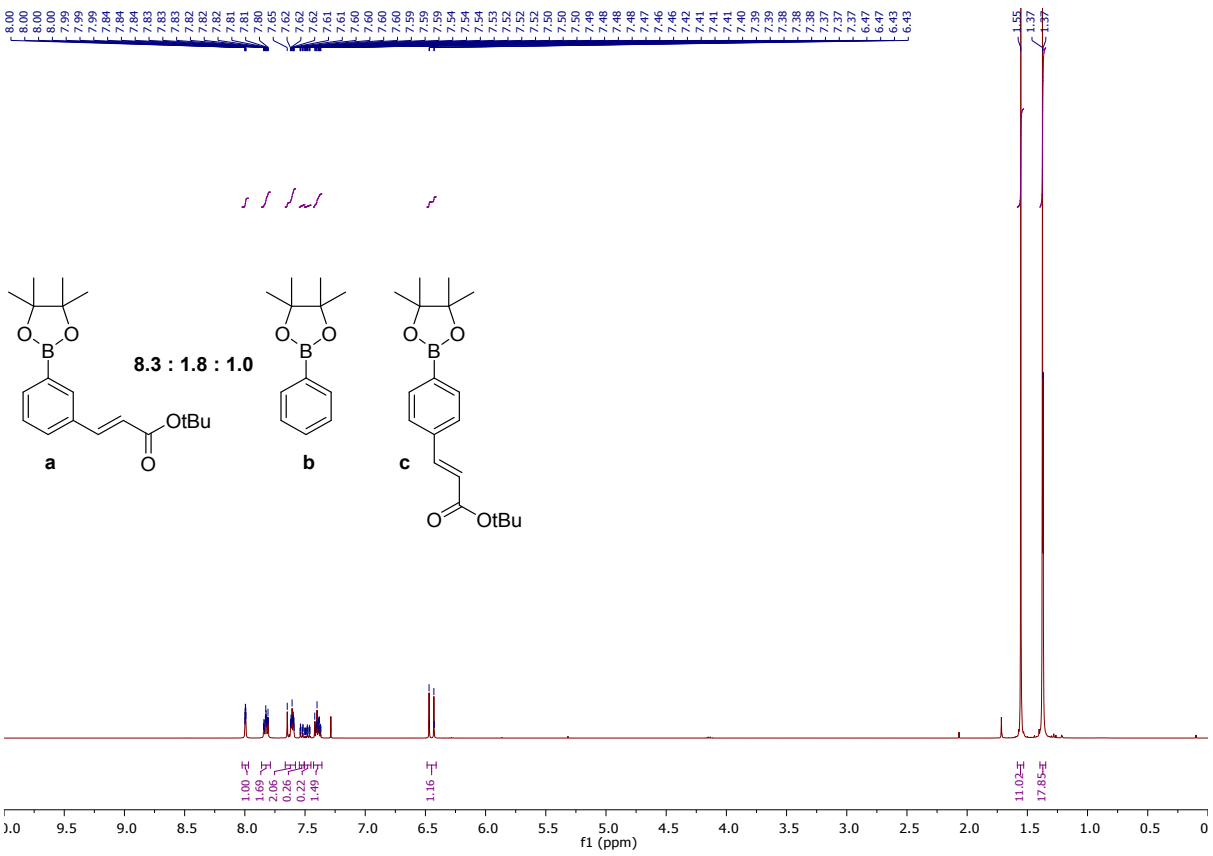

6.0 : 1.0
a
b
f1 (ppm)

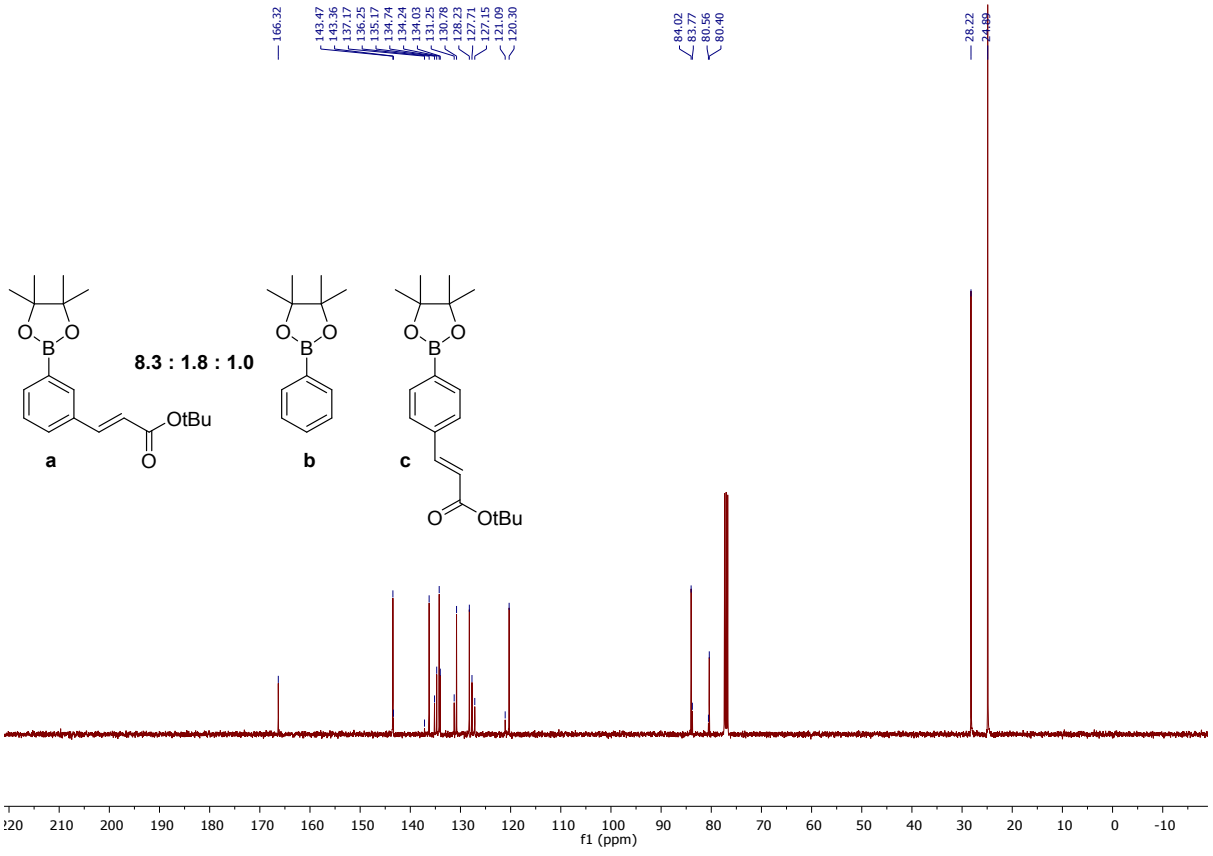

30.60
6.0 : 1.0
a
b
f1 (ppm)

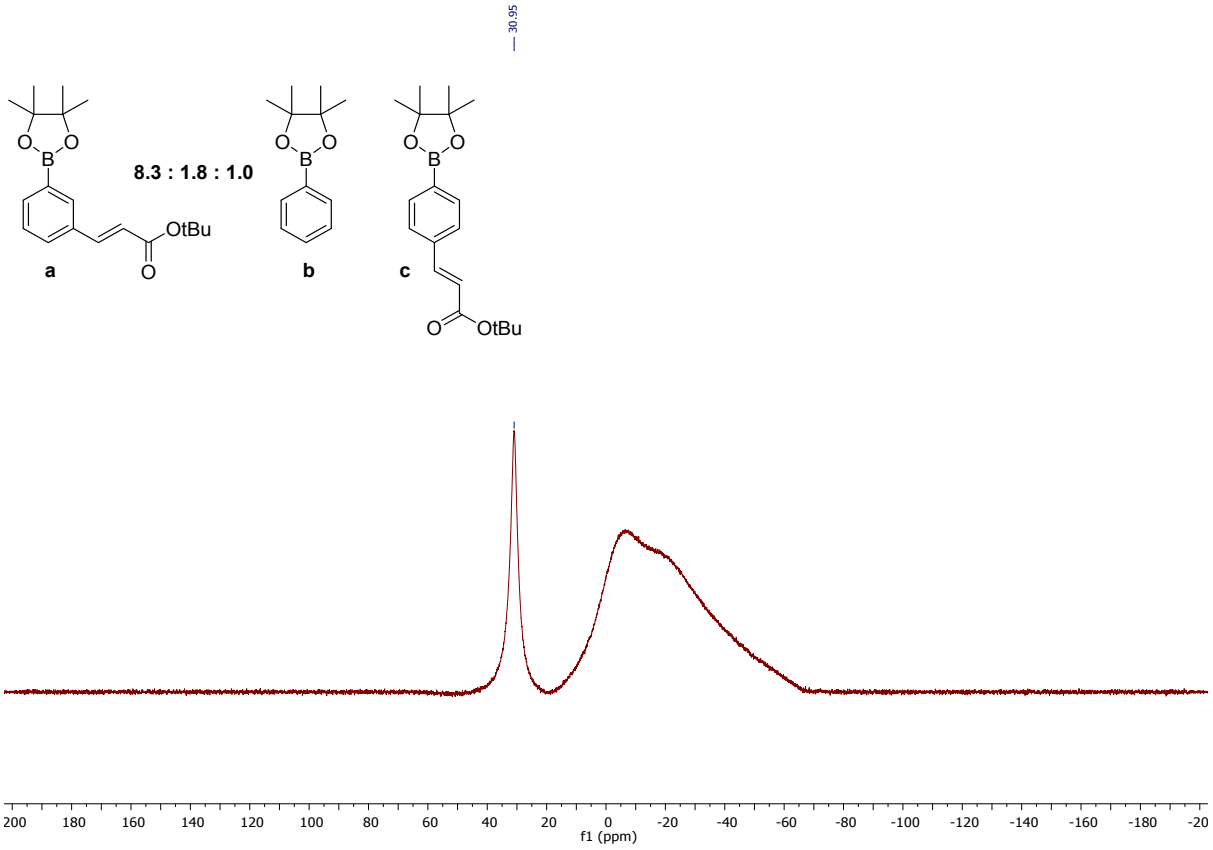

5.9 : 1.0
CO2Me
a
b
f1 (ppm)

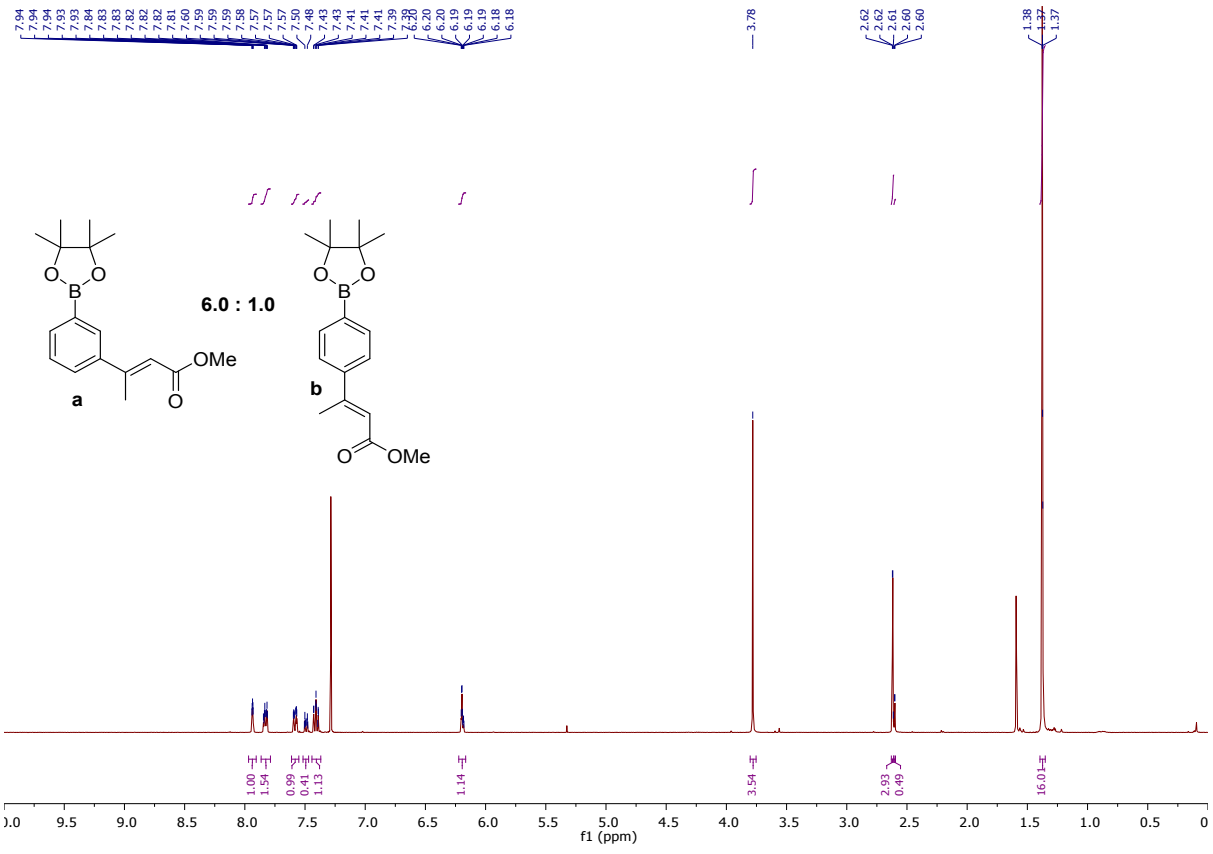

165.24
165.14
148.50
145.21
144.34
139.06
138.98
135.03
133.59
132.79
129.67
127.83
126.43
83.69
83.63
51.32
50.28
50.08
34.22
34.06
32.26
32.20
24.92
24.89
5.9 : 1.0
a
b
CO2Me
CO2Me
f1 (ppm)

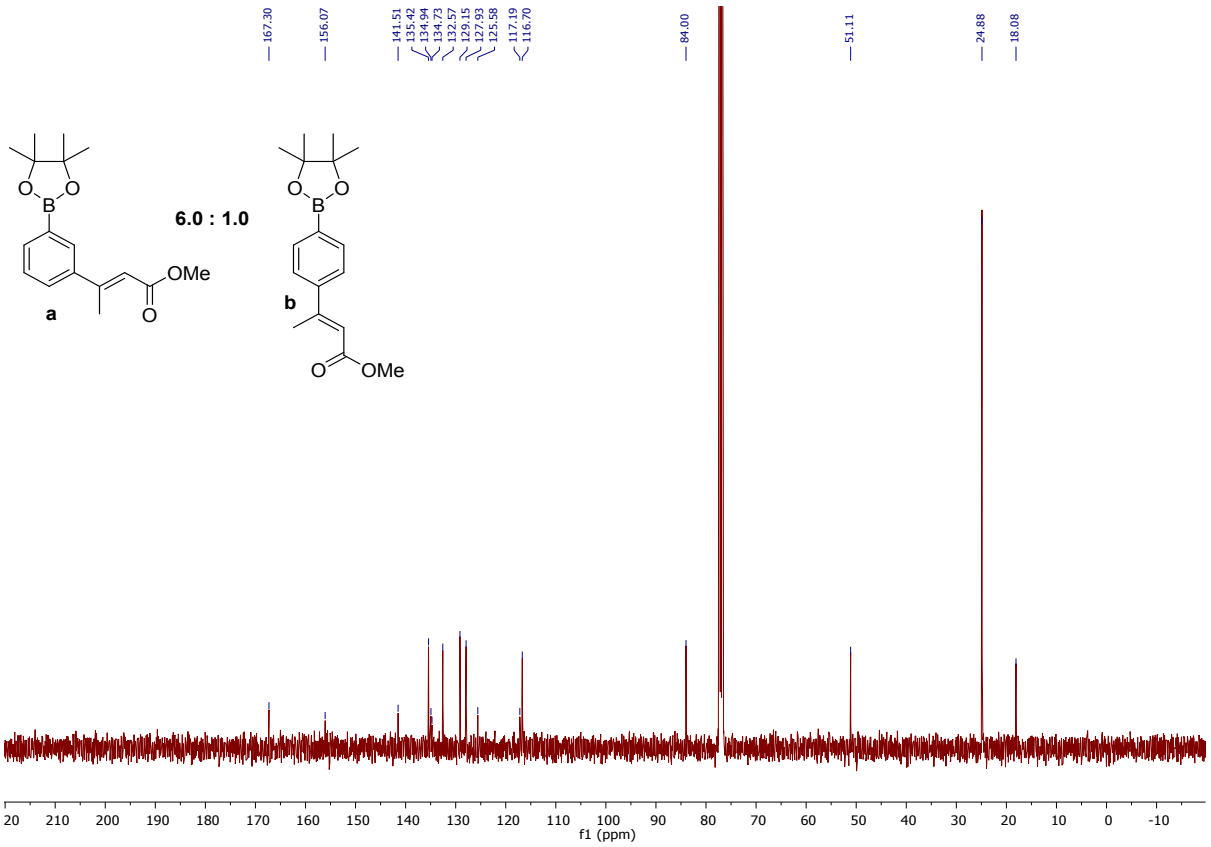

30.86
5.9 : 1.0
a
b
CO2Me
CO2Me
f1 (ppm)

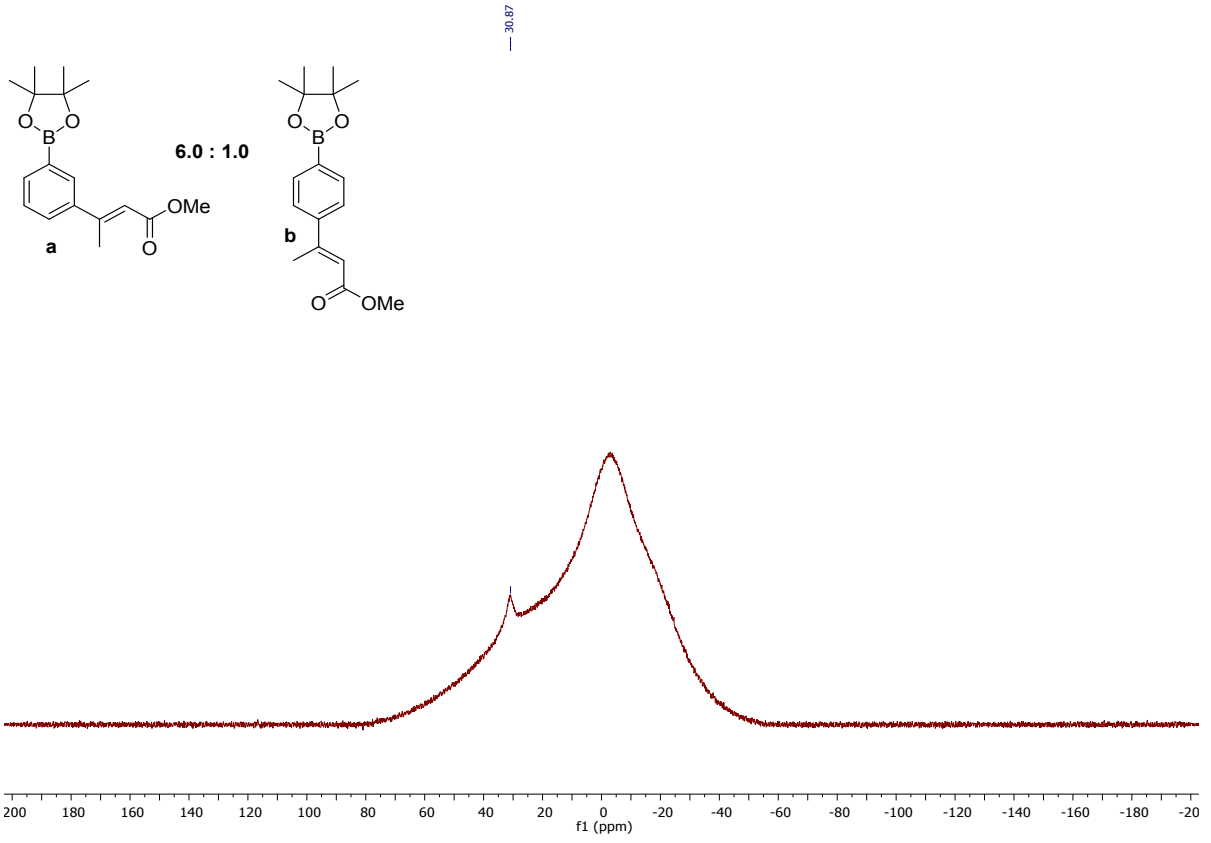

8.3 : 1.8 : 1.0
OtBu
O
a
b
c
OtBu
f1 (ppm)

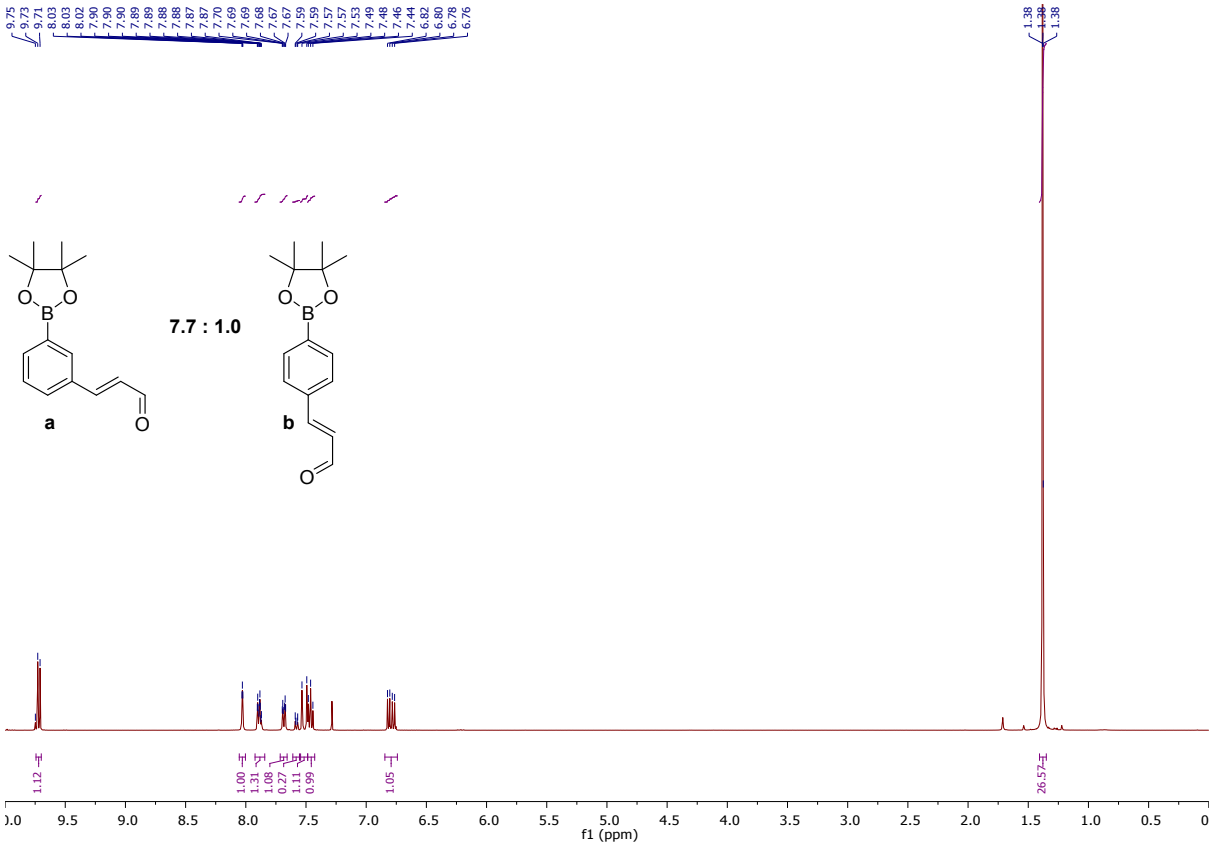

8.3 : 1.8 : 1.0
OtBu
O
a
b
c
OtBu
f1 (ppm)

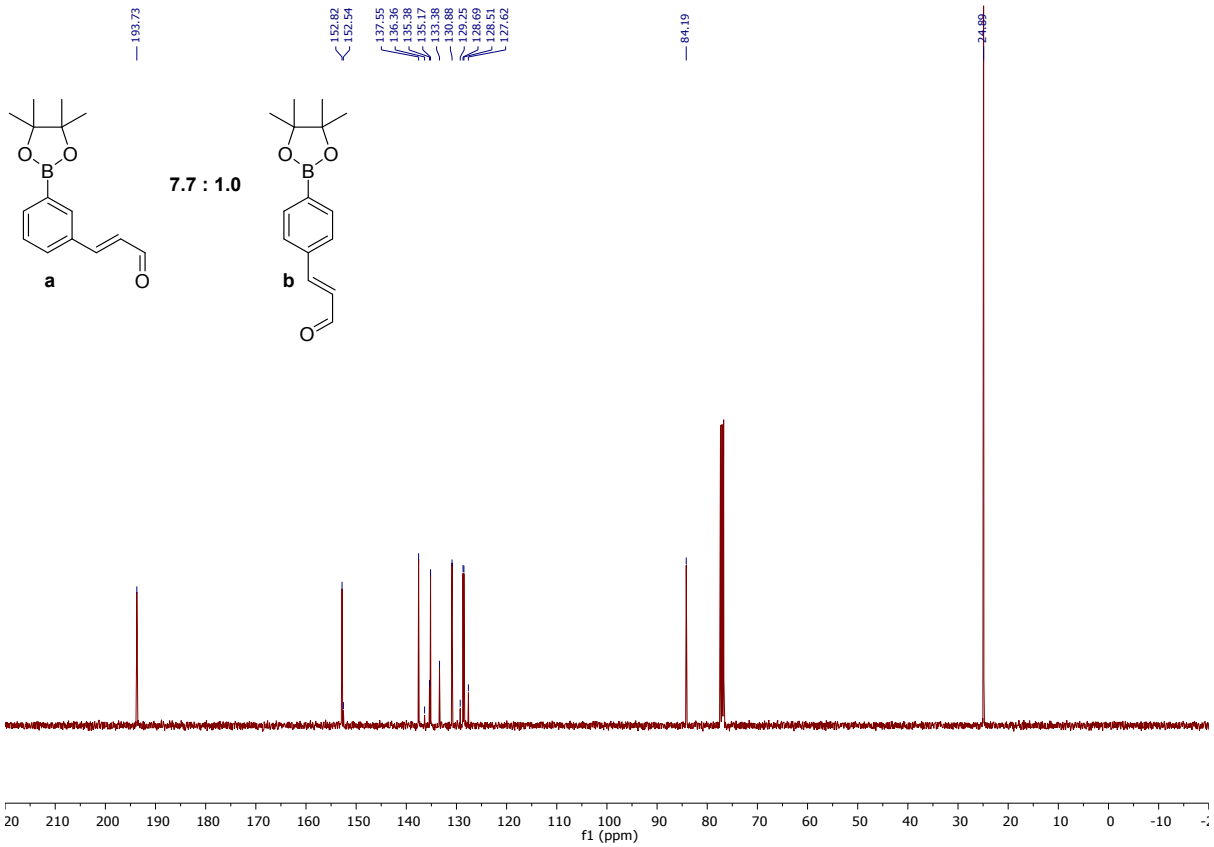

30.95
8.3 : 1.8 : 1.0
OtBu
a
b
c
OtBu
f1 (ppm)

