

Reactivity of 1,3-enyne MIDA Boronates, Exploration of novel 1,2-Alkyne Shift via *gem*-Difluorination and Synthesis of diverse Iterative Coupling Partners

Samir Manna, Debasis Aich, Subrata Hazra, Shivam Khandelwal, Santanu Panda*

Supporting information

Table of Contents

General Information	S1
Synthesis of 1,3-enyne boronates	S2-S6
Optimization Table 3,4-hydroboration	S6-S7
Synthesis of Starting materials	S7-S9
General procedure	S9-S12
¹ H-NMR & ¹³ C-NMR data for synthesized compounds	S12-S35
Crystallography data	S35-S37
Reference	S37-S38
¹ H-NMR & ¹³ C-NMR Spectra	S38-S1578

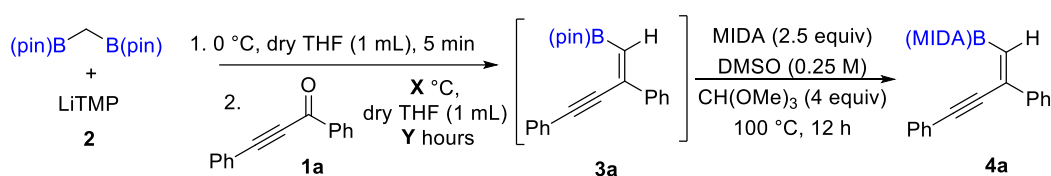
General Information: Unless otherwise stated, reactions were performed under nitrogen using freshly purified solvents. All reactions were monitored by thin-layer chromatography with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Flash chromatography was performed with indicated solvents using silica gel. The NMR spectra were recorded with a Bruker 400, 500 MHz NMR instrument. Data for ¹H NMR are reported as follows: chemical shift (ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublet of doublets, ddd = doublet of doublets of doublets and m = multiplet), and coupling constant (Hz). Mass spectra were acquired on an Agilent technologies 1200 series LC/MS using indicated ionization methods. The known compounds were characterized by ¹H NMR, ¹³C NMR, ¹¹B NMR, and ¹⁹F NMR. For all the known compounds copy of ¹H-NMR, ¹³C NMR and the appropriate references are given.

Materials: Chemicals were purchased from Aldrich, Alfa Aesar, Spectrochem, Avra, TCI and used without purification unless otherwise noted.

➤ Synthesis of 1,3-enyne boronates:

We hypothesized that if the boron-Wittig reaction of enynal with geminal B(pin) would be able to give 1,3-enyne MIDA boronates after transesterification, then our initial target of transition metal-free strategy would be conceived. However, such a strategy has to face some challenges related to the stereoselectivity issues when reacted with a ketone.¹ At the onset of our hypothesis, we began our finding with propargylic ketones. To find out our optimized reaction condition, we have done thorough optimization by varying the reaction temperature and concentration of the reaction and found that the temperature had a significant role in the progress of the reaction.

To optimized the stereoselective outcome of our designed targeted moiety, we have done through screening of all the reaction parameters. As the 1,3-enyne B(pin) (**3**) was highly unstable in the column chromatography, we have performed the transesterification with the crude reaction mixture. We also optimized the transesterification step and observed that the equivalences of MIDA ligand should be equal or higher than the 2.5 equiv.² Also the amount of proton source should be equal or higher than 4 equivalents. For the transesterification, we have optimized several temperatures out of them 100 °C is the best yielding in 12 hours. After fixed all the parameters, we have optimized the best yield 76% (Table 1, entry 7).



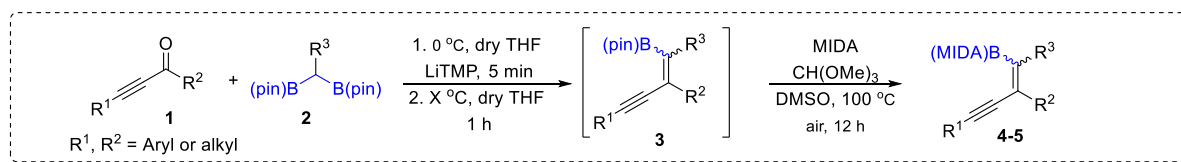
Entry ^{a,b}	2 & 3 (equiv)	1 (equiv)	Temperature (X °C)	Time (Y hours)	isolated Yield %
1	1.2	1	-78 °C	4 h	0
2	1.2	1	0 °C	2 h	50
3	1.2	1	RT	1 h	messy
4	1.2	1	0 °C	4 h	50
5	1.2	1	0 °C to RT	1 h	62
6	1.4	1	0 °C to RT	1 h	72
7	1.5	1	0 °C to RT	1 h	76
8	1.7	1	0 °C to RT	1 h	71

Table 1: LiTMP was made *in situ* using *n*-BuLi (1.5 equiv) and HTMP (1.5 equiv) at -78 °C, 30 min then 0 °C, 30 min; all the reactions was carried out at 0.475 mmol of **1a**.

(Please note that the used HTMP should be highly dried, otherwise yield of this reaction was drastically diminished.)

The optimized condition reveals that the addition of propargylic ketone at 0 °C to the α -bis(boryl)carbanions and then warming up to room temperature is the best yielding (76%) after the transesterification using MIDA in DMSO. Interestingly, the outcome of this boron-Wittig reaction with propargylic ketone gives only one isomer. The structure of all types of 1,3-enyne boronates were confirmed by the X-ray data (**4i**, **4r** and **6i**). However, the previous literature on the boron-Wittig

reaction of ketone showed poor stereoselectivity and dependency on the presence of amine additives to improve the stereoselective outcome.¹



Scope of propargylic Ketone:^{a,b,e,f}

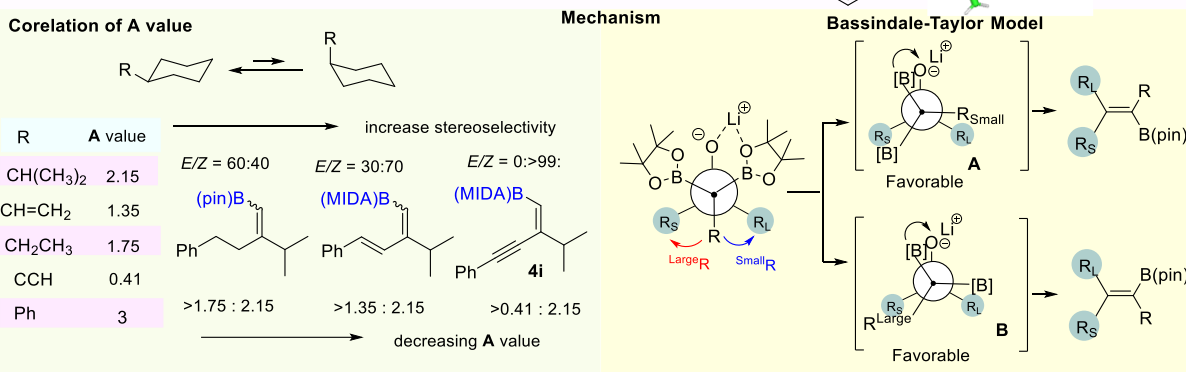
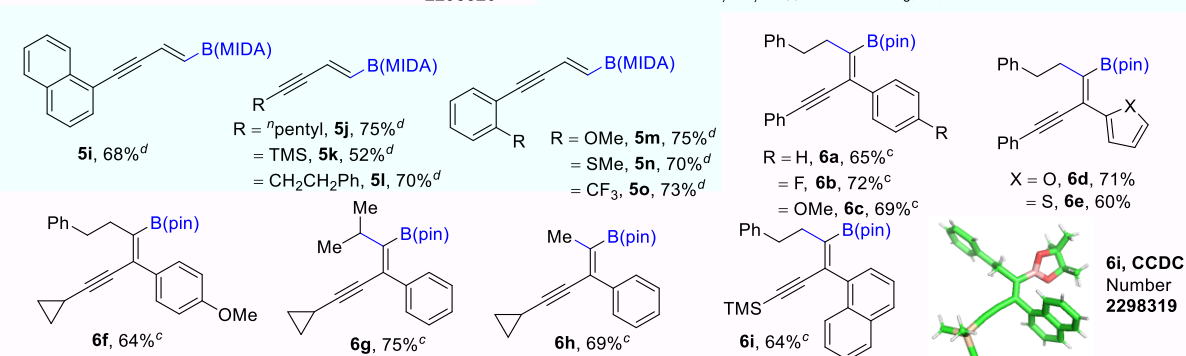
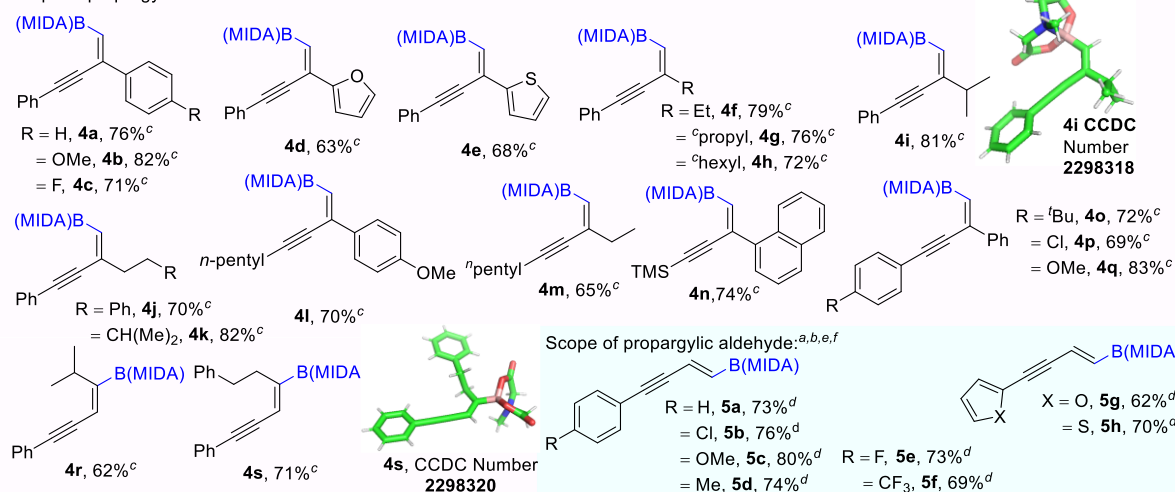


Table 2: Substrate Scope and Mechanism investigation^a LiTMP was made *in situ* using HTMP and *n*-BuLi at -78 °C, 30 min then 0 °C, 30 min; ^b**1** (0.472 mmol), **2** (0.709 mmol), LiTMP (0.709 mmol); ^c**1** was added at 0 °C then warm up to RT for 1 h; ^d**1** was added at -78 °C and stirred for 4h; ^e all the cases crude enyne B(pin) was used for transesterification; ^fMIDA (1.18 mmol, 2.5 equiv), CH(OMe)₃ (1.88 mmol, 4 equiv), DMSO (2 mL)

Having optimized reaction conditions in hand, we have explored substrate scope by varying different propargylic ketones and substituted geminal B(pin). Aryl propargylic ketones with both electron-

¹ S. Namirembe, C. Gao, R. P. Wexler and J. P. Morken, *Org. Lett.*, 2019, **21**, 4392–4394

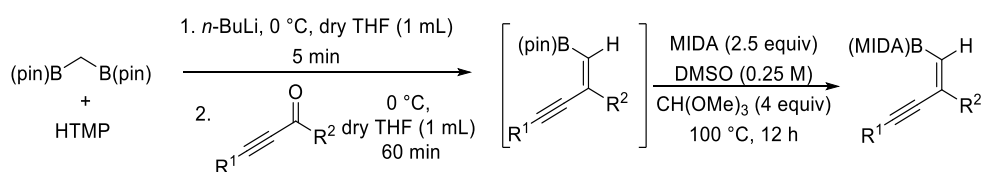
² E. M. Woerly, J. E. Miller and M. D. Burke, *Tetrahedron*, 2013, **69**, 7732–7740.

³ J. R. Coombs, L. Zhang and J. P. Morken, *Org. Lett.*, 2015, **17**, 1708.

donating and electron-withdrawing group works well with high yield and diastereoselectivity (**4b** and **4c**). Most importantly, the reaction tolerated the heteroaromatic propargylic ketones efficiently with high yield and excellent diastereoselectivity (**4d** and **4e**). Further, when we employed sterically-biased aliphatic propargylic ketones, we were also able to get high diastereoselectivity and good yield (**4f-4j**). Variation of the aryl group attached to alkyne did not have any effect on the yield as well as stereoselectivity (**4n-4p**). Additionally, to make tri-substituted 1,3-enyne MIDA boronates, we examined the reactivity of substituted lithiated geminal bis(boronate)s with propargylic aldehyde and noticed the opposite selectivity (reverse with unsubstituted geminal bis(boronate) (**4q** and **4r**). We have proposed a steric model to explain the stereoselectivity outcome, which will be discussed later. Further, we explored the scope with propargylic aldehydes. Following the previous condition as reported by the Morken group,³ we found the desired products (after the transesterification) with high yield and excellent selectivity (**5a-5n**). After successfully encountered di- and tri-substituted 1,3-enyne B(MIDA) compounds, we tuned our attention towards tetra substituted 1,3-enyne boronates. Using our optimized condition for propargyl ketone, we investigated the stereoselectivity outcome by reacting substituted geminal bis(boronate) compounds with propargylic ketones. We observed the steric-controlled Z-selective product (**6a-6i**). As such tetra substituted 1,3-enyne B(pin) are stable in column chromatography, so we are not interested in transesterification. Here, we also found the reflection of the steric model for explaining the stereoselectivity.

To get the exact reason for this excellent stereoselectivity, we have prepared three ketones with the same number of carbon as of **4i** (aliphatic, α,β -unsaturated and alkyne) and employed them in our optimized reaction condition (Table 1, entry 7). The outcome of this boron-Wittig reaction demonstrated that the stereoselectivity is increasing from aliphatic one to α,β -unsaturated to alkyne. To get a rough idea about the steric model, we have introduced the 'A' value of the R group of cyclohexane ring in the chair form (Table 2).⁴ The 'A' value signifies the amount of energy cost of a 'R' group to stay at the axial position of the cyclohexane ring. As the 'A' value decreases from left (aliphatic) to right (alkyne), which correlates with the increasing stereoselectivity. This result suggested that the boron-Wittig reaction of propargylic ketone is controlled mostly by the steric model. To consolidate our hypothesis, we took the help of the well-known Bassindale and Taylor model of the addition of prochiral anion to prochiral aldehyde.⁵ According to the model, the anion will approach the carbonyl group in such a way that the smallest substituent will be positioned between the two carbonyl substituents as shown in table 2. This preference will automatically position the smaller carbanion substituent next to the carbonyl compound's biggest substituent. Our result also fits with this model and signifies the dominion of a steric model.

1. General procedure (GP1): Synthesis of tri-substituted 1,3-enyne B(MIDA) (**4**):

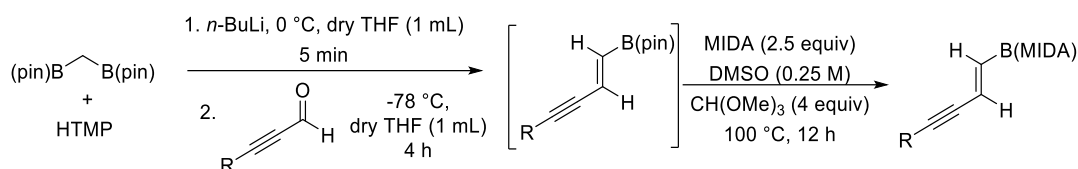


A 20 mL flame-dried reaction tube was first evacuated and backfilled with nitrogen three times then the tube was charged with a THF (1ml) solution of 2,2,6,6-tetramethylpiperidine (100 mg, 0.715 mmol, 1.5 equiv). After cooling the reaction tube at -78 °C, *n*-BuLi (1.2 M in hexanes, 0.6 mL, 0.709 mmol, 1.4 equiv) was added dropwise resulting in a light-yellow solution. The reaction mixture was stirred for

30 min²utes at -78 °C and then 30 minutes at 0 °C. After that, a THF (1 mL) solution of bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (190 mg, 0.715 mmol, 1.5 equiv) was added drop wisely. The resulting mixture was stirred for 5 min at the same temperature then a solution of propargylic ketone (0.475 mmol, 1 equiv) in THF (1 mL) was added. The reaction tube was allowed to stir at room temperature for additional 1 hours. Upon completion, the reaction mixture was quenched by water and extracted with ethyl acetate. The organic layer was dried over Na₂SO₄, filtrated and concentrated under reduced pressure. The crude mixture was then undergoing a celite filtration using hexane as an eluent. The filtrate was the concentrated under reduced pressure and goes for the next step.

To an oven-dried schlenk tube equipped with a stir bar was added crude enyne boronates, anhydrous DMSO (2 mL), CH(OMe)₃ (4.0 equiv) and *N*-methyliminodiacetic acid (104 mg, 0.708 mmol, 2.5 equiv). The resulting mixture was stirred at 100 °C for 12 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (10 mL) and water (10 mL). The organic phase was seperated and the aqueous layer was extracted with ethyl acetate (10 mL) for three times. The combined organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with a mixture of petroleum ether and ethyl acetate (1:3) as eluent to give 1,3-enyne MIDA boronates.

2. General procedure (GP2): Synthesis of di-substituted 1,3-enyne B(MIDA) (5):



A 20 mL flame-dried reaction tube was first evacuated and backfilled with nitrogen three times then the tube was charged with a THF (1ml) solution of 2,2,6,6-tetramethylpiperidine (80 mg, 0.57 mmol, 1.2 equiv). After cooling the reaction tube at -78 °C, *n*-BuLi (1.2 M in hexanes, 0.6 mL, 0.709 mmol, 1.4 equiv) was added dropwise resulting in a light-yellow solution. The reaction mixture was stirred for 30 minutes at -78 °C and then 30 minutes at 0 °C. After that, a THF (1ml) solution of bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (152 mg, 0.57 mmol, 1.2 equiv) was added drop wisely. The resulting mixture was stirred for 5 min at the same temperature then the reacture tube was transferred to -78 °C. After cooling at -78 °C, a solution of ynone (0.475 mmol, 1 equiv) in THF (1ml) was added. The reaction tube was allowed to stir at the same temperature for additional 4 hours. Upon completion, the reaction mixture was quenched by water and extracted with ethyl acetate. The organic layer was dried over Na₂SO₄, filtrated and concentrated under reduced pressure. The crude mixture was

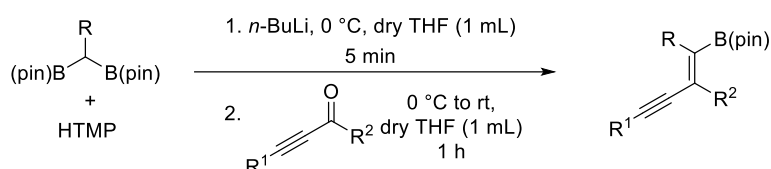
⁴ P. Muller, *Pure and Applied Chemistry*. 1994, **66**, 1077.

⁵ A. R. Bassindale, R. J. Ellis, J. C.-Y. Lau and P. G. Taylor, *J. Chem. Soc. Chem. Commun.*, 1986, **98**.

then undergoing a celite filtration using hexane as an eluent. The filtrate was concentrated under reduced pressure and goes for the next step.

To an oven-dried schlenk tube equipped with a stir bar was added crude enyne boronates, anhydrous DMSO (2 mL), CH(OMe)₃ (4.0 equiv) and *N*-methyliminodiacetic acid (104 mg, 0.708 mmol, 2.5 equiv). The resulting mixture was stirred at 100 °C for 12 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (10 mL) and water (10 mL). The organic phase was separated and the aqueous layer was extracted with ethyl acetate (10 mL) for three times. The combined organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with a mixture of petroleum ether and ethyl acetate (1:3) as eluent to give 1,3-enyne MIDA boronates.

3. General procedure (GP3): Synthesis of tetra-substituted 1,3-enyne B(pin) (**6**):

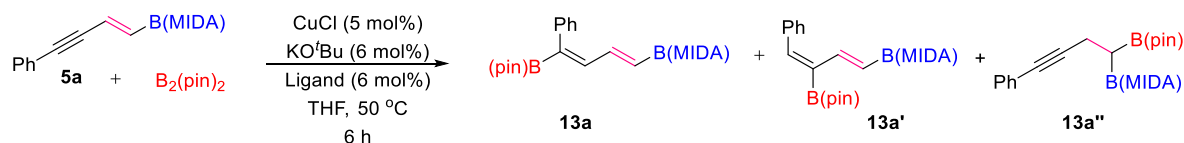


A 20 mL flame-dried reaction tube was first evacuated and backfilled with nitrogen three times then the tube was charged with a THF (1ml) solution of 2,2,6,6-tetramethylpiperidine (100 mg, 0.715 mmol, 1.5 equiv). After cooling the reaction tube at -78 °C, *n*-BuLi (1.2 M in hexanes, 0.6 mL, 0.709 mmol, 1.5 equiv) was added dropwise resulting in a light-yellow solution. The reaction mixture was stirred for 30 minutes at -78 °C and then 30 minutes at 0 °C. After that, a THF (1ml) solution of substituted geminal B(pin) (0.715 mmol, 1.5 equiv.) was added drop wisely. The resulting mixture was stirred for 5 min at the same temperature then a solution of ynone (0.472 mmol, 1 equiv) in THF (1ml) was added. The reaction tube was allowed to stir at room temperature for additional 1.5 hours. Upon completion, the reaction mixture was quenched by water and extracted with ethyl acetate. The organic layer was dried over Na₂SO₄, filtrated and concentrated under reduced pressure. The tetra substituted 1,3-enyne boronates were purified by flash chromatography on silica using a mixture of ethyl acetate and hexane as eluent.

1. Optimization table of 3,4-hydroboration of 1,3-Enyne MIDA boronates:

To optimized the stereoselective 3,4-hydroboration of 1,3-enyne B(MIDA), we have screened both the solvents and ligands, which were listed in the table 2. From this optimization table, we observed that such kind of copper catalysis was more efficient without the proton source (MeOH) and high concentration dependent. After the vigorous optimization, we found that the reaction was highly stereoselective using 0.02 M THF solvent and *p*-anisyl phosphine as a ligand at 50 °C temperature.

3,4-hydroboration of 1,3-enyne B(MIDA):

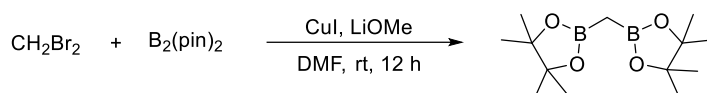


Entry	solvent	ligand	Yield % (13a : 13a')	Entry	solvent	ligand	Yield % (13a : 13a')
1	THF (1 M), MeOH (2 equiv)	PPh_3	40 (55:45)	7	THF (1 M)	$(p\text{-anisyl})_3\text{P}$	70 (75:25)
2	THF (1 M), MeOH (2 equiv)	$(p\text{-anisyl})_3\text{P}$	43 (75:25)	8	THF (0.5 M)	$(p\text{-anisyl})_3\text{P}$	73 (80:20)
3	THF (1 M), MeOH (2 equiv)	$(p\text{-tolyl})_3\text{P}$	43 (65:35)	9	THF (0.02 M)	$(p\text{-anisyl})_3\text{P}$	72 (>99:00)
4	THF (1 M), MeOH (2 equiv)	$(\text{furyl})_3\text{P}$	43 (60:40)				
5	THF (1 M), MeOH (2 equiv)	$(\text{Cy})_3\text{P}$	nd				
6	THF (1 M), MeOH (2 equiv)	Xantphos	nd				

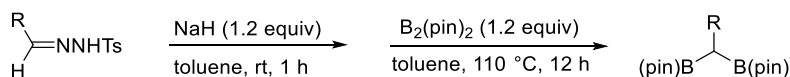
Table 3: **5a** (0.1 mmol, 1 equiv), $B_2(\text{pin})_2$ (0.12 mmol, 1.2 equiv), nd = not detected

➤ Synthesis of Stating Materials:

1. Synthesis of geminal B(pin):



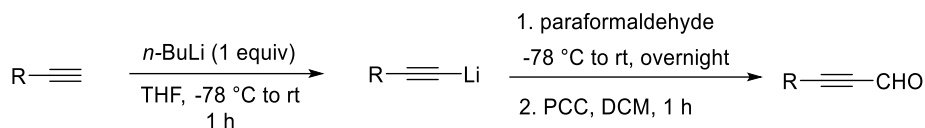
To an oven-dried 250 mL round-bottomed flask equipped with a Teflon coated magnetic stirbar, copper iodide (1.0 g, 5.5 mmol), LiO^tBu (5.2 g, 137.5 mmol) and bis(pinacolato)diboron (25 g, 100 mmol) were added. The flask was evacuated and filled with argon (three cycles). DMF (150 mL) and dibromomethane (9.6 g, 55 mmol) were added *via* syringe under an argon atmosphere. The reaction mixture was stirred at 40 °C for 24 h, and then diluted with n-hexane (150 mL). The organic phase was washed with H_2O (200 mL) and the aqueous layer was extracted with n-hexane (200 mL x 3). The combined organic layers were dried over MgSO_4 , filtered through silica gel and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel to give expected product (9.4 g, 70 %) as a white solid.¹



A modified Schlenk tube was charged with N -tosylhydrazone (1 mmol), 60% NaH (1.2 mmol, 48 mg). After degassed and filled with N_2 , the tube was charged with toluene (8 mL). The mixture was stirred at room temperature for 1 h. Then a solution of $B_2\text{pin}_2$ (1.2 mmol, 305 mg) in toluene (2 mL) was added *via* syringe. Then the tube was sealed and heated at 110 for 12 h. After cooled to room temperature, 10 mL of Et_2O and 10 mL of H_2O were added. The mixture was stirred vigorously for 10 minutes. After separation of organic layer, the aqueous layer was extracted with Et_2O (5 mL x 2). The combined organic

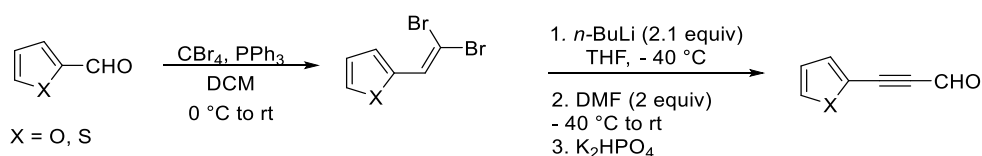
solution was washed with saturated brine (10 mL) and dried over anhydrous Na₂SO₄. After the solvent was evaporated, the crude product was purified by silica gel chromatography.²

2. Synthesis of Propargylic aldehyde and ketone:



First Step: To an oven-dried 250 mL round-bottomed flask equipped with a Teflon coated magnetic stirbar and alkyne (10 mmol) in THF (25 ml) was cooled to -78 °C and charged with *n*-BuLi (1 equiv). The reaction mixture was stirred at the same temperature for 30 min then at room temperature for another 30 min. After that solid paraformaldehyde was added to the reaction mixture at -78 °C then the reaction mixture was transferred to room temperature and stirred for overnight. After the completion of the reaction, water was added and extracted the propargylic alcohol using ethyl acetate (3 times). The crude reaction mixture was dried over anhydrous Na₂SO₄ and concentrated in rotary evaporator. For the next step, the crude propargylic alcohol was used without purification.

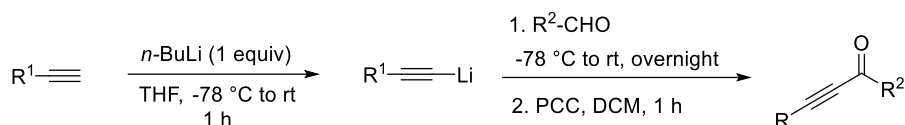
Second Step: In a round-bottomed flask equipped with a Teflon coated magnetic stirbar and crude propargylic alcohol (1 equiv) in DCM was treated with PCC (1.5 equiv) at room temperature. After 1 h of stirring, the reaction was filtered through a silica pad using DCM solvent. Then the crude reaction mixture was concentrated in rotary evaporator and performed a flash column chromatography using 4 % ethyl acetate/hexane as eluent.



First Step: To a solution of aldehyde (1.0 equiv.) and CBr₄ (1.05 equiv.) in anhydrous DCM (0.45 M) cooled down to 0 °C was added Ph₃P (2.1 equiv.) as a solid in small portions. The resultant yellow reaction mixture was then stirred at ambient temperature for 3 h. Solvent was removed in vacuo, and the residue was dissolved in *n*-hexane. Triphenylphosphine oxide was filtered off by suction. The filtrate was concentrated under reduced pressure, and the crude gem-dibromide was purified by flash chromatography on silica gel using *n*-hexane/EtOAc as eluent.

Second Step: A well-stirred solution of gem-dibromide (1.0 equiv.) in anhydrous THF (0.4 M) was cooled down to -40 °C. *n*-BuLi (1.6 M solution in hexanes, 2.1 equiv.) was then added dropwise *via* syringe. The solution was stirred at -50 °C for 15 min, and anhydrous DMF (2.0 equiv.) was added in one portion. The mixture was allowed to slowly reach ambient temperature. After stirring for further 1 h, the reaction mixture was poured into a vigorously stirred mixture of KH₂PO₄ and tert-butyl methyl

ether. The layers were separated and the aqueous layer was extracted with *tert*-butyl methyl ether. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude oil was purified by flash chromatography on silica gel using *n*-hexane/EtOAc as eluent.³

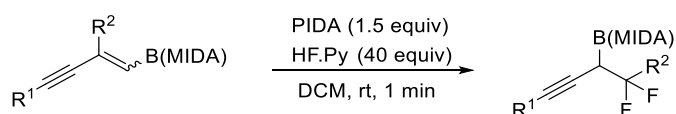


First Step: To an oven-dried 250 mL round-bottomed flask equipped with a Teflon coated magnetic stirbar and alkyne (10 mmol) in THF (25 ml) was cooled to -78 °C and charged with *n*-BuLi (1 equiv). The reaction mixture was stirred at the same temperature for 30 min then at room temperature for another 30 min. After that aldehyde was added to the reaction mixture at -78 °C then the reaction mixture was transferred to room temperature and stirred for 1.5 h. After the completion of the reaction, water was added and extracted the propargylic alcohol using ethyl acetate (3 times) as a solvent. The crude reaction mixture was dried over anhydrous Na₂SO₄ and concentrated in rotary evaporator. For the next step, the crude propargylic alcohol was used without purification.