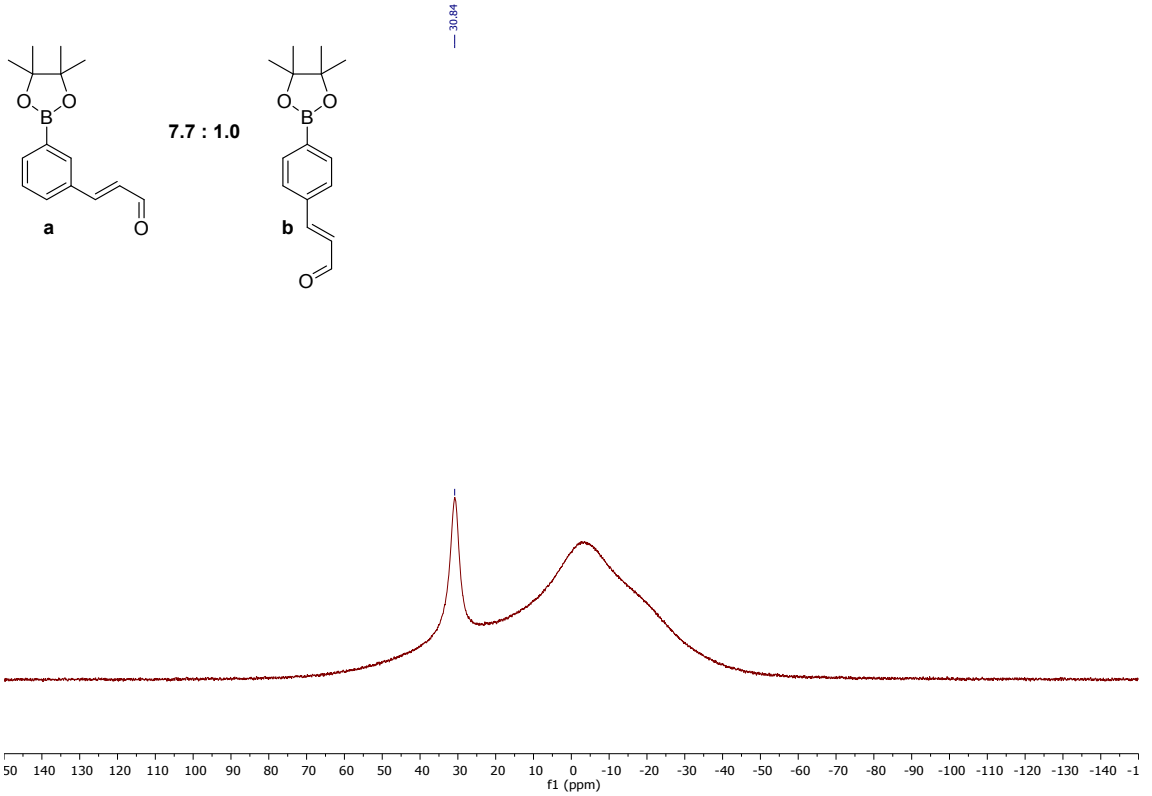

3.78
2.62
2.61
2.60
1.38
1.37
6.0 : 1.0
OMe
a
b
OMe
1.00
1.54
0.99
0.41
1.13
1.14
3.54
2.93
0.49
16.01
f1 (ppm)

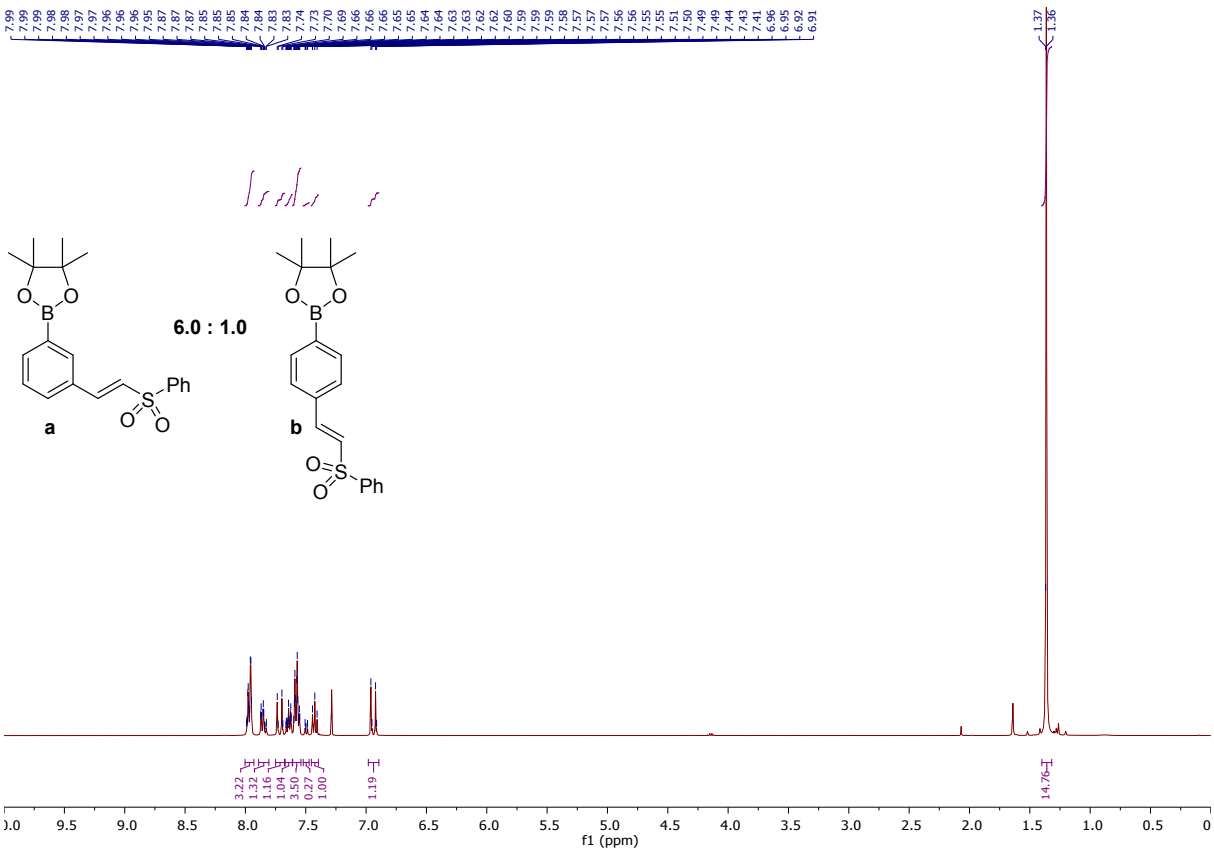

167.30
156.07
141.51
135.42
134.94
134.73
132.57
129.15
127.93
125.58
117.19
116.70
84.00
51.11
24.88
18.08
6.0 : 1.0
a
b
OMe
O
B
f1 (ppm)

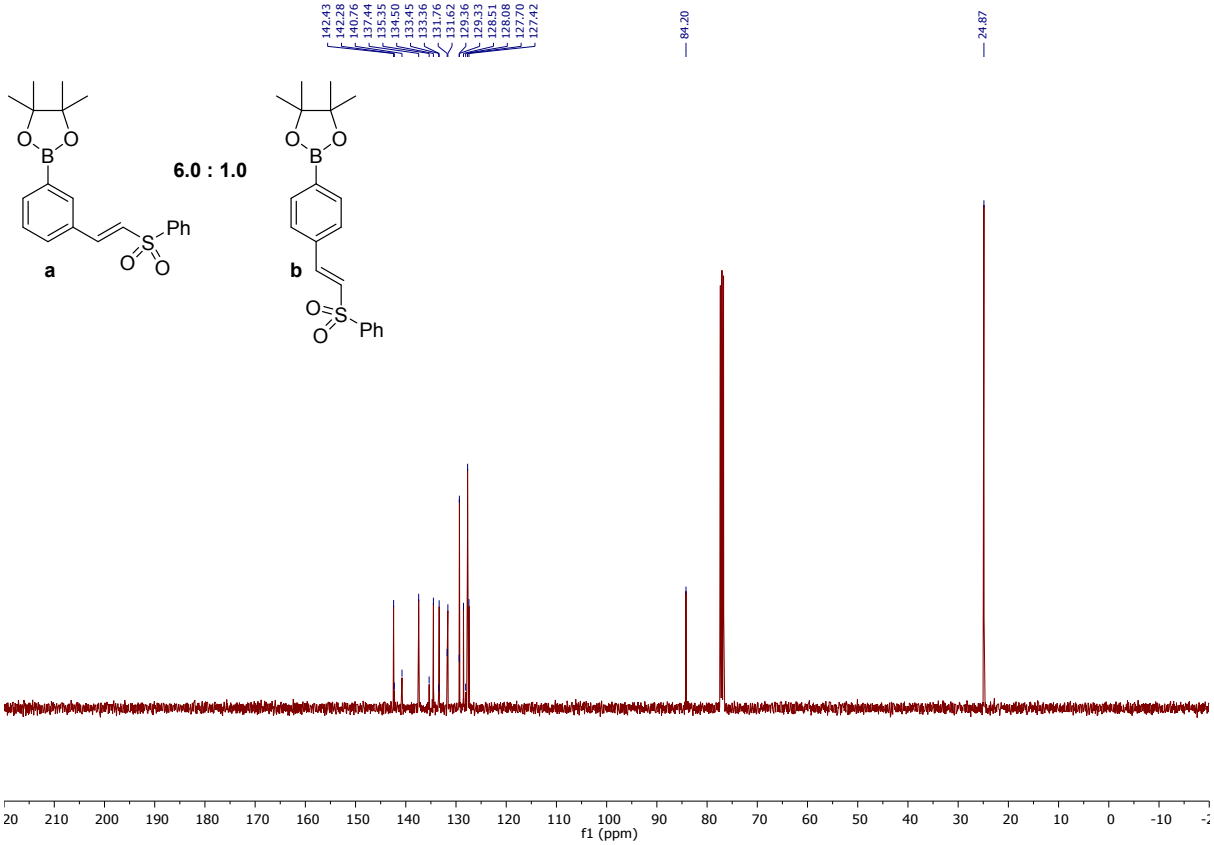

30.87
6.0 : 1.0
a
b
OMe
O
B
f1 (ppm)

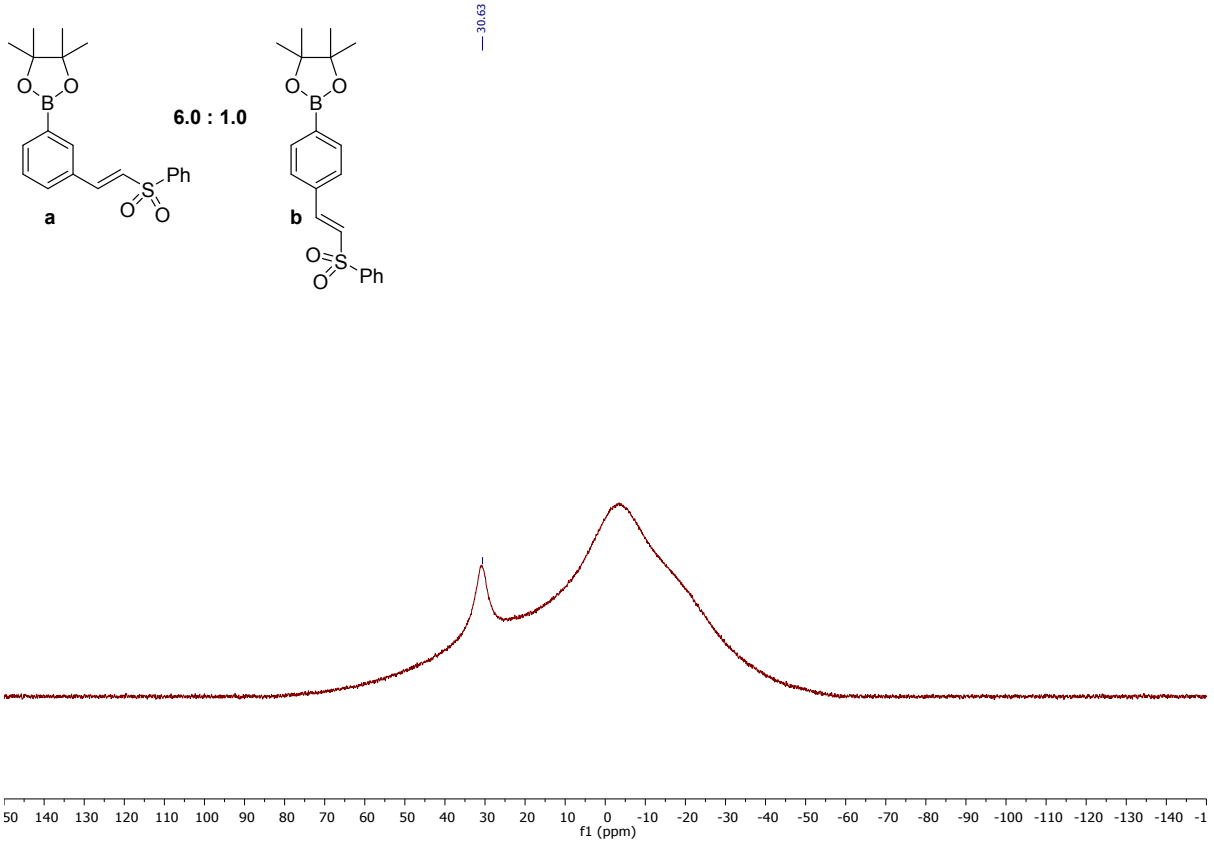

9.75
9.73
9.71
8.03
8.02
7.90
7.89
7.88
7.87
7.70
7.69
7.68
7.67
7.59
7.57
7.53
7.49
7.48
7.46
7.44
6.82
6.80
6.78
6.76
1.38
7.7 : 1.0
a
b
1.12
1.00
1.31
1.08
0.27
1.11
0.99
1.05
26.57
f1 (ppm)

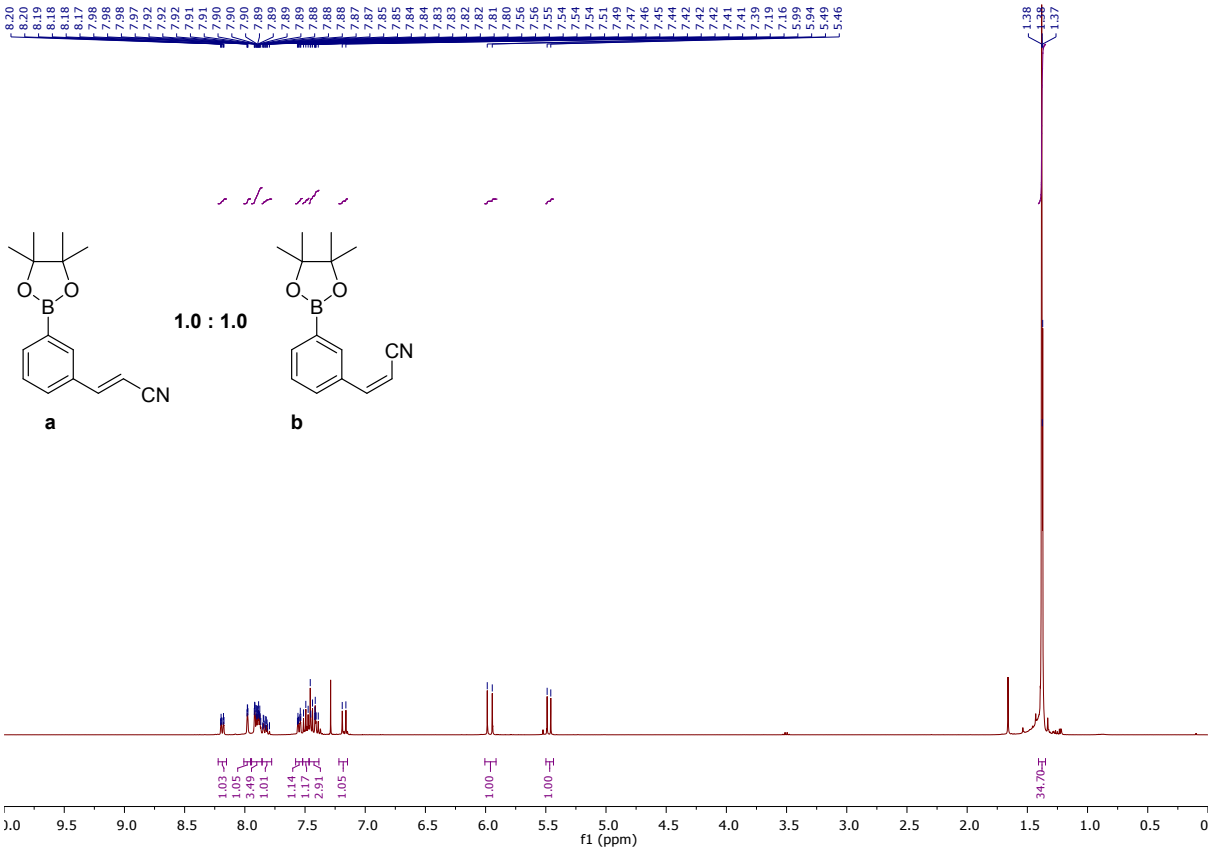

193.73
152.82
152.54
137.55
136.36
135.38
135.17
133.38
130.88
129.25
128.69
128.51
127.62
84.19
24.89
7.7 : 1.0
a
b
f1 (ppm)

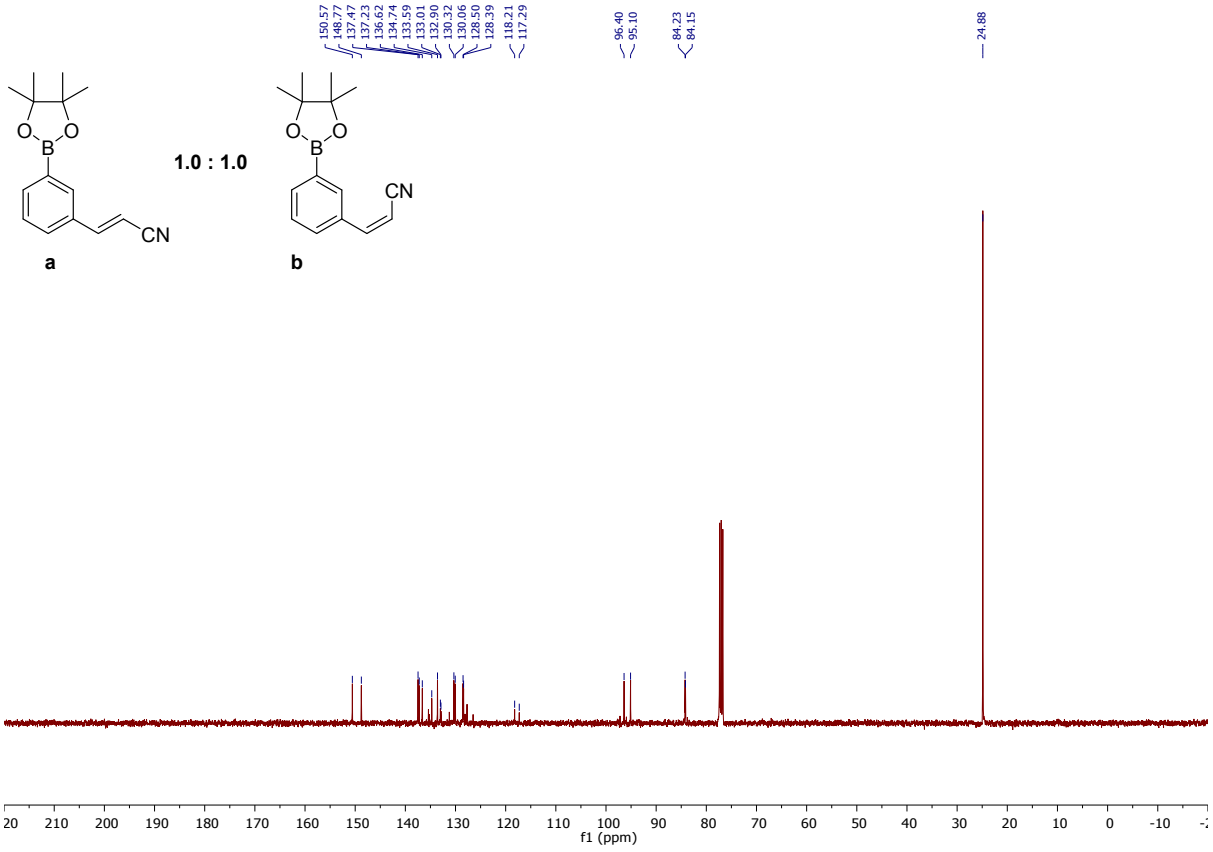

30.84
7.7 : 1.0
a
b
f1 (ppm)

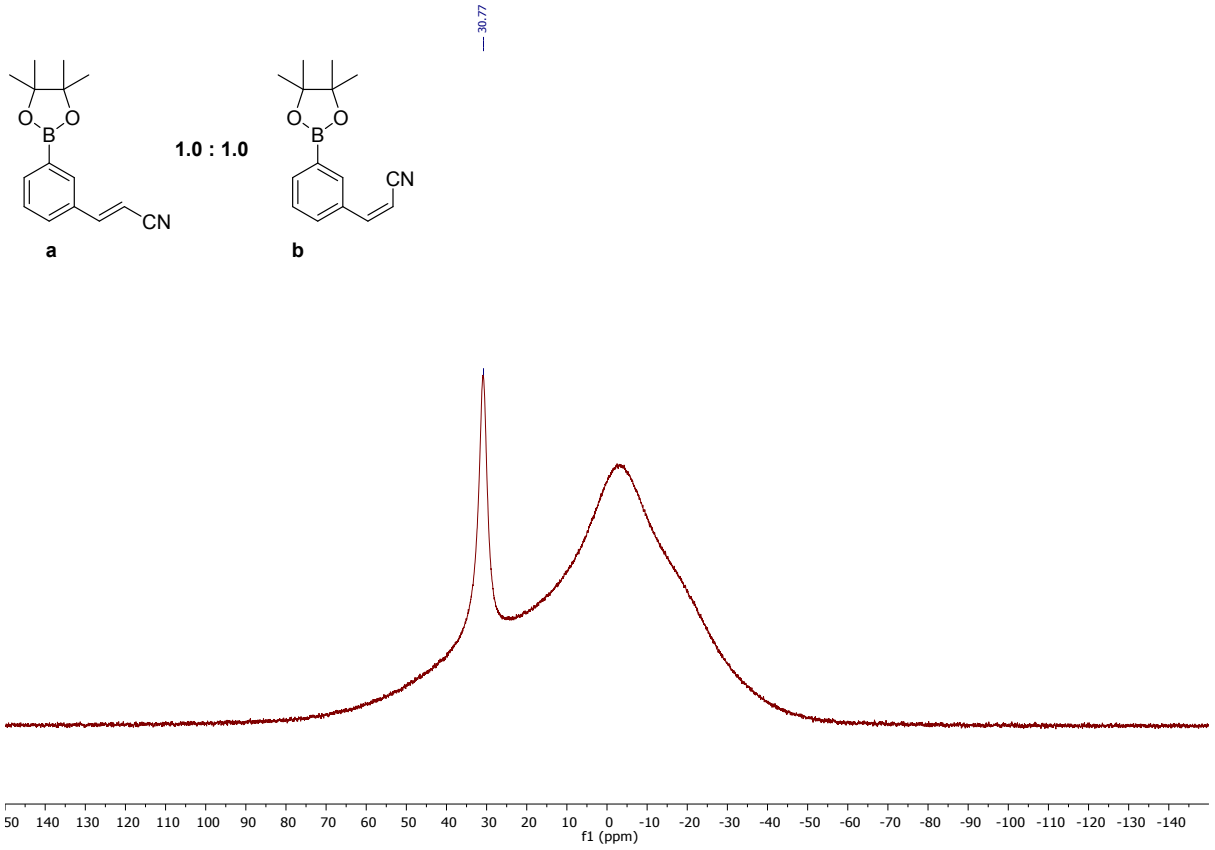

6.0 : 1.0
a
b
Ph
f1 (ppm)

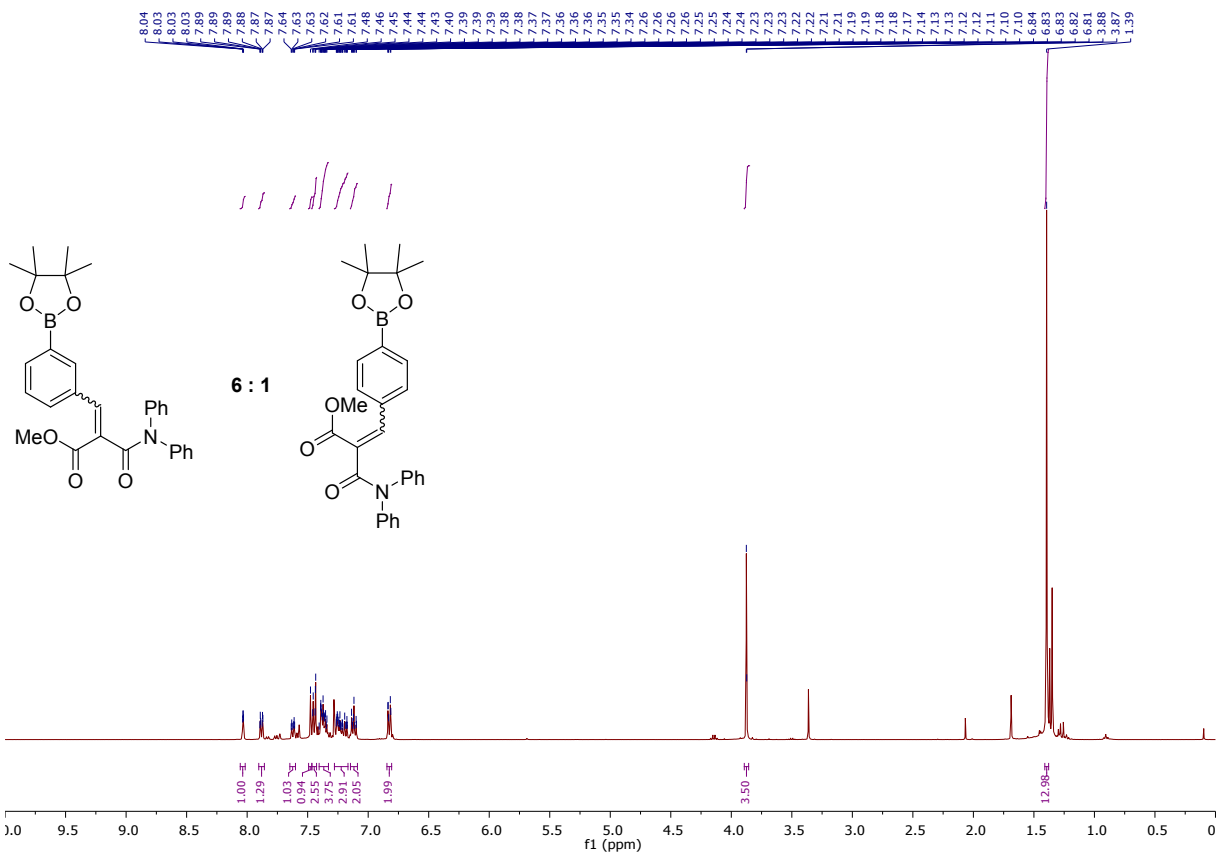

142.43
142.28
140.76
137.44
135.35
134.50
133.45
133.36
131.76
131.62
129.36
129.33
128.51
128.08
127.70
127.42
84.20
24.87
6.0 : 1.0
a
b
Ph
f1 (ppm)