Second Step: In a round-bottomed flask equipped with a Teflon coated magnetic stirbar and crude propargylic alcohol (1 equiv) in DCM was treated with PCC (1.5 equiv) at room temperature. After 1 h of stirring, the reaction was filtered through a silica pad using DCM solvent. Then the crude reaction mixture was concentrated in rotary evaporator and performed a flash column chromatography using 2 % ethyl acetate/hexane as eluent.

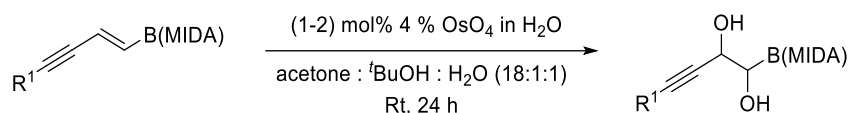
➤ General Procedure:

A. General procedure (A): geminal difluorination via 1,2-alkyne migration (7):



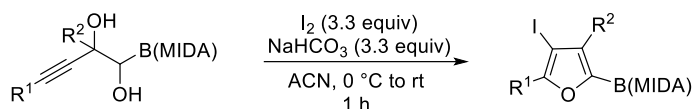
To a stirred solution of 1,3-enyne MIDA boronates (1.0 equiv), PhI(OAc)₂ (2 equiv) in DCM (0.1 M) in a 15 mL of Schlenk tube under ambient atmosphere was added Py.HF (40.0 equiv) in one portion. The reaction was allowed to stir at 25 °C until the complete consumption of boronates as monitored by TLC analysis (typically 1 min). The reaction mixture was directly purified by flash column chromatography on silica with an appropriate solvent to afford the pure product.

B. Synthesis of 1,2-boryl alcohol:



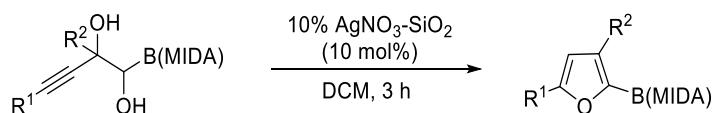
The pure 1,3-enyne MIDA boronate was dissolved in an 18:1:1 solvent mixture of acetone:*tert*-butanol:water (0.1 M) in an oven dried round bottom flask equipped with a magnetic stir bar. A solution of 4% wt of OsO₄ in H₂O (1 – 2 mol%) was added followed by the addition of *N*-methylmorpholine *N*-oxide (1.5 equiv.) at room temperature under nitrogen atmosphere. The resulting reaction mixture was allowed to stir at room temperature for 24 – 36 hours until complete starting material consumption as indicated by TLC analysis. Upon completion, most of the solvent was removed in vacuo to afford an oil residue. The crude product then undergoes a quick flash column chromatograph using 50% acetone/hexane as eluent.

C. General procedure (B): Synthesis of furan *via* iodocyclisation (**9**):



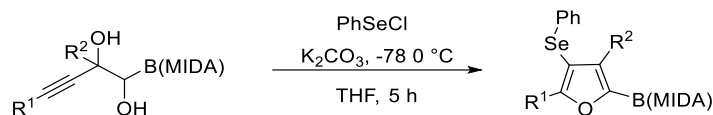
In a 10 ml dried round bottom flask containing a magnetic bar was treated with 1,2-boryl alcohol in acetonitrile solvent (0.1 M). The reaction chamber was then cooled to 0 °C and charged with NaHCO₃ (3.3 equiv) and stirred for 5 min at the same temperature. After that, a solid I₂ (3.3 equiv) was added into the mixture and stirred for another 5 min at the same temperature. Then the cooling bath was removed and stirring continued at room temperature until the total consumption of starting material. After that saturated thiosulphate solution was added until the color of iodine disappears. The crude reaction mixture was then concentrate under reduce pressure and extracted with ethyl acetate (3 times). The oily crude product further undergoes flash column chromatograph using 60% ethyl acetate/hexane as an eluent.

D. General procedure (C): Synthesis of substituted furan BCMs (**10**) using AgNO₃-SiO₂:



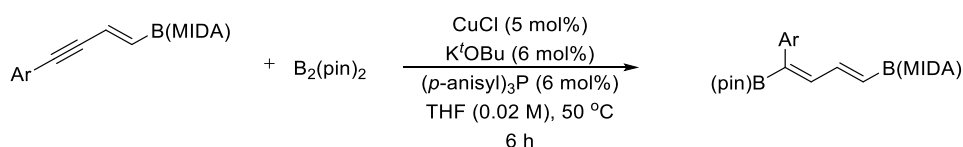
Following that, the 1,2-boryl alcohol was exposed to a *5-endo-dig* cyclization process utilizing 10 mol% commercial 10% w/w silver(I) nitrate on silica gel in DCM (0.1 M) at room temperature for roughly 3 hours. After 3 hours of stirring at room temperature, the crude reaction mixture was run through a flash column chromatograph with an eluent of 60% ethyl acetate/hexane.

E. General procedure (D): Synthesis of furan *via* selenocyclisation (**11**):



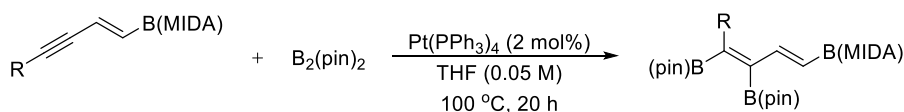
In a 10 ml dried round bottom flask containing a magnetic bar was treated with 1,2-boryl alcohol in THF solvent (0.1 M). The reaction chamber was then cooled to $-78\text{ }^{\circ}\text{C}$ and charged with K_2CO_3 (1.1 equiv) and PhSeCl (1.2 equiv). Then, the mixture was stirred for 5 h at the same temperature. After that saturated thiosulphate solution was added to quench the reaction. The crude reaction mixture was then extracted with ethyl acetate and water (3 times). The oily crude product further undergoes a flash column chromatograph using 60% ethyl acetate/hexane as an eluent.

F. General procedure (E): 3,4-hydroboration of 1,3-enyne MIDA boronates (13):



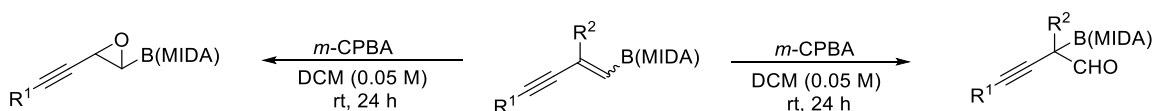
In a 10 ml reaction tube containing a stir bar was treated with CuCl (5 mol%), $\text{K}'\text{OBu}$ (6 mol%), and $(p\text{-anisyl})_3\text{P}$ (6 mol%). The reaction tube was degassing with nitrogen three times before adding THF (2 ml). Then the reaction mixture was stirred at room temperature for 10 min to form the black color solution. After that 1,3-enyne MIDA boronate (1 equiv, 0.1 mmol) and $\text{B}_2(\text{pin})_2$ (1.2 equiv, 0.12 mmol) in THF (2 ml) was added in reaction mixture and stirred at $50\text{ }^{\circ}\text{C}$ for 5-8 h. After the reaction was completed, the reaction mixture was directly subjected to flash column chromatography to give the corresponding bisboronate as a colorless oil or color oil.

G. General procedure (F): 3,4-diboration of 1,3-enyne MIDA boronates (14):



In a 10 ml reaction tube containing a stir bar was treated with 1,3-enyne MIDA boronates (1 equiv), $\text{Pt}(\text{PPh}_3)_4$ (2 mol%), and $\text{B}_2(\text{pin})_2$ (1.2 equiv). The reaction tube was degassing with nitrogen three times before adding THF (0.05 M). Then the reaction mixture was stirred at $100\text{ }^{\circ}\text{C}$ for 20 h to complete the conversion. After the reaction was completed, the reaction mixture was directly subjected to flash column chromatography to give the corresponding trisboronate as a white powder or gammy oil.

E. General procedure (G): epoxidation of 1,3-enyne B(MIDA):

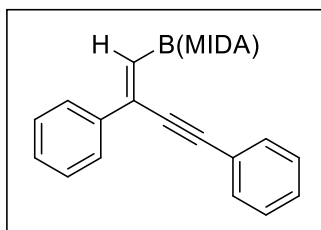


To a stirred solution of 1,3-enyne MIDA boronates in DCM (0.05M) at room temperature m-CPBA (2.2 equiv) was added and stirred for 24 h. When the reaction was completed (confirmed by TLC), the reaction mixture was quenched by aqueous NaHCO₃ solution and extracted using DCM (2 times). Then the crude reaction was directly subjected to flash column chromatography to give the corresponding epoxide or quaternary aldehyde.

➤ **¹H-NMR & ¹³C-NMR data of Synthesized compounds:**

(Z)-2-(2,4-diphenylbut-1-en-3-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**4a**):

According's to the **general procedure GP1**, white solid, 76% yield. ¹H NMR (500 MHz, DMSO) δ

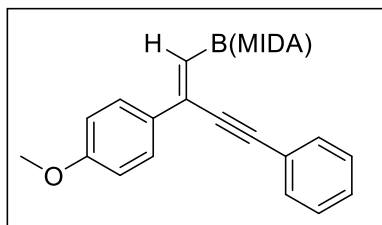


7.79 (d, *J* = 8 Hz, 2H), 7.59-7.58 (m, 2H), 7.46-7.42 (m, 5H), 7.39-7.36 (t, *J* = 7 Hz, 1H), 6.52 (s, 1H), 4.36 (d, *J* = 17 Hz, 2H), 4.10 (d, *J* = 17 Hz, 2H), 2.92 (s, 3H). ¹³C NMR (126 MHz, DMSO) δ 169.06, 139.18, 133.68, 131.50, 128.76, 128.49, 128.44, 128.28, 125.91, 122.34, 94.49, 88.69, 62.27, 47.18. ¹¹B NMR (160 MHz, DMSO) δ 10.06. HRMS (ESI)

m/z cal. for (M + H)⁺ 360.1402, found 360.1409.

(Z)-2-(2-(4-methoxyphenyl)-4-phenylbut-1-en-3-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**4b**):

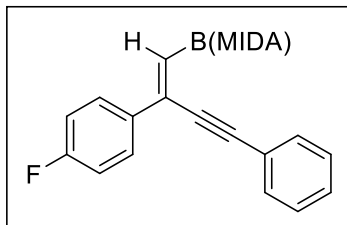
According's to the **general procedure GP1**, yellow semi solid, 82 % yield. ¹H NMR (500 MHz,



DMSO) δ 7.72 (m, 2H), 5.56 (m, 2H), 7.41 (m, 3H), 6.99 (m, 2H), 6.37 (s, 1H), 4.33 (d, *J* = 13.6 Hz, 2H), 4.07 (d, *J* = 14 Hz, 2H), 3.79 (s, 3H), 2.89 (s, 3H). ¹³C NMR (126 MHz, DMSO) δ 169.08, 159.47, 133.08, 131.60, 131.48, 128.72, 128.49, 127.21, 122.41, 113.81, 94.27, 88.89, 62.26, 55.18, 47.19. ¹¹B NMR (160 MHz,

DMSO) δ 10.31. HRMS (ESI) *m/z* cal. for (M+ NH₄)⁺ 407.1773, found 407.1881.

(Z)-2-(2-(4-fluorophenyl)-4-phenylbut-1-en-3-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione

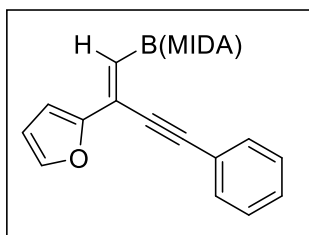


(**4c**): According's to the **general procedure GP1**, white semi solid, 71 % yield. ¹H NMR (500 MHz, DMSO) δ 7.83 (dd, *J* = 5.5 Hz, 2H), 7.59 (dd, *J* = 3.5 Hz, 2H), 7.43-7.42 (m, 3H), 7.27 (t, *J* = 9 Hz, 2H), 6.48 (s, 1H), 4.35 (d, *J* = 17 Hz, 2H), 4.09 (d, *J* = 17 Hz, 2H), 2.91 (s, 3H). ¹³C NMR (126 MHz, DMSO) δ 169.04, 163.10, 161.14, 135.63 (d, *J* = 3.0

Hz), 132.45, 131.52, 128.82, 128.49, 128.02 (d, *J* = 8.3 Hz), 122.23, 115.27 (d, *J* = 21.6 Hz), 94.61, 88.47, 62.23, 47.16. ¹¹B NMR (160 MHz, DMSO) δ 10.24. HRMS (ESI) *m/z* cal. for (M + H)⁺ 378.1307, found 378.1317.

(E)-2-(2-(furan-2-yl)-4-phenylbut-1-en-3-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**4d**):

According's to the **general procedure GP1**, pale brown oil, 63 % yield. ¹H NMR (500 MHz, DMSO)

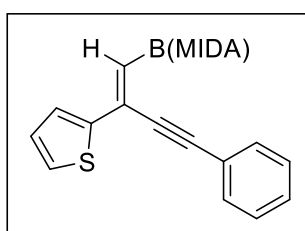


δ 7.73 (d, $J = 1$ Hz, 1H), 7.60-7.58 (m, 2H), 7.42-7.41 (m, 3H), 6.73 (d, $J = 3$ Hz, 1H), 6.58 (dd, $J = 2$ Hz, 1H), 6.38 (s, 1H), 4.32 (d, $J = 17$ Hz, 2H), 4.07 (d, $J = 17$ Hz, 2H), 2.87 (s, 3H). ¹³C NMR (126 MHz, DMSO) δ 168.96, 152.74, 143.80, 131.59, 128.90, 128.46, 123.66, 122.01, 111.95, 108.75, 92.81, 86.22, 62.14, 47.16. ¹¹B NMR (160 MHz, DMSO) δ 10.27.

HRMS (ESI) m/z cal. for (M + H)⁺ 350.1194, found 350.1200.

(E)-6-methyl-2-(4-phenyl-2-(thiophen-2-yl)but-1-en-3-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**4e**):

According's to the **general procedure GP1**, pale yellow semi solid, 68 % yield. ¹H NMR (500 MHz,

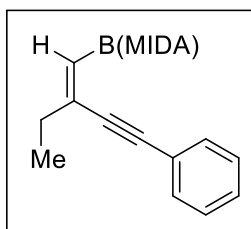


DMSO) δ 7.59-7.57 (m, 2H), 7.54-7.53 (m, 1H), 7.45-7.42 (m, 4H), 7.07 (dd, $J = 4$ Hz, 1H), 6.34 (s, 1H), 4.33 (d, $J = 17$ Hz, 2H), 4.08 (d, $J = 17$ Hz, 2H), 2.89 (s, 3H). ¹³C NMR (126 MHz, DMSO) δ 169.00, 144.66, 131.54, 128.98, 128.54, 127.97, 127.48, 126.60, 125.32, 121.98, 93.60, 87.59, 62.25, 47.25. ¹¹B NMR (160 MHz, DMSO) δ 10.06. HRMS (ESI)

m/z cal. for (M + H)⁺ 366.0966, found 366.0965.

(Z)-2-(2-ethyl-4-phenylbut-1-en-3-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**4f**):

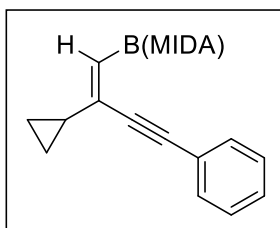
According's to the **general procedure GP1**, yellow solid, 79 % yield. ¹H NMR (500 MHz, DMSO) δ



7.48-7.46 (m, 2H), 7.39-7.37 (m, 3H), 5.73 (s, 1H), 4.29 (d, $J = 17$ Hz, 2H), 4.00 (d, $J = 17$ Hz, 2H), 2.84 (s, 3H), 2.34-2.30 (m, 2H), 1.14 (t, $J = 7.5$ Hz, 3H). ¹³C NMR (126 MHz, DMSO) δ 169.00, 137.32, 131.40, 128.46, 128.42, 122.58, 93.08, 89.84, 62.15, 47.13, 33.55, 13.05. ¹¹B NMR (160 MHz, DMSO) δ 10.31. HRMS (ESI) m/z cal. for (M + H)⁺ 312.1402, found 312.1390.

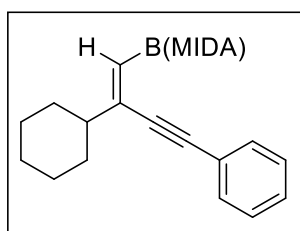
(Z)-2-(2-cyclopropyl-4-phenylbut-1-en-3-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**4g**):

According's to the **general procedure GP1**, pale yellow oil, 76 % yield. ¹H NMR (400 MHz, CDCl₃)



δ 7.46-7.45 (m, 2H), 7.35-7.33 (m, 3H), 5.90 (s, 1H), 3.87 (br. s, 4H), 2.93 (s, 3H), 1.29-1.27 (m, 1H), 0.88-0.87 (m, 2H), 0.79-0.77 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 167.40, 131.93, 131.86, 128.86, 128.49, 122.16, 99.99, 85.60, 62.88, 47.31, 24.93, 6.62. ¹¹B NMR (160 MHz, CDCl₃) δ 10.54. HRMS (ESI) m/z cal. for (M + H)⁺ 324.1402, found 324.1407.

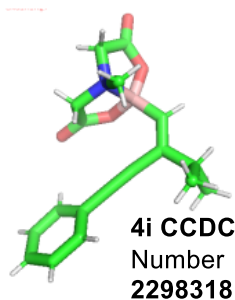
(Z)-2-(2-cyclohexyl-4-phenylbut-1-en-3-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**4h**):



According's to the **general procedure GP1**, pale yellow oil, 72 % yield. ^1H NMR (400 MHz, DMSO) δ 7.46-7.38 (m, 5H), 5.71 (s, 1H), 4.28 (d, $J = 17.2$ Hz, 2H), 3.98 (d, $J = 17.2$ Hz, 2H), 2.81 (s, 3H), 2.18-2.17 (m, 1H), 1.77-1.67 (m, 5H), 1.40-1.18 (m, 5H). ^{13}C NMR (101 MHz, DMSO) δ 169.64, 131.89, 128.97, 128.96, 123.15, 123.13, 117.68, 62.72, 48.51, 47.71, 47.69, 32.21, 32.21, 32.20, 32.18, 32.17, 26.24, 26.20. ^{11}B NMR (160 MHz, DMSO) δ 10.05. HRMS (ESI) m/z cal. for $(\text{M} + \text{NH}_4)^+$ 383.2137, found 383.2154.

(*Z*)-2-(2-isopropyl-4-phenylbut-1-en-3-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**4i**):

According's to the **general procedure GP1**, yellow white solid, 81 % yield. ^1H NMR (500 MHz, DMSO) δ 7.47-7.45 (m, 2H), 7.39-7.38 (m, 3H), 5.73 (s, 1H), 4.28 (d, $J = 17$ Hz, 2H), 4.00 (d, $J = 17$ Hz, 2H), 2.82 (s, 3H), 2.56-2.52 (m, 1H), 1.13 (t, $J = 7$ Hz, 6H). ^{13}C NMR (126 MHz, DMSO) δ 169.58, 142.81, 131.93, 128.99, 123.15, 94.44, 89.16, 62.75, 47.70, 31.14, 22.19. ^{11}B NMR (160 MHz, DMSO) δ 10.51. HRMS (ESI) m/z cal. for $(\text{M} + \text{H})^+$ 326.1558, found 326.1551.

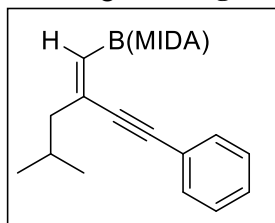


(*Z*)-6-methyl-2-(2-phenethyl-4-phenylbut-1-en-3-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**4j**):

According's to the **general procedure GP1**, yellow solid, 70 % yield. ^1H NMR (400 MHz, CDCl_3) δ 7.52-7.24 (m, 10H), 5.63 (s, 1H), 3.81 (d, $J = 17.2$ Hz, 2H), 3.67 (d, $J = 17.2$ Hz, 2H), 3.01 (m, 2H), 2.75-2.73 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.48, 141.18, 137.42, 131.86, 128.78, 128.59, 128.50, 128.36, 125.99, 122.54, 95.27, 89.04, 62.58, 46.65, 42.59, 34.15. ^{11}B NMR (160 MHz, CDCl_3) δ 10.65. HRMS (ESI) m/z cal. for $(\text{M} + \text{NH}_4)^+$ 405.1980, found 405.1984.

(*Z*)-6-methyl-2-(4-methyl-2-(phenylethynyl)pent-1-en-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**4k**):

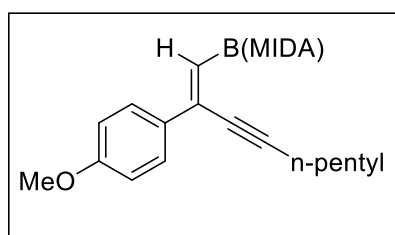
According's to the **general procedure GP1**, pale yellow oil, 82 % yield. ^1H NMR (400 MHz, DMSO)



δ 7.45-7.37 (m, 5H), 5.70 (s, 1H), 4.29 (d, $J = 18$ Hz, 2H), 4.01 ($J = 18$ Hz, 2H), 2.83 (s, 3H), 2.18 (d, $J = 6.8$ Hz, 2H), 2.01-1.98 (m, 1H), 0.93 (d, $J = 6$ Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 169.64, 135.55, 131.92, 129.02, 128.98, 123.07, 93.48, 90.48, 62.72, 50.58, 47.78, 27.25, 22.60. HRMS (ESI) m/z cal. for $(M + H)^+$ 340.1715, found 340.1745.

(*Z*)-2-(2-(4-methoxyphenyl)non-1-en-3-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**4l**):

According's to the **general procedure GP1**, colorless oil, 70 % yield. ^1H NMR (500 MHz, DMSO) δ

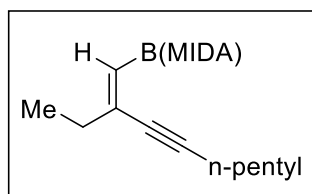


7.57 (d, $J = 8.5$ Hz, 2H), 6.89 (d, $J = 8.5$ Hz, 2H), 6.17 (s, 1H), 4.26 (d, $J = 17$ Hz, 2H), 3.93 (d, $J = 17$ Hz, 2H), 3.73 (s, 3H), 2.81 (s, 3H), 2.32 (t, $J = 7.5$ Hz, 2H), 1.52-1.47 (m, 2H), 1.35-1.24 (m, 4H), 0.86-0.84 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ

168.99, 159.31, 133.95, 131.88, 127.02, 113.57, 96.18, 79.82, 62.55, 55.12, 47.22, 30.61, 27.54, 21.50, 18.91, 13.74. HRMS (ESI) m/z cal. for $(M + H)^+$ 384.1977, found 384.1985.

(*Z*)-2-(2-ethylnon-1-en-3-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**4m**):

According's to the **general procedure GP1**, colorless oil, 65 % yield. ^1H NMR (500 MHz, DMSO) δ

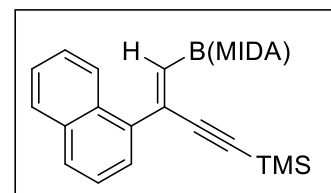


5.54 (s, 1H), 4.24 (d, $J = 17$ Hz, 2H), 3.88 (d, $J = 17$ Hz, 2H), 2.78 (s, 3H), 2.24 (t, $J = 7$ Hz, 2H), 2.15 (q, $J = 7.5$ Hz, 2H), 1.48-1.42 (m, 2H), 1.33-1.27 (m, 4H), 1.03 (t, $J = 7.5$ Hz, 3H), 0.87 (t, $J = 7$ Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 174.23, 143.60, 99.94, 86.15, 67.67, 52.38, 38.91,

35.80, 32.85, 26.78, 24.08, 19.03, 18.23. HRMS (ESI) m/z cal. for $(M + H)^+$ 306.1871, found 306.1878.

(*Z*)-6-methyl-2-(2-(naphthalen-1-yl)-4-(trimethylsilyl)but-1-en-3-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**4n**):

According's to the **general procedure GP1**, colorless oil, 74 % yield. ^1H NMR (500 MHz, DMSO) δ

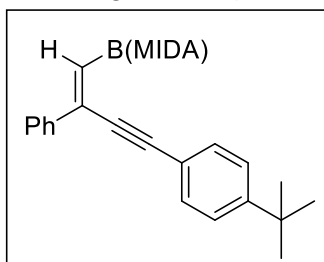


8.21 (d, $J = 7.2$ Hz, 1H), 7.95 (d, $J = 8.4$ Hz, 1H), 7.90 (d, $J = 8.3$ Hz, 1H), 7.56-7.45 (m, 4H), 6.14 (s, 1H), 4.39 (d, $J = 17$ Hz, 2H), 4.04 (d, $J = 17$ Hz, 2H), 3.04 (s, 3H), 0.11 (s, 9H). ^{13}C NMR (101 MHz, DMSO) δ 169.52, 140.21, 134.92, 133.73, 130.22, 128.80, 128.67, 126.53,

126.22, 126.08, 125.68, 105.79, 100.76, 63.15, 47.94, 0.06. HRMS (ESI) m/z cal. for $(M + H)^+$ 406.1640, found 406.1652.

(Z)-2-(4-(4-(tert-butyl)phenyl)-2-phenylbut-1-en-3-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**4o**):

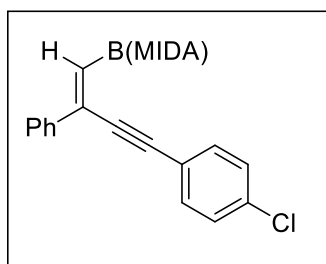
According's to the **general procedure GP1**, white solid, 72 % yield. ^1H NMR (500 MHz, DMSO) δ



7.65 (d, $J = 7.5$ Hz, 2H), 7.39 (d, $J = 8.5$ Hz, 2H), 7.32-7.30 (m, 4H), 7.24 (t, $J = 7.5$ Hz, 1H), 6.36 (s, 1H), 4.23 (d, $J = 17$ Hz, 2H), 3.96 (d, $J = 17$ Hz, 2H), 2.79 (s, 3H), 1.17 (s, 9H). ^{13}C NMR (126 MHz, DMSO) δ 169.07, 151.60, 139.26, 133.88, 131.30, 128.44, 128.27, 125.90, 125.35, 119.37, 94.70, 88.15, 62.34, 47.21, 34.51, 30.83. HRMS (ESI) m/z cal. for (M + H) $^+$ 416.2028, found 416.2045.

(Z)-2-(4-(4-chlorophenyl)-2-phenylbut-1-en-3-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**4p**):

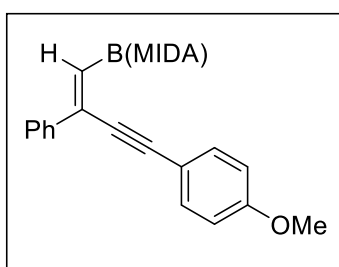
According's to the **general procedure GP1**, pale yellow oil, 69 % yield. ^1H NMR (500 MHz, DMSO)



δ 7.77 (d, $J = 7.5$ Hz, 2H), 7.60 (d, $J = 8.5$ Hz, 2H), 7.50 (d, $J = 8.5$ Hz, 2H), 7.44 (t, $J = 7.5$ Hz, 2H), 7.37 (t, $J = 7.5$ Hz, 1H), 6.54 (s, 1H), 4.35 (d, $J = 17$ Hz, 2H), 4.10 (d, $J = 17$ Hz, 2H), 2.91 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 169.70, 139.50, 134.07, 133.92, 133.75, 129.22, 129.02, 128.89, 126.45, 121.78, 93.73, 90.21, 62.74, 47.72. HRMS (ESI) m/z cal. for (M + H) $^+$ 394.1012, found 394.1049.

(Z)-2-(4-(4-methoxyphenyl)-2-phenylbut-1-en-3-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**4q**):

According's to the **general procedure GP1**, yellow gammy solid ($E/Z = 05:95$), 83 % yield. ^1H NMR

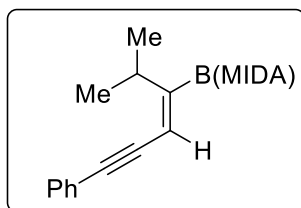


(500 MHz, DMSO) δ 7.78 (d, $J = 7.5$ Hz, 2H), 7.52 (d, $J = 8.5$ Hz, 2H), 7.44 (d, $J = 7.5$ Hz, 2H), 7.36 (t, $J = 7.5$ Hz, 1H), 6.99 (d, $J = 8.5$ Hz, 2H), 6.44 (s, 1H), 4.35 (d, $J = 17.5$ Hz, 2H), 4.09 (d, $J = 17.5$ Hz, 2H), 3.80 (s, 3H), 2.91 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 169.67, 160.17, 139.86, 134.52, 133.65, 128.96, 128.77, 126.44, 114.84, 114.74, 95.32, 88.03, 62.83, 55.77, 47.73. HRMS (ESI) m/z cal. for (M

+ H) $^+$ 407.1773, found 407.1780.

(Z)-6-methyl-2-(2-methyl-6-phenylhex-3-en-5-yn-3-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**4r**):

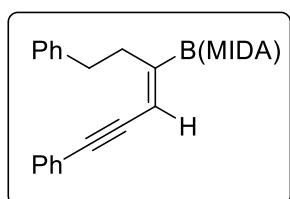
According's to the **general procedure GP2**, brown oil, 62 % yield. ^1H NMR (400 MHz, CDCl_3) δ 7.43-



7.39 (m, 5H), 5.91 (s, 1H), 4.28 (d, $J = 17.6$ Hz, 2H), 4.11 (d, $J = 17.6$ Hz, 2H), 2.82 (s, 3H), 2.77 (t, $J = 6.8$ Hz, 1H), 1.24 (d, $J = 6.8$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.18, 131.77, 129.79, 129.51, 123.99, 115.50, 96.87, 89.36, 63.14, 48.43, 32.23, 22.08. HRMS (ESI) m/z cal. for $(\text{M} + \text{H})^+$ 326.1558, found 326.1550.

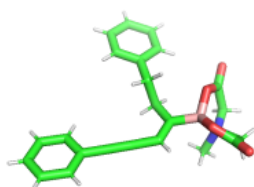
(*Z*)-2-(1,6-diphenylhex-3-en-5-yn-3-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**4s**):

According's to the **general procedure GP2**, pale yellow, 71 % yield. ^1H NMR (500 MHz, CDCl_3) δ



7.49-7.47 (m, 2H), 7.37-7.36 (m, 2H), 7.30-7.17 (m, 6H), 6.22 (s, 1H), 3.88 (d, $J = 16.5$ Hz, 2H), 3.74 (d, $J = 16.5$ Hz, 2H), 2.91 (t, $J = 8.5$ Hz, 2H), 2.81 (s, 3H), 2.61 (t, $J = 8.5$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ

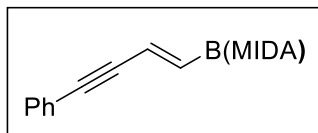
167.49, 142.40, 131.56, 128.56, 128.47, 125.95, 123.30, 118.99, 96.60, 86.92, 62.02, 46.94, 35.84, 35.81. HRMS (ESI) m/z cal. for $(\text{M} + \text{NH}_4)^+$ 405.1980, found 405.1984.



4s, CCDC Number
2298320

(*E*)-2-(4-(4-phenylbut-1-en-3-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**5a**):⁴

According's to the **general procedure GP2**, yellow solid, 73 % yield. ^1H NMR (500 MHz, DMSO) δ

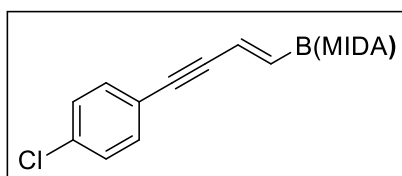


7.46-7.45 (m, 2H), 7.40-7.39 (m, 3H), 6.28 (d, $J = 18.5$ Hz, 1H), 6.14 (d, $J = 18.5$ Hz, 1H), 4.26 (d, $J = 17$ Hz, 2H), 4.05 (d, $J = 17$ Hz, 2H), 2.82 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 169.01, 131.27, 128.74, 128.69,

122.43, 120.70, 89.77, 61.51, 46.82. HRMS (ESI) m/z cal. for $(\text{M} + \text{H})^+$ 284.1089, found 284.1044.

(*E*)-2-(4-(4-chlorophenyl)but-1-en-3-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**5b**):

According's to the **general procedure GP2**, yellow solid, 76 % yield. ^1H NMR (500 MHz, DMSO) δ

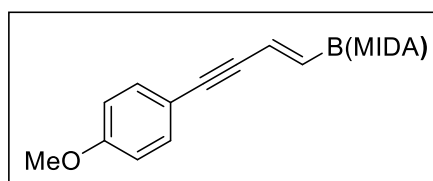


7.47 (m, 4H), 6.31 (d, $J = 18.4$ Hz, 1H), 6.13 (d, $J = 18.4$ Hz, 1H), 4.27 (d, $J = 17.2$ Hz, 2H), 4.05 (d, $J = 17.2$ Hz, 2H), 2.82 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 168.86, 133.34, 133.03, 132.91, 128.81, 121.28, 120.42, 90.72, 88.48, 61.48, 46.78. HRMS (ESI)

m/z cal. for $(\text{M} + \text{H})^+$ 318.0699, found 318.0694.

(*E*)-2-(4-(4-methoxyphenyl)but-1-en-3-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**5c**):

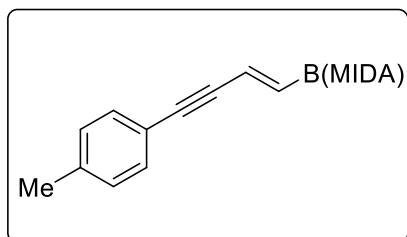
According's to the **general procedure GP2**, yellow solid, 80 % yield. ^1H NMR (400 MHz, DMSO) δ



7.38 (d, $J = 6.4$ Hz, 2H), 6.94 (d, $J = 6.4$ Hz, 2H), 6.16 (dt, $J = 18, 8, 2\text{H}$), 4.25 (d, $J = 16.4$ Hz, 2H), 4.04 (d, $J = 16.8$ Hz, 2H), 3.78 (s, 3H), 2.81 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ

168.87, 159.43, 132.76, 121.04, 114.39, 114.29, 89.99, 88.43, 61.45, 55.18, 46.77. HRMS (ESI) m/z cal. for $(\text{M} + \text{H})^+$ 314.1194, found 314.1180.

(*E*)-6-methyl-2-(4-(*p*-tolyl)but-1-en-3-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**5d**):

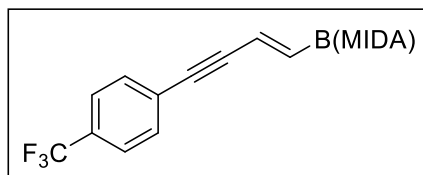


According's to the **general procedure GP2**, yellow solid, 74 % yield. ^1H NMR (400 MHz, DMSO) δ 7.32 (d, $J = 8$ Hz, 2H), 7.11 (d, $J = 8$ Hz, 2H), 6.33 (d, $J = 18.4$ Hz, 1H), 6.16 (d, $J = 18.4$ Hz, 1H), 4.03 (d, $J = 17.2$ Hz, 2H), 3.74 (d, $J = 17.2$ Hz, 2H), 2.87 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.76, 138.71,

131.57, 129.16, 124.17, 119.89, 91.61, 88.58, 61.65, 47.05, 21.45. HRMS (ESI) m/z cal. for $(\text{M} + \text{NH}_4)^+$ 315.1511, found 315.1520.

(*E*)-6-methyl-2-(4-(4-(trifluoromethyl)phenyl)but-1-en-3-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**5f**):

According's to the **general procedure GP2**, pale yellow oil, 69 % yield. ^1H NMR (400 MHz, DMSO)

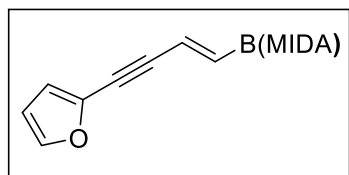


δ 7.75 (d, $J = 8$ Hz, 2H), 7.67 (d, $J = 8$ Hz, 2H), 6.39 (d, $J = 18$ Hz, 1H), 6.18 (d, $J = 18$ Hz, 1H), 4.28 (d, $J = 17.2$ Hz, 2H), 4.07 (d, $J = 17.2$ Hz, 2H), 2.84 (s, 3H). ^{13}C NMR (101 MHz, DMSO)

δ 169.48, 132.52, 132.46, 132.43, 126.12, 126.05, 126.02, 125.97, 120.66, 120.63, 99.98, 92.64, 88.62, 62.06, 62.05, 62.00, 47.34, 47.30. ^{19}F NMR (471 MHz, DMSO) δ -61.38. ^{11}B NMR (160 MHz, DMSO) δ 10.31. HRMS (ESI) m/z cal. for $(\text{M} + \text{H})^+$ 369.1228, found 369.1239.

(*E*)-2-(4-(furan-2-yl)but-1-en-3-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**5g**):

According's to the **general procedure GP2**, brown oil, 62 % yield. ^1H NMR (400 MHz, CDCl_3) δ 6.76

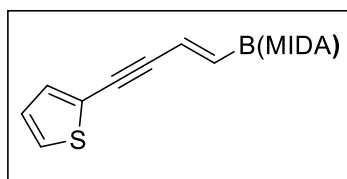


(d, $J = 18$ Hz, 1H), 6.63 (d, $J = 3.6$ Hz, 1H), 6.29 (d, $J = 3.2$ Hz, 1H), 6.14 (d, $J = 18.4$ Hz, 1H), 4.02 (d, $J = 16.8$ Hz, 2H), 3.76 (d, $J = 16.8$ Hz, 2H), 3.46 (s, 1H), 2.88 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ

167.47, 154.12, 135.90, 130.68, 118.20, 110.37, 82.73, 74.14, 61.60, 46.95. HRMS (ESI) m/z cal. for $(\text{M} + \text{H})^+$ 274.0887, found 274.0880.

(*E*)-6-methyl-2-(4-(thiophen-2-yl)but-1-en-3-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**5h**):

According's to the **general procedure GP2**, yellow solid, 60 yield. ^1H NMR (500 MHz, DMSO) δ 7.27

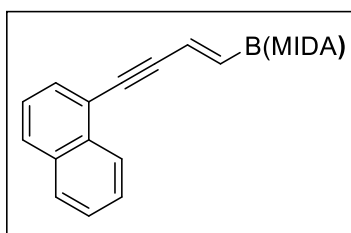


(d, $J = 13.5$ Hz, 1H), 7.08 (d, $J = 4$ Hz, 1H), 6.93 (d, $J = 18$ Hz, 1H), 6.03 (d, $J = 18$ Hz, 1H), 4.58 (s, 1H), 4.25 (d, $J = 17$ Hz, 2H), 4.06 (d, $J = 17$ Hz, 2H), 2.81 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 169.54, 146.23, 134.47, 133.84, 127.17, 120.53, 86.24, 77.54, 61.98, 47.28.

HRMS (ESI) m/z cal. for $(\text{M} + \text{H})^+$ 290.0653, found 290.0653.

(*E*)-6-methyl-2-(4-(naphthalen-1-yl)but-1-en-3-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**5i**):

According's to the **general procedure GP2**, yellow solid, 68% yield. ^1H NMR (500 MHz, DMSO) δ

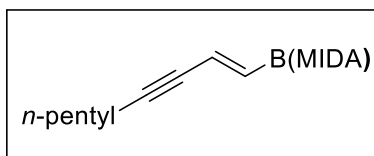


8.23 (d, $J = 8$ Hz, 1H), 7.71 (d, $J = 8$ Hz, 2H), 7.55 (d, $J = 7$ Hz, 1H), 7.42 (t, $J = 7$ Hz, 1H), 7.38 (t, $J = 7.5$ Hz, 1H), 7.18 (t, $J = 8$ Hz, 1H), 6.41 (d, $J = 18$ Hz, 1H), 6.23 (d, $J = 18$ Hz, 1H), 3.99 (d, $J = 17$ Hz, 2H), 3.68 (d, $J = 17$ Hz, 2H), 2.77 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 168.02, 133.16, 130.63, 129.03, 128.31, 126.95, 126.53,

126.09, 125.29, 124.03, 120.58, 94.10, 89.42, 77.29, 77.03, 76.78, 61.98, 61.74, 47.15. HRMS (ESI) m/z cal. for $(\text{M} + \text{H})^+$ 334.1245, found 334.1246.

(*E*)-6-methyl-2-(non-1-en-3-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**5j**):⁴

According's to the **general procedure GP2**, yellow solid, 75 % yield. ^1H NMR (400 MHz, CDCl_3)

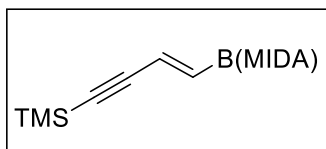


6.04 (d, $J = 18.4$ Hz, 2H), 4.08 (d, $J = 16.8$ Hz, 2H), 3.74 (d, $J = 16.8$ Hz, 2H), 2.87 (s, 3H), 2.31 (t, $J = 6$ Hz, 2H), 1.56-1.52 (m, 2H), 1.36-1.33 (m, 4H), 0.93-0.90 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 168.34, 124.77, 93.03, 80.53, 61.69, 47.20, 31.20, 28.44, 22.26,

19.50, 14.02. HRMS (ESI) m/z cal. for $(\text{M} + \text{H})^+$ 278.1558, found 278.1498.

(*E*)-6-methyl-2-(4-(trimethylsilyl)but-1-en-3-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**5k**):⁴

According's to the **general procedure GP2**, yellow solid, 52 % yield. ^1H NMR (500 MHz, DMSO) δ

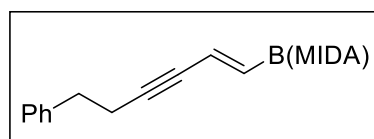


6.23 (d, $J = 18.4$ Hz, 1H), 5.91 (d, $J = 18.4$ Hz, 1H), 4.23 (d, $J = 17.2$ Hz, 2H), 4.02 (d, $J = 17.2$ Hz, 2H), 2.78 (s, 3H), 0.17 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 168.51, 120.46, 105.24, 94.28, 61.10, 46.39, -0.50.

HRMS (ESI) m/z cal. for $(\text{M} + \text{K})^+$ 318.0730, found 318.0869.

(*E*)-6-methyl-2-(6-phenylhex-1-en-3-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**5l**):

According's to the **general procedure GP2**, yellow solid, 70 % yield. ^1H NMR (500 MHz, DMSO) δ

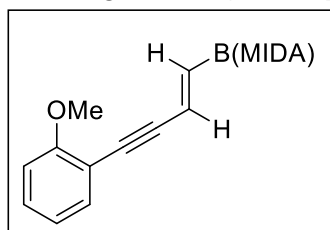


7.33-7.23 (m, 5H), 6.09 (d, $J = 18.4$ Hz, 1H), 6.01 (d, $J = 18.4$ Hz, 1H), 4.06 (d, $J = 17.2$ Hz, 2H), 3.72 (d, $J = 17.2$ Hz, 2H), 2.81 (s, 3H), 2.66-2.60 (m, 2H), 1.28-1.24 (m, 2H). ^{13}C NMR (101 MHz,

CDCl₃) δ 168.39, 140.60, 128.49, 128.44, 126.37, 124.40, 91.93, 81.13, 61.59, 47.10, 34.98, 21.64. HRMS (ESI) m/z cal. for (M + H)⁺ 312.1402, found 312.1410.

(*E*)-2-(4-(2-methoxyphenyl)but-1-en-3-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**5m**):⁴

According's to the **general procedure GP2**, brown solid, 75% yield. ¹H NMR (400 MHz, CDCl₃) δ

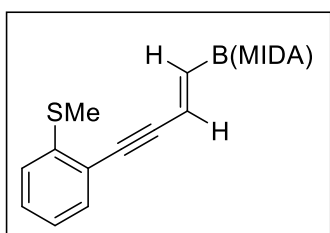


7.43 (d, $J = 7.2$ Hz, 1H), 7.34-7.29 (m, 1H), 6.95-6.89 (m, 2H), 6.42 (d, $J = 18.4$ Hz, 1H), 6.21 (d, $J = 18.4$ Hz, 1H), 3.97 (d, $J = 16.8$ Hz, 2H), 3.90 (s, 3H), 3.75 (d, $J = 16.8$ Hz, 2H), 2.90 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 167.03, 159.99, 133.66, 130.05, 124.58, 120.55, 110.77, 93.05, 87.85, 61.55, 55.83, 46.83. ¹¹B NMR (160 MHz, CDCl₃)

δ 9.73. HRMS (ESI) m/z cal. for (M + H)⁺ 314.1194, found 314.1180.

(*E*)-6-methyl-2-(4-(2-(methylthio)phenyl)but-1-en-3-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**5n**):

According's to the **general procedure GP2**, yellow solid, 70 % yield. ¹H NMR (500 MHz, CDCl₃) δ

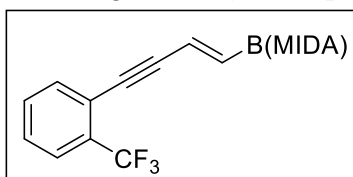


7.39 (d, $J = 7.5$ Hz, 1H), 7.30-7.28 (m, 1H), 7.14 (d, $J = 7.5$ Hz, 1H), 7.07 (t, $J = 7.5$ Hz, 1H), 6.39 (d, $J = 18$ Hz, 1H), 6.24 (d, $J = 18$ Hz, 1H), 3.99 (d, $J = 17$ Hz, 2H), 3.74 (d, $J = 17$ Hz, 2H), 2.86 (s, 3H), 2.47 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 167.65, 141.74, 132.51, 129.05, 124.33, 124.17, 123.88, 121.03, 95.46, 88.71, 61.66, 47.03, 15.04. ¹¹B

NMR (160 MHz, CDCl₃) δ 10.03. HRMS (ESI) m/z cal. for (M + H)⁺ 347.1237, found 347.1235.

(*E*)-6-methyl-2-(4-(2-(trifluoromethyl)phenyl)but-1-en-3-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**5o**):

According's to the **general procedure GP2**, pale yellow oil, 73 % yield. ¹H NMR (400 MHz, DMSO)

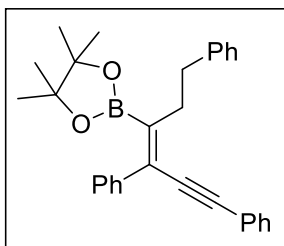


δ 7.80-7.58 (m, 4H), 6.38 (d, $J = 18$ Hz, 1H), 6.18 (d, $J = 18$ Hz, 1H), 4.28 (d, $J = 18$ Hz, 2H), 4.09 (d, $J = 18$ Hz, 2H), 2.84 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 169.49, 134.41, 133.05, 130.32, 130.02, 129.42, 126.52, 120.68, 95.37, 85.76, 62.09, 47.32. ¹⁹F NMR (471

MHz, DMSO) δ -61.01. ¹¹B NMR (160 MHz, DMSO) δ 10.06. HRMS (ESI) m/z cal. for (M + NH₄)⁺ 369.1228, found 369.1235.

(*Z*)-4,4,5,5-tetramethyl-2-(1,4,6-triphenylhex-3-en-5-yn-3-yl)-1,3,2-dioxaborolane (**6a**):

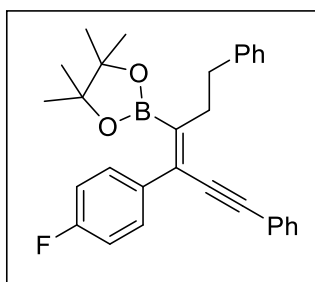
According's to the **general procedure GP3**, colorless oil, 65 % yield. ¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, $J = 7$ Hz, 2H), 7.35 (m, 2H), 7.25-7.19 (m, 10H), 7.13-7.09 (m, 1H), 2.88-2.84 (m, 2H), 2.81-2.78 (m, 2H), 1.10 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 142.36, 140.78, 133.26, 131.60, 131.47,



128.62, 128.57, 128.42, 128.29, 128.26, 128.17, 127.84, 127.62, 125.76, 123.65, 96.39, 88.93, 83.67, 37.64, 35.71, 24.65. ^{11}B NMR (160 MHz, CDCl_3) δ 30.18. HRMS (ESI) m/z cal. for $(\text{M} + \text{H})^+$ 435.2490, found 435.2484.

(*Z*)-2-(4-(4-fluorophenyl)-1,6-diphenylhex-3-en-5-yn-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6b**):

According's to the **general procedure GP3**, colorless liquid, 72 % yield. ^1H NMR (500 MHz, CDCl_3)

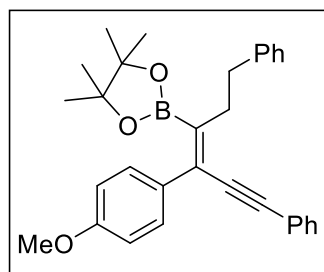


δ 7.36-7.34 (m, 4H), 7.23-7.18 (m, 7H), 7.11-7.09 (m, 1H), 6.92 (t, $J = 8.5$ Hz, 2H), 2.87-2.84 (m, 2H), 2.80-2.76 (m, 2H), 1.10 (s, 12H). ^{13}C NMR (126 MHz, CDCl_3) δ 162.55 (d, $J = 246$ Hz), 142.25, 136.84, 132.41, 131.59, 130.28 (d, $J = 8$ Hz), 128.62, 128.56, 128.30, 128.18, 125.80, 123.45, 114.61 (d, $J = 21.8$ Hz), 96.68, 88.77, 83.72, 37.60, 35.70, 24.65. ^{11}B NMR (160 MHz, CDCl_3) δ 30.35. HRMS (ESI) m/z cal. for

$(\text{M} + \text{H})^+$ 453.2396, found 453.2400.

(*Z*)-2-(4-(4-methoxyphenyl)-1,6-diphenylhex-3-en-5-yn-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6c**):

According's to the **general procedure GP3**, white yellow solid, 69% yield. ^1H NMR (400 MHz,



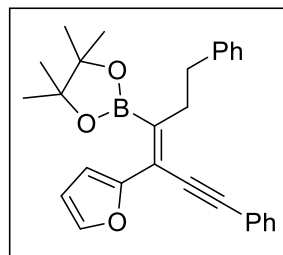
CDCl_3) δ 7.46-7.44 (m, 3H), 7.37-7.29 (m, 7H), 7.24-7.20 (m, 2H), 6.88 (d, $J = 8.8$ Hz, 2H), 3.85 (s, 3H), 2.94 (t, $J = 4.8$ Hz, 2H), 2.89 (t, $J = 3.2$ Hz, 2H), 1.23 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 159.36, 142.42, 133.34, 132.84, 131.60, 129.77, 128.62, 128.30, 128.29, 128.17, 125.75, 123.64, 113.24, 96.17, 89.08, 83.66, 55.36, 37.77, 35.82, 24.70.

^{11}B NMR (160 MHz, CDCl_3) δ 30.20. HRMS (ESI) m/z cal. for $(\text{M} +$

$\text{H})^+$ 465.2596, found 465.2583.

(*E*)-2-(4-(furan-2-yl)-1,6-diphenylhex-3-en-5-yn-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6d**):

According's to the **general procedure GP3**, pale brown oil, 71 % yield. ^1H NMR (400 MHz, CDCl_3)

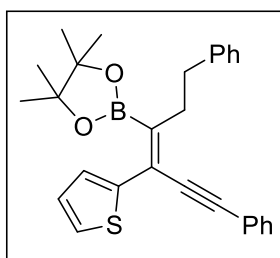


δ 7.67 (br. s, 1H), 7.52-7.51 (m, 2H), 7.44-7.43 (m, 3H), 7.29-7.17 (m, 5H), 6.59-6.55 (m, 2H), 2.78 (br. s, 4H), 1.32 (s, 12H). ^{13}C NMR (126 MHz, CDCl_3) δ 152.01, 142.77, 141.24, 131.31, 128.92, 128.73, 128.26, 128.18, 125.86, 122.07, 118.54, 111.82, 108.54, 93.83, 84.97, 83.81, 36.70, 34.74, 24.61. ^{11}B NMR (160 MHz, CDCl_3) δ 30.69. HRMS (ESI) m/z cal. for $(\text{M} +$

$\text{H})^+$ 425.2283, found 425.2290.

(*E*)-2-(1,6-diphenyl-4-(thiophen-2-yl)hex-3-en-5-yn-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6e**):

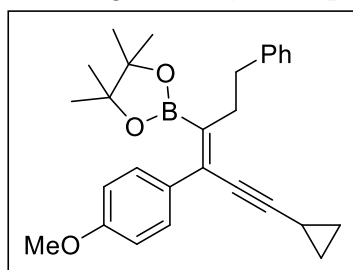
According's to the **general procedure GP3**, pale yellow oil, 60 % yield. ¹H NMR (500 MHz, CDCl₃)



δ 7.37 (t, $J = 3.5$ Hz, 2H), 7.24-7.21 (m, 3H), 7.20-7.14 (m, 6H), 7.11-7.00 (m, 1H), 6.87 (t, $J = 4$ Hz, 1H), 2.84-2.82 (m, 2H), 2.79-2.77 (m, 2H), 1.17 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 143.52, 142.23, 131.62, 128.58, 128.36, 128.34, 128.32, 126.60, 126.52, 125.83, 125.52, 125.12, 123.37, 95.77, 88.32, 83.90, 37.80, 35.59, 24.79. ¹¹B NMR (160 MHz, CDCl₃) δ 30.36. HRMS (ESI) m/z cal. for (M + H)⁺ 441.2054, found 441.2045.

(*Z*)-2-(6-cyclopropyl-4-(4-methoxyphenyl)-1-phenylhex-3-en-5-yn-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6f**):

According's to the **general procedure GP3**, colorless oil, 64 % yield. ¹H NMR (400 MHz, CDCl₃) δ

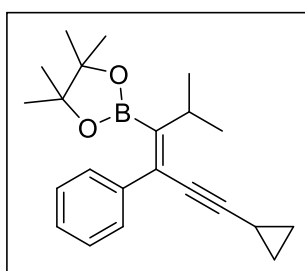


7.37-7.25 (m, 6H), 7.24-7.16 (m, 1H), 6.85 (d, $J = 8.5$ Hz, 2H), 3.84 (s, 3H), 2.81 (s, 4H), 1.49-1.46 (m, 1H), 1.21 (s, 12H), 0.89-0.87 (m, 2H), 0.77-0.76 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 159.34, 142.77, 134.16, 133.58, 129.79, 128.64, 128.36, 125.76, 113.24, 101.10, 83.54, 55.43, 37.49, 35.83, 24.78, 9.10, 0.69. ¹¹B NMR (160 MHz, CDCl₃) δ 30.35. HRMS (ESI) m/z cal. for (M + H)⁺ 429.2596,

found 429.2590.

(*Z*)-2-(6-cyclopropyl-2-methyl-4-phenylhex-3-en-5-yn-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6g**):

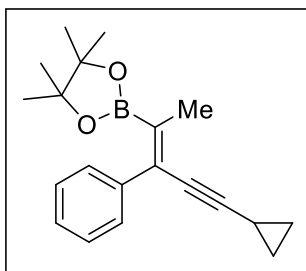
According's to the **general procedure GP3**, colorless oil, 75 % yield. ¹H NMR (400 MHz, CDCl₃) δ



7.40 (d, $J = 6.4$ Hz, 2H), 7.28-7.25 (m, 3H), 3.23-3.19 (m, 1H), 1.43 (m, 1H), 1.28-1.12 (m, 18H), 0.85-.074 (m, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 141.31, 128.95, 127.97, 127.24, 126.57, 99.51, 82.90, 33.77, 24.30, 21.48, 8.31, -0.00. ¹¹B NMR (160 MHz, CDCl₃) δ 30.35. HRMS (ESI) m/z cal. for (M + H)⁺ 337.2283, found 337.2279.

(*Z*)-2-(5-cyclopropyl-3-phenylpent-2-en-4-yn-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6h**):

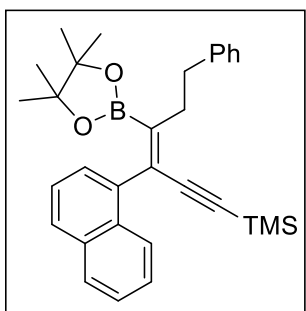
According's to the **general procedure GP3**, colorless oil, 69 % yield. ^1H NMR (400 MHz, CDCl_3) δ



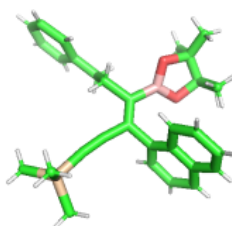
7.39-7.37 (m, 2H), 7.28-7.26 (m, 3H), 2.09 (s, 3H), 1.48-1.44 (m, 1H), 1.16 (s, 12H), 0.87-0.77 (m, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ 140.84, 132.97, 128.89, 127.88, 127.82, 127.10, 126.68, 101.24, 82.85, 23.96, 19.85, 8.48, -0.00. ^{11}B NMR (160 MHz, CDCl_3) δ 30.18. HRMS (ESI) m/z cal. for $(\text{M} + \text{Na})^+$ 331.1840, found 331.1736.

(Z)-trimethyl(3-(naphthalen-1-yl)-6-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-3-en-1-yn-1-yl)silane (**6i**):

According's to the **general procedure GP3**, colorless oil, 64 % yield. ^1H NMR (500 MHz, CDCl_3) δ



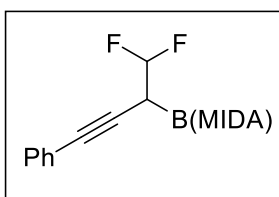
7.83-7.81 (m, 1H), 7.66-7.59 (m, 3H), 7.32-7.21 (m, 6H), 7.10-7.07 (m, 2H), 2.85-2.74 (m, 4H), 0.67 (s, 12H), 0.00 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 142.24, 138.43, 133.54, 131.99, 131.49, 128.78, 128.73, 128.31, 128.26, 127.80, 127.63, 126.61, 126.39, 125.83, 125.73, 125.56, 125.47, 125.07, 104.20, 101.96, 83.13, 36.61, 35.63, 24.26, -0.00. ^{11}B NMR (160 MHz, CDCl_3) δ 30.11. HRMS (ESI) m/z cal. for $(\text{M} + \text{K})^+$ 519.2287, found 519.2290.



6i, CCDC
Number
2298319

2-(1,1-difluoro-4-phenylbut-3-yn-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**7a**):

According's to the **general procedure A**, colourless oil, 58% yield. ^1H NMR (500 MHz, DMSO) δ

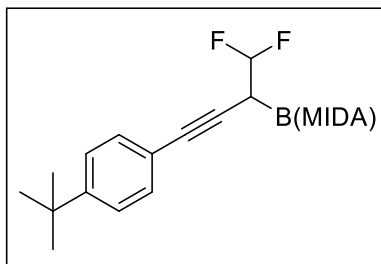


7.36 (m, 5H), 6.12 (td, $J = 56.5$, 3 Hz, 1H), 4.45 (d, $J = 17$ Hz, 1H), 4.36 (d, $J = 17$ Hz, 1H), 4.10 (d, $J = 17$ Hz, 1H), 4.00 (d, $J = 16$ Hz, 1H), 3.11 (s, 3H), 3.06-2.98 (m, 1H). ^{13}C NMR (126 MHz, DMSO) δ 168.91, 168.65, 131.81, 129.06, 128.83, 123.07, 116.85, 84.23, 63.06, 62.71, 46.91. ^{19}F NMR (471 MHz, DMSO) δ -109.95 (d, $J = 270$ Hz), -114.46 (d, $J = 270$ Hz). ^{11}B

NMR (160 MHz, DMSO) δ 10.20. HRMS (ESI) m/z cal. for $(\text{M} + \text{NH}_4)^+$ 339.1322, found 339.1332.

2-(4-(4-(tert-butyl)phenyl)-1,1-difluorobut-3-yn-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**7b**):

According's to the **general procedure A**, colourless oil, 52% yield. ^1H NMR (400 MHz, DMSO) δ

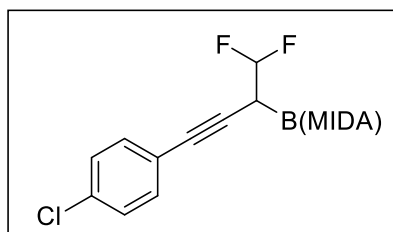


7.38 (d, $J = 7.2$ Hz, 2H), 7.30 (d, $J = 7.2$ Hz, 2H), 6.12 (td, $J = 53.6$, 3 Hz, 1H), 4.46 (d, $J = 17.2$ Hz, 1H), 4.34 (d, $J = 17.2$ Hz, 1H), 4.10 (d, $J = 17.2$ Hz, 1H), 3.97 (d, $J = 17.2$ Hz, 1H), 3.10 (s, 3H), 3.04-2.95 (m, 1H), 1.27 (s, 9H). ^{13}C NMR (126 MHz, DMSO) δ 169.02, 168.68, 151.66, 131.64, 125.96, 120.19, 116.94, 84.36, 63.15, 62.78, 46.93, 35.02, 31.44. ^{19}F NMR (471 MHz, DMSO) δ -109.96

(d, $J = 270$ Hz), -114.46 (d, $J = 270$ Hz). ^{11}B NMR (160 MHz, DMSO) δ 10.24. HRMS (ESI) m/z cal. for $(\text{M} + \text{NH}_4)^+$ 395.1948, found 395.1964.