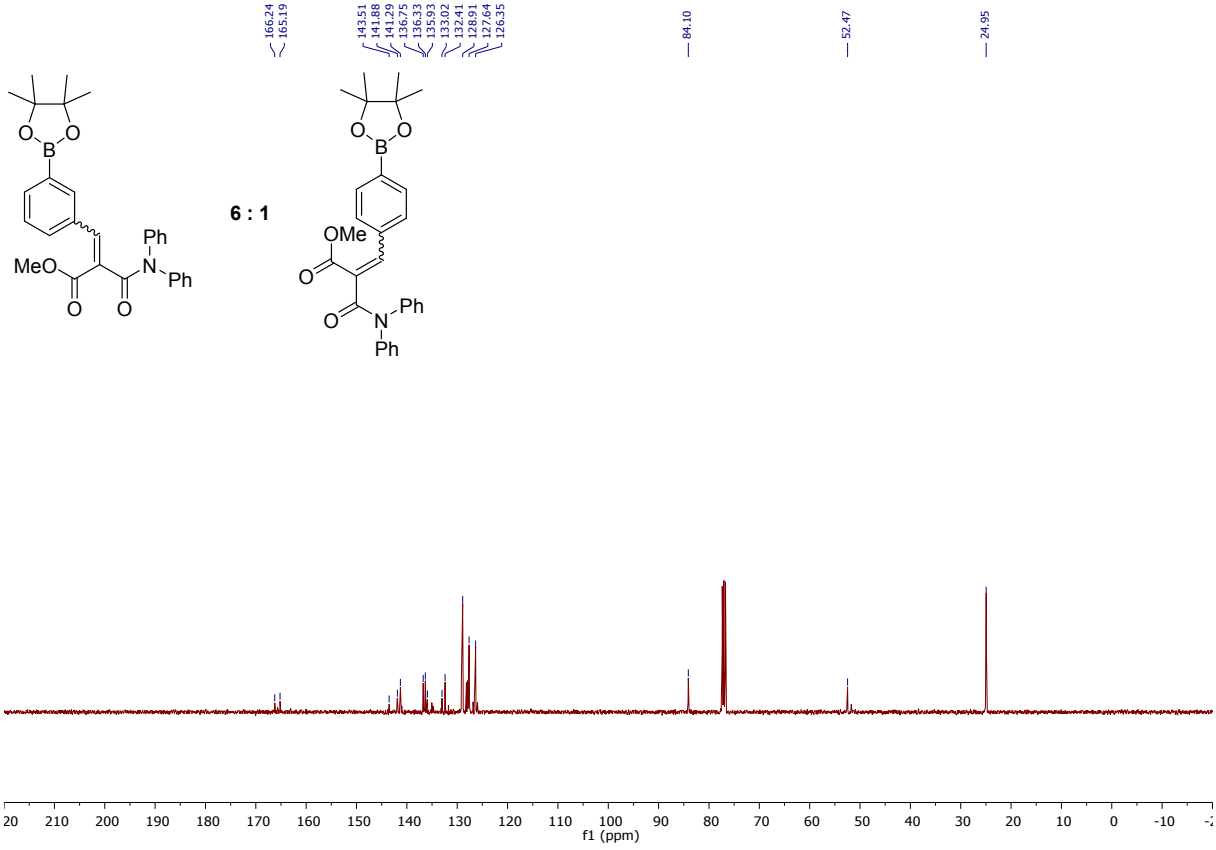

30.63
6.0 : 1.0
a
b
Ph
f1 (ppm)

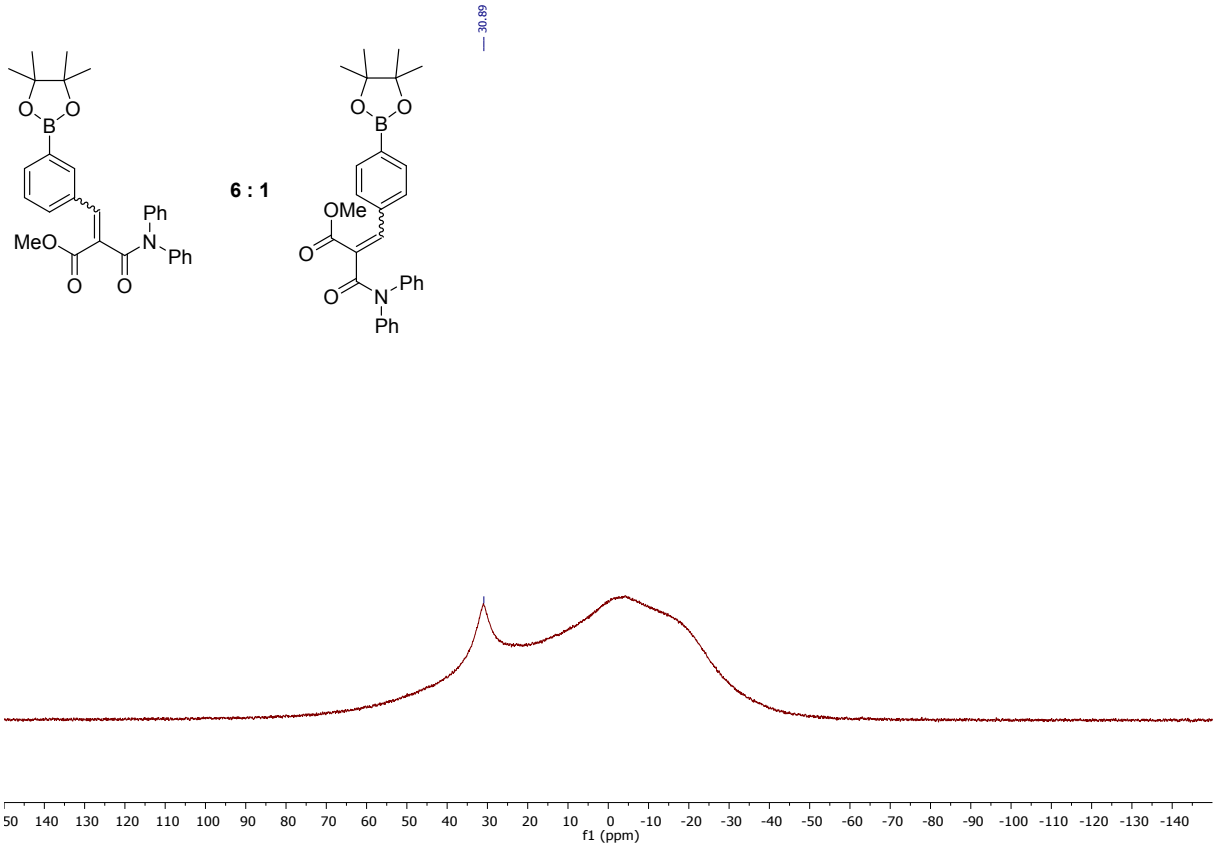

1.0 : 1.0
a
b
f1 (ppm)


1.0 : 1.0
a
b
f1 (ppm)

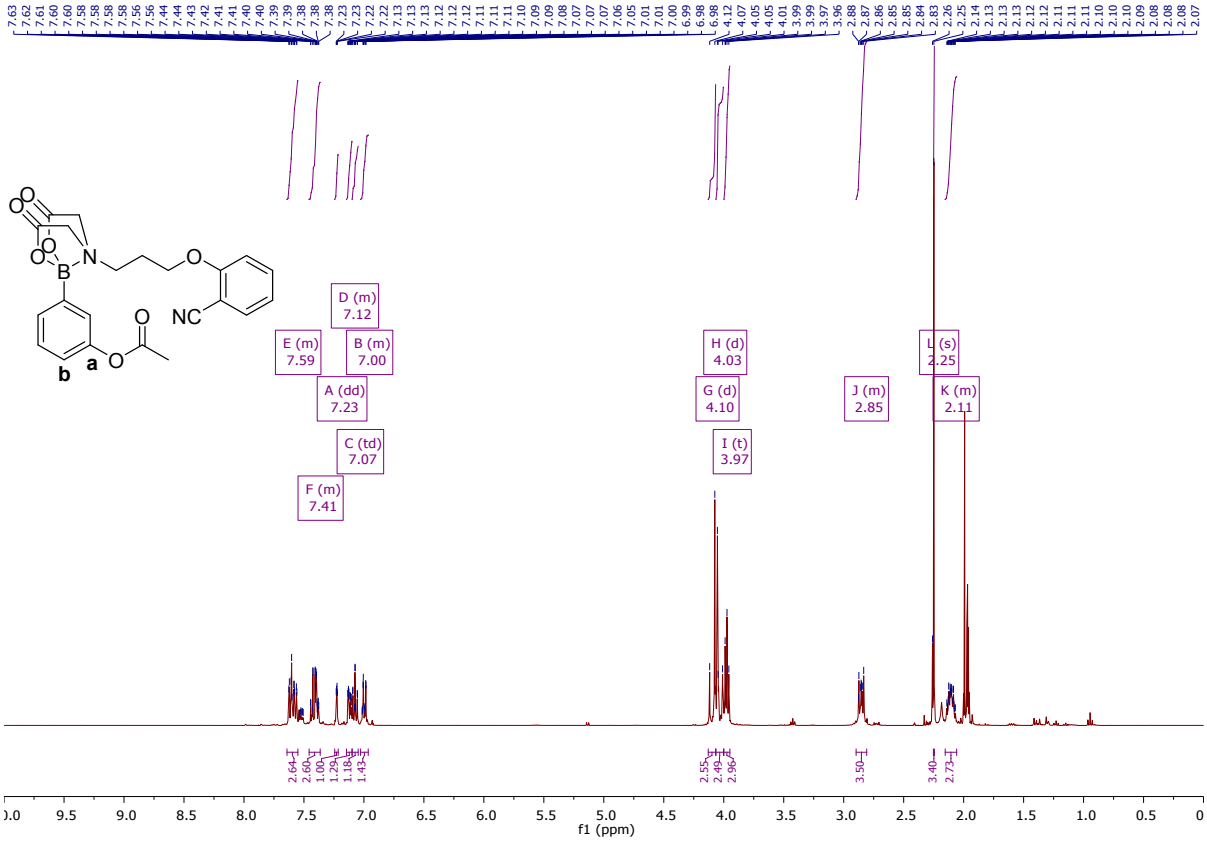

30.77
1.0 : 1.0
CN
CN
a
b
f1 (ppm)

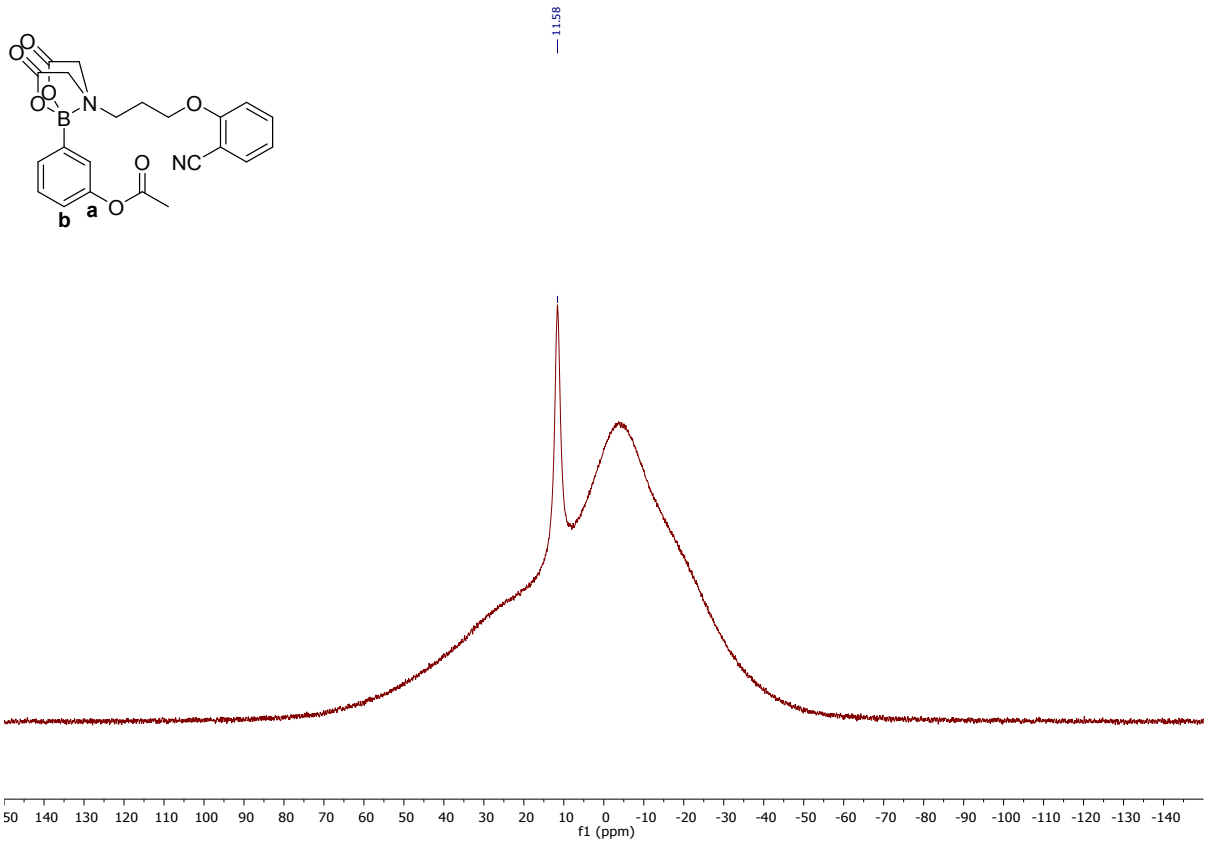

6 : 1
Ph
N
Ph
MeO
O
O
OMe
O
O
N
Ph
Ph
f1 (ppm)

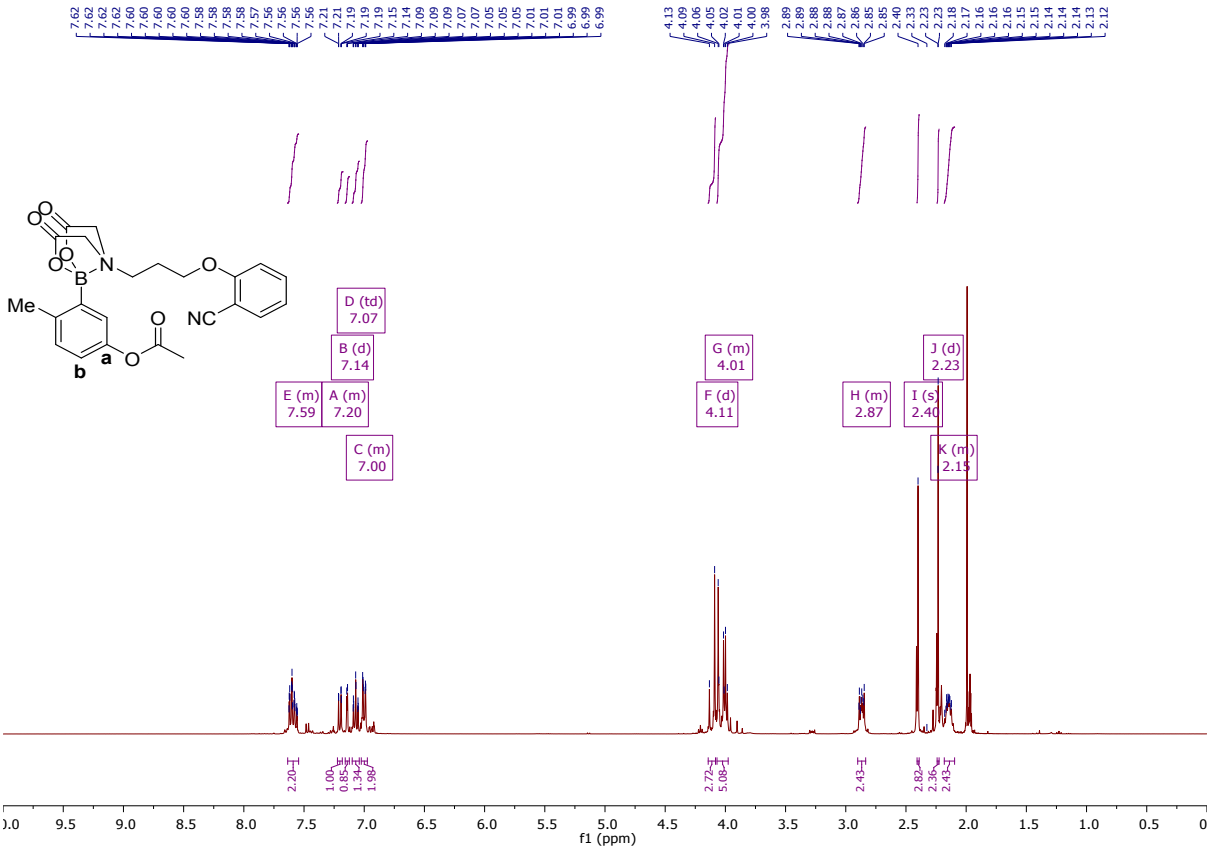

166.24
165.19
143.51
141.88
141.29
136.75
136.33
135.93
133.02
132.41
128.91
127.64
126.35
84.10
52.47
24.95
6 : 1
MeO
Ph
N
Ph
O
O
O
OMe
O
O
N
Ph
Ph
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

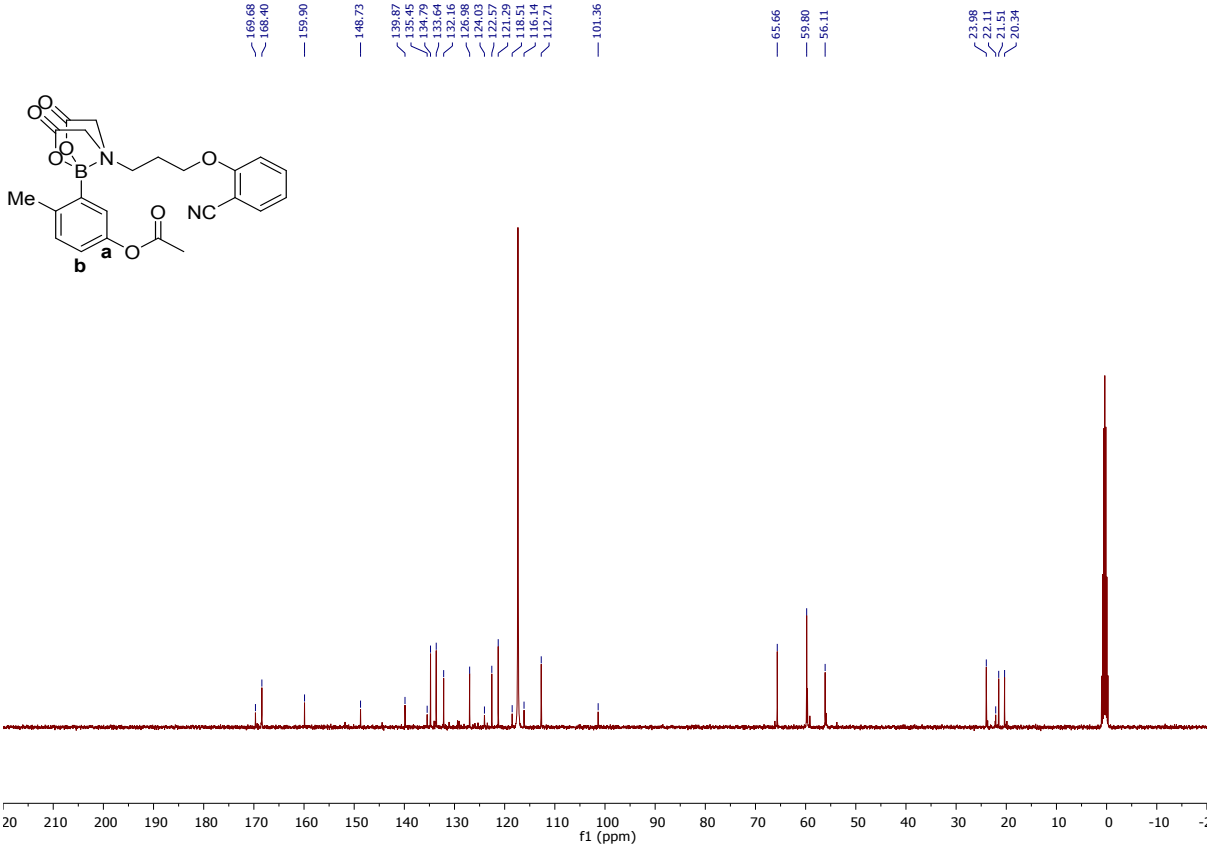

30.89
6 : 1
MeO
Ph
N
Ph
O
O
O
OMe
O
O
N
Ph
Ph
50 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)

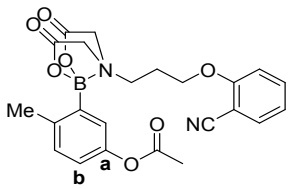
Acetoxylated Aryl Boronic Acid MIDA-DG Ester NMR Spectra



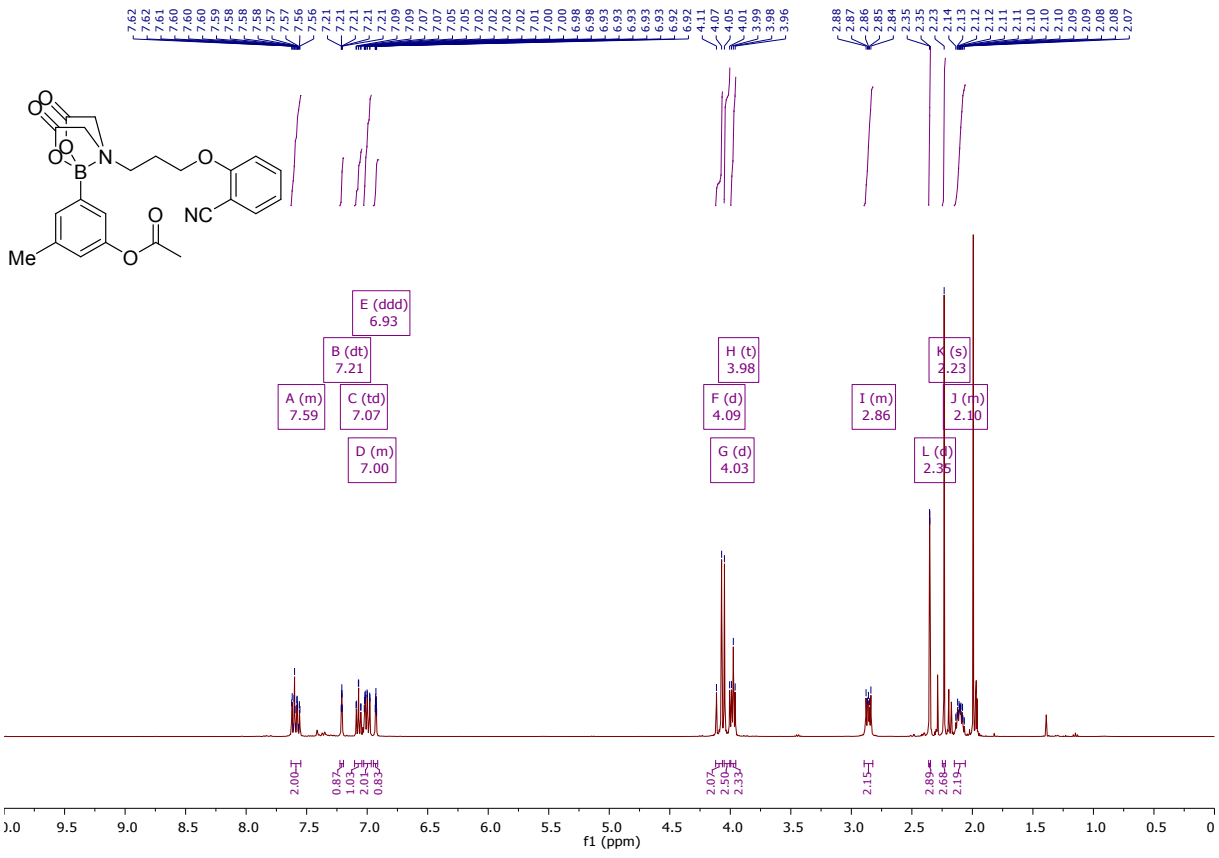


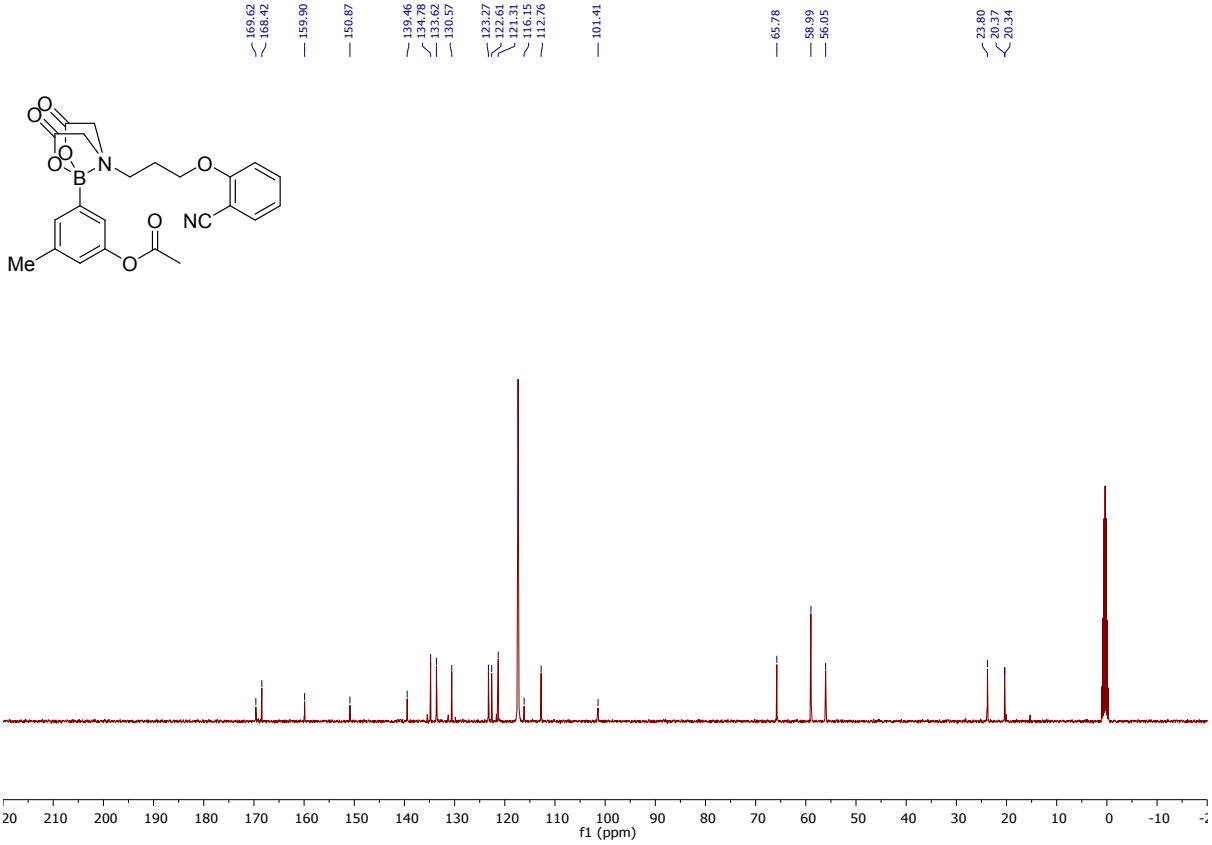

D (td)
7.07
B (d)
7.14
E (m)
7.59
A (m)
7.20
C (m)
7.00
G (m)
4.01
F (d)
4.11
H (m)
2.87
I (s)
2.40
J (d)
2.23
K (m)
2.15
Me
NC
a
b
f1 (ppm)

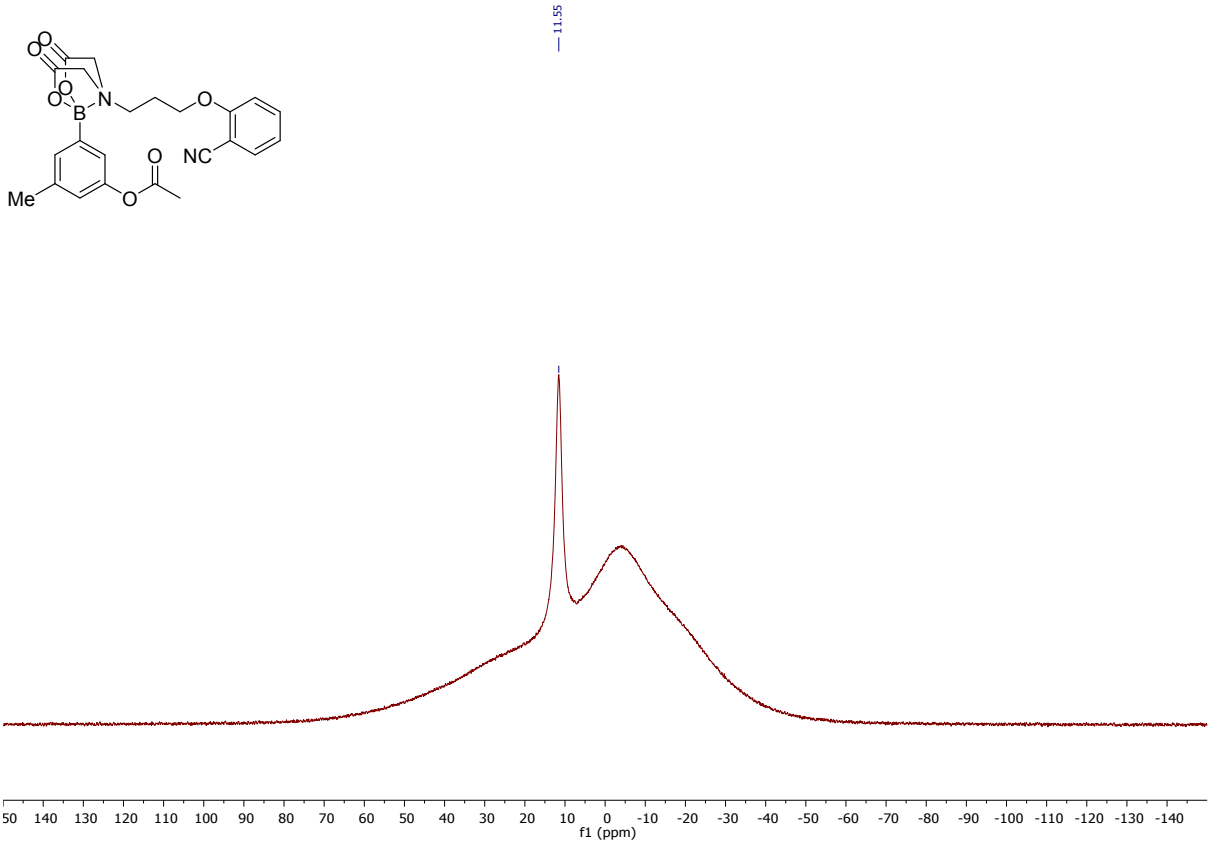

169.68
168.40
159.90
148.73
139.87
135.45
134.79
133.64
132.16
126.98
124.03
122.57
121.29
118.51
116.14
112.71
101.36
65.66
59.80
56.11
23.98
22.11
21.51
20.34
Me
NC
a
b
f1 (ppm)

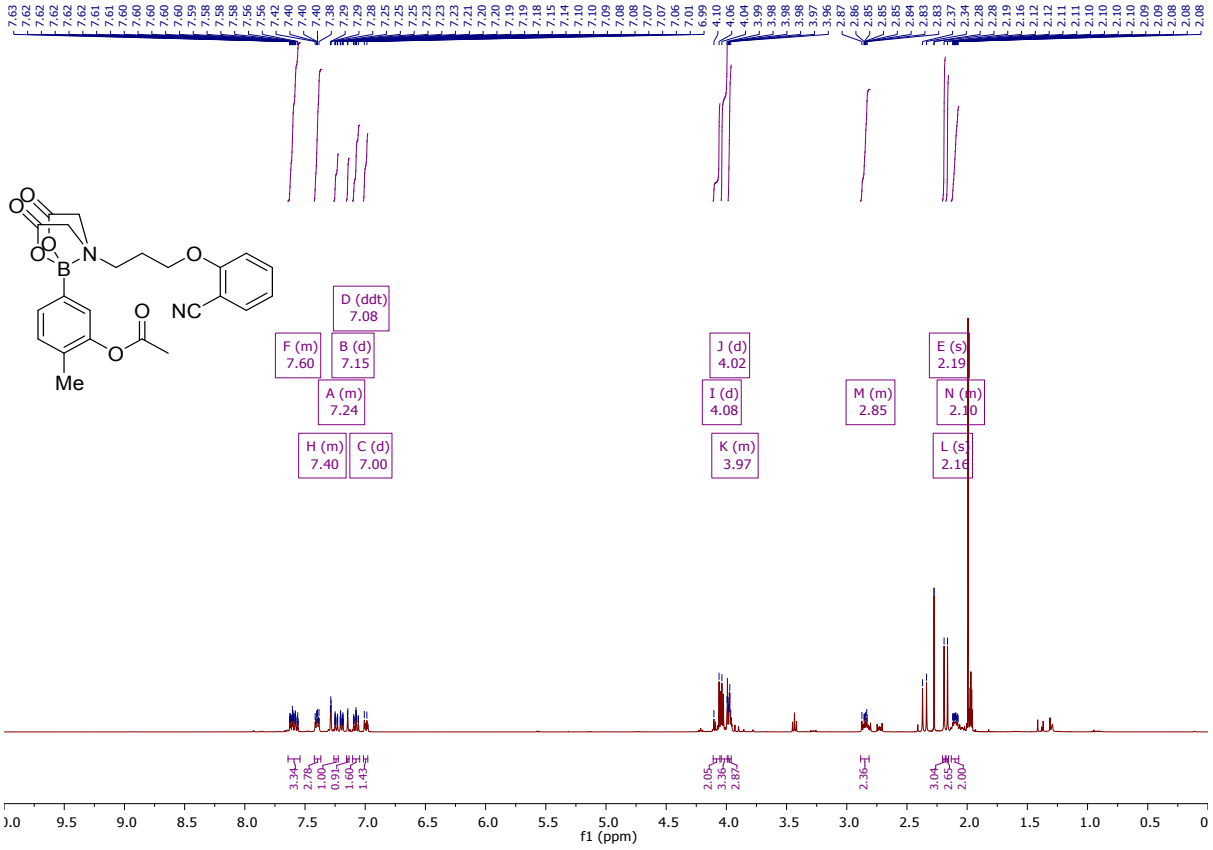

O
O
O
B
N
O
Me
NC
O
a
O
b

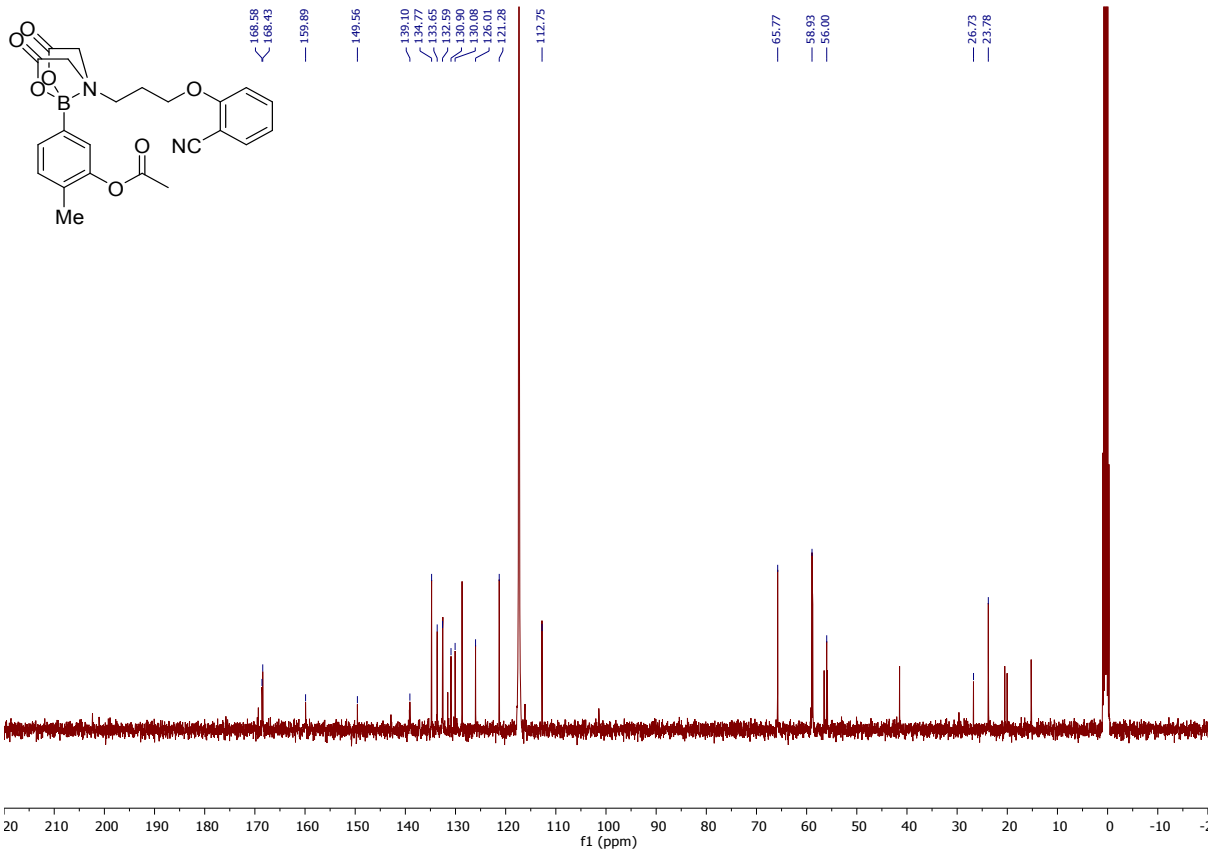
12.25
190 170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190
f1 (ppm)

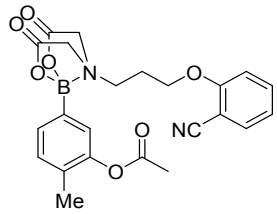

7.62 7.62 7.61 7.60 7.60 7.60 7.59 7.58 7.58 7.58 7.57 7.57 7.56 7.56 7.21 7.21 7.21 7.21 7.21 7.09 7.09 7.07 7.07 7.07 7.05 7.05 7.02 7.02 7.02 7.02 7.01 7.00 7.00 6.98 6.98 6.93 6.93 6.93 6.93 6.92 6.92 4.11 4.07 4.05 4.01 3.99 3.98 3.96 2.88 2.87 2.86 2.85 2.84 2.35 2.35 2.23 2.14 2.13 2.12 2.12 2.11 2.11 2.10 2.10 2.10 2.09 2.09 2.09 2.08 2.08 2.07
O
O
O
B
N
O
NC
O
Me
E (ddd) 6.93
B (dt) 7.21
A (m) 7.59
C (td) 7.07
D (m) 7.00
H (t) 3.98
F (d) 4.09
G (d) 4.03
I (m) 2.86
K (s) 2.23
J (m) 2.10
L (d) 2.35
2.00 0.87 1.03 2.01 0.83 2.07 2.50 2.33 2.15 2.80 2.68 2.19
f1 (ppm)


169.62
168.42
159.90
150.87
139.46
134.78
133.62
130.57
123.27
122.61
121.31
116.15
112.76
101.41
65.78
58.99
56.05
23.80
20.37
20.34
O
O
O
O
B
N
O
NC
O
Me
O
f1 (ppm)

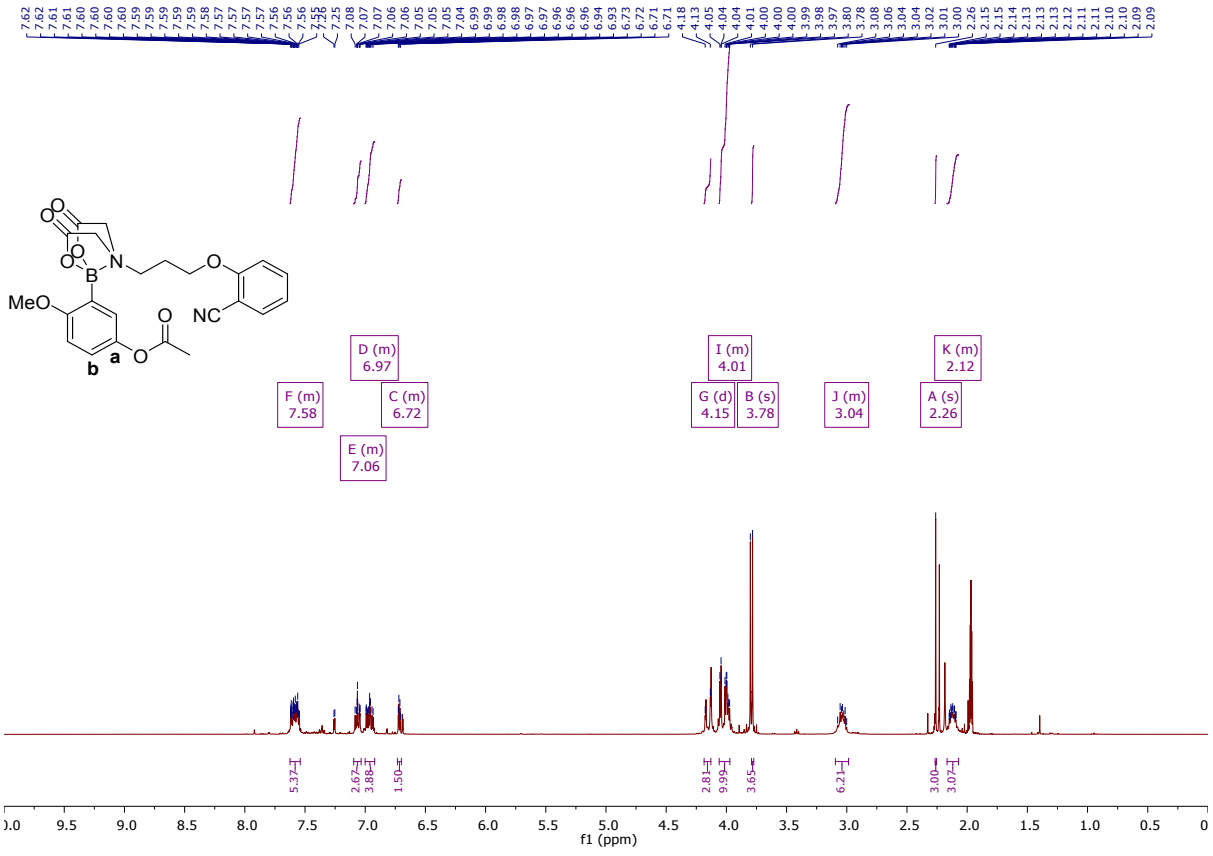

11.55
O
O
O
O
B
N
O
NC
O
Me
O
f1 (ppm)

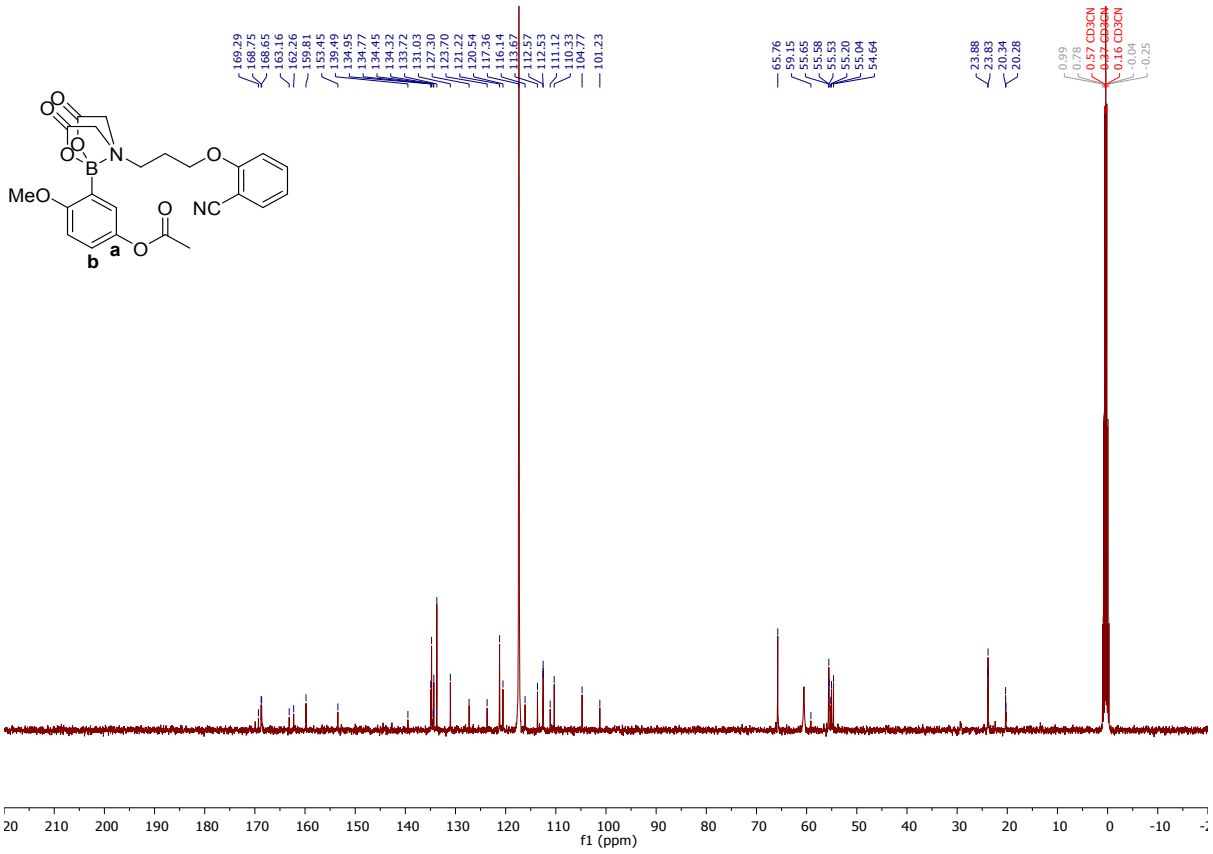

D (ddt)
7.08
F (m)
7.60
B (d)
7.15
A (m)
7.24
H (m)
7.40
C (d)
7.00
J (d)
4.02
I (d)
4.08
K (m)
3.97
M (m)
2.85
E (s)
2.19
N (m)
2.10
L (s)
2.16
f1 (ppm)

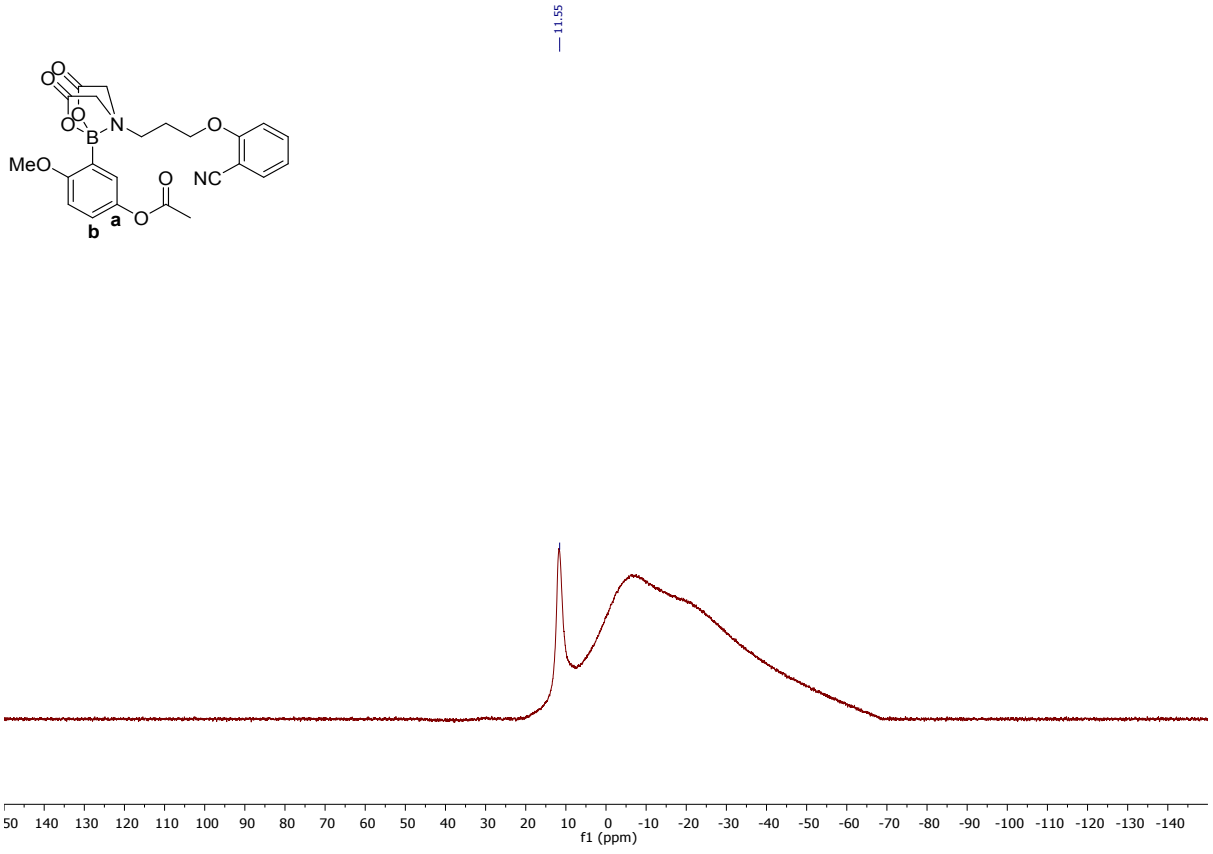

168.58
168.43
159.89
149.56
139.10
134.77
133.65
132.59
130.90
130.08
126.01
121.28
112.75
65.77
58.93
56.00
26.73
23.78
f1 (ppm)