2-(4-(4-chlorophenyl)-1,1-difluorobut-3-yn-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**7c**):

According's to the **general procedure A**, colourless oil, 62% yield. ^1H NMR (400 MHz, DMSO) δ

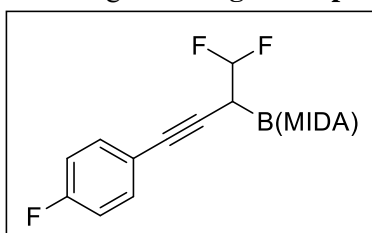


7.45-7.38 (m, 4H), 6.12 (td, $J = 55.6$, 2.8 Hz, 1H), 4.40 (d, $J = 17.2$ Hz, 1H), 4.35 (d, $J = 17.2$ Hz, 1H), 4.09 (d, $J = 17.2$ Hz, 1H), 4.00 (d, $J = 17.2$ Hz, 1H), 3.09 (s, 3H), 3.06-2.98 (m, 1H). ^{13}C NMR (126 MHz, DMSO) δ 173.60, 173.40, 138.31, 138.29, 133.95, 126.68, 87.88, 84.41, 84.14, 83.88, 67.78, 67.48, 51.68.

^{19}F NMR (471 MHz, DMSO) δ -109.91 (d, $J = 270$ Hz), -114.50 (d, $J = 271$ Hz). ^{11}B NMR (160 MHz, DMSO) δ 11.52. HRMS (ESI) m/z cal. for $(\text{M} + \text{NH}_4)^+$ 373.0932, found 373.0963.

2-(4-(4-fluorophenyl)-1,1-difluorobut-3-yn-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**7d**):

According's to the **general procedure A**, colourless oil, 57% yield. ^1H NMR (400 MHz, CDCl_3) δ

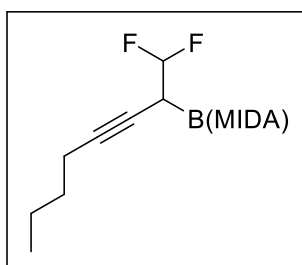


7.39-7.34 (m, 2H), 7.04-7.00 (m, 2H), 6.12 (td, $J = 56$, 2.8 Hz, 1H), 4.15-3.90 (m, 4H), 3.22 (s, 3H), 2.83-2.74 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.25, 163.71, 137.49, 133.58 (d, $J = 8.5$ Hz), 130.22, 115.84 (d, $J = 22$ Hz), 100.00, 84.46, 62.93, 62.87, 46.02.

^{19}F NMR (471 MHz, CDCl_3) δ -109.96 (s), 111.46 (d, $J = 275$ Hz), -113.77 (d, $J = 195$ Hz). ^{11}B NMR (160 MHz, DMSO) δ 10.26. HRMS (ESI) m/z cal. for $(\text{M} + \text{NH}_4)^+$ 357.1228, found 357.1234.

2-(1,1-difluorooct-3-yn-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**7e**):

According's to the **general procedure A**, colourless oil, 60% yield. ^1H NMR (400 MHz, CDCl_3) δ

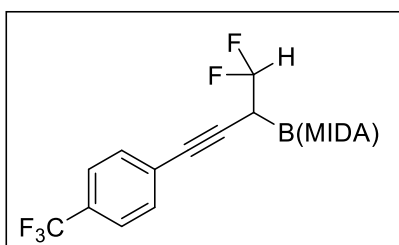


5.99 (td, $J = 56, 2.8$ Hz, 1H), 4.10-3.90 (m, 4H), 3.19 (s, 3H), 2.93-2.85 (m, 1H), 2.54-2.24 (m, 2H), 1.44-1.35 (m, 4H), 0.93 (t, $J = 2.4$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.44, 166.73, 116.17, 100.00, 85.87, 62.80, 62.71, 45.77, 45.76, 30.73, 21.96, 21.85, 18.39, 13.45, 13.44. ^{19}F NMR (471 MHz, CDCl_3) δ -111.89 (d, $J = 273$ Hz), -114.07 (d, $J = 273$ Hz). ^{11}B NMR (160 MHz, DMSO) δ 10.30. HRMS (ESI) m/z cal. for (M

+ NH_4) $^+$ 319.1635, found 319.1642.

2-(1,1-difluoro-4-(4-(trifluoromethyl)phenyl)but-3-yn-2-yl)-6-methyl-1,3,6,2-dioxaborocane-4,8-dione (**7f**):

According's to the **general procedure A**, colourless oil, 56% yield. ^1H NMR (400 MHz, DMSO) δ

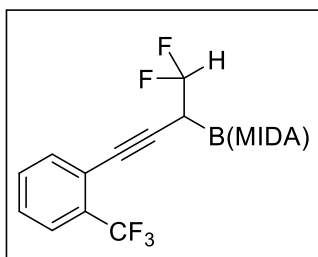


7.74 (d, $J = 8.8$ Hz, 2H), 7.59 (d, $J = 8.8$ Hz, 2H), 6.15 (td, $J = 56, 3.6$ Hz, 1H), 4.47-4.35 (m, 2H), 4.14-4.02 (m, 2H), 3.12 (s, 3H), 3.07-3.02 (m, 1H). ^{13}C NMR (101 MHz, DMSO) δ 168.92, 168.80, 132.59, 128.65, 127.38, 125.95, 125.91, 119.16, 116.75, 82.99, 63.00, 62.73, 46.99. ^{19}F NMR (471 MHz, DMSO) δ -61.93 (s) -

111.09 (d, $J = 273$ Hz), -115.89 (d, $J = 273$ Hz). ^{11}B NMR (160 MHz, DMSO) δ 10.30. HRMS (ESI) m/z cal. for (M + NH_4) $^+$ 407.1196, found 407.1160.

2-(1,1-difluoro-4-(2-(trifluoromethyl)phenyl)but-3-yn-2-yl)-6-methyl-1,3,6,2-dioxaborocane-4,8-dione (**7g**):

According's to the **general procedure A**, colourless oil, 42% yield. ^1H NMR (400 MHz, CDCl_3) δ

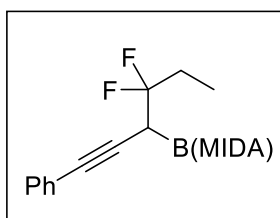


7.91-7.57 (m, 4H), 6.12 (td, $J = 56, 3.2$ Hz, 1H), 4.45-4.36 (m, 2H), 4.13-3.94 (m, 2H), 3.11 (s, 3H), 3.05-3.00 (m, 1H). ^{13}C NMR (101 MHz, DMSO) δ 168.76, 168.63, 134.78, 132.94, 129.07, 126.30, 80.01, 79.75, 79.43, 79.10, 79.09, 62.83, 62.64, 46.75. ^{19}F NMR (471 MHz, CDCl_3) δ

-60.93 (s), -110.09 (d, $J = 272$ Hz), -114.89 (d, $J = 270$ Hz). ^{11}B NMR (160 MHz, DMSO) δ 11.81. HRMS (ESI) m/z cal. for (M + NH_4) $^+$ 407.1196, found 407.1180.

2-(4,4-difluoro-1-phenylhex-1-yn-3-yl)-6-methyl-1,3,6,2-dioxaborocane-4,8-dione (**7h**):

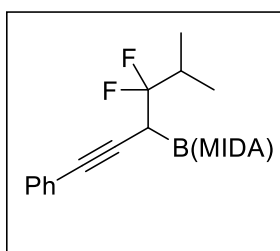
According's to the **general procedure A**, colourless oil, 53% yield. ^1H NMR (400 MHz, DMSO) δ



7.37 (m, 5H), 4.44 (d, $J = 17.2$ Hz, 1H), 4.32 (d, $J = 17.8$ Hz, 1H), 4.09 (d, $J = 17.2$ Hz, 1H), 3.95 (d, $J = 17.2$ Hz, 1H), 3.12 (s, 3H), 3.01-2.98 (m, 1H), 2.20-1.99 (m, 2H), 1.02 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 169.16, 168.67, 131.71, 129.09, 128.86, 122.97, 83.95, 73.98, 63.05, 62.52, 46.66, 42.56, 25.41, 6.65. ^{19}F NMR (471 MHz, DMSO) δ -92.70. ^{11}B NMR (160 MHz, DMSO) δ 9.73. HRMS (ESI) m/z cal. for $(\text{M} + \text{NH}_4)^+$ 367.1635, found 367.1649.

2-(4,4-difluoro-5-methyl-1-phenylhex-1-yn-3-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**7i**):

According's to the **general procedure A**, colourless oil, 59% yield. ^1H NMR (400 MHz, DMSO) δ

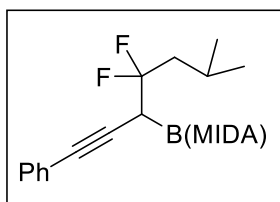


7.37 (m, 5H), 4.43 (d, $J = 17.2$ Hz, 1H), 4.31 (d, $J = 16.8$ Hz, 1H), 4.09 (d, $J = 17.2$ Hz, 1H), 3.94 (d, $J = 16.2$ Hz, 1H), 3.13 (s, 3H), 3.06-2.96 (m, 1H), 2.47-2.41 (m, 1H), 1.09 (d, $J = 6.8$ Hz, 3H), 1.02 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 169.06, 168.61, 131.63, 129.06, 128.78, 126.55, 123.08, 87.19, 83.98, 79.42 (t, $J = 33$ Hz), 63.08, 62.59, 46.65, 34.33 (t, $J = 25.9$ Hz), 16.55 (q, $J = 3.1$ Hz), 15.94 (t, $J = 4.9$ Hz). ^{19}F NMR (471 MHz,

DMSO) δ -97.69 (d, $J = 249$ Hz), -104.27 (d, $J = 235$ Hz). ^{11}B NMR (160 MHz, DMSO) δ 10.08. HRMS (ESI) m/z cal. for $(\text{M} + \text{NH}_4)^+$ 381.1792, found 381.1804.

2-(4,4-difluoro-6-methyl-1-phenylhept-1-yn-3-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**7j**):

According's to the **general procedure A**, colourless oil, 65% yield. ^1H NMR (400 MHz, CDCl_3) δ

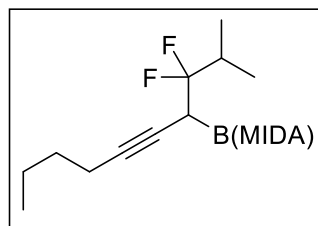


7.39-7.29 (m, 5H), 4.01-3.88 (m, 4H), 3.19 (s, 3H), 2.87-2.80 (m, 1H), 2.12-2.08 (m, 2H), 1.30-1.26 (m, 1H), 1.02 (d, $J = 6$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.20, 166.49, 131.56, 130.12, 128.60, 128.55, 128.49, 128.46, 122.45, 84.97, 62.92, 62.87, 45.98, 44.35, 23.74, 23.40. ^{19}F NMR (471 MHz, CDCl_3) δ -89.90 (m). ^{11}B NMR (160 MHz, DMSO) δ 10.04.

HRMS (ESI) m/z cal. for $(\text{M} + \text{NH}_4)^+$ 395.1948, found 395.1961.

2-(3,3-difluoro-2-methyldec-5-yn-4-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**7k**):

According's to the **general procedure A**, colourless oil, 60% yield. ^1H NMR (400 MHz, CDCl_3) δ

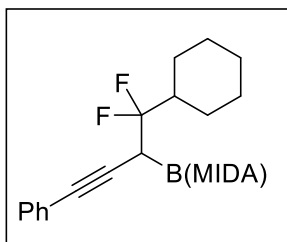


4.03-3.89 (m, 4H), 3.20 (s, 3H), 3.01-2.88 (m, 1H), 2.55-2.44 (m, 1H), 2.16 (t, $J = 6.8$ Hz, 2H), 1.54-1.45 (m, 1H), 1.33-1.26 (m, 4H), 1.09-1.04 (m, 4H), 0.92-0.90 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 93.75, 62.85, 62.68, 45.96, 31.08, 28.35, 22.10, 18.68, 13.99, 13.99, 13.98. ^{19}F NMR (471 MHz, CDCl_3) δ -98.58 (d, $J = 240$ Hz), -108.04 (d, $J = 230$

Hz). ^{11}B NMR (160 MHz, CDCl_3) δ 10.08. HRMS (ESI) m/z cal. for $(\text{M} + \text{NH}_4)^+$ 361.2105, found 361.2061.

2-(1-cyclohexyl-1,1-difluoro-4-phenylbut-3-yn-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**7l**):

According's to the **general procedure A**, white solid, 55% yield. ^1H NMR (400 MHz, DMSO) δ 7.37

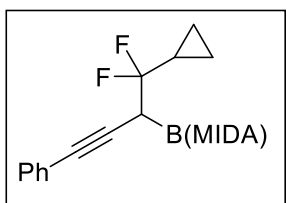


(m, 5H), 4.41 (d, $J = 17.6$ Hz, 1H), 4.41 (d, $J = 17.6$ Hz, 1H), 4.04 (d, $J = 17.6$ Hz, 1H), 3.94 (d, $J = 17.6$ Hz, 1H), 3.11 (s, 3H), 3.02-2.89 (m, 1H), 2.13-1.64 (m, 6H), 1.22-1.07 (m, 5H). ^{13}C NMR (101 MHz, DMSO) δ 169.17, 168.74, 131.64, 129.16, 129.15, 129.12, 128.83, 123.04, 79.74, 79.41, 63.02, 62.50, 46.61, 25.89, 25.62, 25.60. ^{19}F NMR (471 MHz, DMSO) δ -97.16 (d, $J = 227$ Hz), -101.94 (d, $J = 230$ Hz). ^{11}B NMR (160

MHz, DMSO) δ 9.88. HRMS (ESI) m/z cal. for $(\text{M} + \text{NH}_4)^+$ 421.2105, found 421.2113.

2-(1-cyclopropyl-1,1-difluoro-4-phenylbut-3-yn-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**7m**):

According's to the **general procedure A**, colourless oil, 51% yield. ^1H NMR (400 MHz, DMSO) δ

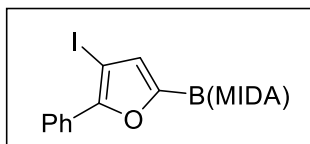


7.31-7.19 (m, 5H), 3.97-3.79 (m, 4H), 3.13 (s, 3H), 2.87 (t, $J = 10.2$ Hz, 1H), 1.20-1.18 (m, 1H), 0.78-0.71 (m, 2H), 0.70-0.58 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 169.23, 168.77, 131.68, 129.12, 128.83, 123.08, 63.04, 62.50, 46.64, 25.43, 2.23. ^{19}F NMR (471 MHz, CDCl_3) δ -94.25 (d, $J = 231$ Hz), -96.79 (d, $J = 233$ Hz). ^{11}B NMR (160 MHz, DMSO) δ 10.20. HRMS

(ESI) m/z cal. for $(\text{M} + \text{NH}_4)^+$ 379.1635, found 379.1644.

2-(4-iodo-5-phenylfuran-2-yl)-6-methyl-1,3,6,2-dioxazaboronane-4,9-dione (**9a**):

According's to the **general procedure B**, white solid, 61 % yield. ^1H NMR (400 MHz, DMSO) δ 7.96

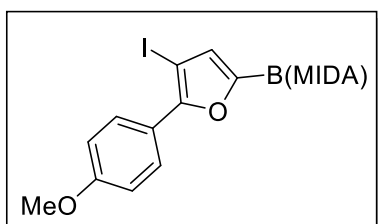


(d, $J = 8$ Hz, 2H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.42-7.38 (m, 1H), 6.86 (s, 1H), 4.39 (d, $J = 17.2$ Hz, 2H), 4.18 (d, $J = 17.2$ Hz, 2H), 2.74 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 169.39, 154.15, 130.47, 129.09, 128.82,

128.68, 126.47, 63.51, 62.04, 47.81. ^{11}B NMR (160 MHz, DMSO) δ 9.66. HRMS (ESI) m/z cal. for $(\text{M} + \text{Na})^+$ 461.9980, found 461.9989.

2-(4-iodo-5-(4-methoxyphenyl)furan-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**9b**):

According's to the **general procedure B**, white solid, 65 % yield. ^1H NMR (400 MHz, DMSO) δ 7.88



(d, $J = 8.8$ Hz, 2H), 7.06 (d, $J = 8.8$ Hz, 2H), 6.82 (s, 1H), 4.39 (d, $J = 17.2$ Hz, 2H), 4.18 (d, $J = 17.2$ Hz, 2H), 3.81 (s, 3H), 2.74 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 169.37, 159.75, 154.46, 128.42, 128.11, 123.15, 114.51, 62.02, 61.77, 55.74, 47.80. ^{11}B NMR (160 MHz, DMSO) δ 9.73. HRMS (ESI) m/z cal. for $(\text{M} +$

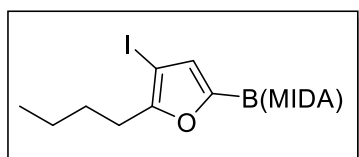
$\text{H})^+$ 456.0110, found 456.0112.



9b, CCDC Number
2298321

2-(5-butyl-4-iodofuran-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**9c**):

According to the **general procedure B**, colorless oil, 69 % yield. ^1H NMR (400 MHz, CDCl_3) δ 6.77

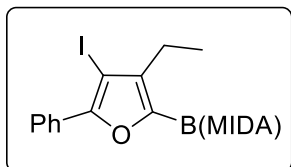


(s, 1H), 4.06 (d, $J = 16.4$ Hz, 2H), 3.83 (t, $J = 16.2$ Hz, 2H), 6.68 (d, $J = 3.2$ Hz, 1H), 4.01 (d, $J = 16.2$ Hz, 1H), 3.92 (d, $J = 16.2$ Hz, 1H), 2.74 (s, 3H), 2.71-2.67 (m, 2H), 1.64-1.58 (m, 2H), 1.35-1.27 (m, 2H), 0.96-0.87 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.35,

160.81, 132.15, 126.60, 62.66, 61.62, 47.19, 31.21, 27.80, 22.18, 13.80. ^{11}B NMR (160 MHz, CDCl_3) δ 10.24. HRMS (ESI) m/z cal. for $(\text{M} + \text{H})^+$ 423.0583, found 423.0587.

2-(3-ethyl-4-iodo-5-phenylfuran-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**9d**):

According to the **general procedure B**, white solid, 75 % yield. ^1H NMR (400 MHz, CDCl_3) δ 7.95

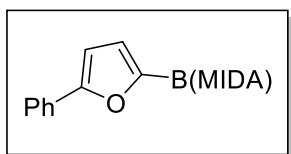


(d, $J = 6.8$ Hz, 2H), 7.46-7.37 (m, 3H), 3.98 (d, $J = 16.4$ Hz, 2H), 3.88 (d, $J = 16.4$ Hz, 2H), 2.78 (s, 3H), 2.62-2.60 (m, 2H), 1.18 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.75, 154.42, 140.90, 130.34, 128.53, 128.46, 126.61, 69.47, 61.64, 46.92, 19.99, 15.77. ^{11}B NMR (160 MHz, CDCl_3) δ

10.03. HRMS (ESI) m/z cal. for $(\text{M} + \text{H})^+$ 454.0317, found 454.0316.

6-methyl-2-(5-phenylfuran-2-yl)-1,3,6,2-dioxazaboronane-4,9-dione (**10a**):⁴

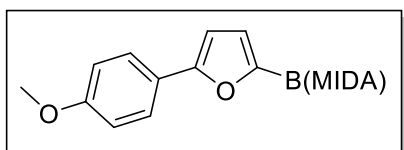
According to the **general procedure C**, colorless oil, 74 % yield. ^1H NMR (400 MHz, CDCl_3) δ 7.69-



7.67 (m, 2H), 7.42-7.38 (m, 2H), 7.31-7.28 (m, 1H), 6.88 (t, $J = 3.2$ Hz, 1H), 6.68 (d, $J = 3.2$ Hz, 1H), 4.01 (d, $J = 16.2$ Hz, 1H), 3.92 (d, $J = 16.2$ Hz, 1H), 2.79 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 169.54, 156.45, 131.00, 129.26, 127.94, 124.20, 120.40, 106.53, 62.01, 61.94, 47.70.

2-(5-(4-methoxyphenyl)furan-2-yl)-6-methyl-1,3,6,2-dioxazaboronane-4,9-dione (**10b**):⁴

According to the **general procedure C**, colorless oil, 80 % yield. ^1H NMR (400 MHz, DMSO) δ 7.66

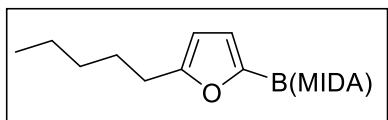


(d, $J = 8.8$ Hz, 2H), 6.98 (d, $J = 8.8$ Hz, 2H), 6.74 (s, 1H), 6.68 (s, 1H), 4.37 (d, $J = 17.2$ Hz, 1H), 4.15 (d, $J = 17.2$ Hz, 1H), 3.77 (s, 3H), 2.68 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 169.48, 159.27,

156.65, 125.76, 124.05, 120.36, 114.72, 104.79, 61.93, 55.67, 47.68. HRMS (ESI) m/z cal. for (M + H)⁺ 344.1495, found 344.1462.

6-methyl-2-(5-pentylfuran-2-yl)-1,3,6,2-dioxazaboronane-4,9-dione (**10c**):⁴

According's to the **general procedure C**, colorless oil, 72 % yield. ¹H NMR (400 MHz, CDCl₃) δ 7.68

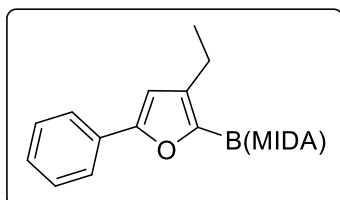


(d, $J = 2.8$ Hz, 2H), 5.99 (d, $J = 2.8$ Hz, 1H), 4.07 (d, $J = 16.8$ Hz, 2H), 3.83 (d, $J = 16.8$ Hz, 2H), 2.71 (s, 3H), 2.65-2.60 (m, 2H), 1.64-1.57 (m, 2H), 1.39-1.27 (m, 4H), 0.95-0.87 (m, 3H). ¹³C NMR

(101 MHz, CDCl₃) δ 167.83, 160.75, 119.96, 105.39, 61.55, 47.10, 31.40, 28.12, 27.85, 27.78, 22.38, 22.29, 13.82. HRMS (ESI) m/z cal. for (M + H)⁺ 344.1495, found 344.1462.

2-(3-ethyl-5-phenylfuran-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**10d**):

According's to the **general procedure C**, colorless oil, 80 % yield. ¹H NMR (400 MHz, CDCl₃) δ 7.63

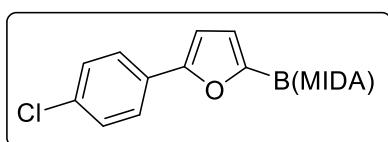


(d, $J = 7.2$ Hz, 2H), 7.39-7.36 (m, 2H), 7.29-7.26 (m, 1H), 6.60 (d, $J = 2$ Hz, 1H), 4.06 (d, $J = 16.4$ Hz, 2H), 3.88 (d, $J = 16.4$ Hz, 2H), 2.73 (s, 3H), 2.64-2.59 (m, 2H), 1.23-1.19 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.50, 156.44, 139.08, 130.70, 128.74, 127.65, 123.95,

107.23, 61.53, 46.84, 18.47, 15.69. ¹¹B NMR (160 MHz, CDCl₃) δ 8.26. HRMS (ESI) m/z cal. for (M + H)⁺ 328.1351, found 328.1259.

2-(5-(4-chlorophenyl)furan-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**10e**):

According's to the **general procedure C**. colourless liquid, 70% yield. ¹H NMR (400 MHz, DMSO) δ

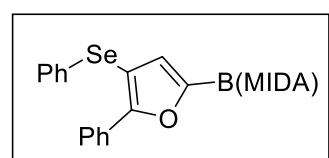


7.76 (d, $J = 8.8$ Hz, 2H), 7.48 (d, $J = 8.8$ Hz, 2H), 6.98-6.96 (m, 1H), 6.75-6.74 (m, 1H), 4.39 (d, $J = 17.2$ Hz, 2H), 4.17 (d, $J = 17.2$ Hz, 2H), 2.70 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 169.51, 155.34, 132.29, 129.84, 129.30, 125.91, 124.21, 120.55, 107.31,

61.96, 47.71. HRMS (ESI) m/z cal. for (M + H)⁺ 334.0648, found 334.0662.

6-methyl-2-(5-phenyl-4-(phenylselanyl)furan-2-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**11a**):

According's to the **general procedure D**, white solid, 67 % yield. ¹H NMR (400 MHz, DMSO) δ 7.92

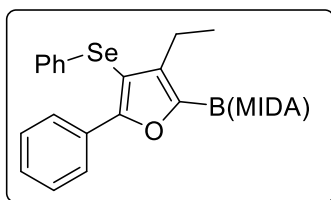


(d, $J = 7.6$ Hz, 2H), 7.48-7.25 (m, 8H), 4.40 (d, $J = 17.2$ Hz, 2H), 4.20 (d, $J = 17.2$ Hz, 2H), 2.77 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 169.46, 156.47, 131.66, 130.43, 130.10, 129.07, 128.85, 127.21, 126.70, 126.56, 103.57, 100.02, 62.10, 47.87. HRMS (ESI) m/z cal. for (M +

H)⁺ 356.0516, found 356.0531.

2-(3-ethyl-5-phenyl-4-(phenylselanyl)furan-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**11b**):

According to the **general procedure D**, white solid, 71 % yield. ^1H NMR (400 MHz, DMSO) δ 7.95

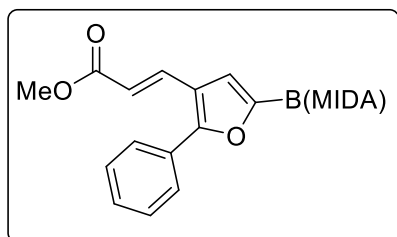


(d, $J = 7.2$ Hz, 2H), 7.42-7.17 (m, 8H), 4.43 (d, $J = 17.2$ Hz, 2H), 4.22 (d, $J = 17.2$ Hz, 2H), 2.75 (s, 3H), 2.51-2.50 (m, 2H), 0.96-0.95 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 169.39, 157.96, 140.34, 132.75, 130.59, 130.01, 128.99, 128.94, 128.14, 126.80, 126.47, 105.07, 62.10, 47.73, 18.34, 16.60. ^{11}B NMR (160 MHz, DMSO) δ 9.58. HRMS

(ESI) m/z cal. for $(\text{M} + \text{NH}_4)^+$ 501.1095, found 501.1249.

methyl(*E*)-3-(5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-phenylfuran-3-yl)acrylate (**9aa**):

Compound **9aa** was synthesized using general heck coupling procedure. **9a** (1 equiv), methyl acrylate

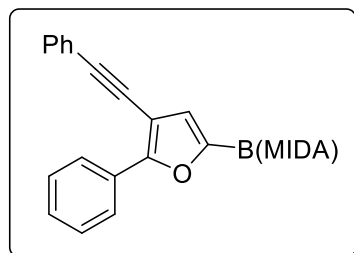


(1.5 equiv), $\text{Pd}(\text{OAc})_2$ (0.02 equiv), PPh_3 (0.15 equiv), Et_3N (2 equiv), DMF (0.1 M), 90 °C, 19 h. colourless oil, 63% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 16$ Hz, 1H), 7.68-7.65 (m, 2H), 7.55-7.53 (m, 1H), 7.48-7.45 (m, 2H), 7.07 (s, 1H), 6.25 (d, $J = 15.5$ Hz, 1H), 3.98 (d, $J = 16.5$ Hz, 2H), 3.86 (d, $J = 16.5$ Hz,

2H), 3.78 (s, 3H), 2.81 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.55, 166.61, 135.50, 132.98, 132.16, 132.06, 131.97, 128.96, 128.59, 128.47, 127.47, 118.73, 118.49, 118.40, 61.71, 51.66, 47.19. ^{11}B NMR (160 MHz, CDCl_3) δ 8.41. HRMS (ESI) m/z cal. for $(\text{M} + \text{H})^+$ 384.1249, found 384.1255.

6-methyl-2-(5-phenyl-4-(phenylethynyl)furan-2-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**9ab**):

Compound **9ab** was synthesized using general sonogashira coupling procedure. **9a** (1 equiv), phenyl

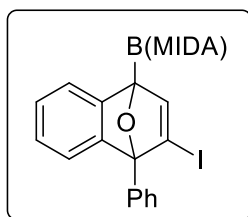


acetylene (1.5 equiv), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.1 equiv), CuI (0.05 equiv), Et_3N (3 equiv), THF (0.1 M), RT, 4 h. Colourless oil, 72% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.11 (d, $J = 7.5$ Hz, 1H), 7.95 (d, $J = 7.5$ Hz, 1H), 7.70-7.53 (m, 2H), 7.46-7.34 (m, 5H), 7.27 (s, 1H), 6.97 (d, $J = 3$ Hz, 1H), 4.07-4.02 (m, 2H), 3.89-3.84 (m, 2H), 2.79 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.83, 157.98, 155.38, 131.38, 130.24,

130.05, 129.62, 128.66, 128.60, 128.53, 128.48, 128.44, 128.34, 126.50, 125.11, 124.15, 103.63, 94.05, 82.48, 61.72, 61.69, 47.27. ^{11}B NMR (160 MHz, CDCl_3) δ 8.60. HRMS (ESI) m/z cal. for $(\text{M} + \text{NH}_4)^+$ 417.1616, found 417.1619.

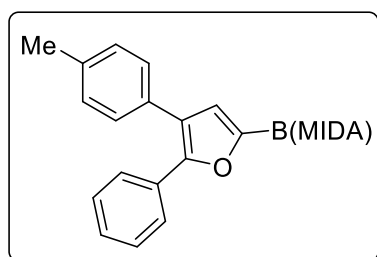
2-(3-iodo-4-phenyl-1,4-epoxynaphthalen-1(4H)-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**9ac**):

Compound **9ac** was synthesized using general [4+2] cyclo addition procedure. **9a** (1 equiv), CsF (5 equiv), 2-(Trimethylsilyl)phenyl trifluoromethanesulfonate (3 equiv), ACN (0.1 M), 60 °C, 24 h. Colourless oil, 68% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 7 Hz, 2H), 7.51-7.43 (m, 4H), 7.38 (d, *J* = 7 Hz, 2H), 7.04-6.97 (m, 2H), 3.92-3.83 (m, 4H), 3.02 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 166.75, 166.68, 153.28, 151.14, 148.56, 134.06, 128.69, 128.19, 127.82, 125.82, 124.72, 121.30, 121.13, 112.02, 96.45, 62.43, 62.38, 46.92. ¹¹B NMR (160 MHz, CDCl₃) δ 8.24. HRMS (ESI) *m/z* cal. for (M + H)⁺ 518.1339, found 518.1310.