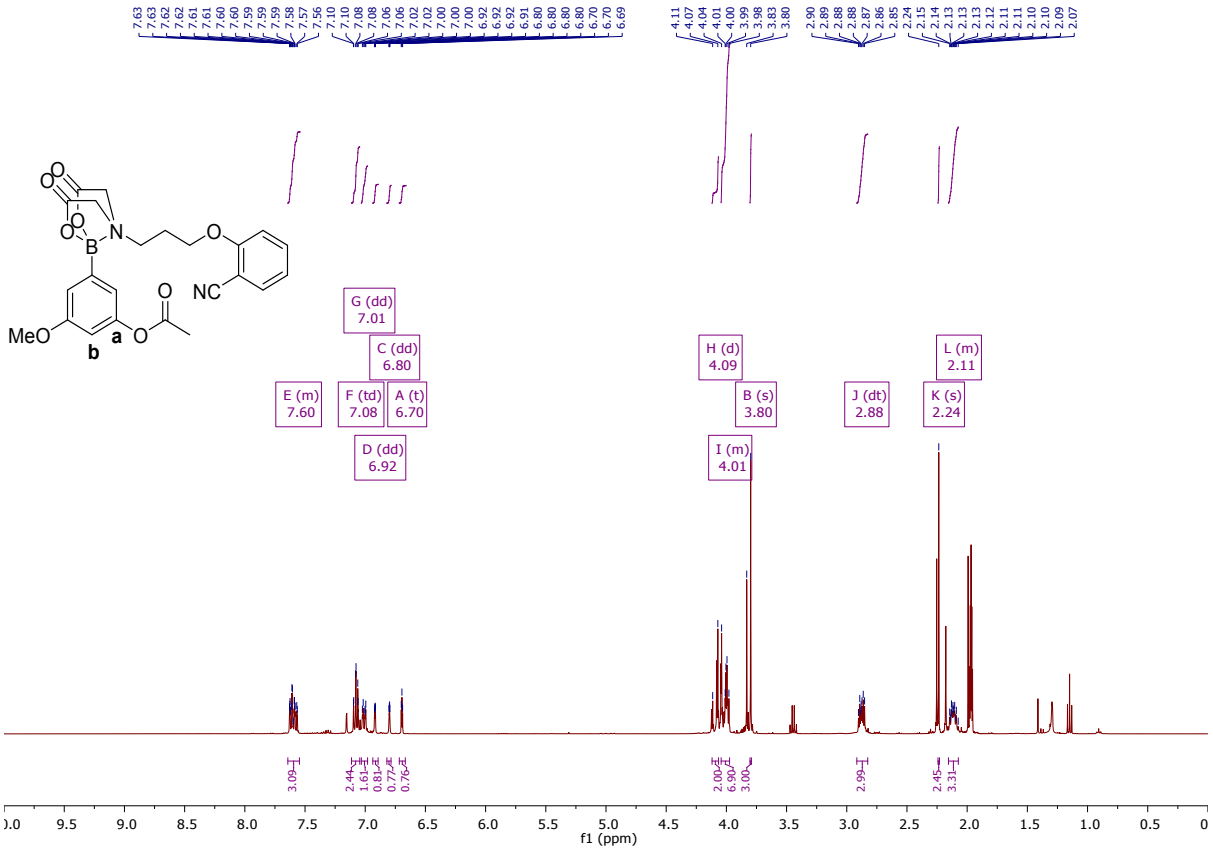

O
O
O
B
N
O
NC
O
O
Me

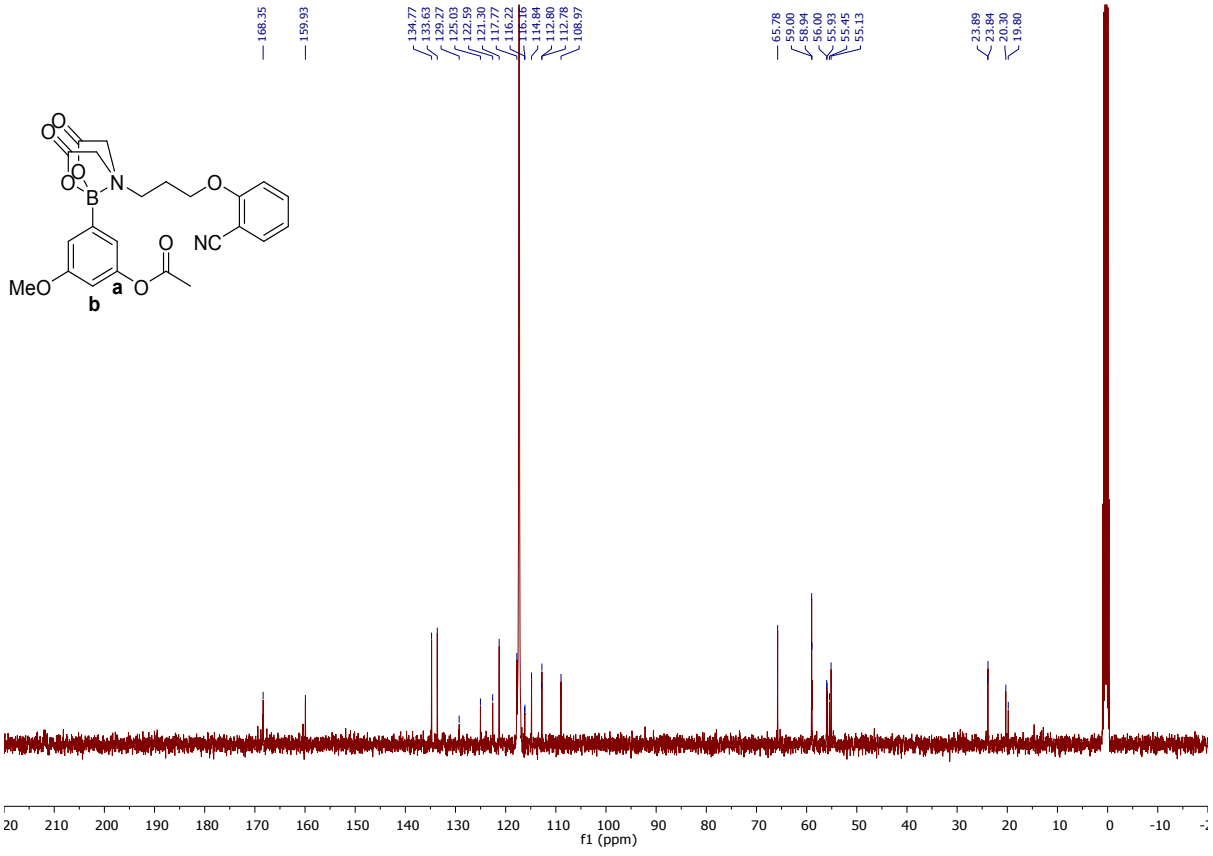
11.89
f1 (ppm)

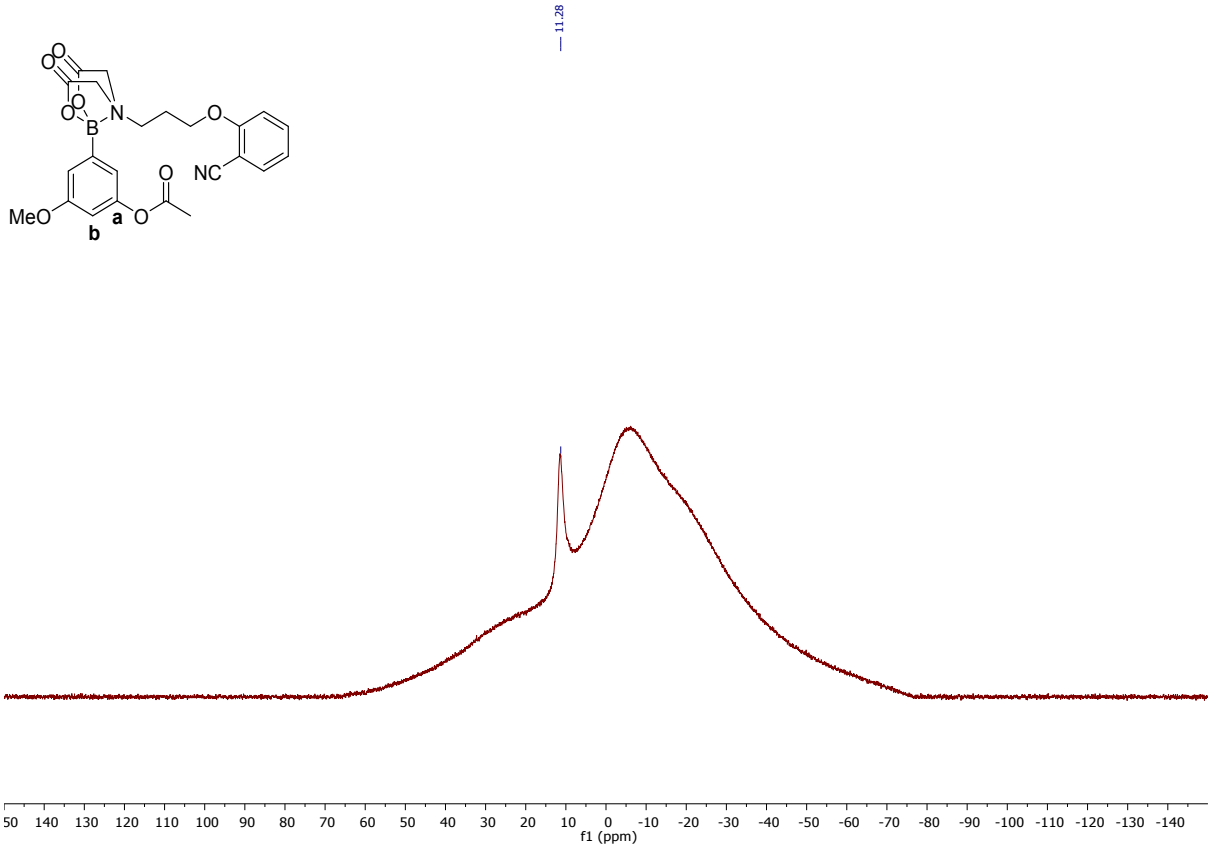

MeO
NC
O
O
B
N
O
O
O
a
b
D (m) 6.97
F (m) 7.58
C (m) 6.72
E (m) 7.06
I (m) 4.01
G (d) 4.15
B (s) 3.78
J (m) 3.04
K (m) 2.12
A (s) 2.26
f1 (ppm)

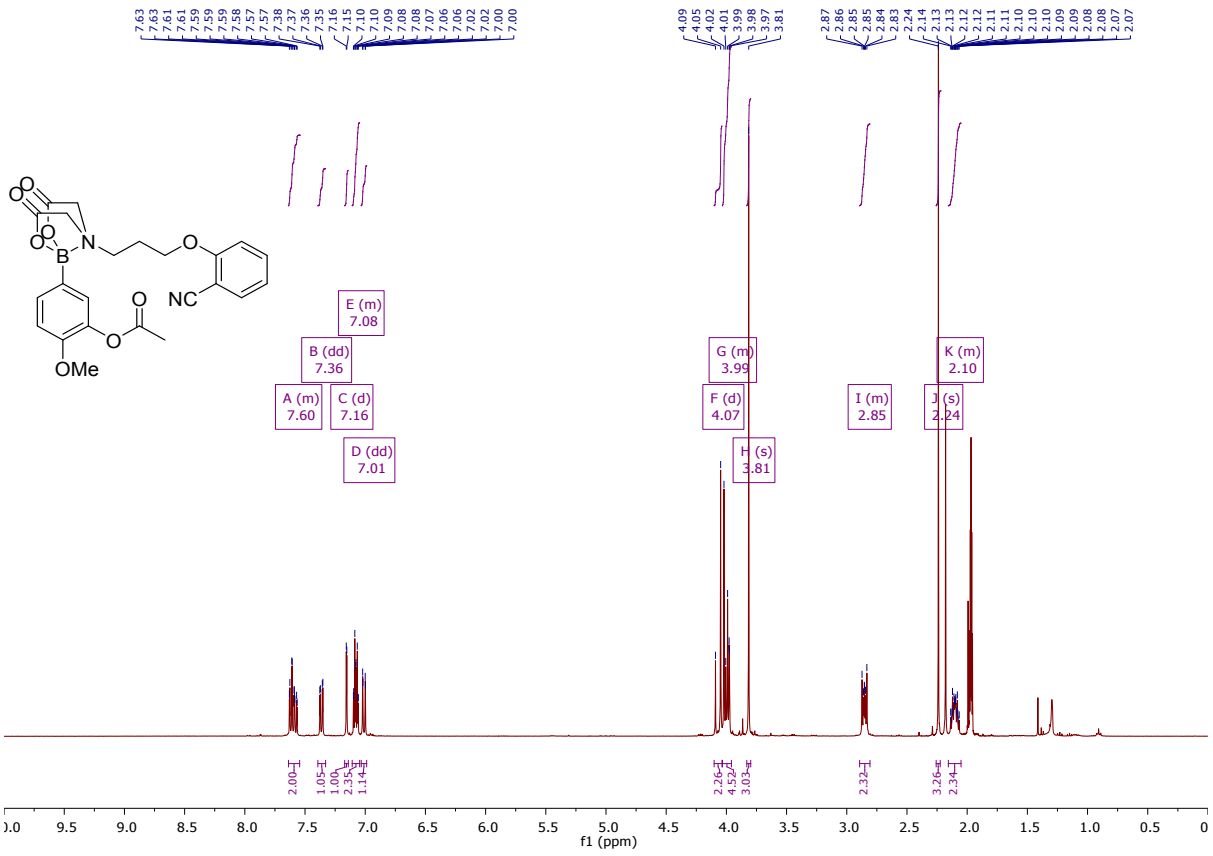

169.29
168.75
168.65
163.16
162.26
159.81
153.45
139.49
134.95
134.77
134.45
134.32
133.72
131.03
127.30
123.70
121.22
120.54
117.36
116.14
113.67
112.57
112.53
111.12
110.33
104.77
101.23
65.76
59.15
55.65
55.58
55.53
55.20
55.04
54.64
23.88
23.83
20.34
20.28
0.99
0.78
0.57 CD3CN
0.32 CD3CN
0.16 CD3CN
0.04
0.25
MeO
NC
a
b
f1 (ppm)

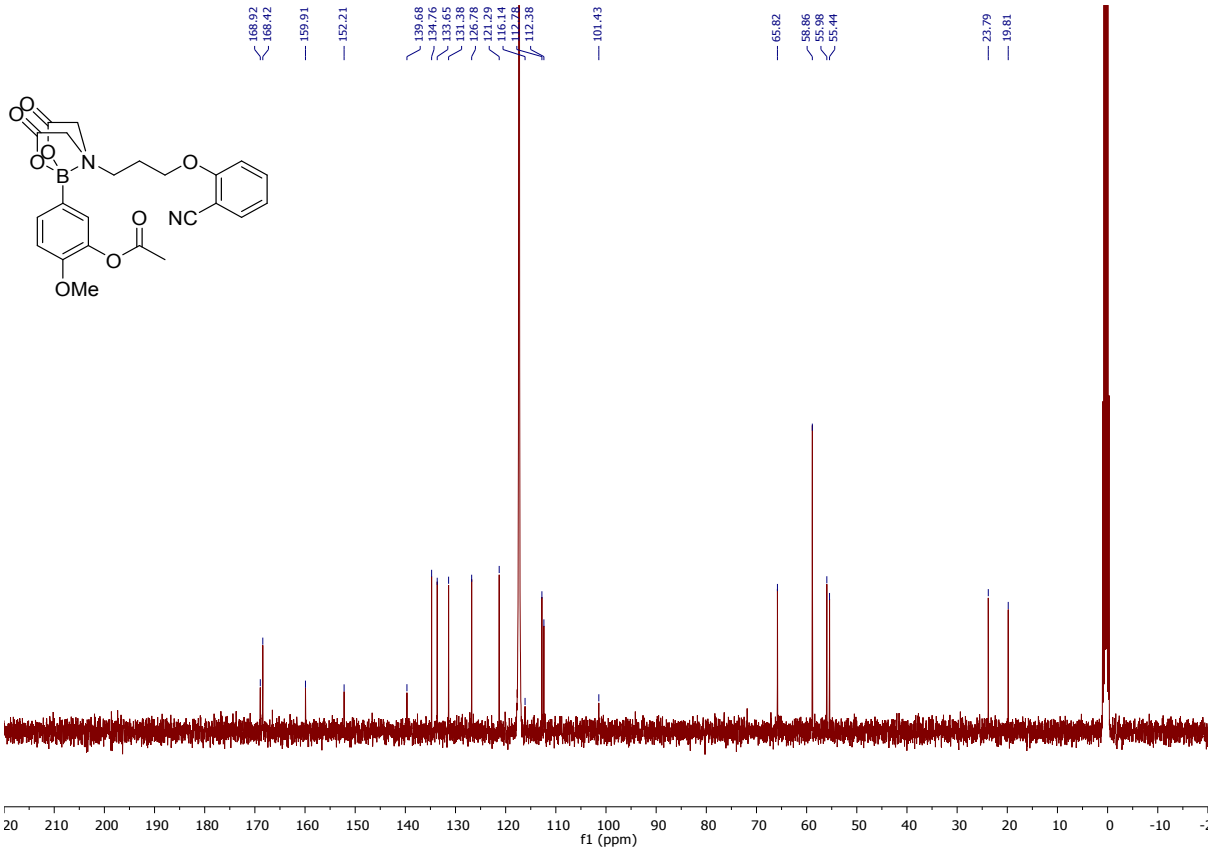

11.55
MeO
NC
a
b
f1 (ppm)

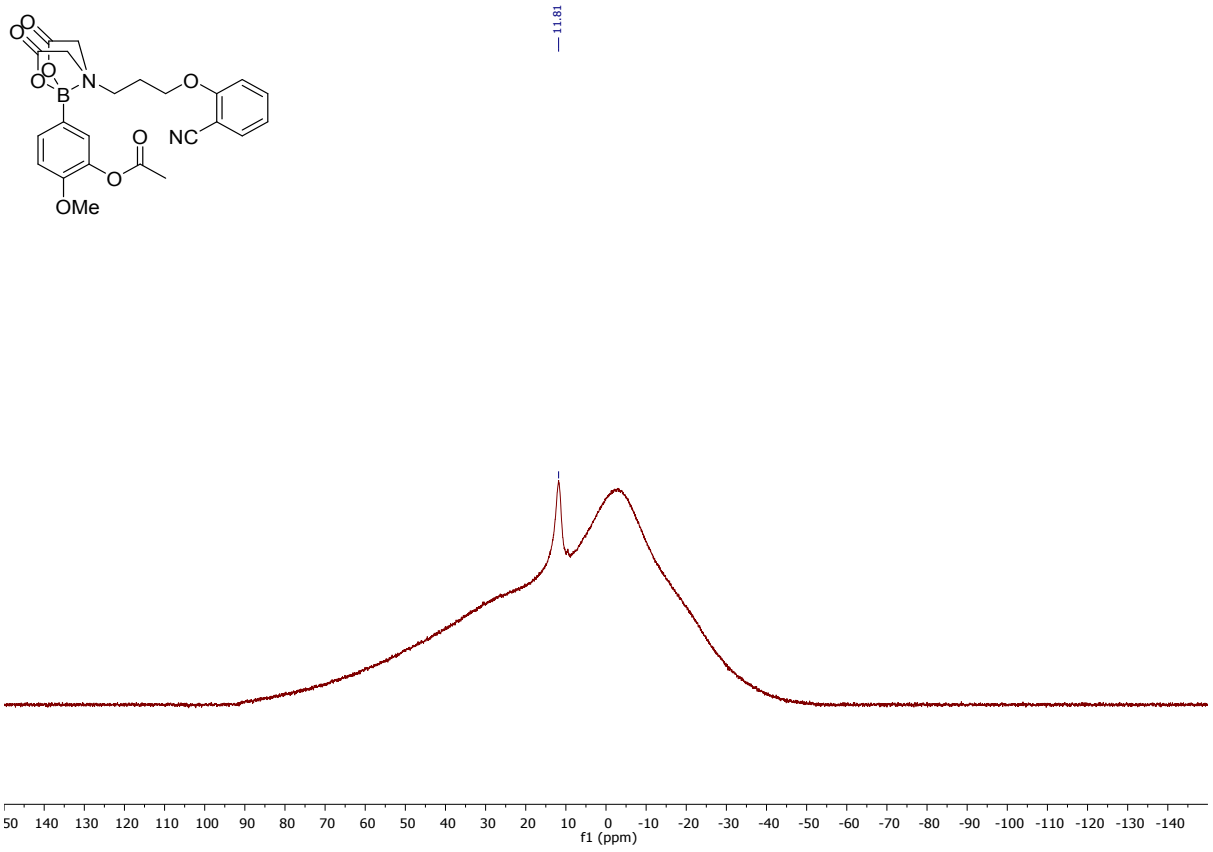

G (dd) 7.01
C (dd) 6.80
E (m) 7.60
F (td) 7.08
A (t) 6.70
D (dd) 6.92
H (d) 4.09
B (s) 3.80
I (m) 4.01
J (dt) 2.88
K (s) 2.24
L (m) 2.11
MeO
a
b
NC
f1 (ppm)

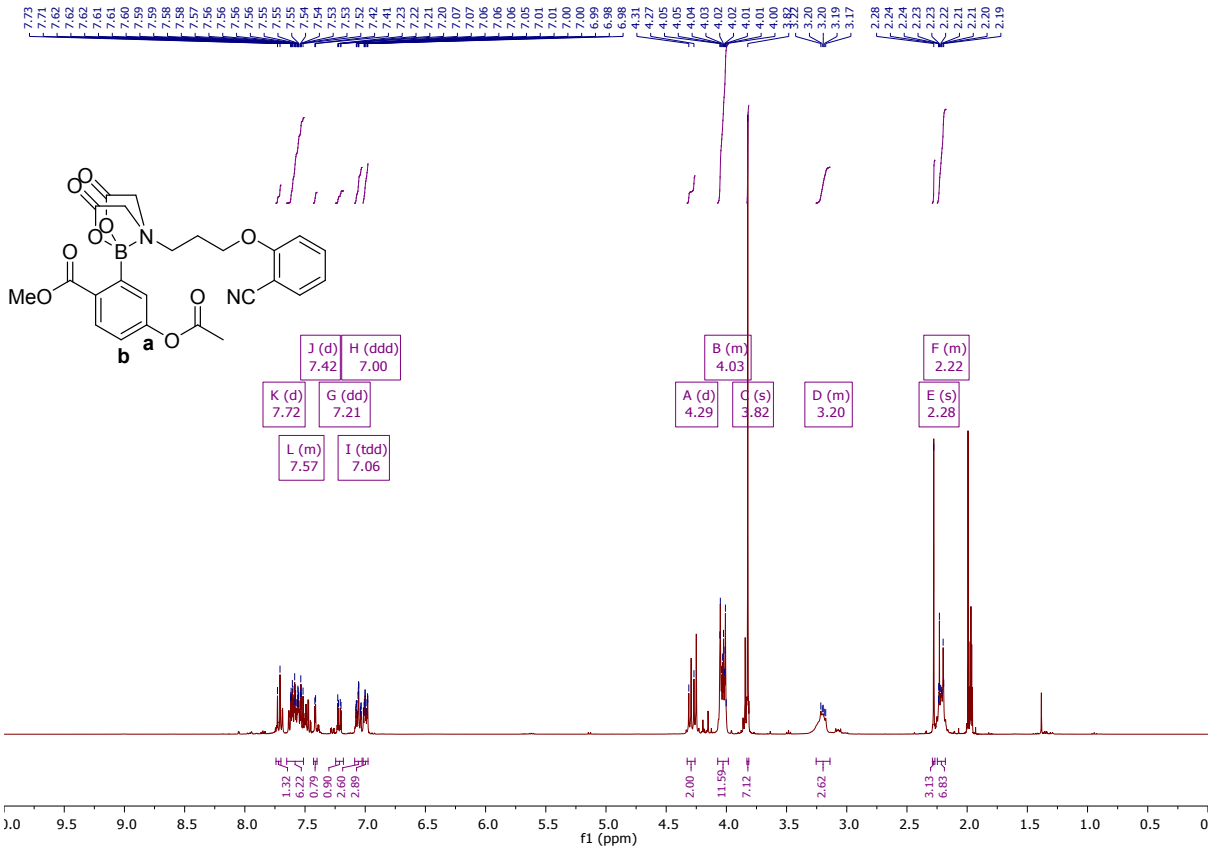

MeO
a
b
NC
f1 (ppm)

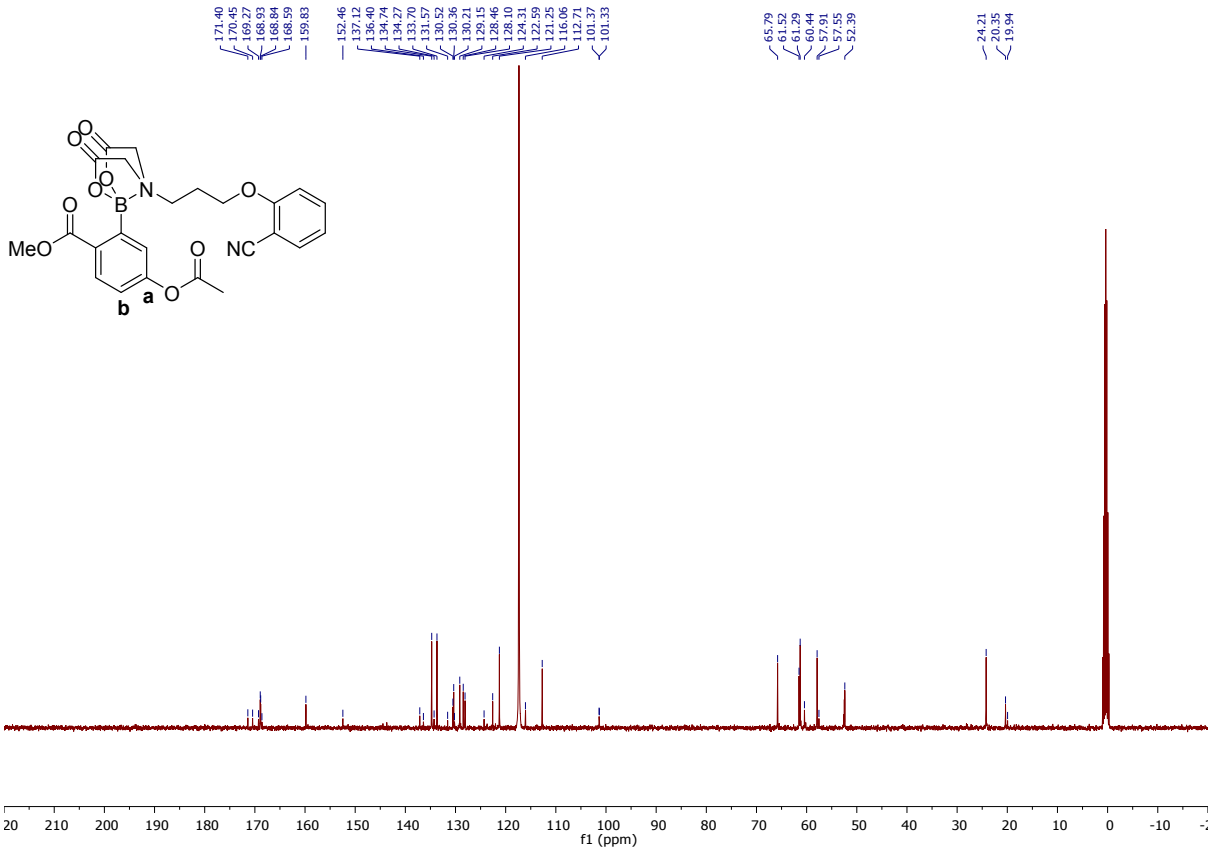

11.28
MeO
a
b
NC
f1 (ppm)

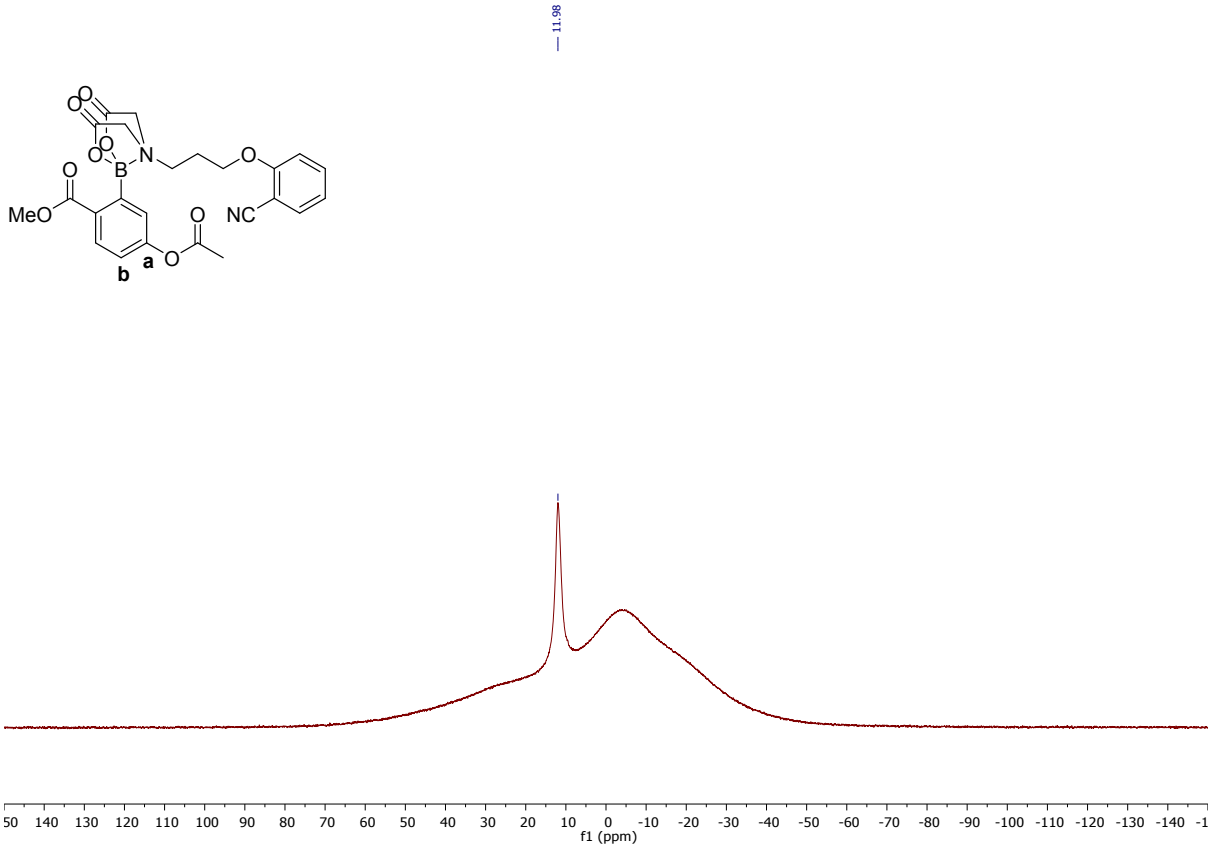

MeO
NC
A (m) 7.60
B (dd) 7.36
C (d) 7.16
D (dd) 7.01
E (m) 7.08
F (d) 4.07
G (m) 3.99
H (s) 3.81
I (m) 2.85
J (s) 2.24
K (m) 2.10
f1 (ppm)

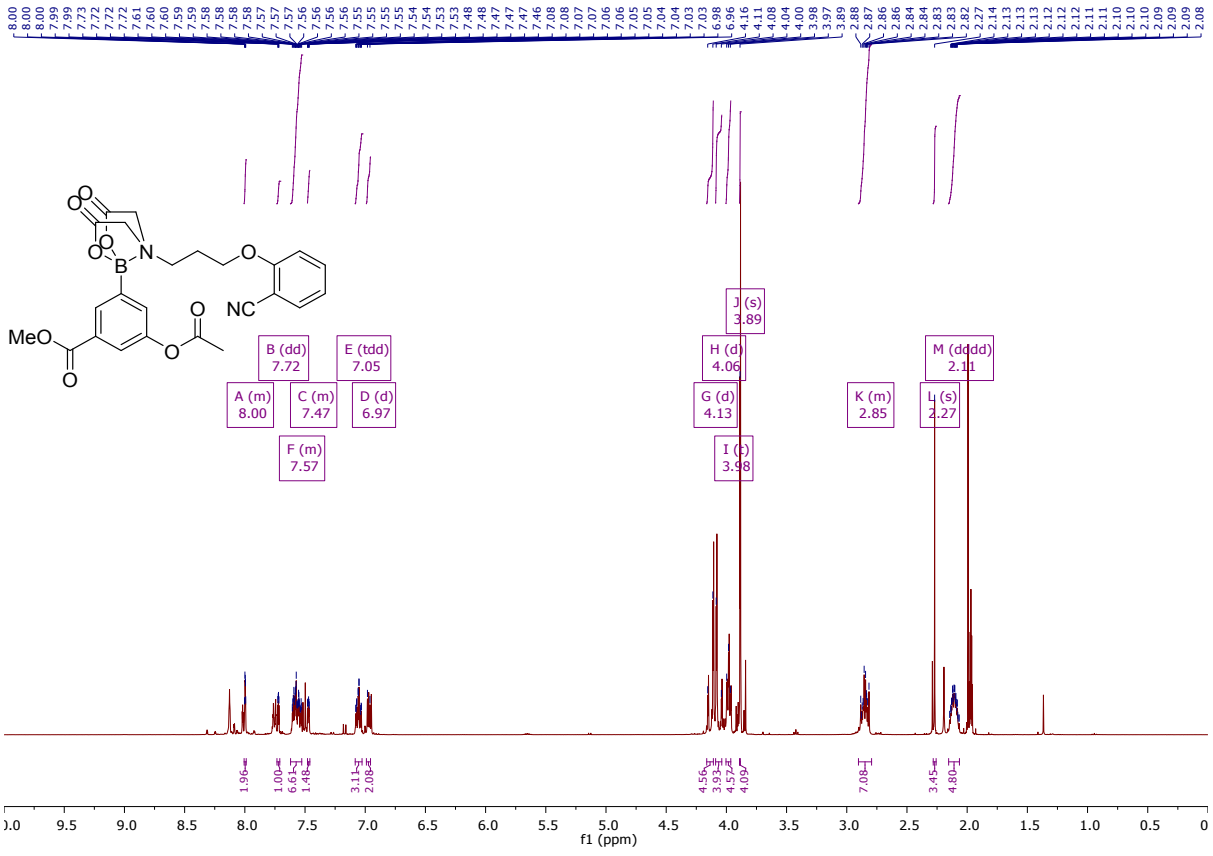

168.92
168.42
159.91
152.21
139.68
134.76
133.65
131.38
126.78
121.29
116.14
112.28
112.38
101.43
65.82
58.86
55.98
55.44
23.79
19.81
O
O
O
B
N
O
NC
O
O
OMe
f1 (ppm)

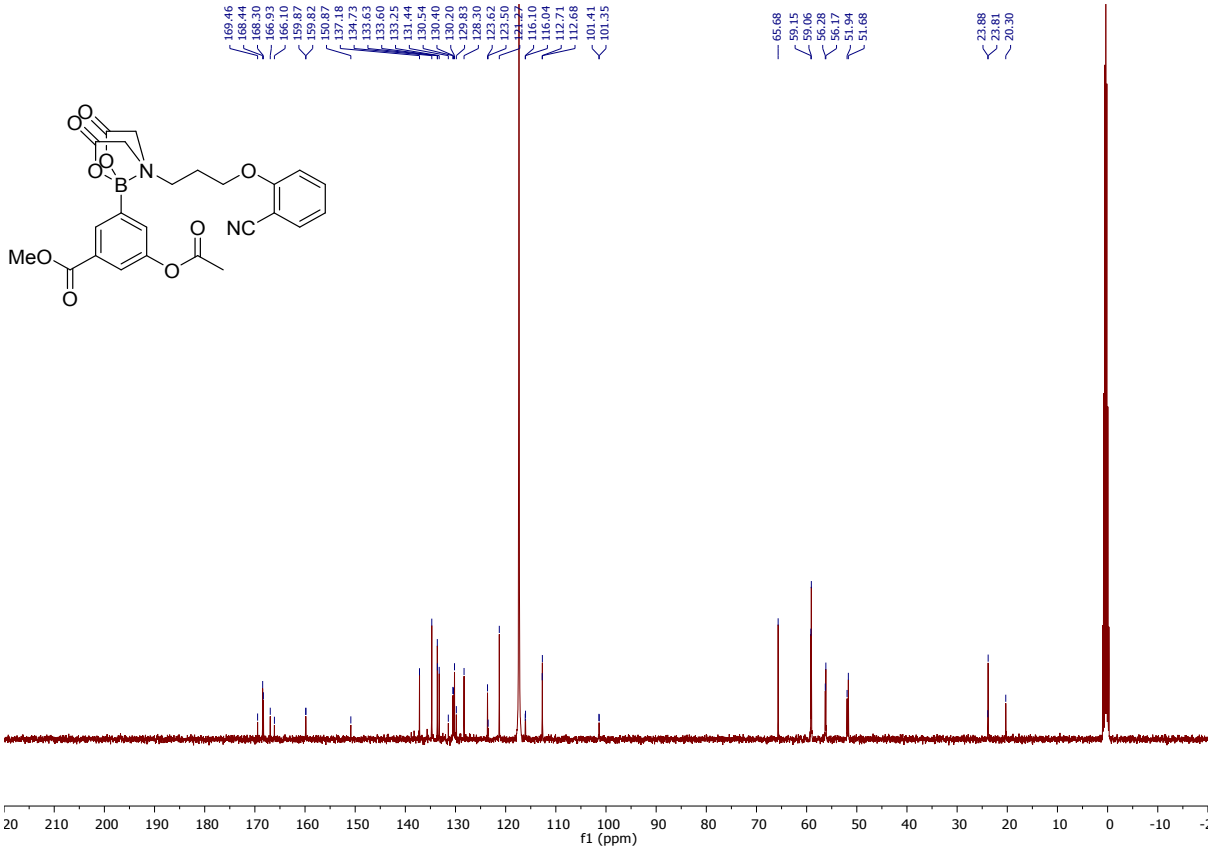

11.81
O
O
O
B
N
O
NC
O
O
OMe
f1 (ppm)

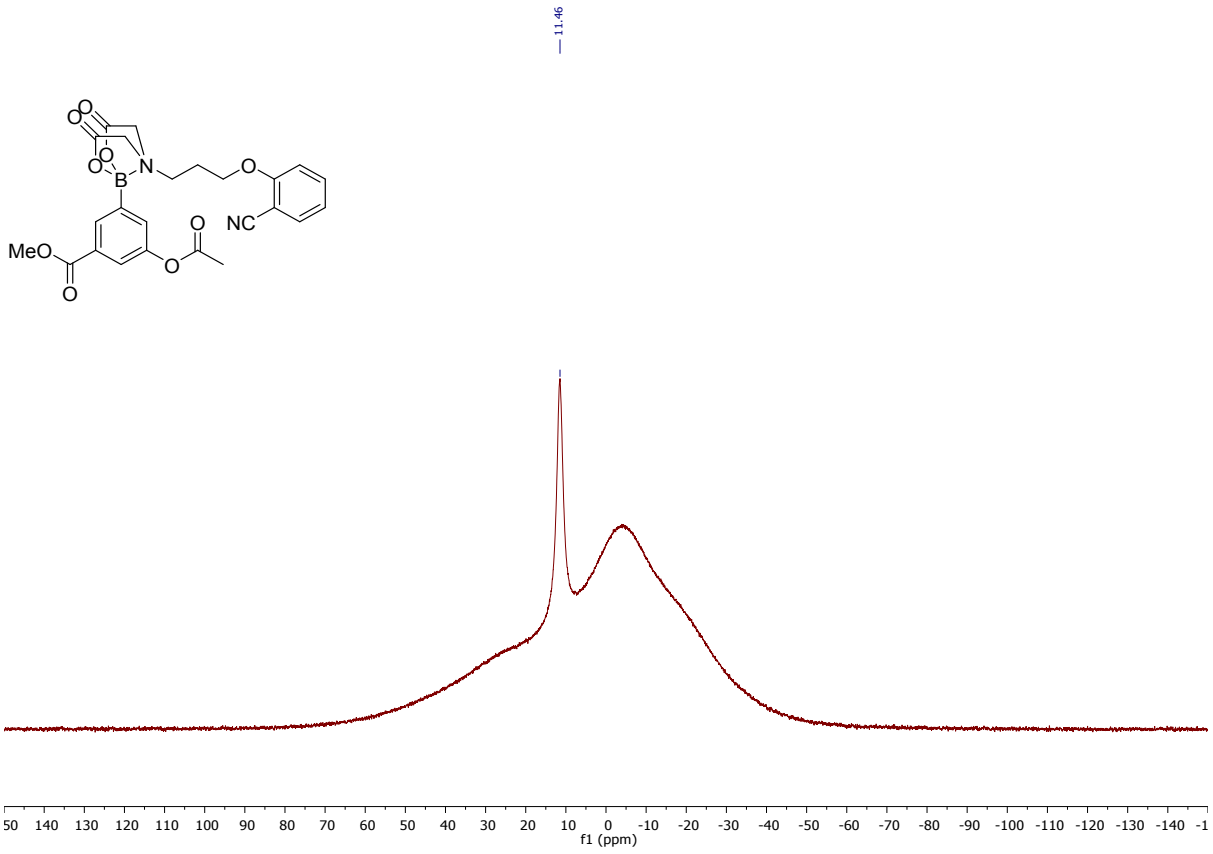

J (d) 7.42
H (ddd) 7.00
K (d) 7.72
G (dd) 7.21
L (m) 7.57
I (tdd) 7.06
B (m) 4.03
A (d) 4.29
C (s) 3.82
D (m) 3.20
F (m) 2.22
E (s) 2.28
f1 (ppm)

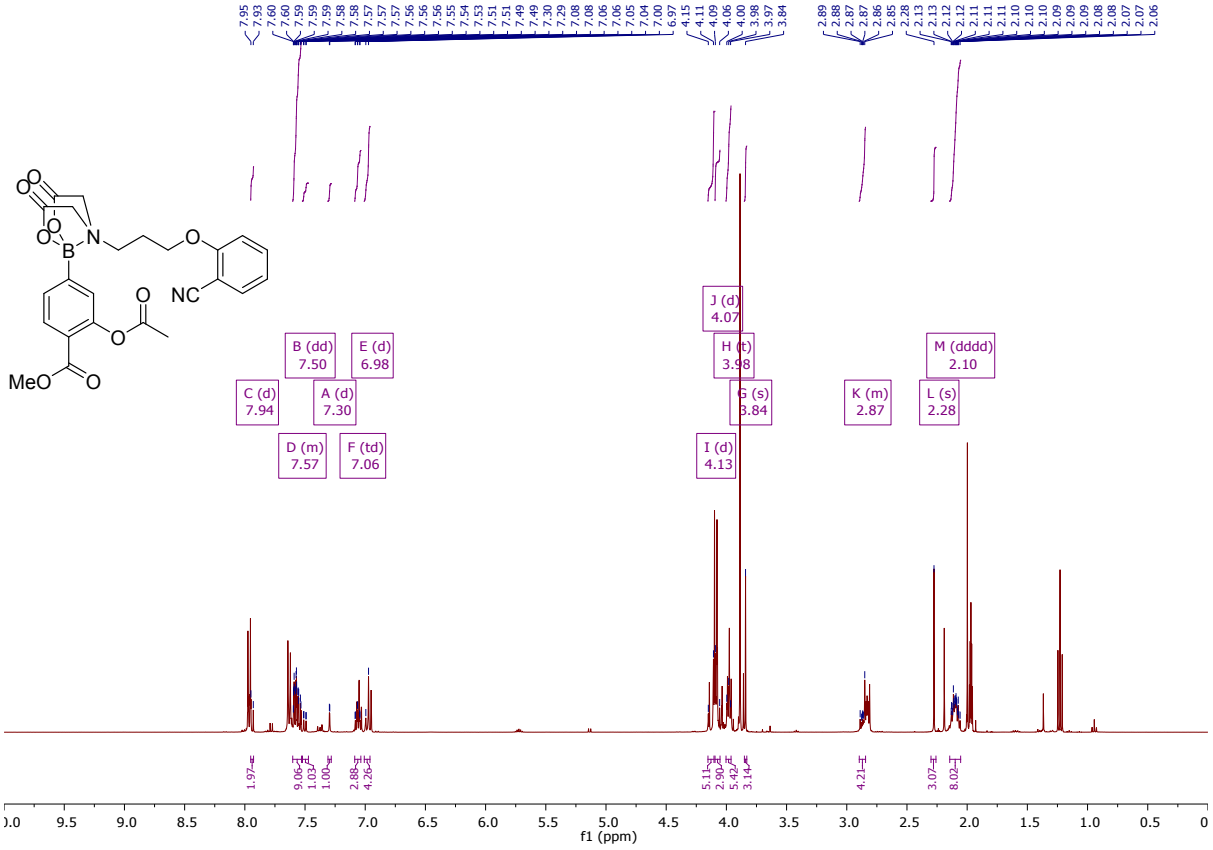

f1 (ppm)

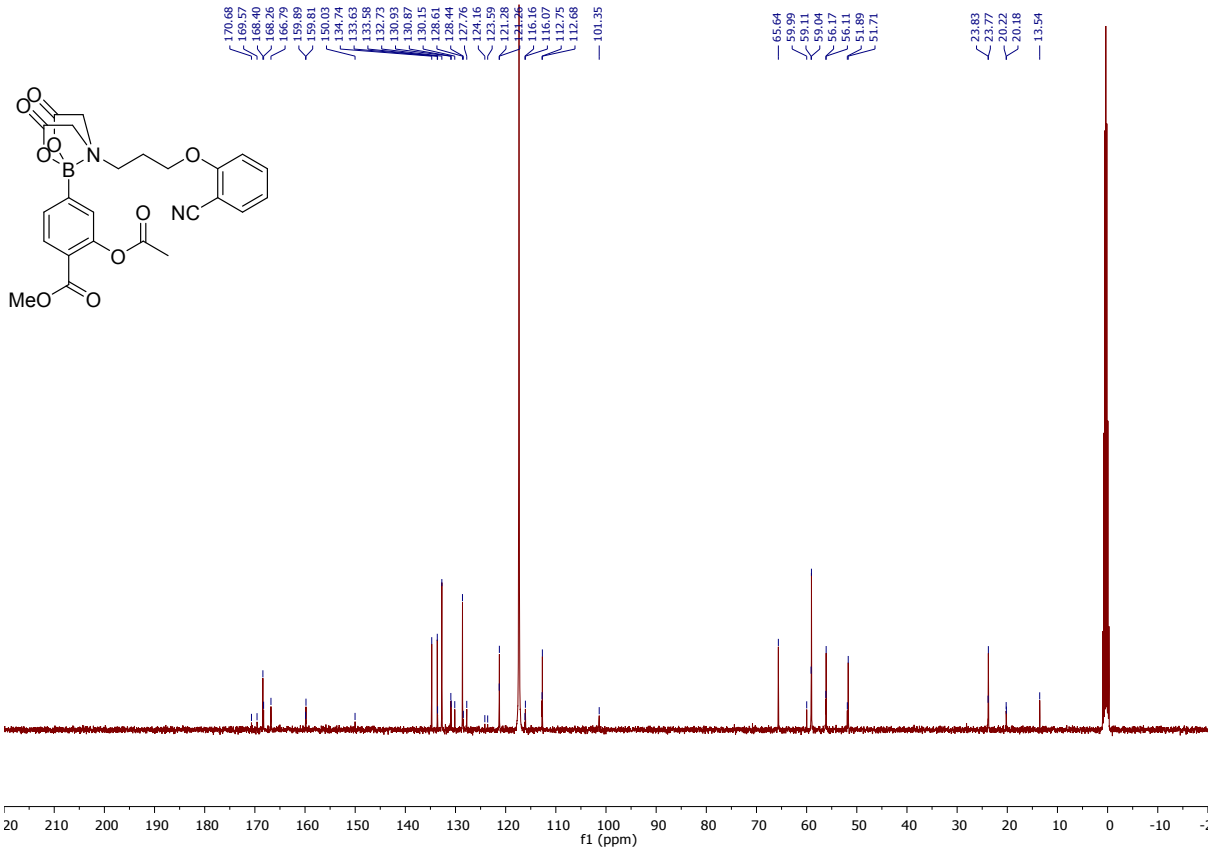

11.98
MeO
NC
a
b
f1 (ppm)

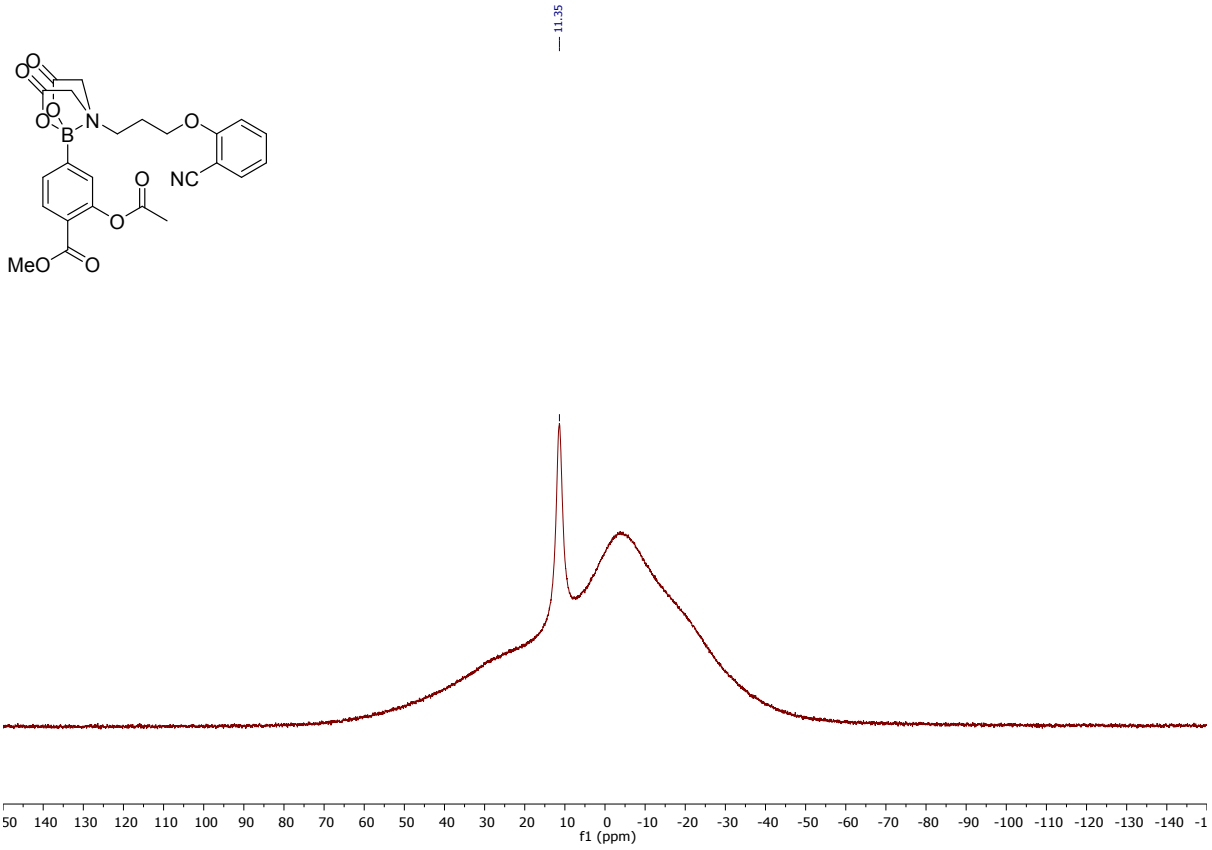

MeO
NC
A (m) 8.00
B (dd) 7.72
C (m) 7.47
D (d) 6.97
E (tdd) 7.05
F (m) 7.57
G (d) 4.13
H (d) 4.06
I (q) 3.98
J (s) 3.89
K (m) 2.85
L (s) 2.27
M (dddd) 2.11
f1 (ppm)


169.46
168.44
168.30
166.93
166.10
159.87
159.82
150.87
137.18
134.73
133.63
133.60
133.25
131.44
130.54
130.40
130.20
129.83
128.30
123.62
123.50
121.27
116.10
116.04
112.71
112.68
101.41
101.35
65.68
59.15
59.06
56.28
56.17
51.94
51.68
23.88
23.81
20.30
MeO
O
NC
B
N
f1 (ppm)