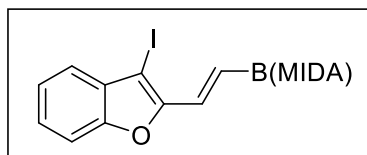
6-methyl-2-(5-phenyl-4-(p-tolyl)furan-2-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**9ad**):

Compound **9ad** was synthesized using general Suzuki coupling procedure. **9a** (1 equiv), 4-methyl phenyl boronic acid (1.5 equiv), Cs₂CO₃ (3 equiv), Pd(OAc)₂ (0.1 equiv), XPhos (0.2 equiv), THF (0.1 M), RT for 24 h. Colourless oil, 75% yield. ¹H NMR (400 MHz, DMSO) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.37-7.36 (m, 2H), 7.30-7.28 (m, 3H), 7.21-7.19 (m, 2H), 6.81 (d, *J* = 3.6 Hz, 1H), 4.40 (d, *J* = 17.2 Hz, 2H), 4.19 (d, *J* = 17.2 Hz, 2H), 2.78 (s, 3H), 2.33 (s, 3H). ¹³C NMR (126 MHz, DMSO) δ 169.43, 150.87, 136.84, 134.65, 131.52, 131.26, 129.78, 129.02, 128.54, 128.24, 126.53, 122.65, 122.35, 62.01, 47.81, 21.22. ¹¹B NMR (160MHz, DMSO) δ 8.63. HRMS (ESI) *m/z* cal. for (M + H)⁺ 390.1507, found 390.1509.



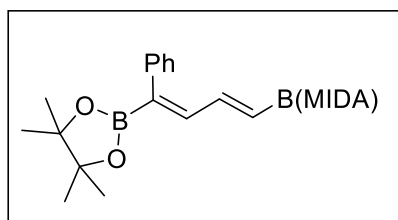
(*E*)-2-(2-(3-iodobenzofuran-2-yl)vinyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**12**):

In a reaction tube containing **5m** (1 equiv) in dry DCM (0.05 M) was cooled to -30 °C and treated with I₂ (1.2 equiv) in dry DCM (0.05). After the stirring for 3 h, the reaction mixture was quenched by using aq. Na₂S₂O₃ and extracted the crude mixture using DCM (2 times). Colourless oil, 76% yield. ¹H NMR (400 MHz, DMSO) δ 7.60-7.57 (m, 1H), 7.41-7.33 (m, 3H), 6.34 (d, *J* = 17.6 Hz, 1H), 5.99 (d, *J* = 17.6 Hz, 1H), 4.26 (d, *J* = 16.8 Hz, 2H), 4.08 (d, *J* = 16.8 Hz, 2H), 2.80 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 169.64, 154.38, 145.19, 144.80, 131.23, 126.67, 124.45, 121.43, 117.61, 111.67, 70.11, 62.06, 47.38. ¹¹B NMR (160 MHz, DMSO) δ 8.73. HRMS (ESI) *m/z* cal. for (M + H)⁺ 535.3528, found 535.3538.



6-methyl-2-((*1E,3Z*)-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,3-dien-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**13a**):

According's to the **general procedure E**, colourless oil, 72% yield. ^1H NMR (500 MHz, DMSO) δ

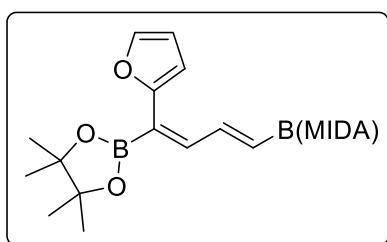


7.43 (m, 2H), 7.31-7.18 (m, 4H), 6.35 (d, $J = 18$ Hz, 1H), 6.19 (d, $J = 18$ Hz, 1H), 3.96 (d, $J = 15$ Hz, 2H), 3.74 (d, $J = 15$ Hz, 1H), 2.88 (s, 3H), 1.27 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.49, 131.68, 128.55, 128.40, 124.21, 122.91, 91.42, 89.02, 83.20, 61.71, 47.04, 24.57. ^{11}B NMR (160 MHz, DMSO) δ 22.53,

13.73. HRMS (ESI) m/z cal. for $(\text{M} + \text{NH}_4)^+$ 429.2363, found 429.2365.

2-((1*E*,3*Z*)-4-(furan-2-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,3-dien-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**13b**):

According's to the **general procedure E**, colourless oil, 76% yield. ^1H NMR (400 MHz, DMSO) δ

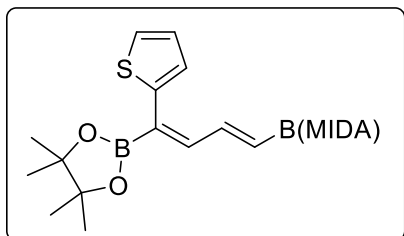


7.05 (d, $J = 18.4$ Hz, 1H), 6.69 (d, $J = 3.6$ Hz, 1H), 6.57-6.55 (m, 2H), 6.20 (d, $J = 18.4$ Hz, 1H), 6.90 (d, $J = 18.4$ Hz, 1H), 4.26 (d, $J = 17.2$ Hz, 2H), 4.06 (d, $J = 17.2$ Hz, 2H), 2.81 (s, 3H), 1.23 (s, 12H). ^{13}C NMR (126 MHz, DMSO) δ 169.54, 154.65, 152.73, 136.37, 129.23, 114.49, 111.68, 83.54, 81.83, 61.93, 47.26, 25.06,

24.95. HRMS (ESI) m/z cal. for $(\text{M} + \text{H})^+$ 402.1890, found 402.1891. The stereochemistry of the structure has been elucidated by observing 2D NOESY NMR.

6-methyl-2-((1*E*,3*Z*)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(thiophen-2-yl)buta-1,3-dien-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**13c**):

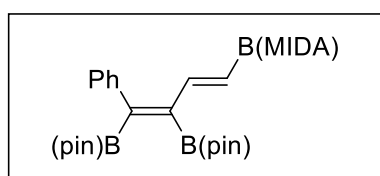
According's to the **general procedure E**, colourless oil, 69% yield. ^1H NMR (500 MHz, DMSO) δ



7.37 (d, $J = 18$ Hz, 1H), 7.21 (d, $J = 3.2$ Hz, 1H), 7.08 (d, $J = 3.6$ Hz, 1H), 6.92 (d, $J = 18$ Hz, 1H), 6.01 (d, $J = 18$ Hz, 1H), 5.71 (d, $J = 18$ Hz, 1H), 4.26 (d, $J = 16.8$ Hz, 2H), 4.06 (d, $J = 16.8$ Hz, 2H), 2.81 (s, 3H), 1.24 (s, 12H). ^{13}C NMR (101 MHz, DMSO) δ 169.58, 145.50, 142.39, 134.44, 130.48, 128.15, 83.60, 61.93,

47.24, 25.06. HRMS (ESI) m/z cal. for $(\text{M} + \text{K})^+$ 456.1220, found 456.1363. The stereochemistry of the structure has been elucidated by observing 2D NOESY NMR.

6-methyl-2-((1*E*,3*Z*)-4-phenyl-3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,3-dien-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**14a**):



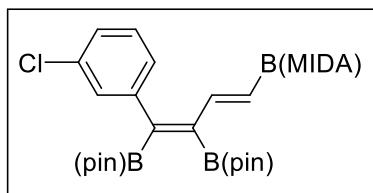
According's to the **general procedure F**, pale yellow solid, 75% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.30 (t, $J = 7.5$ Hz, 2H), 7.21 (t, $J = 7$ Hz, 1H), 7.00 (d, $J = 7$ Hz, 2H), 6.53 (d, $J = 18$ Hz, 1H), 5.80 (d, $J = 18$ Hz, 1H), 4.14 (d, $J = 17.5$ Hz, 2H), 3.90 (d, $J = 17$

Hz, 2H), 2.72 (s, 3H), 1.32 (s, 8H), 1.20 (s, 8H), 1.16 (s, 4H), 1.07 (s, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ 169.39, 142.61, 141.43, 129.31, 128.13, 126.74, 84.14, 84.04, 81.86, 74.05, 61.75, 47.14, 25.53,

25.38, 24.93, 24.87. ^{11}B NMR (160 MHz, CDCl_3) δ 22.23, 20.09, 11.30. HRMS (ESI) m/z cal. for $(\text{M} + \text{H})^+$ 538.2949, found 538.2890.

2-((1*E*,3*Z*)-4-(3-chlorophenyl)-3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,3-dien-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**14b**):

According's to the **general procedure F**, colourless liquid, 63% yield. ^1H NMR (400 MHz, CDCl_3) δ

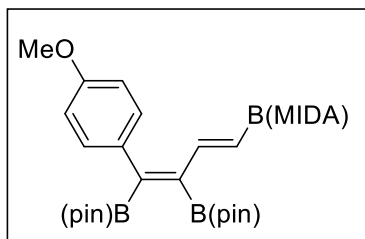


7.71-7.66 (m, 2H), 7.56 (d, $J = 7.6$ Hz, 1H), 7.51-7.29 (m, 1H), 6.42 (d, $J = 18.2$ Hz, 1H), 5.90 (d, $J = 18.2$ Hz, 1H), 3.87 (d, $J = 16.4$ Hz, 2H), 3.70 (d, $J = 16.4$ Hz, 2H), 2.92 (s, 3H), 1.29 (s, 12H), 1.28 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.12, 132.14, 132.05, 131.98, 129.26, 129.11, 128.56, 128.48, 127.28, 126.70, 84.26,

84.21, 83.15, 61.95, 61.25, 45.68, 26.16, 25.27, 24.73, 24.57. HRMS (ESI) m/z cal. for $(\text{M} + \text{H})^+$ 589.2835, found 589.2841.

2-((1*E*,3*Z*)-4-(4-methoxyphenyl)-3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,3-dien-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**14c**):

According's to the **general procedure F**, colourless liquid, 79% yield. ^1H NMR (500 MHz, CDCl_3) δ

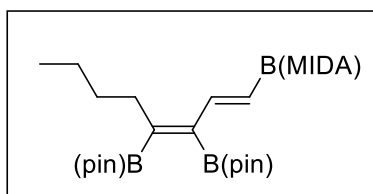


7.04 (d, $J = 8.6$ Hz, 2H), 6.81 (d, $J = 8.6$ Hz, 2H), 6.76 (d, $J = 18.5$ Hz, 1H), 5.84 (d, $J = 18.5$ Hz, 1H), 3.88 (d, $J = 16.5$ Hz, 2H), 3.79 (s, 3H), 3.66 (d, $J = 16.5$ Hz, 2H), 2.88 (s, 3H), 1.37 (s, 9H), 1.27 (s, 9H), 1.23 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.62, 158.39, 145.08, 133.19, 132.15, 132.07, 130.47, 128.57, 128.47, 113.25,

84.03, 84.00, 83.14, 61.89, 61.21, 55.17, 46.56, 25.29, 24.78, 24.54. ^{11}B NMR (160 MHz, CDCl_3) δ 22.49, 12.03. HRMS (ESI) m/z cal. for $(\text{M} + \text{H})^+$ 585.3320, found 585.3339.

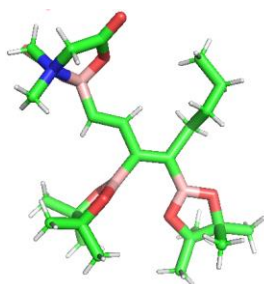
2-((1*E*,3*Z*)-3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octa-1,3-dien-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**14d**):

According's to the **general procedure F**, white solid, 81% yield. ^1H NMR (400 MHz, DMSO) δ 6.92



(d, $J = 18$ Hz, 1H), 5.72 (d, $J = 18$ Hz, 1H), 4.22 (d, $J = 17.2$ Hz, 2H), 3.98 (d, $J = 17.2$ Hz, 2H), 2.75 (s, 3H), 2.24 (br. s, 2H), 1.28 (s, 12H), 1.21 (s, 12H), 1.19-1.17 (m, 4H), 0.86 (m, 3H). ^{13}C NMR (126 MHz, DMSO) δ 169.58, 140.71, 131.99, 131.91, 129.26,

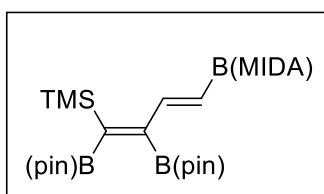
129.17, 83.74, 83.62, 61.86, 47.21, 32.30, 25.54, 25.11, 24.91, 22.47, 14.29. ^{11}B NMR (160 MHz, DMSO) δ 22.41, 9.07. HRMS (ESI) m/z cal. for $(\text{M} + \text{H})^+$ 535.3528, found 535.3538.



14d, CCDC Number **2298322**

2-((1E,3Z)-3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trimethylsilyl)buta-1,3-dien-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**14e**) :

According's to the **general procedure F**, colourless oil, 69% yield. ^1H NMR (400 MHz, DMSO) δ 6.89

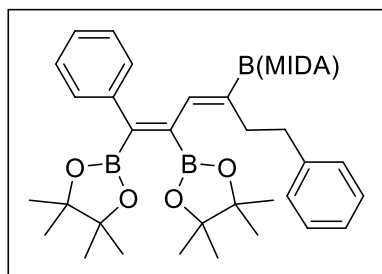


(d, $J = 18$ Hz, 1H), 5.81 (d, $J = 18$ Hz, 1H), 4.23 (d, $J = 17.2$ Hz, 2H), 3.96 (d, $J = 17.2$ Hz, 2H), 2.76 (s, 3H), 1.26 (s, 12H), 1.23 (s, 12H), 0.14 (s, 9H). ^{13}C NMR (101 MHz, DMSO) δ 169.55, 131.99, 131.89, 129.27, 129.15, 83.93, 83.60, 61.73, 47.07, 25.34, 25.25, 1.79. ^{11}B NMR (160

MHz, DMSO) δ 22.53, 13.73. HRMS (ESI) m/z cal. for $(\text{M} + \text{H})^+$ 551.3297, found 551.3314.

2-((3Z,5Z)-1,6-diphenyl-5,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-3,5-dien-3-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**14f**):

According's to the **general procedure F**, colourless oil, 75% yield. ^1H NMR (400 MHz, DMSO) δ

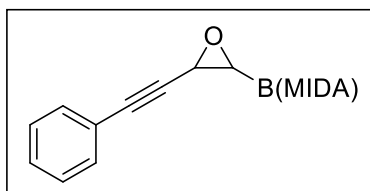


7.30-7.17 (m, 10H), 6.47 (s, 1H), 3.63 (d, $J = 16.4$ Hz, 2H), 3.44 (d, $J = 16.4$ Hz, 2H), 2.66-2.62 (m, 2H), 2.05 (s, 3H), 2.02-2.00 (m, 2H), 1.32 (s, 12H), 1.30 (s, 12H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.52, 143.46, 142.91, 140.89, 128.64, 128.42, 128.17, 127.88, 126.25, 125.47, 83.99, 83.92, 83.15, 61.22, 45.47, 35.39, 34.34, 24.91, 24.85, 24.56. ^{11}B NMR (160 MHz, DMSO) δ 22.53,

11.21. HRMS (ESI) m/z cal. for $(\text{M} + \text{NH}_4)^+$ 659.3841, found 659.3869.

6-methyl-2-(3-(phenylethynyl)oxiran-2-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**15a**):⁴

According's to the **general procedure G**, white pale white-yellow solid, 59% yield. ^1H NMR (400

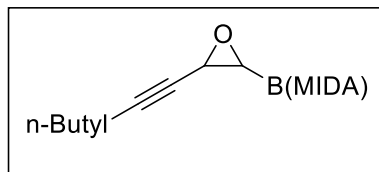


MHz, CDCl_3) δ 7.44 (dd, $J = 5.4, 1.9$ Hz, 2H), 7.33-7.28 (m, 3H), 4.06 (dd, $J = 17.2, 7.2$ Hz, 2H), 3.92 (d, $J = 17.2$ Hz, 1H), 3.81 (d, $J = 17.2$ Hz, 1H), 3.64 (d, $J = 2.8$ Hz, 1H), 3.15 (s, 3H), 2.64 (d, $J = 2.8$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 168.10, 166.82, 131.91,

128.78, 128.33, 121.97, 86.31, 83.53, 62.17, 62.11, 46.25, 44.57.

2-(3-(hex-1-yn-1-yl)oxiran-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**15b**):⁴

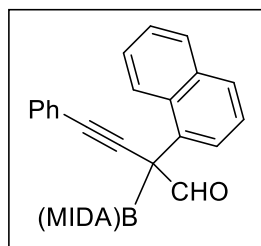
According's to the **general procedure G**, colourless oil, 59% yield. ^1H NMR (400 MHz, CDCl_3) δ



3.92 (m, 4H), 3.43 (q, $J = 1.6$ Hz, 1H), 3.15 (s, 3H), 2.48 (d, $J = 2.8$ Hz, 1H), 2.23 (t, $J = 6.8$ Hz, 2H), 1.53-1.27 (m, 4H), 0.92 (d, $J = 7.6$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.62, 166.28, 84.87, 62.07, 61.99, 46.03, 44.74, 30.42, 21.89, 18.39, 13.52.

2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-(naphthalen-1-yl)-4-phenylbut-3-ynal (**16a**):

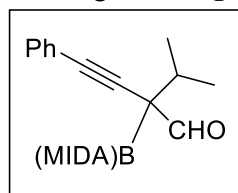
According's to the **general procedure G**, white solid, 56% yield. ^1H NMR (500 MHz, CDCl_3) δ 9.57



(s, 1H), 8.32 (d, $J = 8.5$ Hz, 1H), 7.92-7.75 (m, 4H), 7.52-7.40 (m, 4H), 7.37-7.32 (m, 2H), 7.32-7.23 (m, 3H), 3.95-3.77 (m, 4H), 3.07 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 198.41, 166.71, 166.62, 134.72, 132.95, 132.11, 131.42, 130.60, 129.54, 129.32, 129.16, 128.88, 128.65, 126.08, 125.67, 125.41, 122.15, 90.39, 87.19, 63.51, 63.41, 47.22, 29.69. ^{11}B NMR (160 MHz, CDCl_3) δ 10.82. HRMS (ESI) m/z cal. for $(\text{M} + \text{NH}_4)^+$ 443.1773 found 443.1791.

2-isopropyl-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-4-phenylbut-3-ynal (**16b**):

According's to the **general procedure G**, white solid, 55% yield. ^1H NMR (400 MHz, CDCl_3) δ 9.72

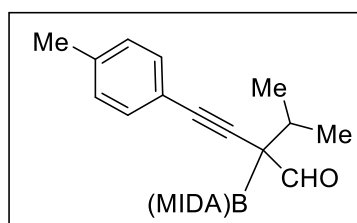


(s, 1H), 7.42-7.39 (m, 2H), 7.32-7.30 (m, 3H), 4.04-3.95 (m, 3H), 3.79 (d, $J = 16.9$ Hz, 1H), 3.04 (s, 3H), 2.58 (m, 1H), 1.24 (d, $J = 5.88$ Hz, 3H), 1.15 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 203.49, 166.58, 166.31, 133.66, 131.53, 130.19, 128.55, 122.61, 88.37, 86.87, 62.95, 46.53, 33.40, 20.13,

19.94. ^{11}B NMR (160 MHz, CDCl_3) δ 10.27. HRMS (ESI) m/z cal. for $(\text{M} + \text{NH}_4)^+$ 359.1773 found 359.1767.

2-isopropyl-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-4-(p-tolyl)but-3-ynal (**16c**):

According's to the **general procedure G**, white solid, 60% yield. ^1H NMR (400 MHz, CDCl_3) δ 9.73

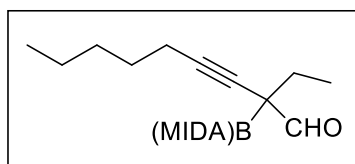


(s, 1H), 7.29 (t, $J = 7.84$ Hz, 2H), 7.14 (d, $J = 7.8$ Hz, 2H), 4.05 (d, $J = 15.9$ Hz, 1H), 3.88-3.83 (m, 2H), 3.75 (d, $J = 16.7$ Hz, 1H), 3.05 (s, 3H), 2.64-2.57 (m, 1H), 2.36 (s, 3H), 1.25 (d, $J = 6.8$ Hz, 3H), 1.19 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 203.60, 166.65, 166.31, 138.76, 131.43, 129.40, 129.31, 119.45, 88.42, 86.02, 62.90,

62.87, 46.47, 33.40, 21.47, 20.16, 19.97. ^{11}B NMR (160 MHz, CDCl_3) δ 10.89. HRMS (ESI) m/z cal. for $(\text{M} + \text{NH}_4)^+$ 373.1929 found 373.1947.

2-ethyl-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)non-3-ynal (**16d**):

According to the **general procedure G**, white solid, 80% yield. ¹H NMR (500 MHz, DMSO) δ 9.46



(s, 1H), 4.40 (d, *J* = 15 Hz, 1H), 4.29 (d, *J* = 15 Hz, 1H), 3.94 (d, *J* = 17.0 Hz, 2H), 2.99 (s, 3H), 2.22 (t, *J* = 14 Hz, 2H), 2.09-2.02 (m, 2H), 1.66-1.73 (m, 1H), 1.46-1.40 (m, 2H), 1.36-1.24 (m, 4H), 0.88-0.82 (m, 6H). ¹³C NMR (126 MHz, DMSO) δ 202.54, 168.63,

168.14, 87.53, 78.05, 63.25, 63.20, 46.70, 30.86, 28.43, 24.33, 22.02, 18.57, 14.27, 10.59. ¹¹B NMR (160 MHz, DMSO) δ 10.87. HRMS (ESI) *m/z* cal. for (M + NH₄)⁺ 339.2086 found 339.2077.

F. Crystallographic Data and Structure Refinements:

Good quality single crystals of each compound were sorted out with the help of a polarizing microscope and immersed in paratone oil, which was then mounted on the tip of glass fiber and cemented using epoxy resin. The single-crystal XRD diffraction data were collected at 298 K on a Bruker AXS (D8 Quest System) X-ray diffractometer, equipped with a PHOTON 100 CMOS detector using graphite-monochromated Mo-K_α radiation (0.71073 Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. Bruker Apex III software was used for data collection, unit cell measurements, absorption corrections, scaling, and integration.⁵ The data were reduced and an empirical absorption correction was applied with the help of SAINTPLUS software and SADABS programs using XPREP, respectively.⁶ The structures were solved by the direct method using SHELXL-2014 in the WinGx programs. The WinGx package of programs was used to carry out the full-matrix least-squares refinement against the function $|F^2|$.⁷ For all the cases, non-hydrogen atoms were refined anisotropically. All other hydrogen atoms were geometrically fixed using the riding atom model and assigned fixed isotropic displacement parameters. The “ACTA” command was used to generate the Crystallographic Information File (CIF). The structural details of all the compounds are presented in **Table S2**. CCDC: 2298318, 2298319, 2298320, 2298321, 2298322 contain the crystallographic data of these compounds 4g, 6i, 4p, 7b, 21d respectively. These data are available from The Cambridge Crystallographic Data Center (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

Table S2: Crystal data and structure refinements for the molecules **4g**, **6i**, **4p**, **7b** and **21d**.

Entry	4i	6i	4s	9b	14d
Empirical formula	C ₁₈ H ₂₀ B N O ₄	C ₃₁ H ₃₇ B O ₂ Si	C _{11.50} H ₁₁ B _{0.5} N _{0.5} O ₂	C ₁₆ H ₁₅ B I N O ₆	C ₂₅ H ₄₂ B ₃ N O ₈
Formula weight	325.16	480.50	193.61	455.00	517.02
Temperature (K)	296(2)	296(2)	296(2)	296(2)	296(2)
Radiation	Mo (<i>k</i> _α)	Mo (<i>k</i> _α)	Mo (<i>k</i> _α)	Mo (<i>k</i> _α)	Mo (<i>k</i> _α)
Wave length (λ)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	triclinic	orthorhombic	monoclinic	orthorhombic

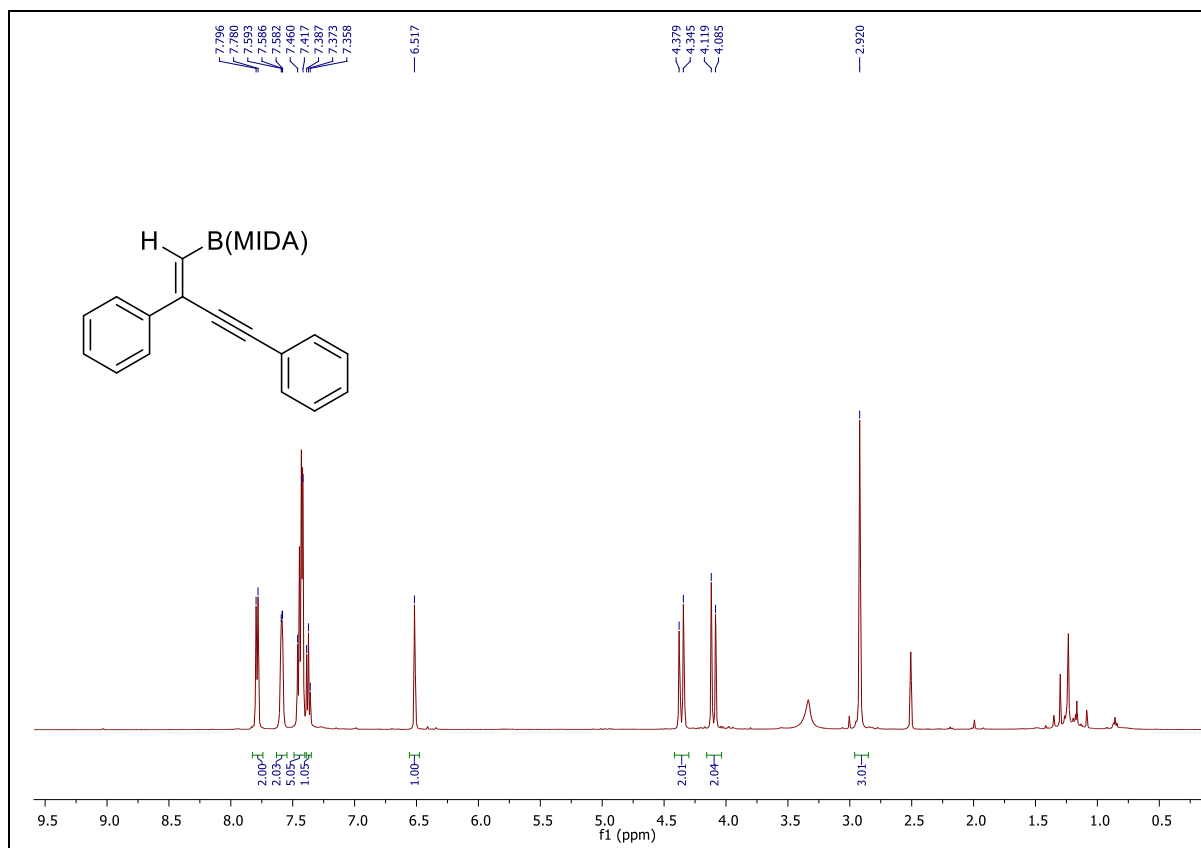
Space group	<i>Pbcn</i>	<i>P</i> $\bar{1}$	<i>Ccc2</i>	<i>P2₁/c</i>	<i>Pbca</i>
<i>a</i> [Å]	10.617(1)	10.562(6)	11.125(7)	19.623(4)	13.492(5)
<i>b</i> [Å]	12.426(1)	12.806(9)	35.01(2)	6.695(2)	16.205(6)
<i>c</i> [Å]	26.89(4)	13.142(1)	10.586(7)	13.524(3)	27.144(1)
α [°]	90	61.44(3)	90	89.84(3)	90
β [°]	90	71.55(3)	90	74.91(3)	90
γ [°]	90	72.89(3)	90	89.96(3)	90
Volume [Å ³]	3548(1)	1459.1(1)	4123(5)	1715.4(8)	5935(4)
Z	8	2	16	4	8
Density (calculated) [Mg m ⁻³]	1.217	1.094	1.248	1.762	1.157
Absorption coefficient [mm ⁻¹]	0.085	0.104	0.084	1.899	0.083
<i>F</i> (000)	1376	516	1632	896	2224
Refl. used [<i>I</i> > 2 σ (<i>I</i>)]	7789	6456	6895	4703	19938
Independent reflections	1606	1967	2597	2169	4625
<i>R</i> _{int}	0.2360	0.1464	0.1563	0.0992	0.2157
Refinement method	full-matrix least squares on <i>F</i> ²	full-matrix least squares on <i>F</i> ²	full-matrix least squares on <i>F</i> ²	full-matrix least squares on <i>F</i> ²	full-matrix least squares on <i>F</i> ²
GOF	0.888	1.038	0.943	0.998	1.228
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0954 <i>wR</i> ₂ = 0.2111	<i>R</i> ₁ = 0.1287 <i>wR</i> ₂ = 0.3592	<i>R</i> ₁ = 0.0643 <i>wR</i> ₂ = 0.1207	<i>R</i> ₁ = 0.0496 <i>wR</i> ₂ = 0.0847	<i>R</i> ₁ = 0.1592 <i>wR</i> ₂ = 0.4519
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.3803 <i>wR</i> ₂ = 0.3293	<i>R</i> ₁ = 0.2941 <i>wR</i> ₂ = 0.4548	<i>R</i> ₁ = 0.2312 <i>wR</i> ₂ = 0.1640	<i>R</i> ₁ = 0.1613 <i>wR</i> ₂ = 0.1078	<i>R</i> ₁ = 0.3775 <i>wR</i> ₂ = 0.5469
CCDC	2298318	2298319	2298320	2298321	2298322