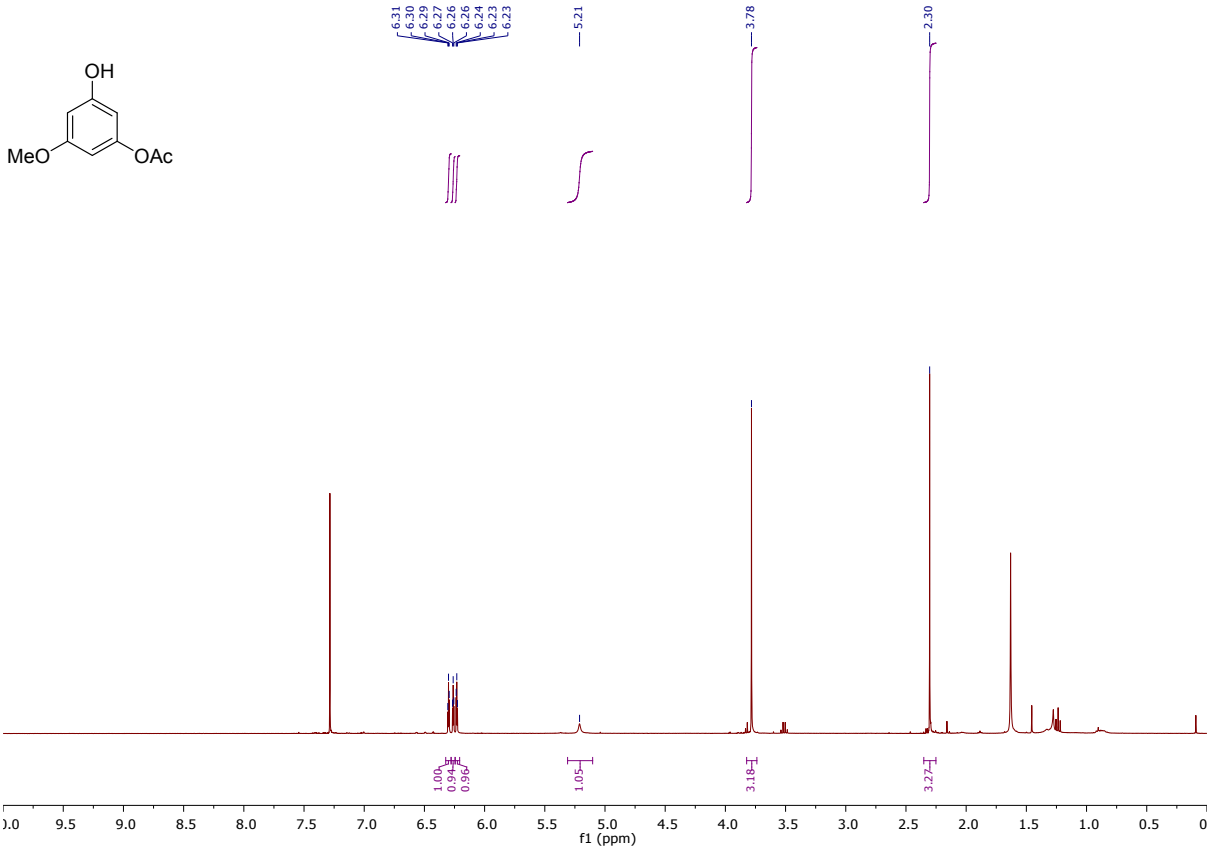

11.46
MeO
O
NC
B
N
f1 (ppm)

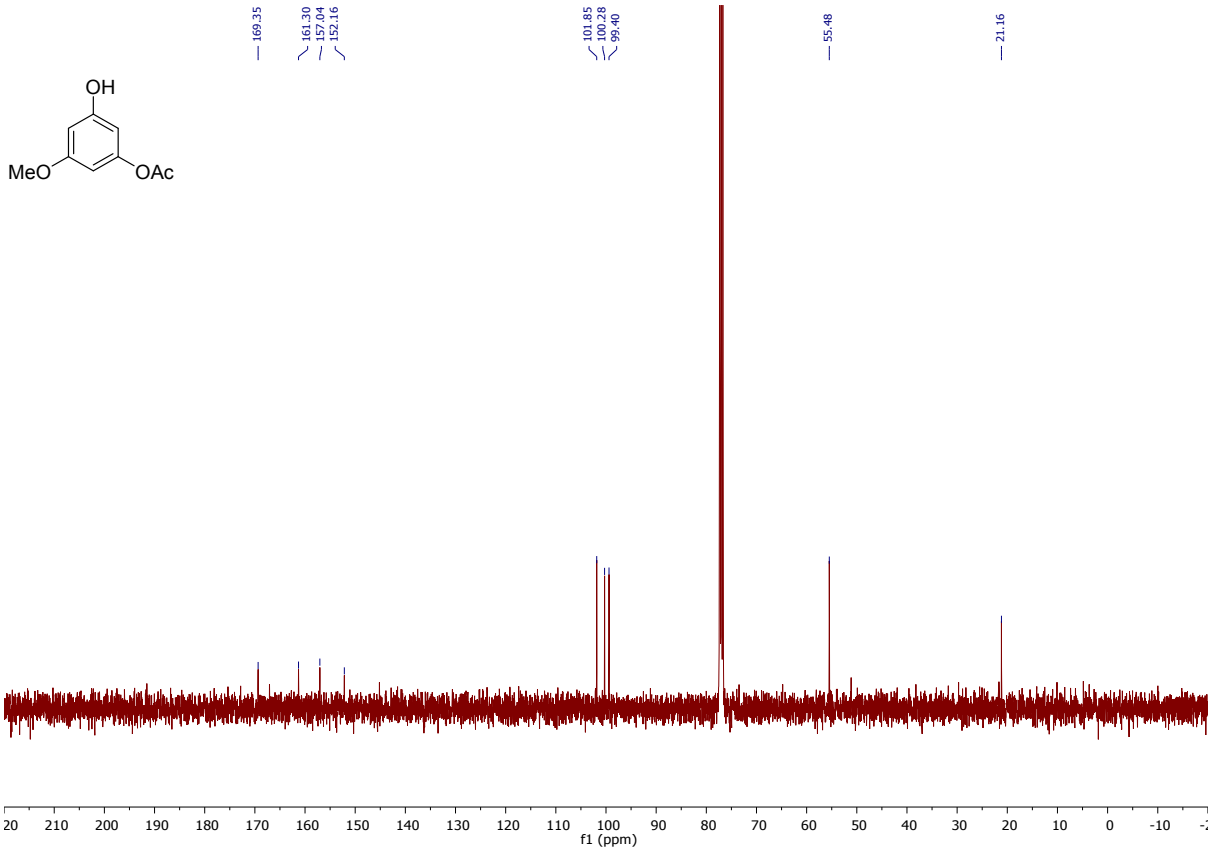

C (d) 7.94
B (dd) 7.50
A (d) 7.30
E (d) 6.98
D (m) 7.57
F (td) 7.06
J (d) 4.07
H (t) 3.98
G (s) 3.84
I (d) 4.13
K (m) 2.87
M (dddd) 2.10
L (s) 2.28
f1 (ppm)


f1 (ppm)

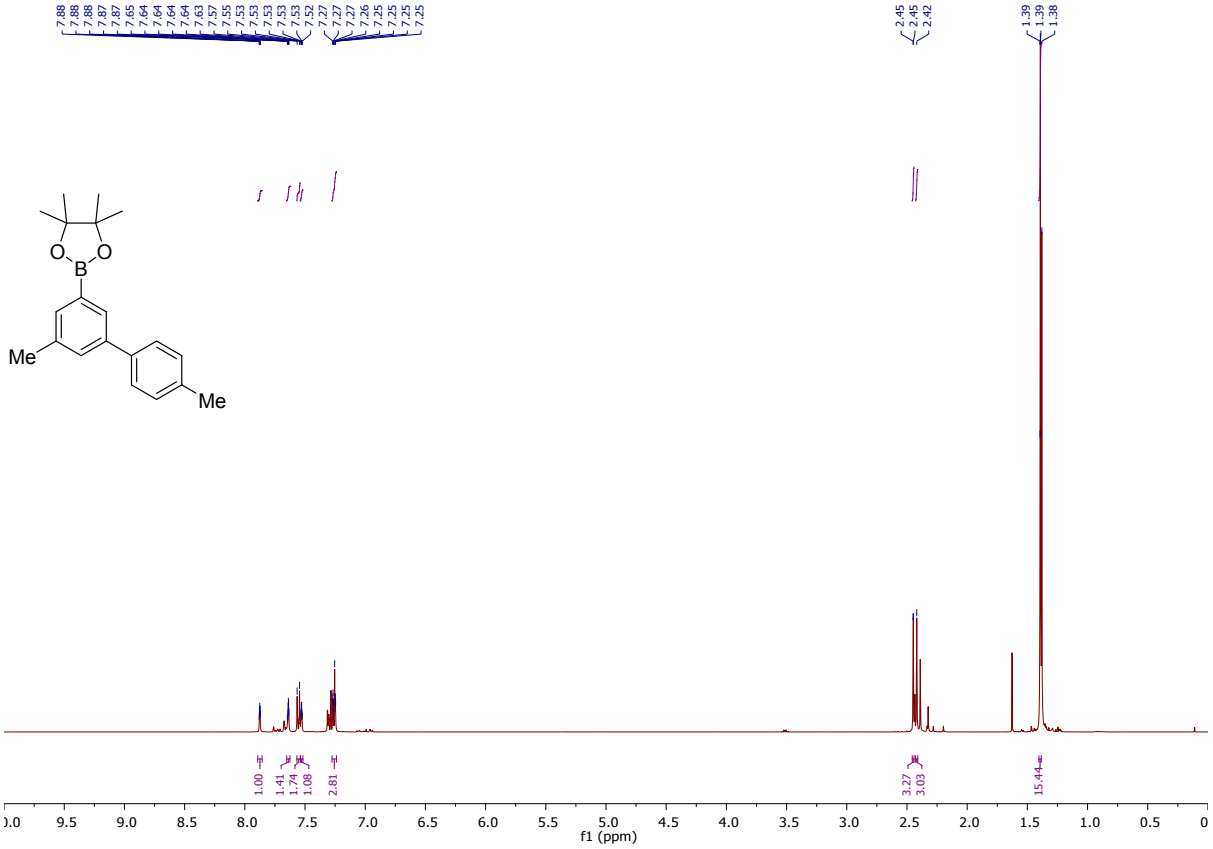


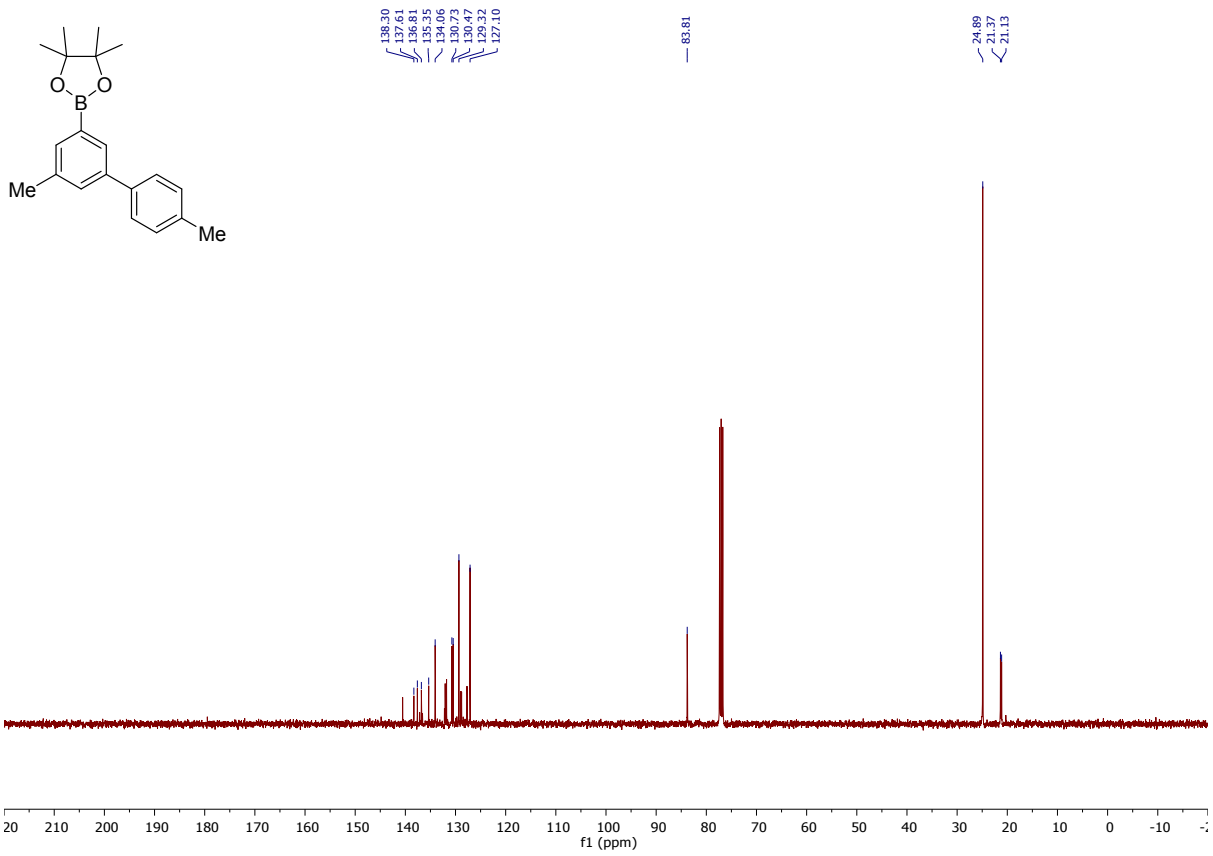
Oxidised Acetoxylated Product NMR Spectra

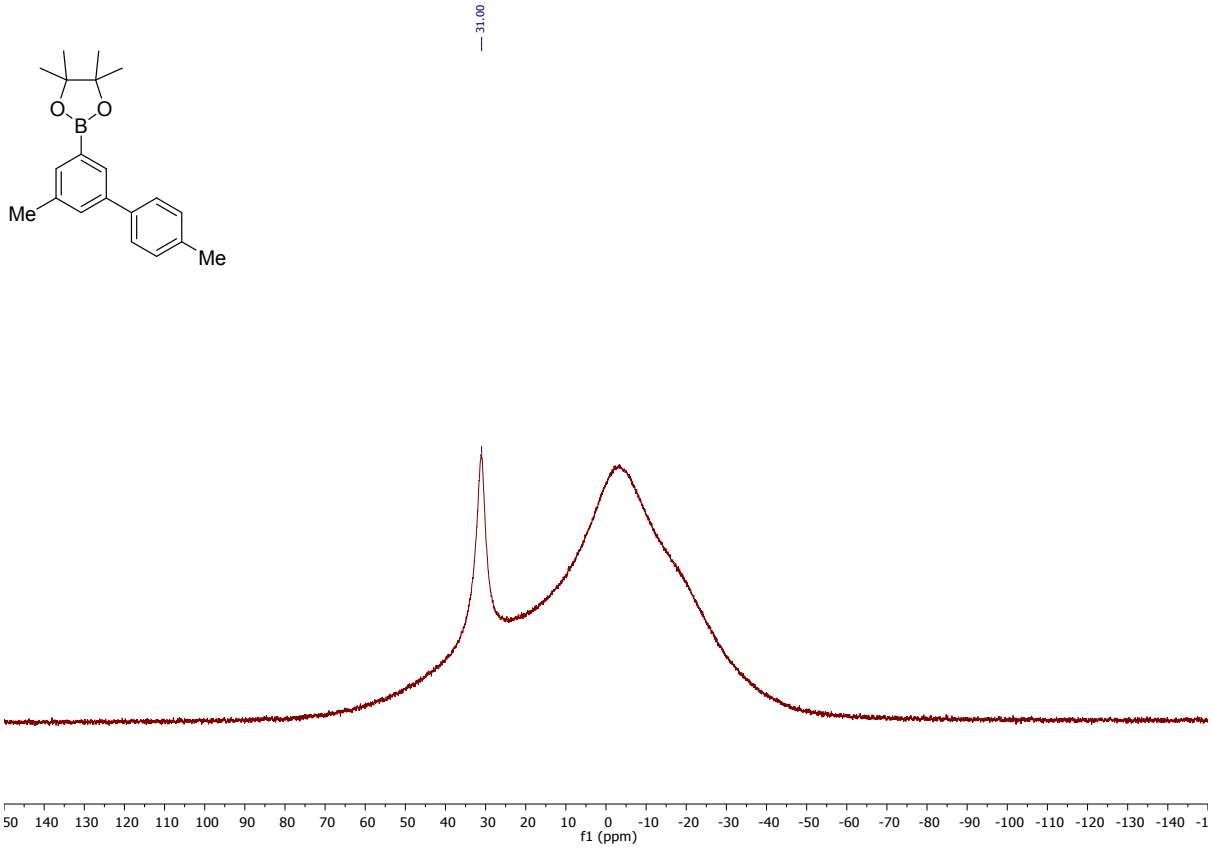



169.35
161.30
157.04
152.16
101.85
100.28
99.40
55.48
21.16
OH
MeO
OAc
f1 (ppm)