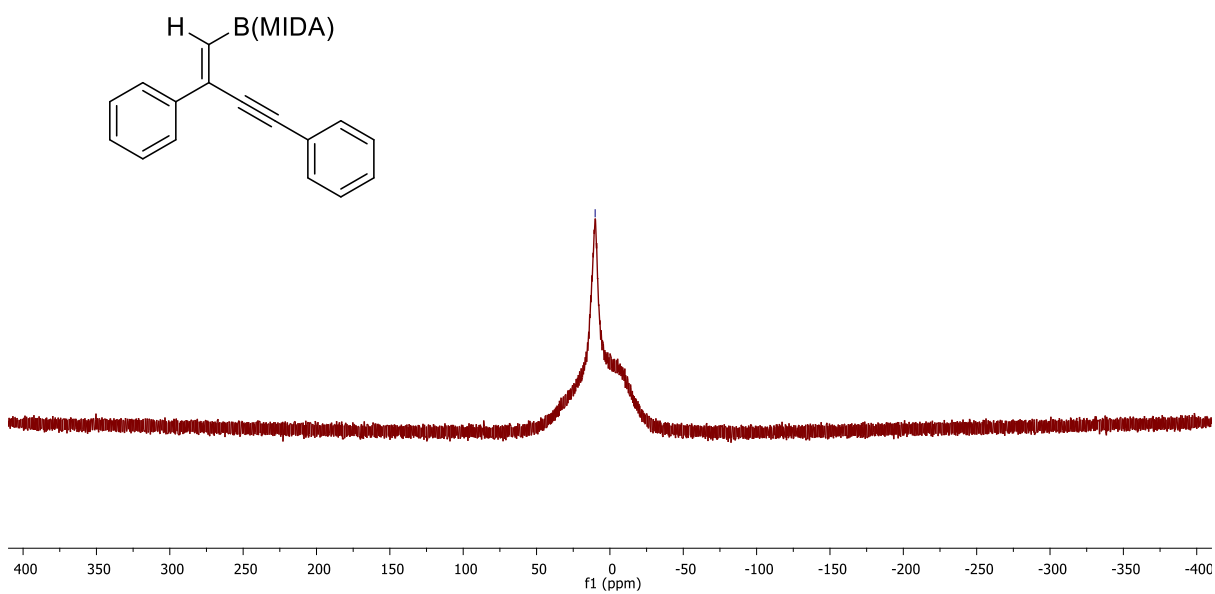
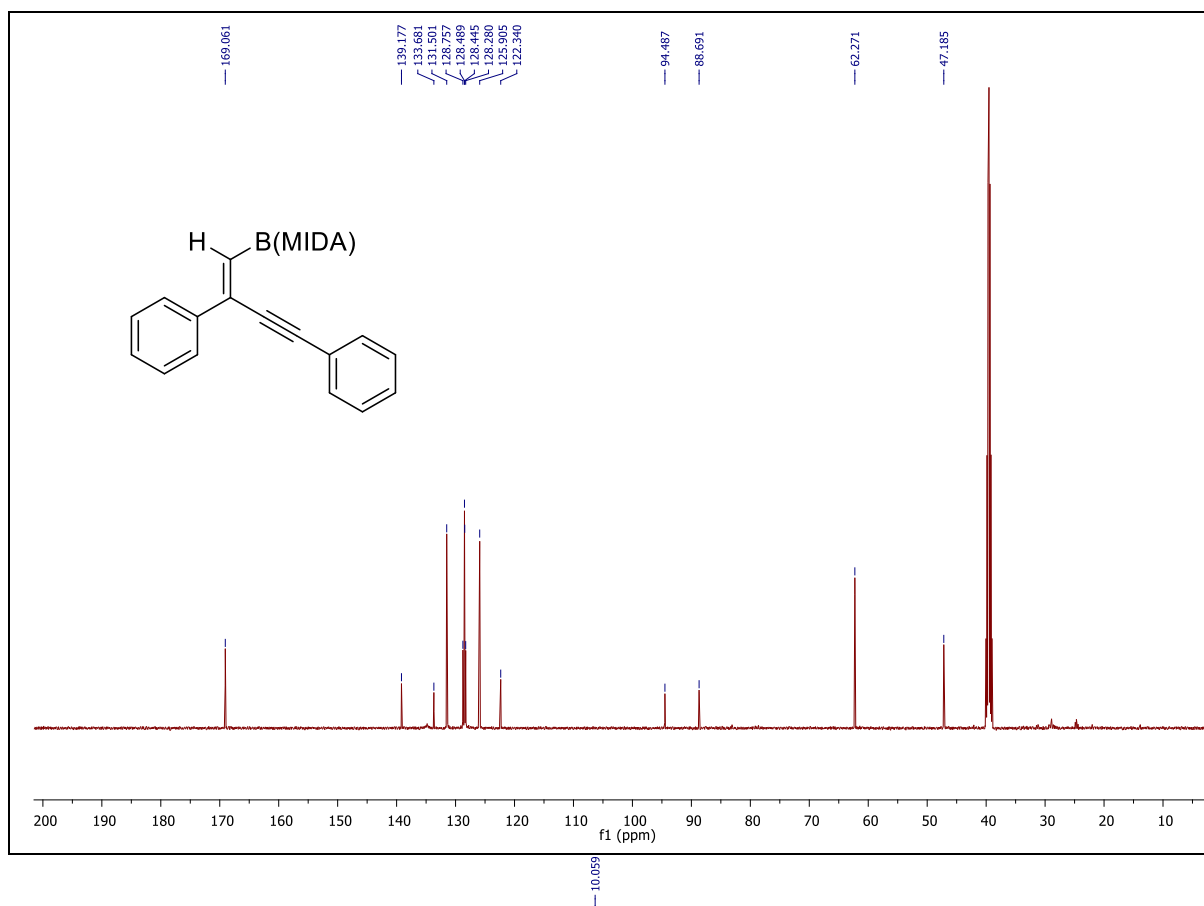
G. Reference

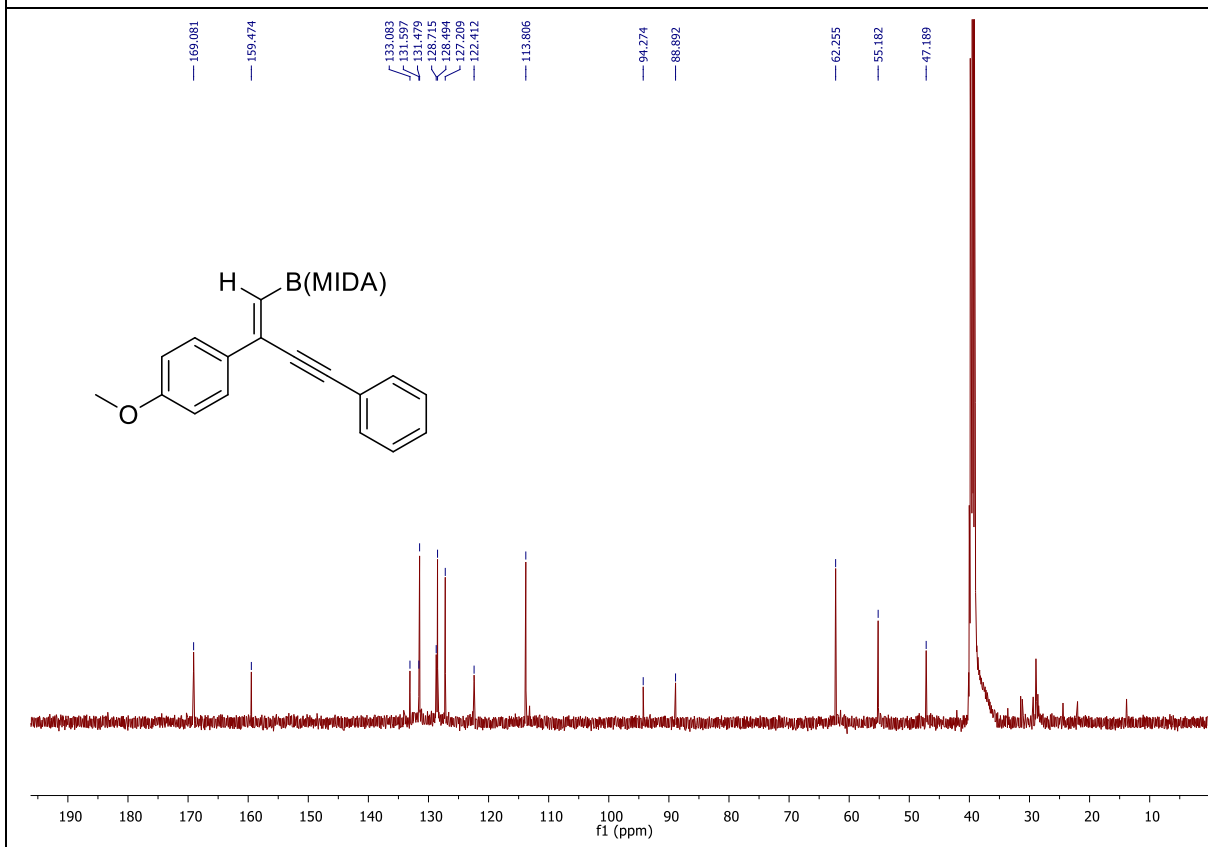
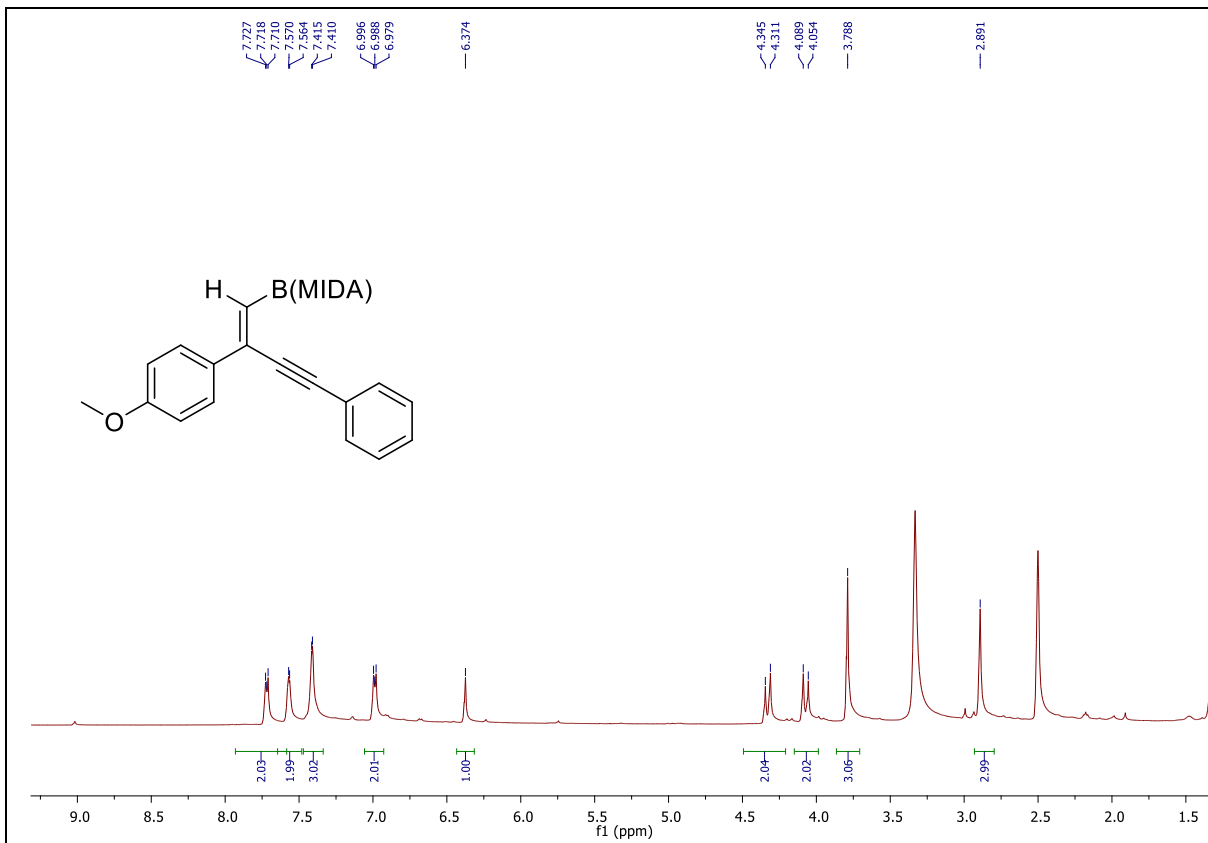
1. C. Hwang, W. Jo and S. H. Cho, *Chem. Commun.* 2017, **53**, 7573-7576.
2. H. Li, X. Shanguan, Z. Zhang, S. Huang, Y. Zhang and J. Wang, *Org. Lett.* 2014, **16**, 448-451.
3. C. Liu, X. Zhang, R. Wang and W. Wang, *Org. Lett.* 2010, **12**, 4948-4951.
4. R. K. Shiroodi, O. Koleda and V. Gevorgyan, *J. Am. Chem. Soc.* 2014, **136**, 13146–13149.
5. (a) Sheldrick, G. M. Siemens Area Correction Absorption Correction Program; University of Göttingen: Göttingen, Germany, **1994**; (b) Farrugia; L. J., WinGx suite for small-molecule single crystal crystallography. *J. Appl. Crystallogr.* **1999**, *32*, 837.
6. (a) SAINT+, 6.02ed, Bruker AXS, Madison, WI, **1999**; (b) XPREP, 5.1 ed. Siemens Industrial Automation Inc., Madison, WI, **1995**,

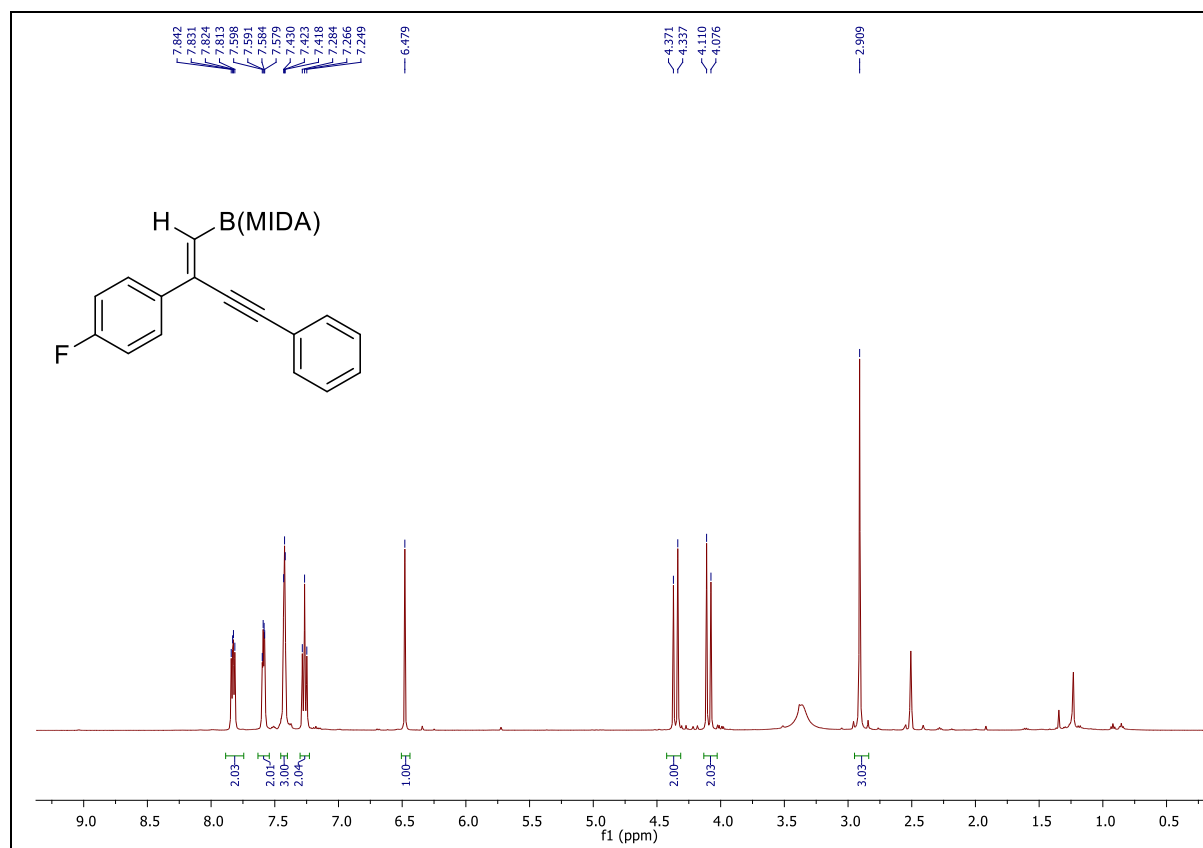
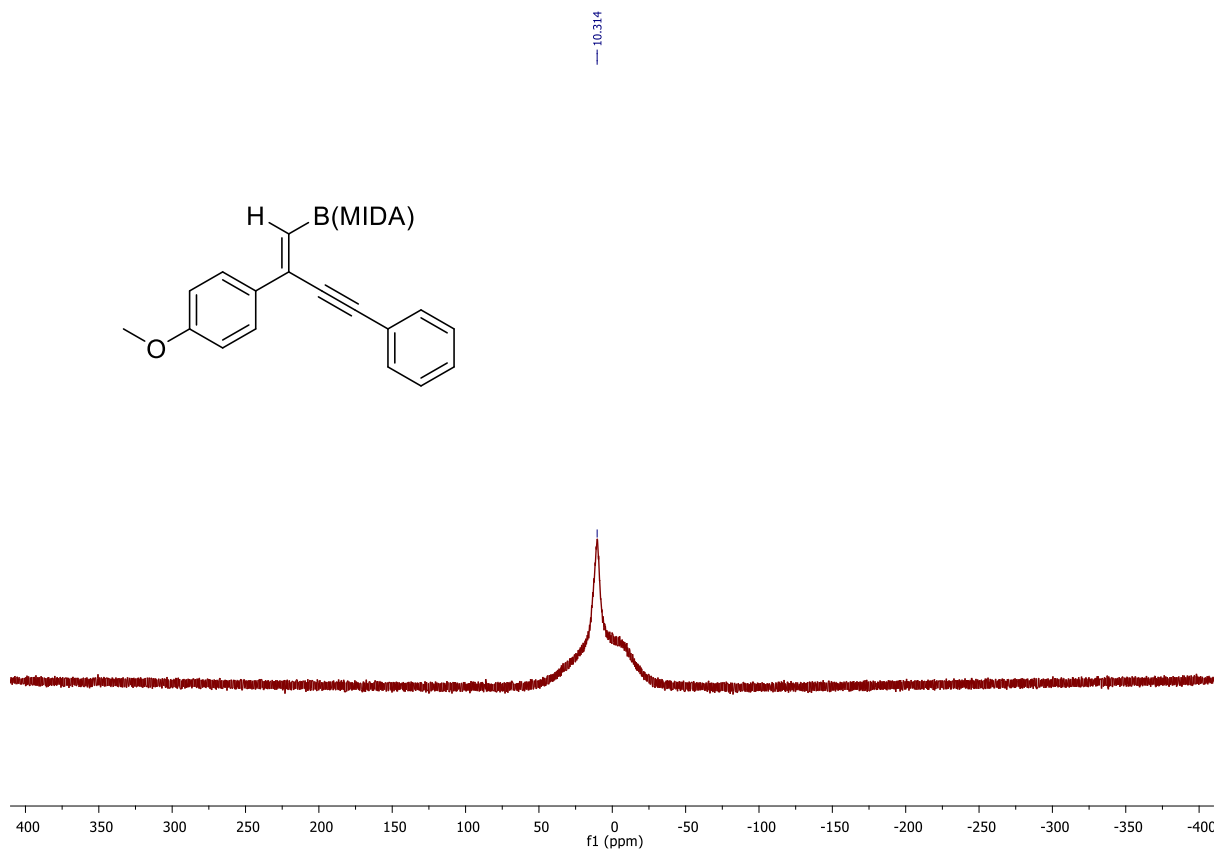
7. (a) Sheldrick; G. M., SHELXL-97 Program for Crystal Structure Solution and Refinement; University of Göttingen: Göttingen, Germany, **1997**; (b) G. M. Sheldrick, Crystal Structure Refinement with SHELXL. *Acta Cryst C* **2015**, *71*, 3–8.

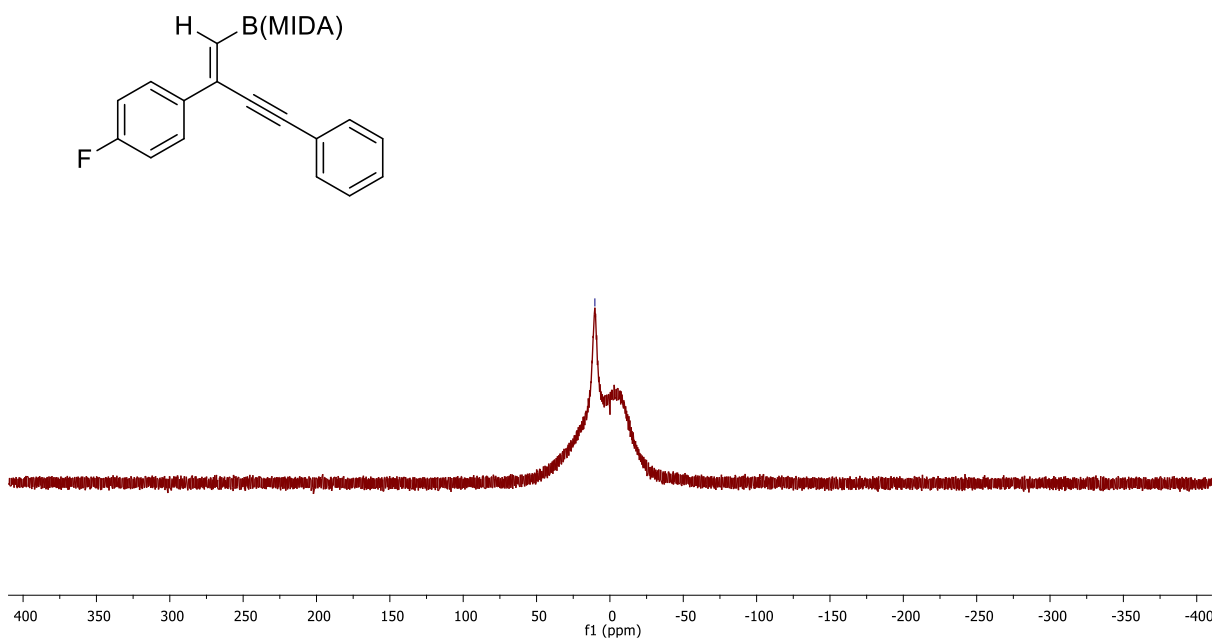
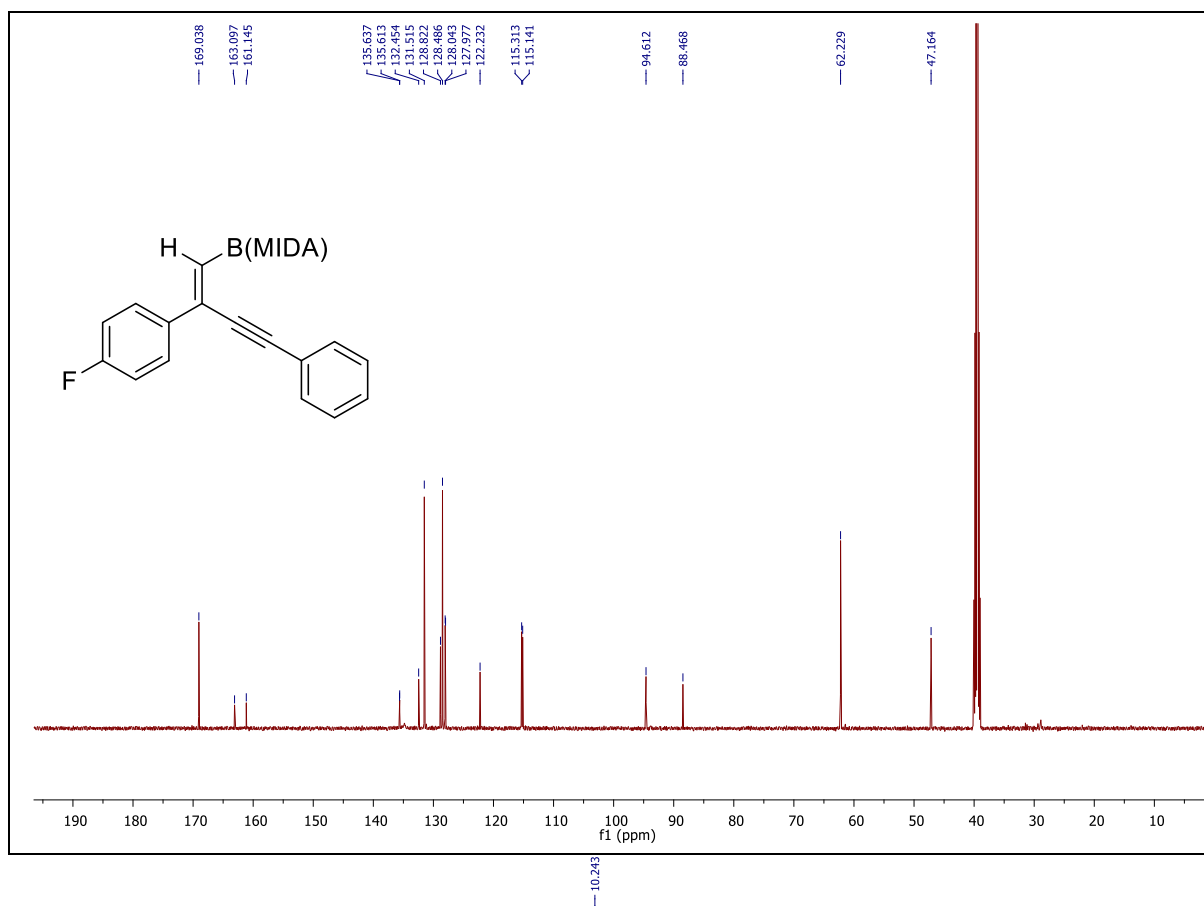
➤ **$^1\text{H-NMR}$ & $^{13}\text{C-NMR}$ Spectra:**

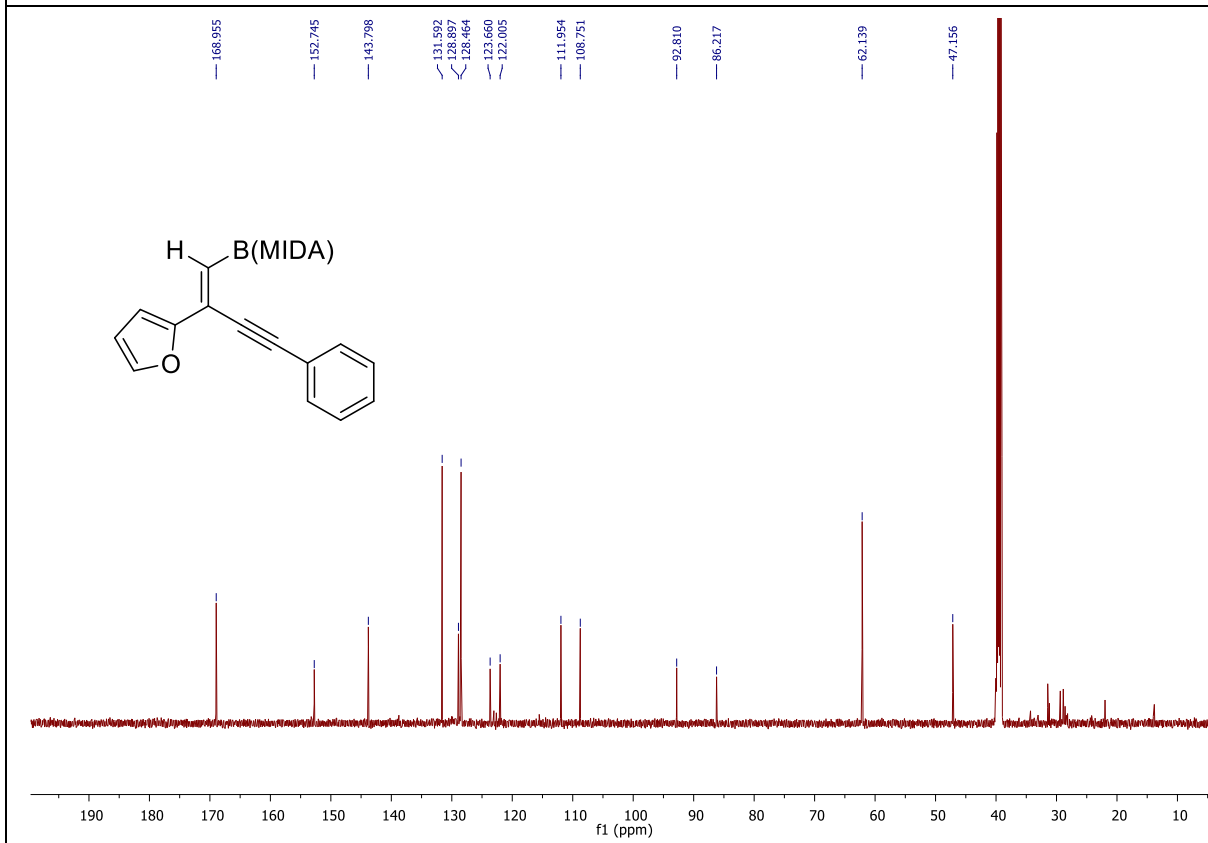
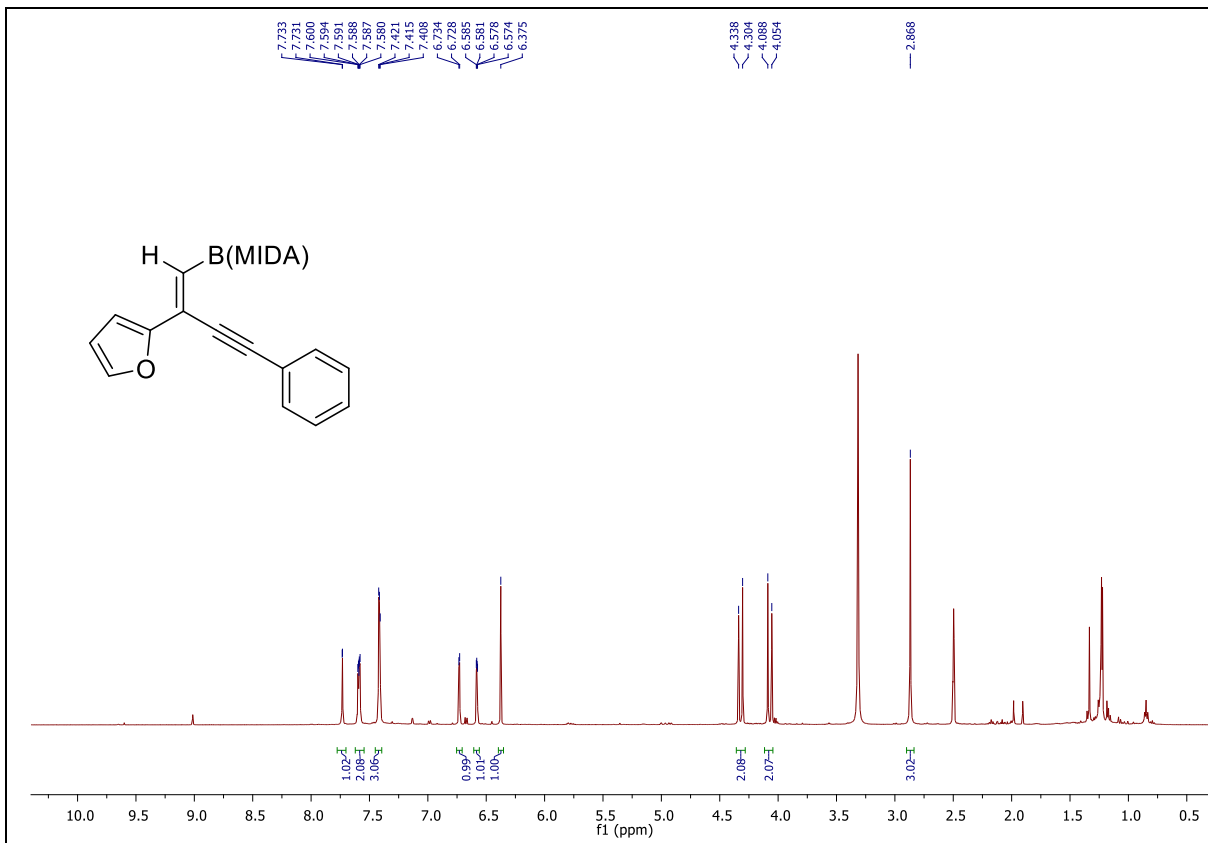


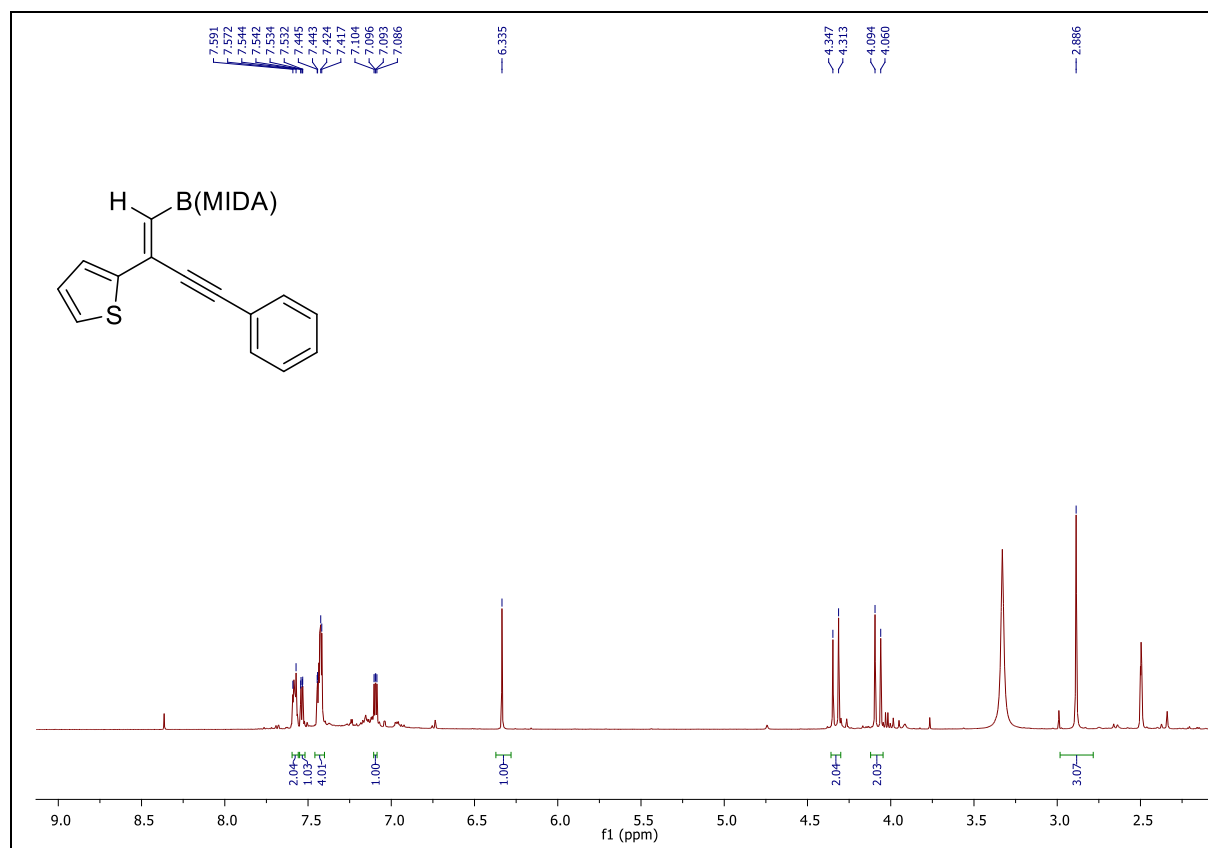
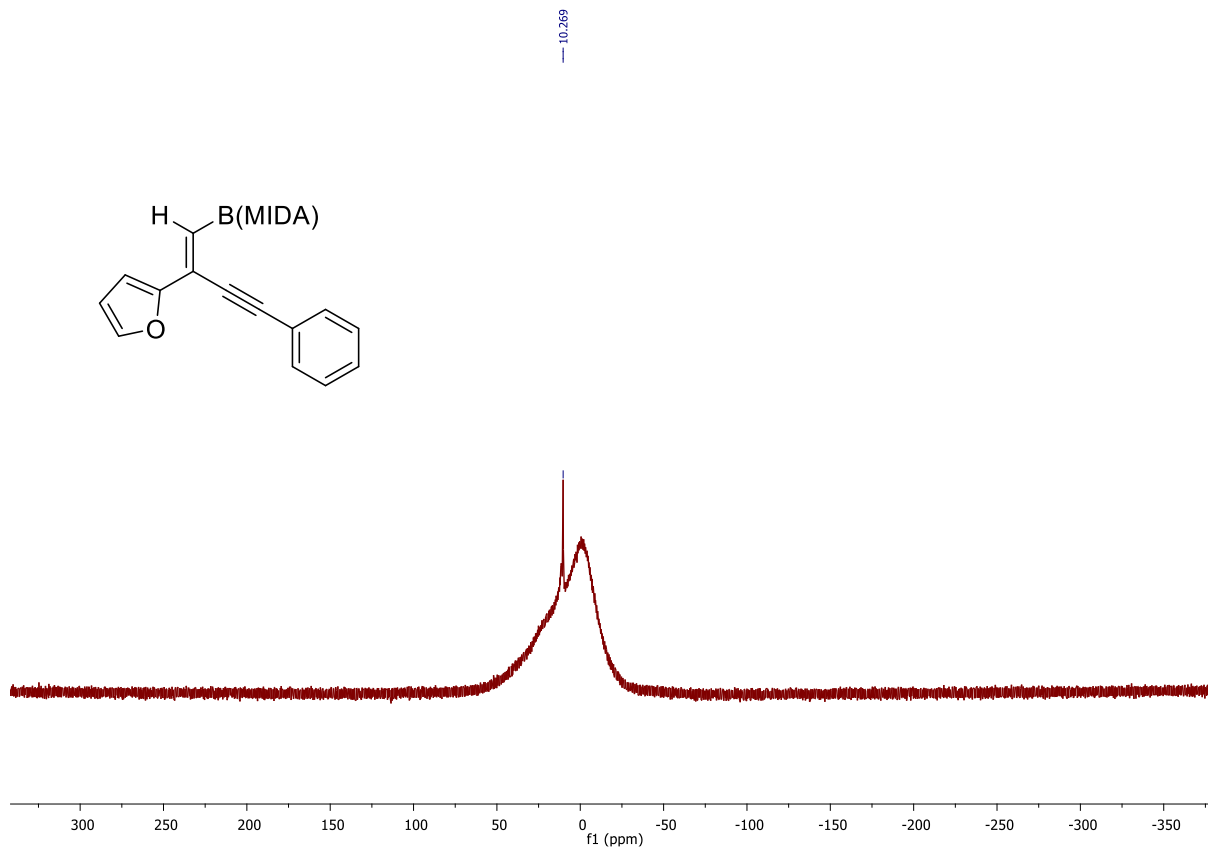












7.591
7.572
7.544
7.542
7.534
7.532
7.445
7.443
7.442
7.417
7.104
7.096
7.093
7.086

6.335

4.347
4.313
4.094
4.060

2.886

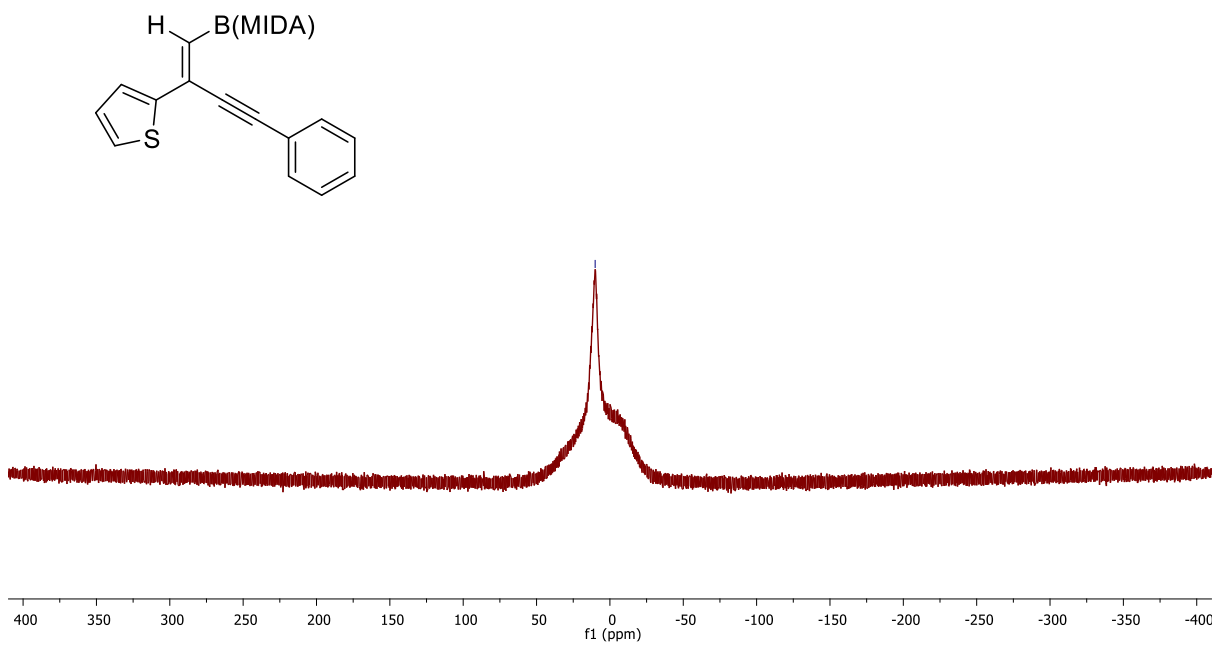
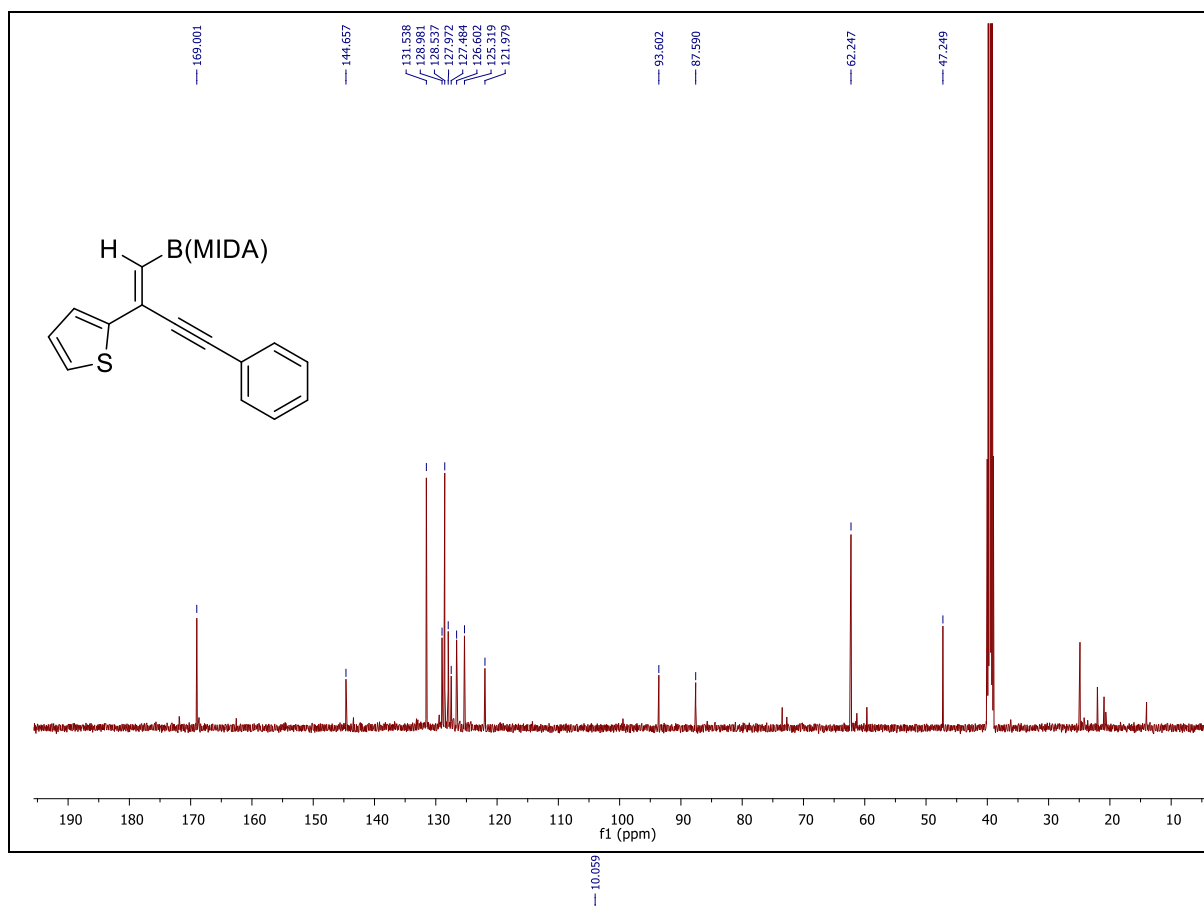
2.04
1.03
4.01

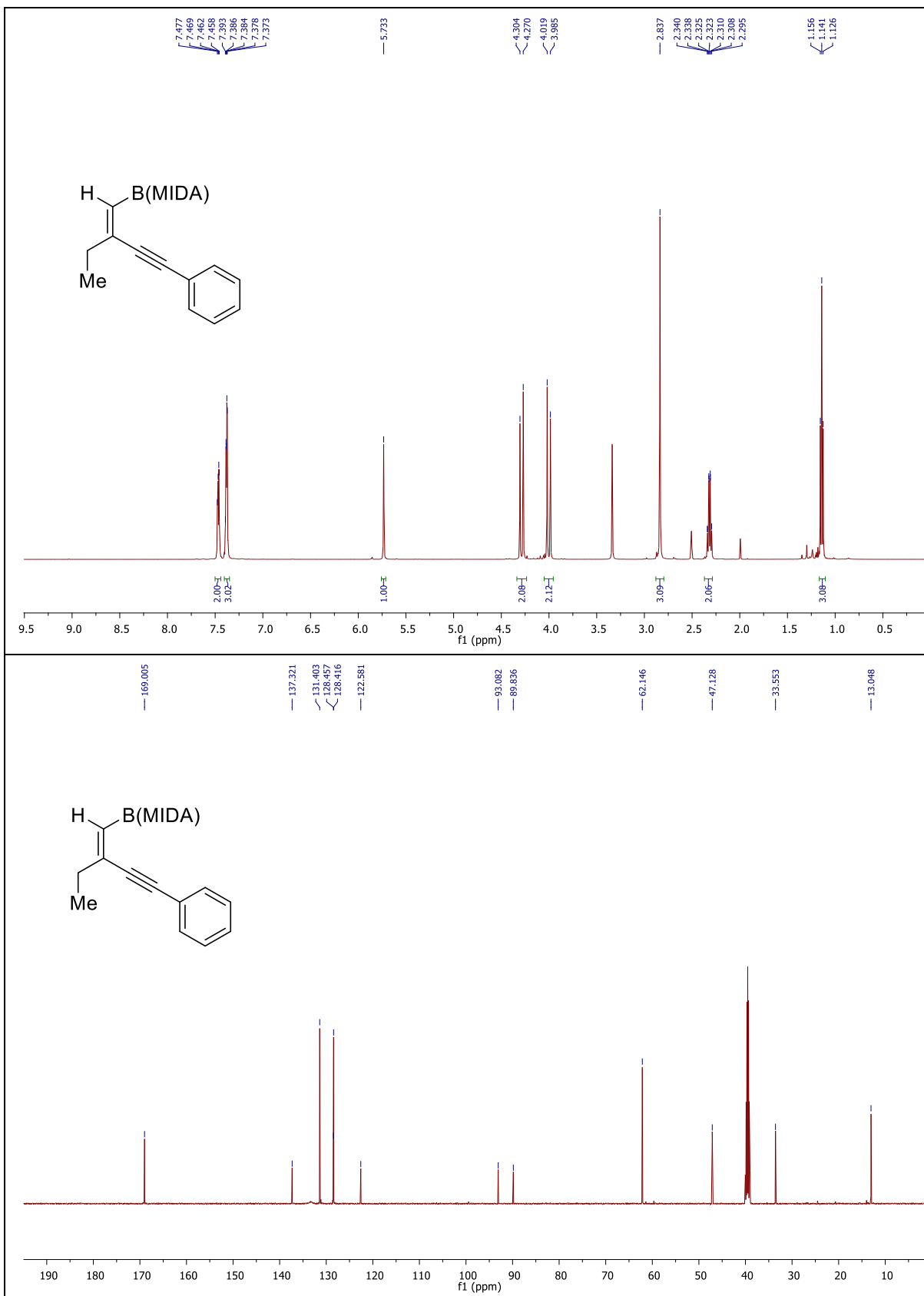
1.00

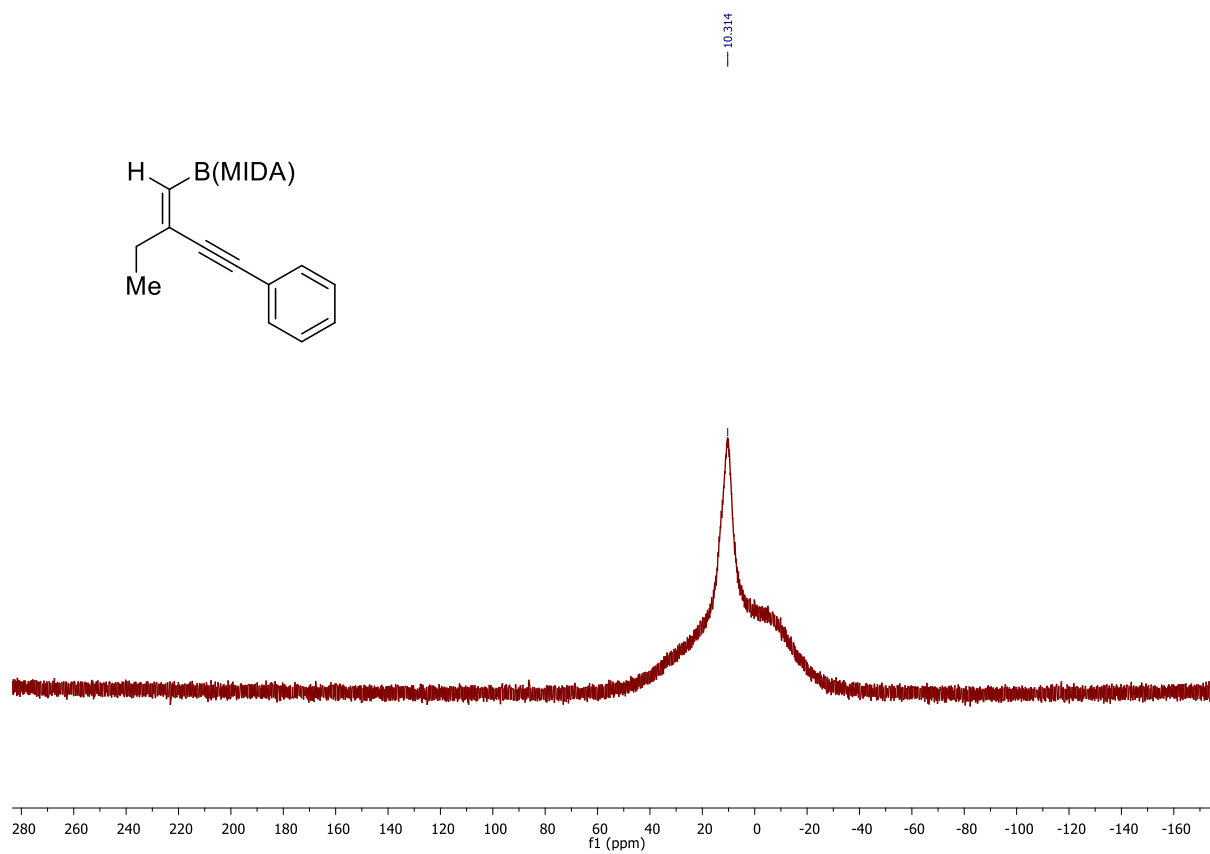
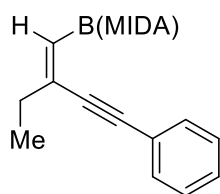
1.00

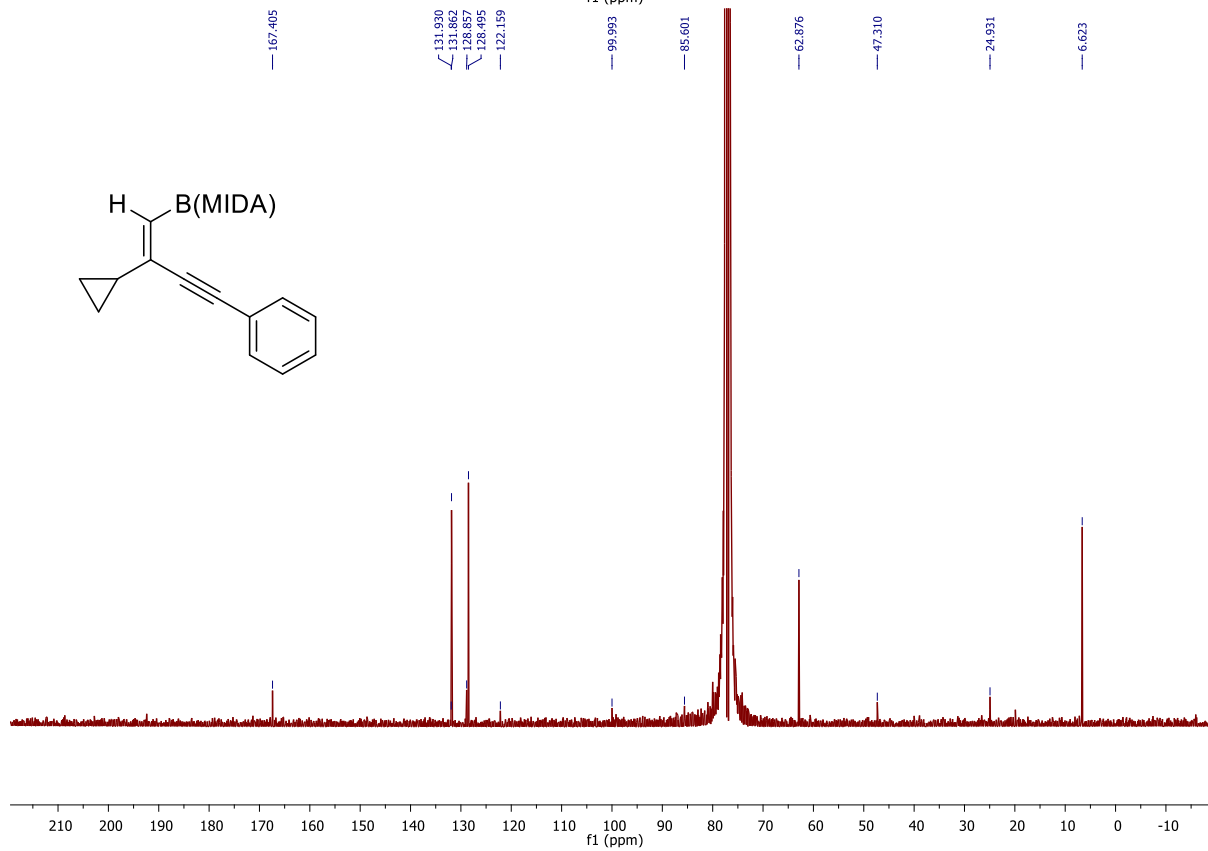
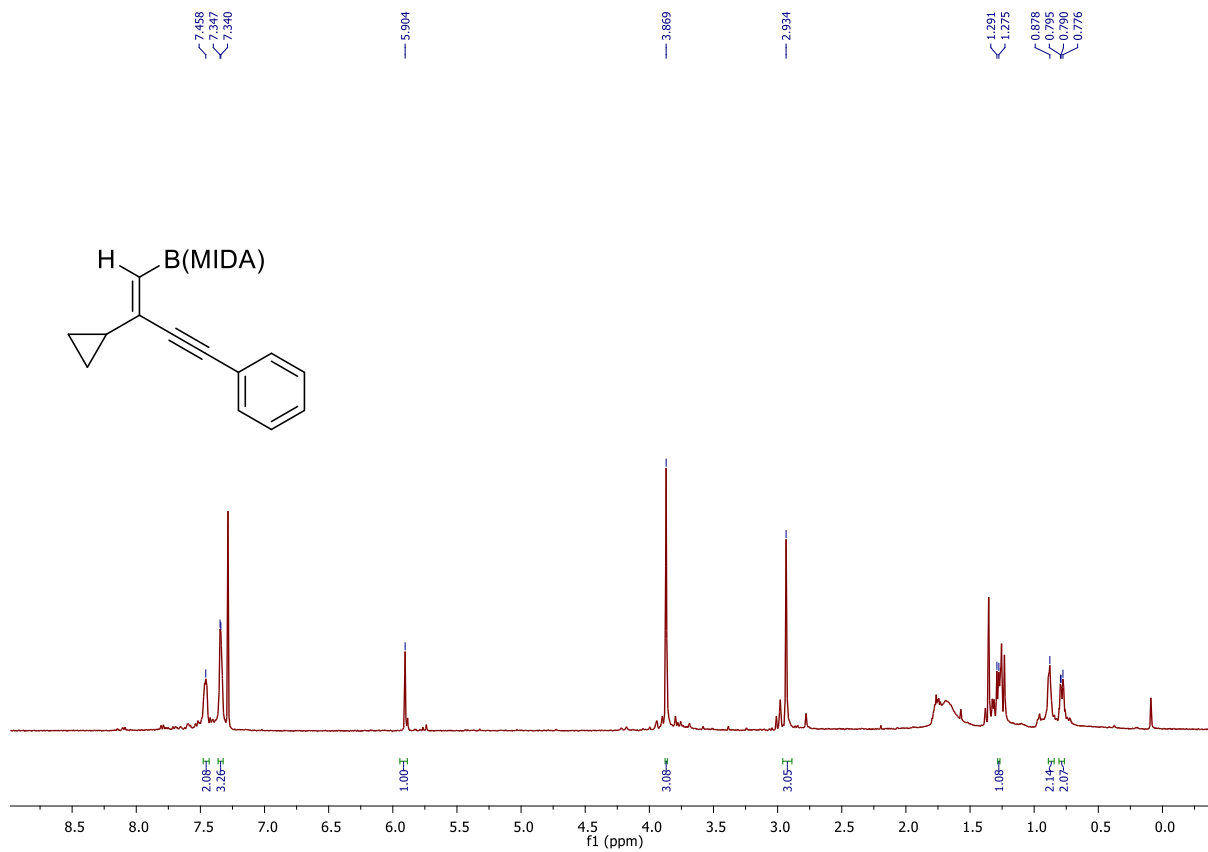
2.04
2.03