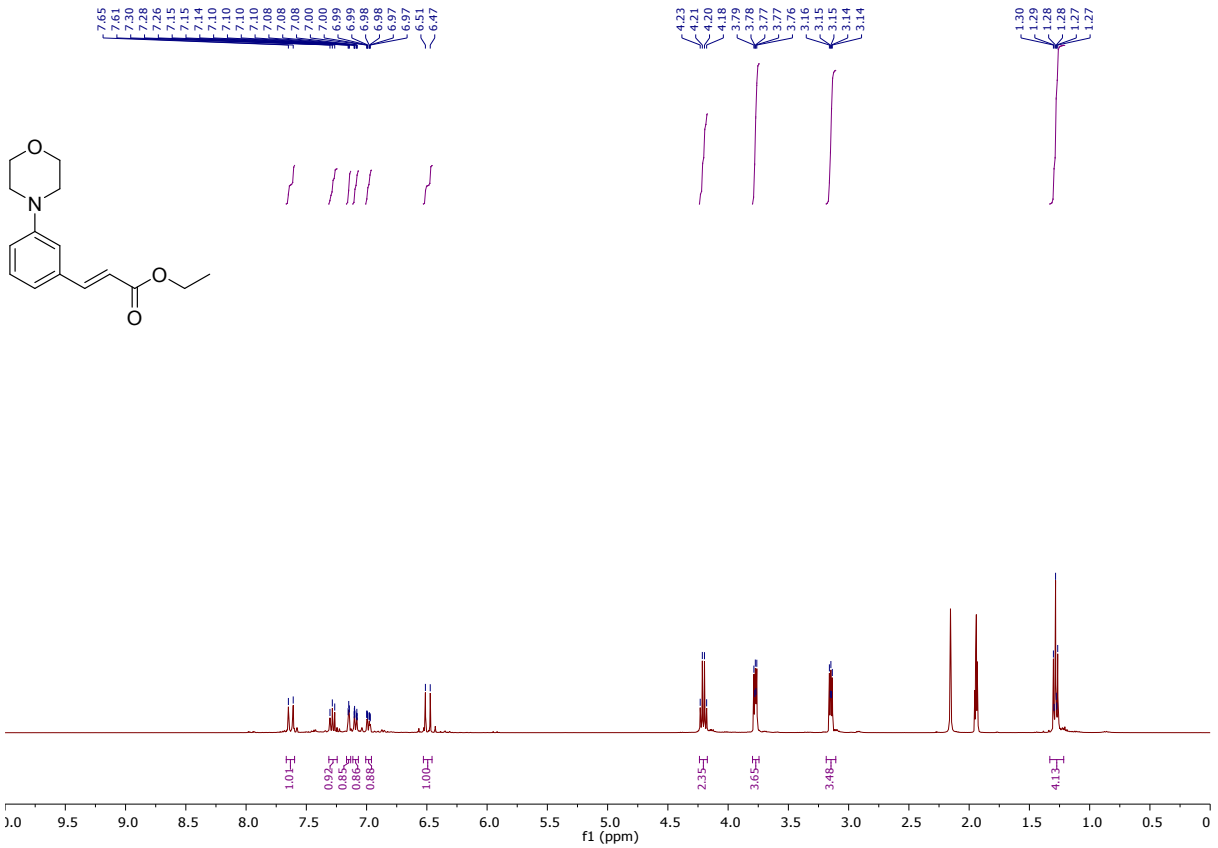
Arylated product NMR Spectra

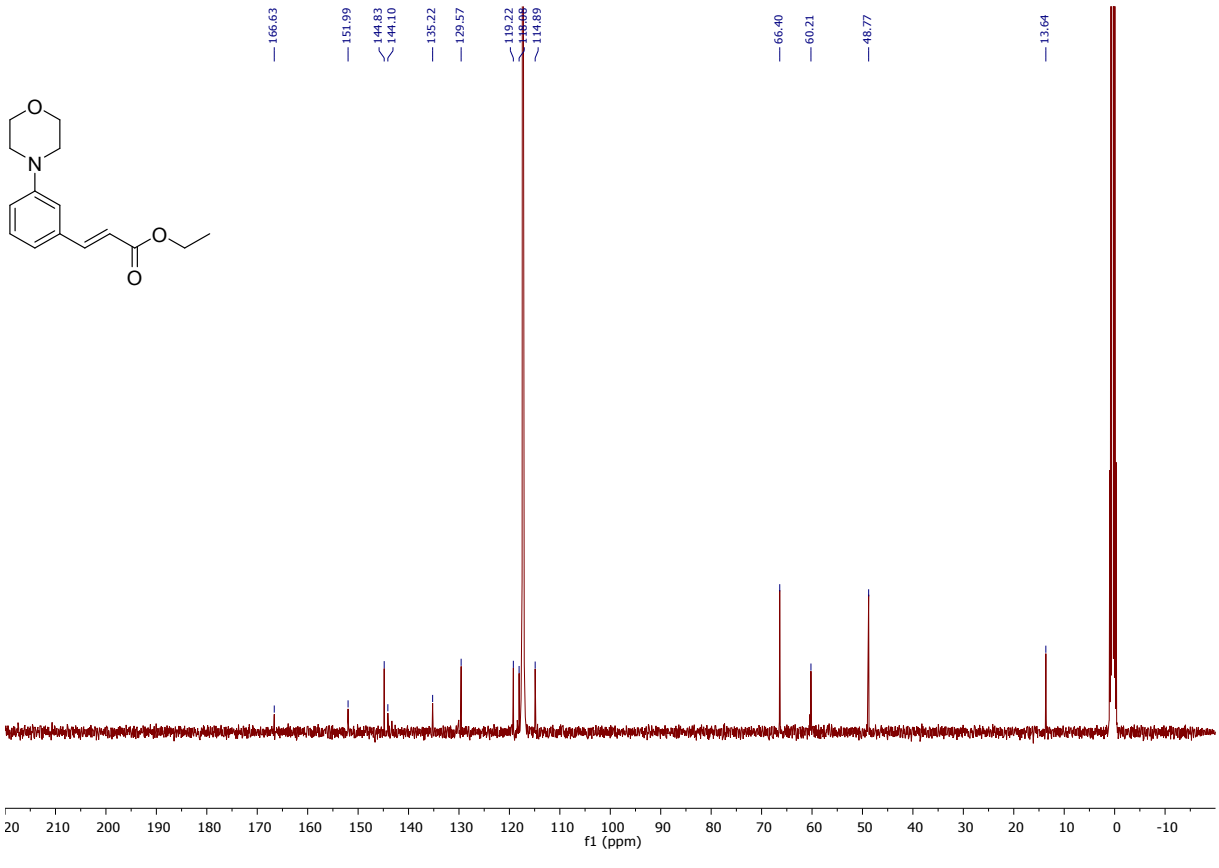


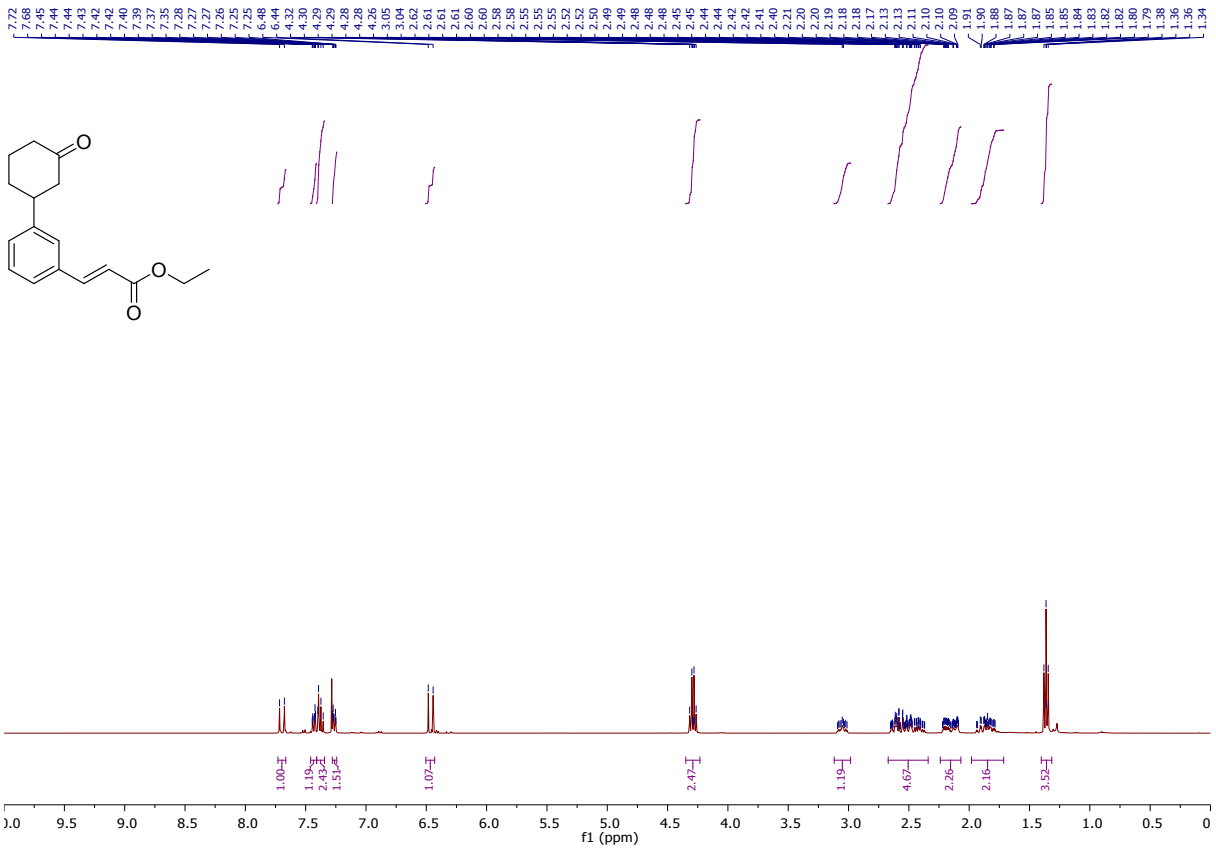


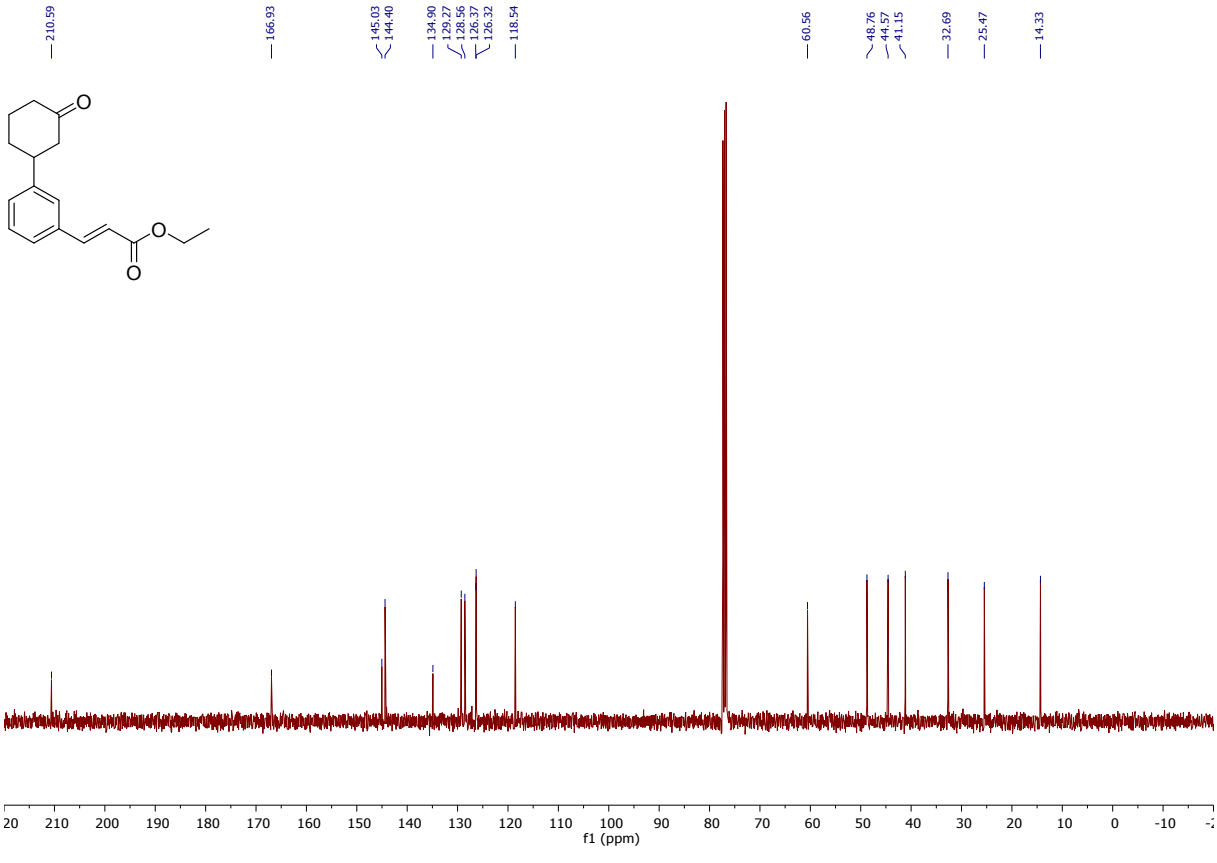

31.00
O
O
B
Me
Me
50 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -1
f1 (ppm)

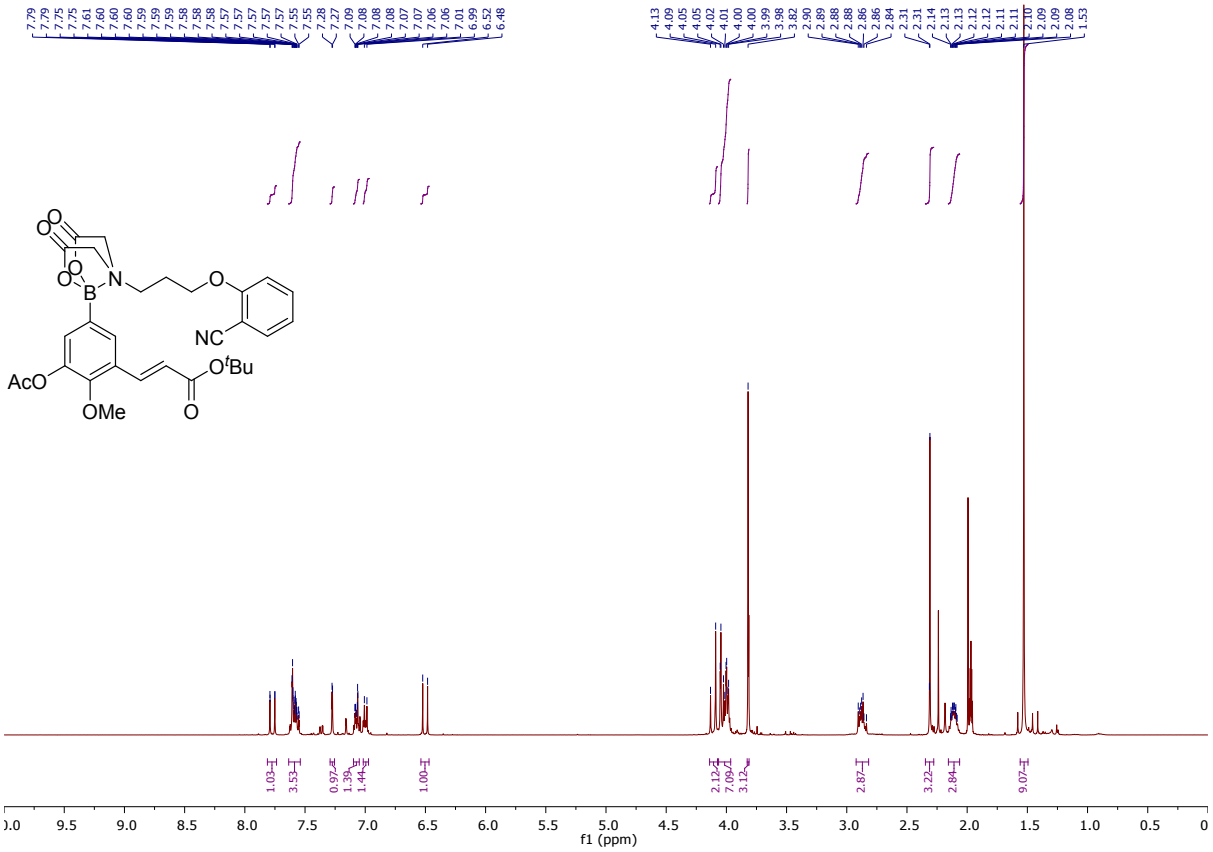
Derivatised products NMR spectra

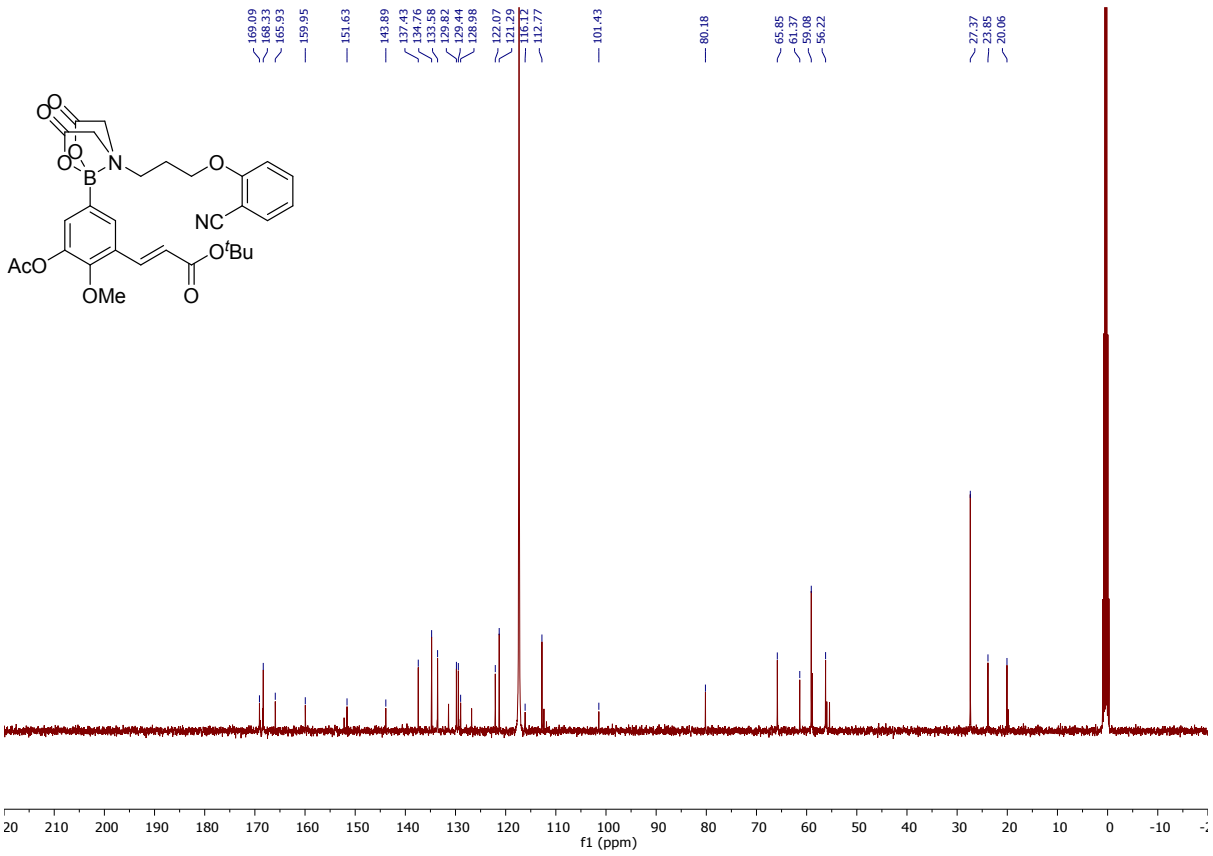


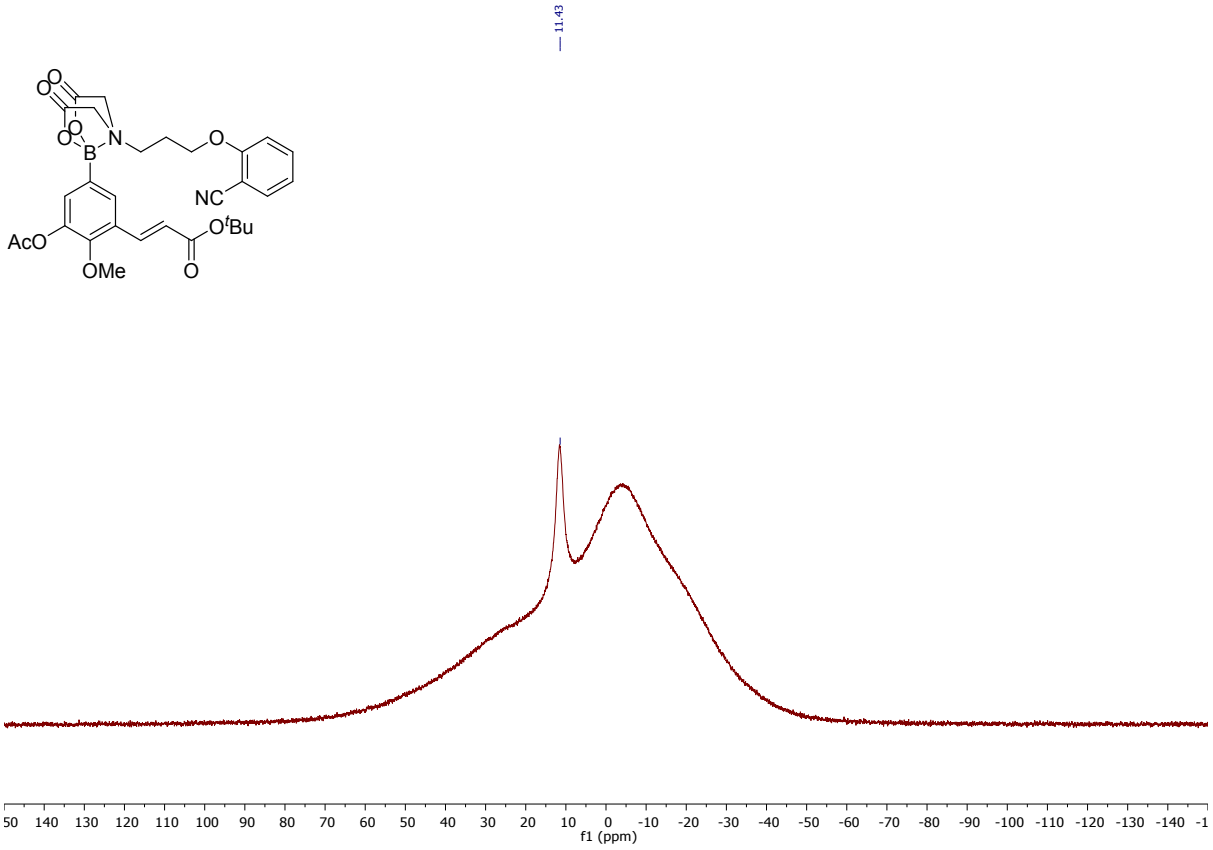


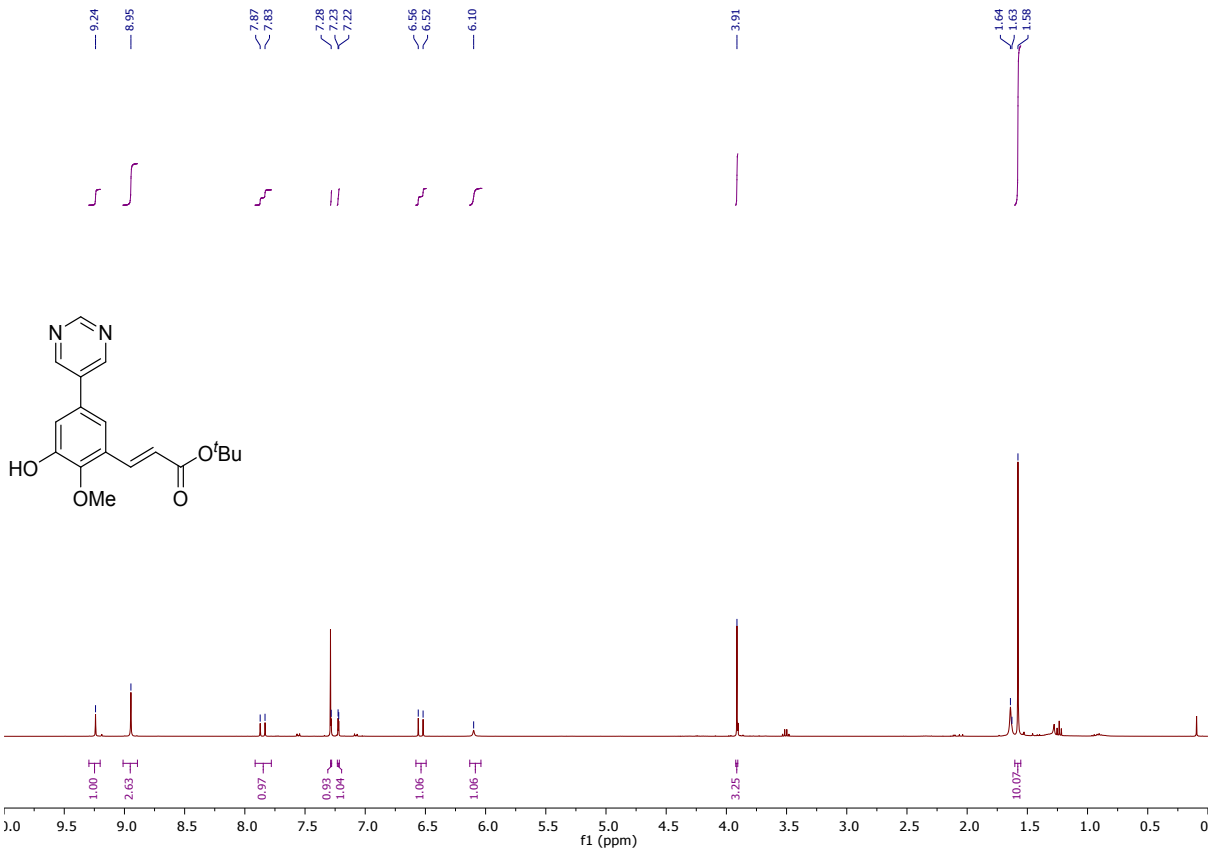

O
O
O
1.00
1.19
2.43
1.51
1.07
2.47
1.19
4.67
2.26
2.16
3.52
f1 (ppm)

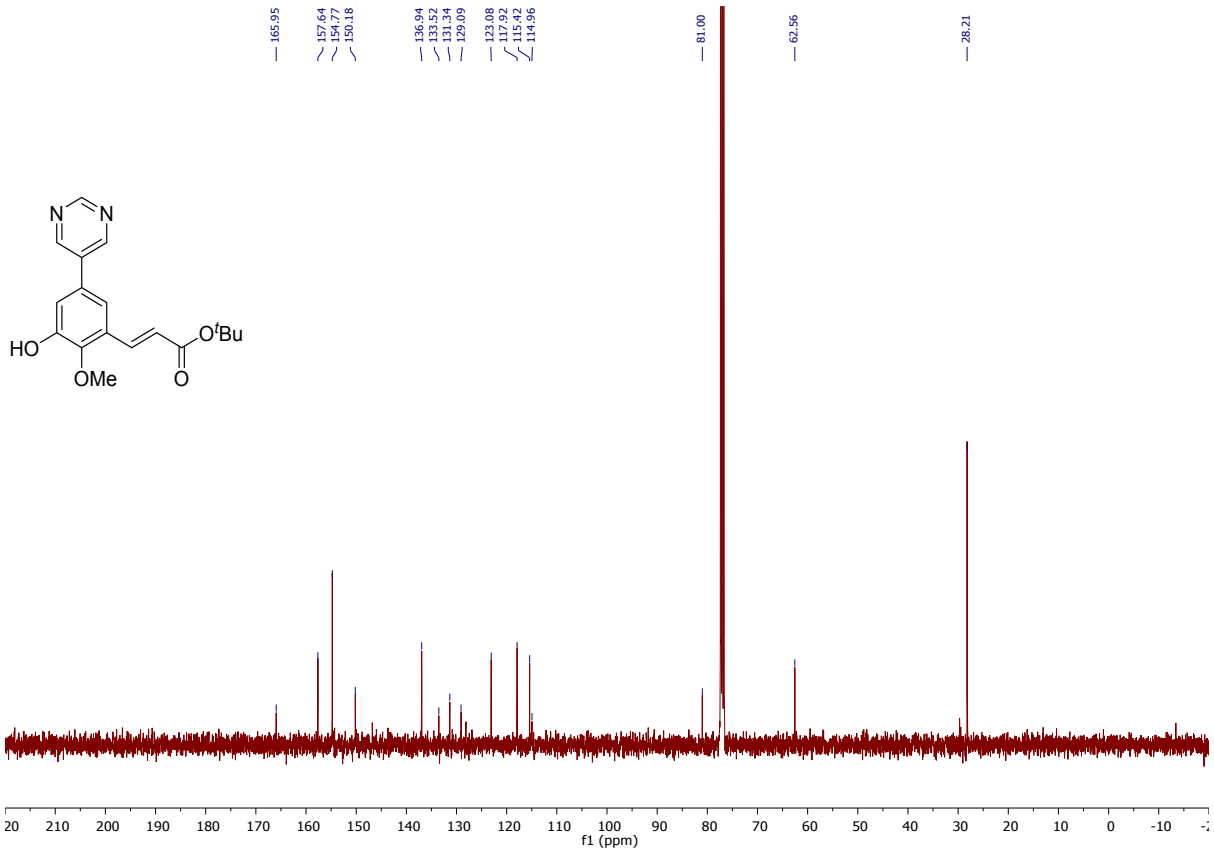

210.59
166.93
145.03
144.40
134.90
129.27
128.56
126.37
126.32
118.54
60.56
48.76
44.57
41.15
32.69
25.47
14.33
O
O
O
f1 (ppm)


f1 (ppm)


f1 (ppm)


11.43
O
O
O
O
B
N
O
NC
AcO
OMe
O
O
tBu
50 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -1
f1 (ppm)


9.24
8.95
7.87
7.83
7.28
7.23
7.22
6.56
6.52
6.10
3.91
1.64
1.63
1.58
N
N
HO
OMe
O
O
tBu
1.00
2.63
0.97
0.93
1.04
1.06
1.06
3.25
10.07
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)


165.95
157.64
154.77
150.18
136.94
133.52
131.34
129.09
123.08
117.92
115.42
114.96
81.00
62.56
28.21
N
N
HO
OMe
O
O^{t}Bu
f1 (ppm)

The X-ray crystal structure of PhB(MIDA-DG) 7.

Crystal data for **7**: $C_{20}H_{19}BN_2O_5$, M = 378.18, monoclinic, $P2_1/c$ (no. 14), a = 9.8085(5), b = 8.9262(4), c = 21.7277(9) Å, β = 99.222(5)°, V = 1877.72(16) Å^3, Z = 4, D_c = 1.338 g cm^{-3}, μ(Mo-Kα) = 0.096 mm^{-1}, T = 173 K, colourless blocky needles, Agilent Xcalibur 3 E diffractometer; 3720 independent measured reflections (R_{int} = 0.0233), F^2 refinement,[X1,X2] R_1(obs) = 0.0439, wR_2(all) = 0.1012, 2805 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, completeness to θ_{full}(25.2°) = 98.6%], 254 parameters. CCDC 1961105. See Figure S12.

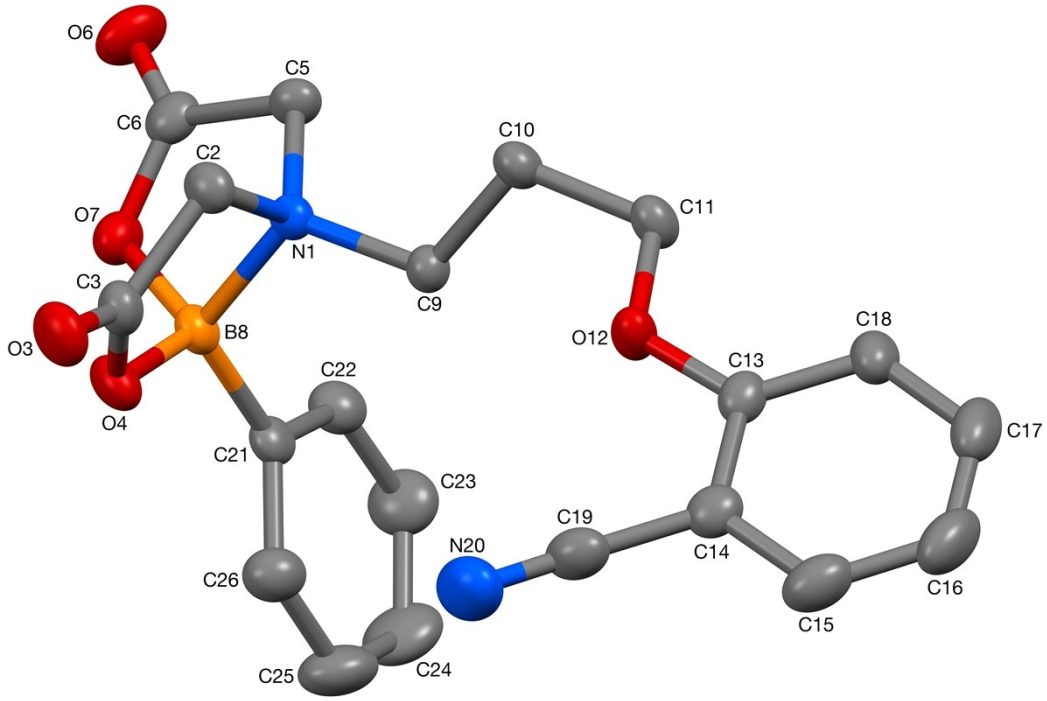


Figure S12 The crystal structure of **7** (50% probability ellipsoids).

Identification code	CJC1801	
Formula	C20 H19 B N2 O5	
Formula weight	378.18	
Temperature	173(2) K	
Diffractometer, wavelength	Agilent Xcalibur 3 E, 0.71073 Å	
Crystal system, space group	Monoclinic, $P2_1/c$	
Unit cell dimensions	a = 9.8085(5) Å	α = 90°
	b = 8.9262(4) Å	β = 99.222(5)°
	c = 21.7277(9) Å	γ = 90°
Volume, Z	1877.72(16) Å^3, 4	
Density (calculated)	1.338 Mg/m^3	
Absorption coefficient	0.096 mm^{-1}	
F(000)	792	

Crystal colour / morphology	Colourless blocky needles
Crystal size	0.756 x 0.225 x 0.125 mm^3
□ range for data collection	2.471 to 28.211°
Index ranges	-13<=h<=13, -7<=k<=11, -18<=l<=28
Reflns collected / unique	6389 / 3720 [R(int) = 0.0233]
Reflns observed [F>4□(F)]	2805
Absorption correction	Analytical
Max. and min. transmission	0.990 and 0.954
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3720 / 0 / 254
Goodness-of-fit on F^2	1.044
Final R indices [F>4□(F)]	R1 = 0.0439, wR2 = 0.0895
R indices (all data)	R1 = 0.0648, wR2 = 0.1012
Largest diff. peak, hole	0.239, -0.203 $eÅ^{-3}$
Mean and maximum shift/error	0.000 and 0.000

Bond lengths [Å] and angles [°] for PhB(MIDA-DG) **7**.

N(1)-C(5)	1.4899(18)
N(1)-C(2)	1.4964(19)
N(1)-C(9)	1.5001(19)
N(1)-B(8)	1.662(2)
C(2)-C(3)	1.506(2)
C(3)-O(3)	1.2027(19)
C(3)-O(4)	1.334(2)
O(4)-B(8)	1.462(2)
C(5)-C(6)	1.513(2)
C(6)-O(6)	1.2025(18)
C(6)-O(7)	1.3272(19)
O(7)-B(8)	1.486(2)
B(8)-C(21)	1.581(2)
C(9)-C(10)	1.520(2)
C(10)-C(11)	1.508(2)
C(11)-O(12)	1.4361(18)
O(12)-C(13)	1.3564(18)
C(13)-C(18)	1.390(2)
C(13)-C(14)	1.398(2)
C(14)-C(15)	1.388(2)
C(14)-C(19)	1.441(3)
C(15)-C(16)	1.380(3)
C(16)-C(17)	1.376(3)
C(17)-C(18)	1.389(2)
C(19)-N(20)	1.142(2)
C(21)-C(26)	1.392(2)
C(21)-C(22)	1.394(2)
C(22)-C(23)	1.383(2)
C(23)-C(24)	1.374(3)
C(24)-C(25)	1.370(3)
C(25)-C(26)	1.388(3)

C(5)-N(1)-C(2)	112.35(12)
C(5)-N(1)-C(9)	113.28(12)
C(2)-N(1)-C(9)	111.81(11)
C(5)-N(1)-B(8)	103.61(11)
C(2)-N(1)-B(8)	101.62(11)
C(9)-N(1)-B(8)	113.34(11)
N(1)-C(2)-C(3)	106.04(13)
O(3)-C(3)-O(4)	123.93(15)
O(3)-C(3)-C(2)	125.19(16)
O(4)-C(3)-C(2)	110.88(13)
C(3)-O(4)-B(8)	113.31(12)
N(1)-C(5)-C(6)	105.31(12)
O(6)-C(6)-O(7)	124.21(16)
O(6)-C(6)-C(5)	124.95(16)
O(7)-C(6)-C(5)	110.82(13)
C(6)-O(7)-B(8)	114.22(12)
O(4)-B(8)-O(7)	111.31(13)
O(4)-B(8)-C(21)	113.85(13)
O(7)-B(8)-C(21)	112.02(13)
O(4)-B(8)-N(1)	102.13(12)
O(7)-B(8)-N(1)	99.32(12)
C(21)-B(8)-N(1)	117.01(13)
N(1)-C(9)-C(10)	113.98(12)

C(11)-C(10)-C(9)	111.44(13)
O(12)-C(11)-C(10)	106.40(12)
C(13)-O(12)-C(11)	118.78(12)
O(12)-C(13)-C(18)	125.14(15)
O(12)-C(13)-C(14)	115.40(14)
C(18)-C(13)-C(14)	119.46(15)
C(15)-C(14)-C(13)	120.32(16)
C(15)-C(14)-C(19)	120.40(16)
C(13)-C(14)-C(19)	119.28(14)
C(16)-C(15)-C(14)	120.00(17)
C(17)-C(16)-C(15)	119.62(17)
C(16)-C(17)-C(18)	121.44(18)
C(17)-C(18)-C(13)	119.15(17)
N(20)-C(19)-C(14)	178.1(2)
C(26)-C(21)-C(22)	116.91(16)
C(26)-C(21)-B(8)	122.58(15)
C(22)-C(21)-B(8)	120.49(14)
C(23)-C(22)-C(21)	121.91(17)
C(24)-C(23)-C(22)	119.79(18)
C(25)-C(24)-C(23)	119.73(18)
C(24)-C(25)-C(26)	120.50(18)
C(25)-C(26)-C(21)	121.14(17)

References

[X1] SHELXTL v5.1, Bruker AXS, Madison, WI, 1998.

[X2] SHELX-2013, G.M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.