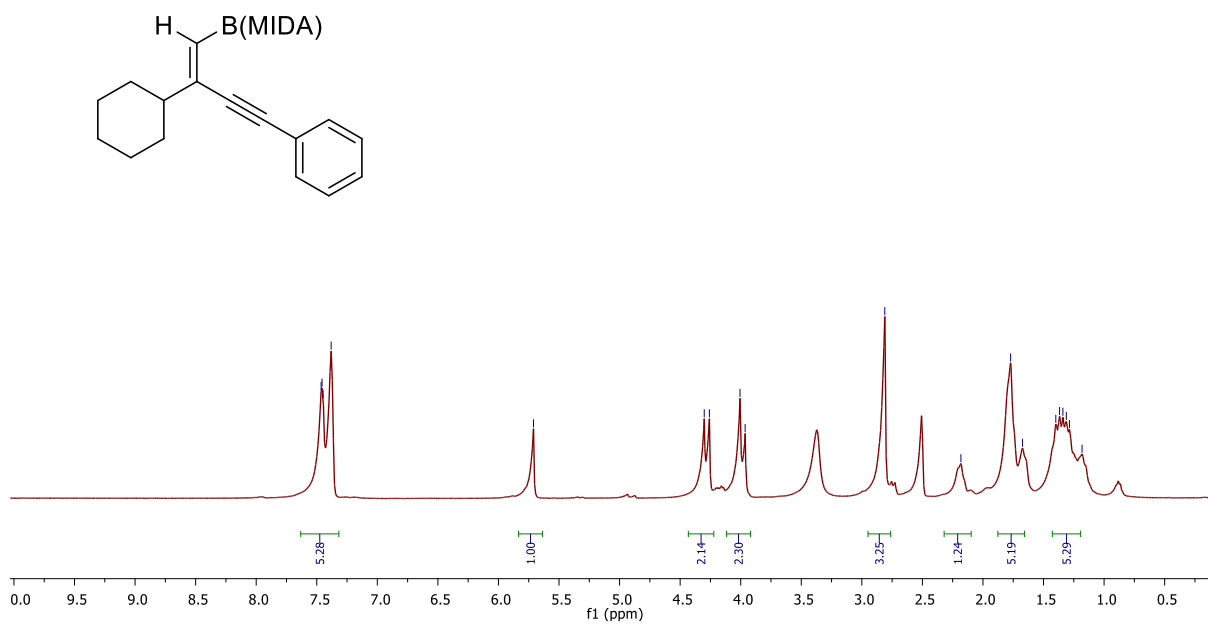
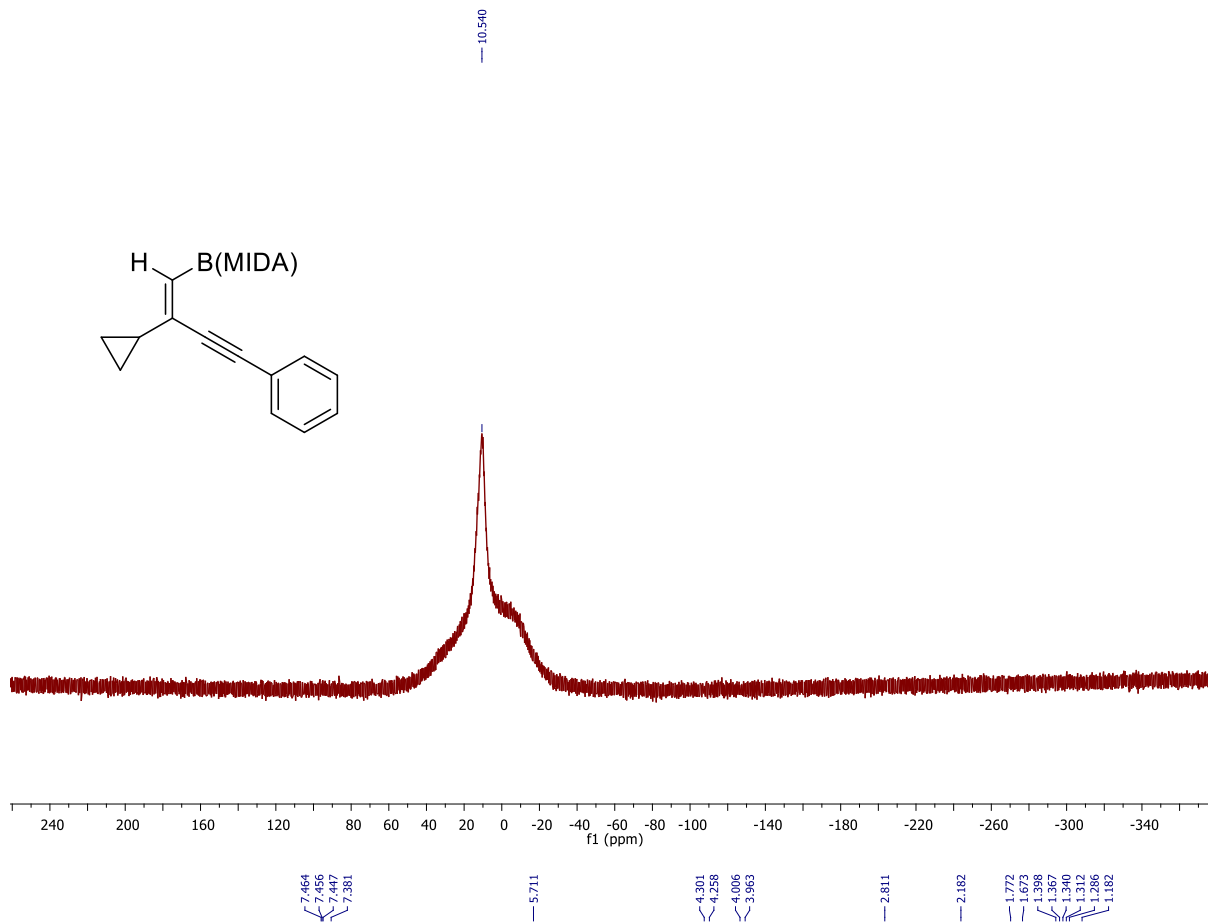
3.07

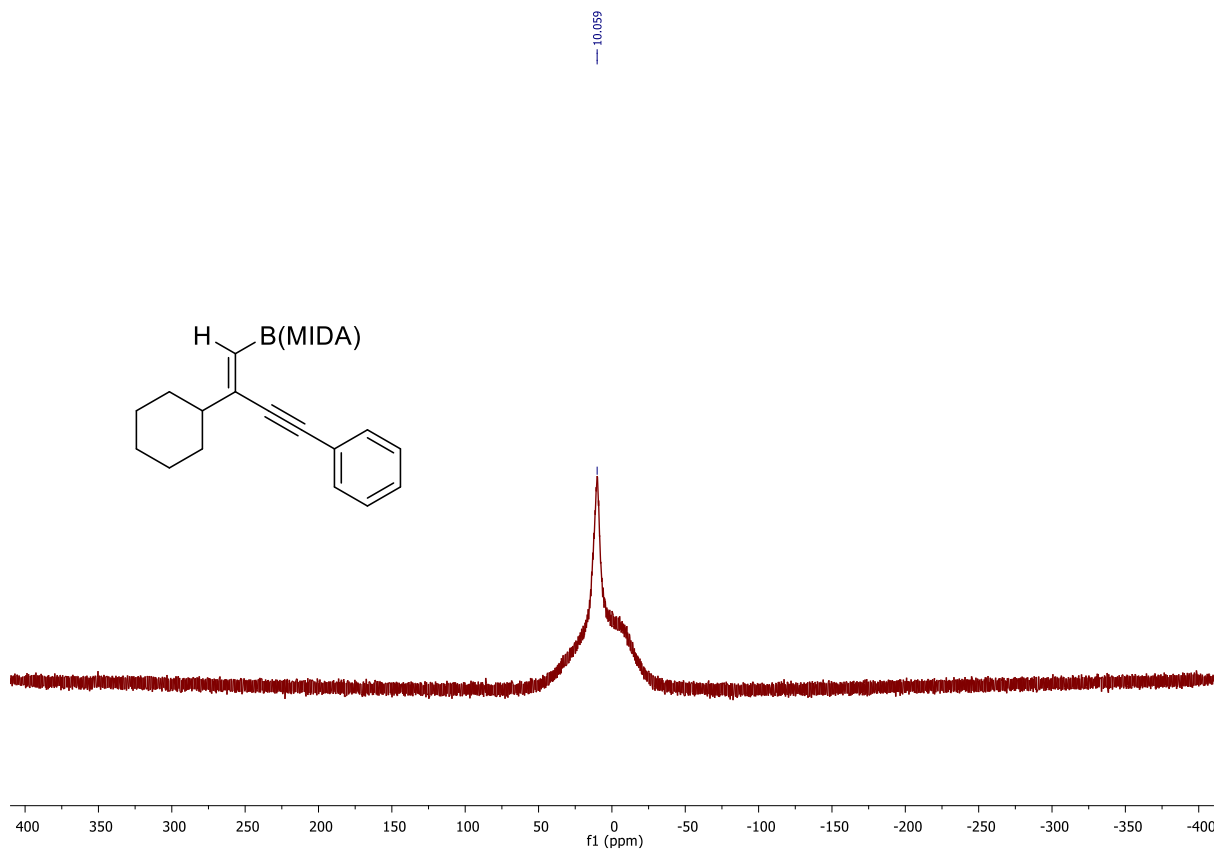
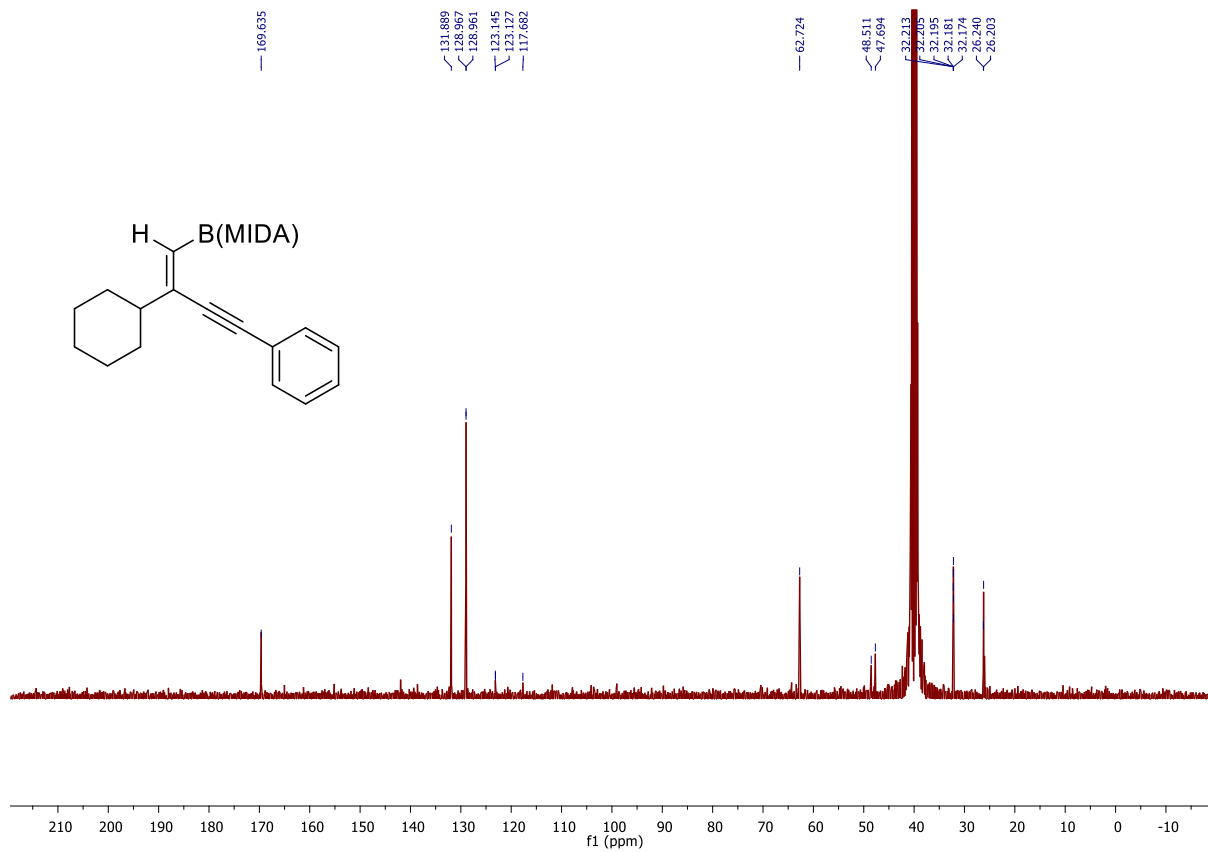


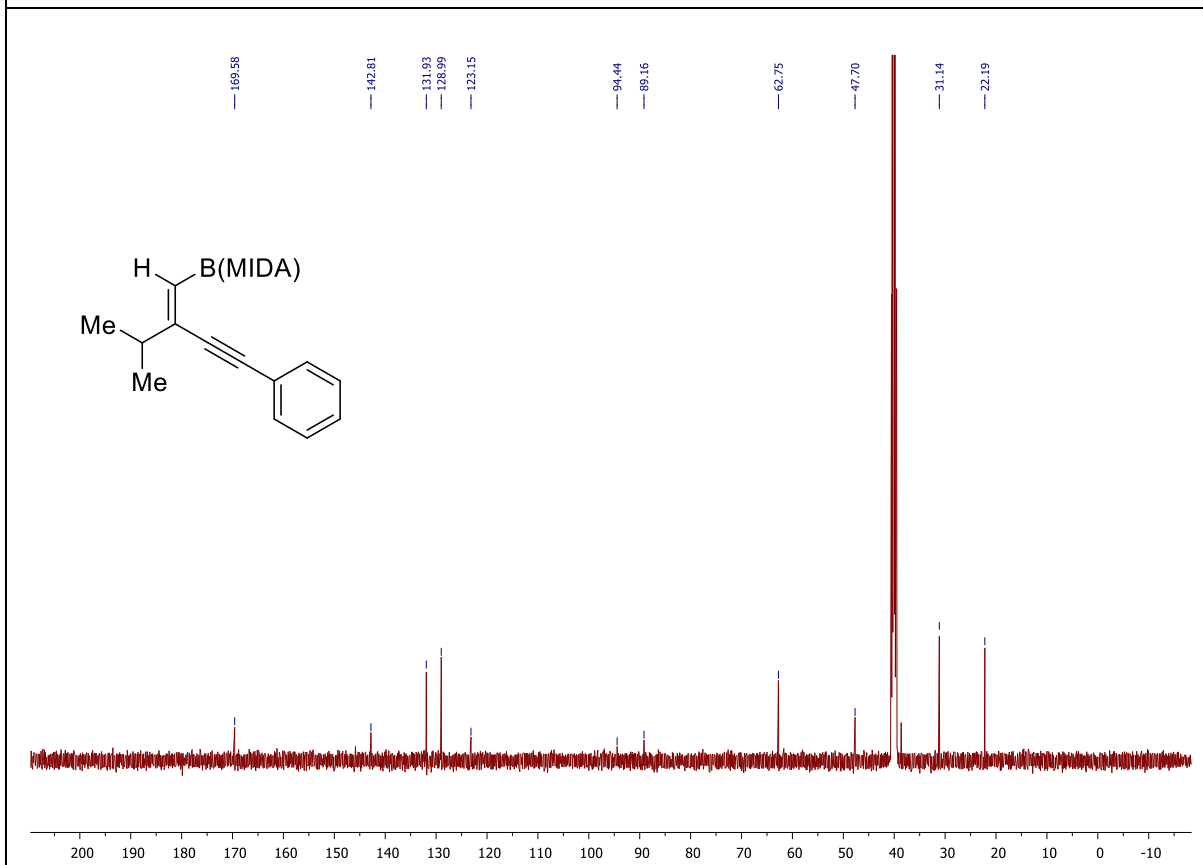
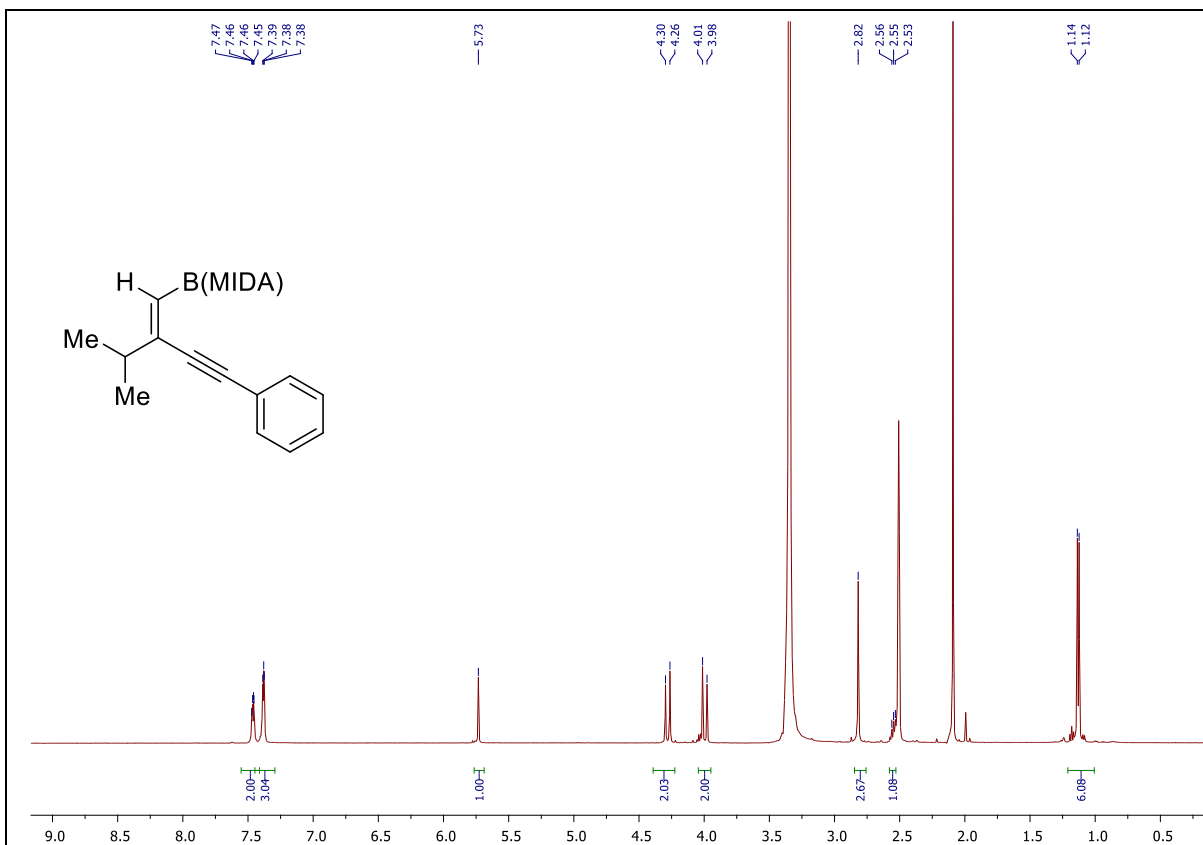


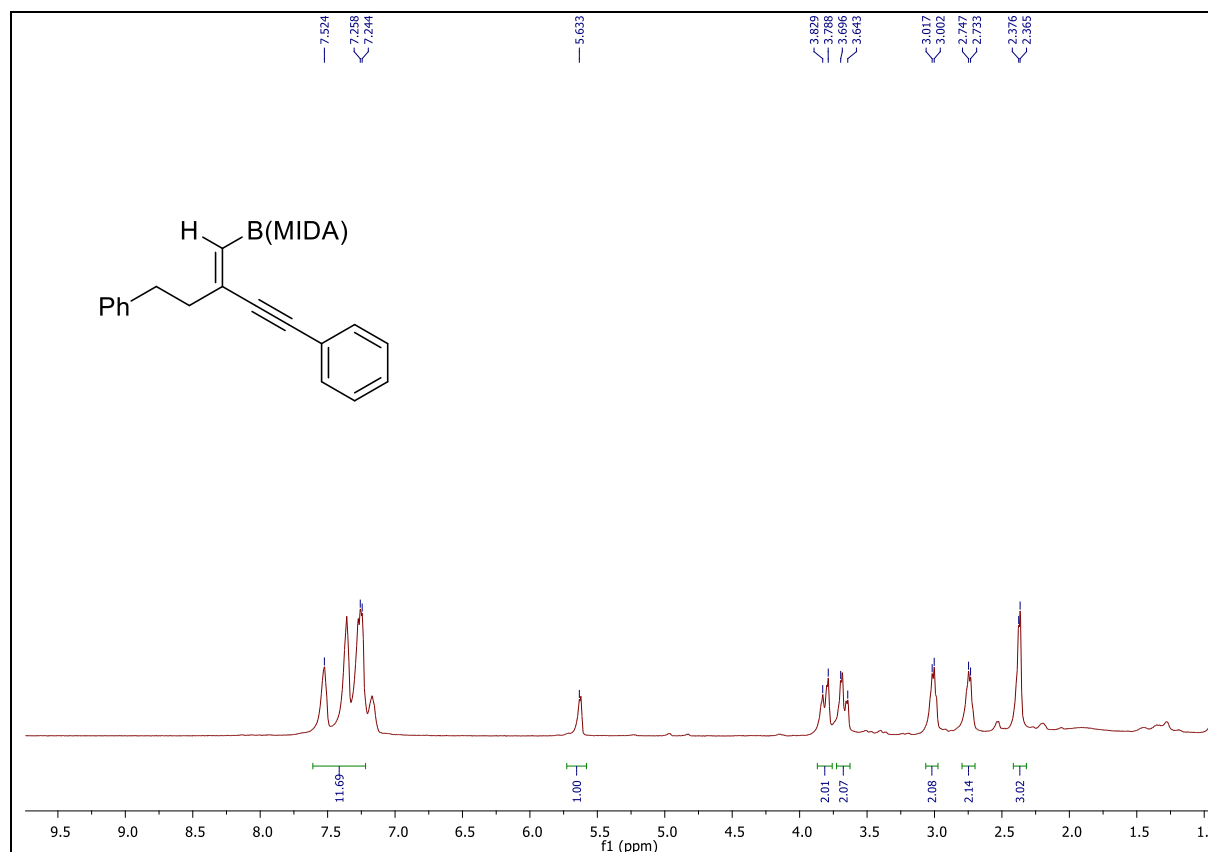
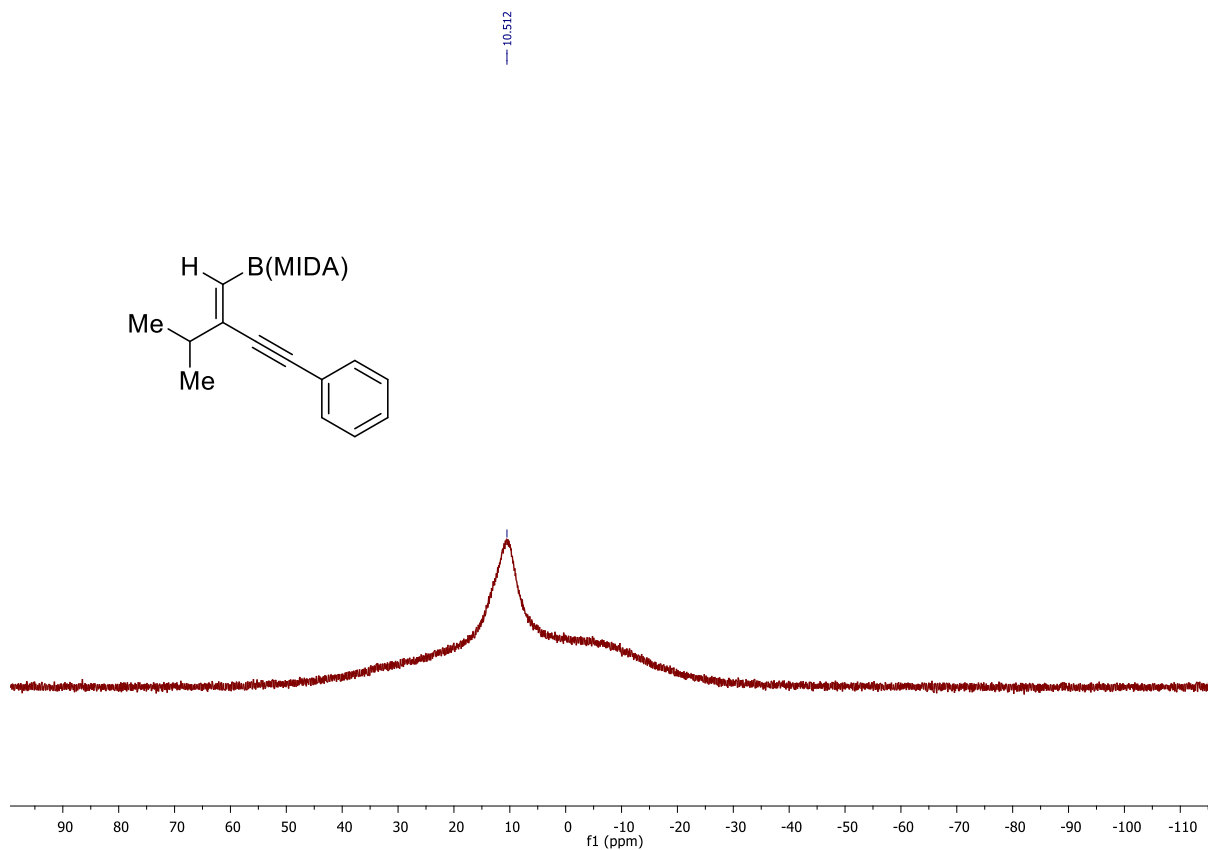


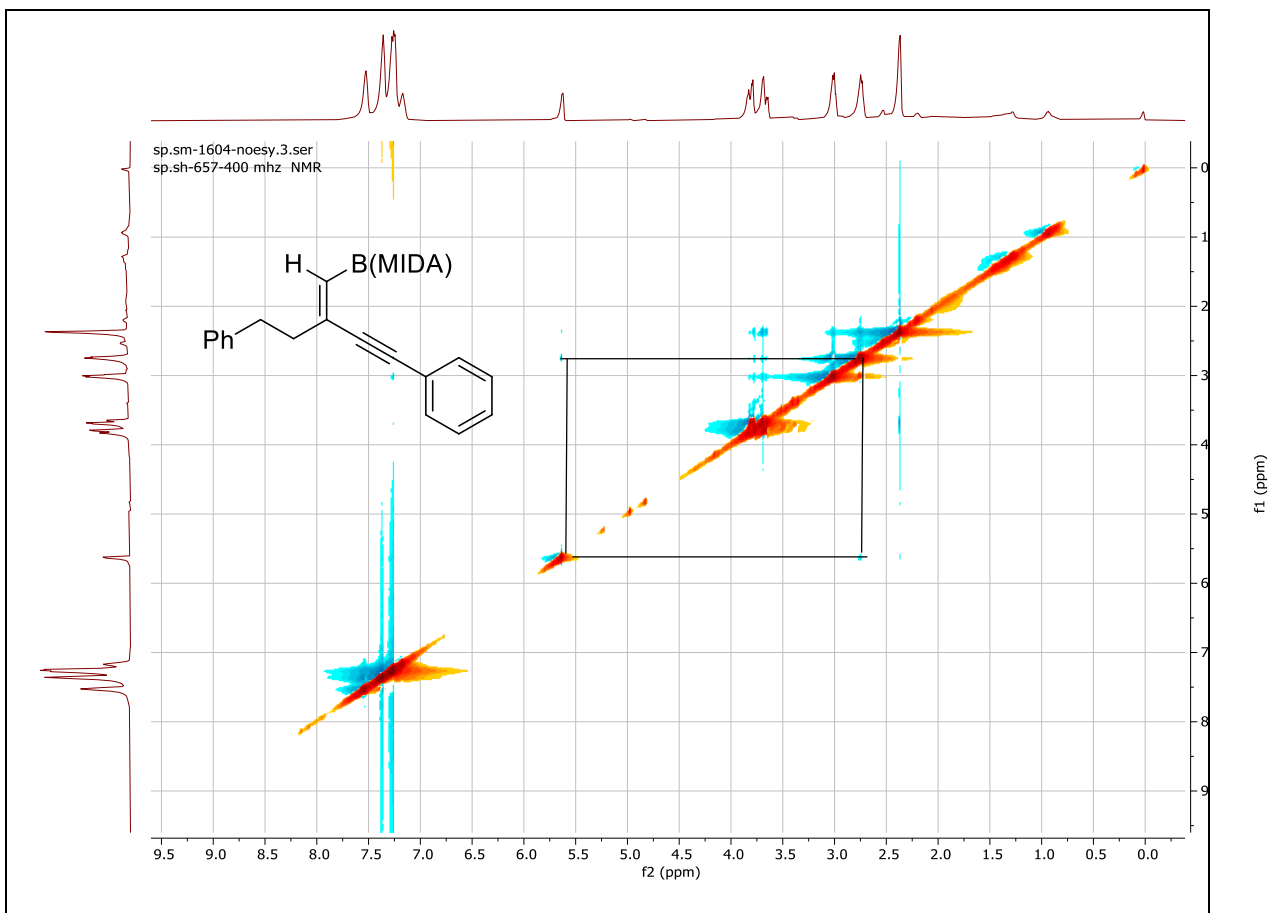
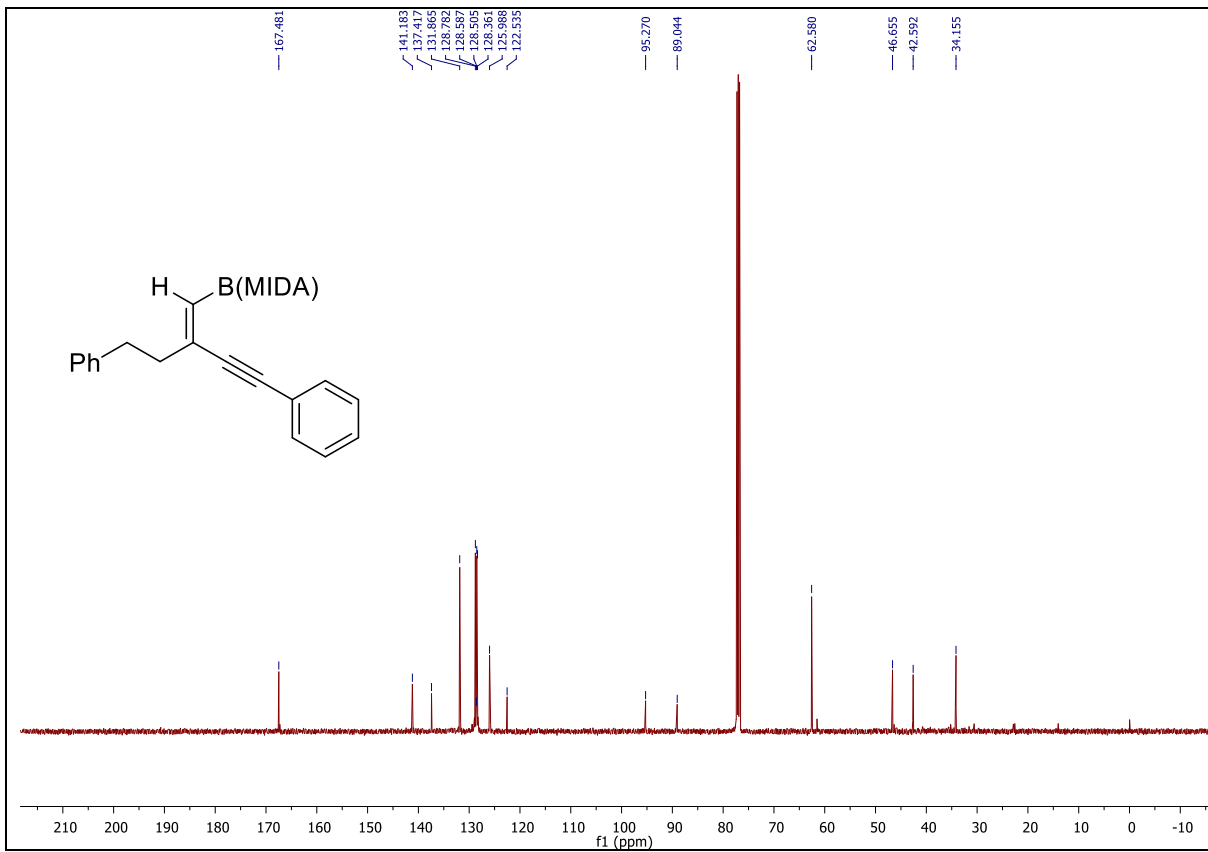


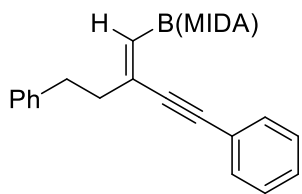




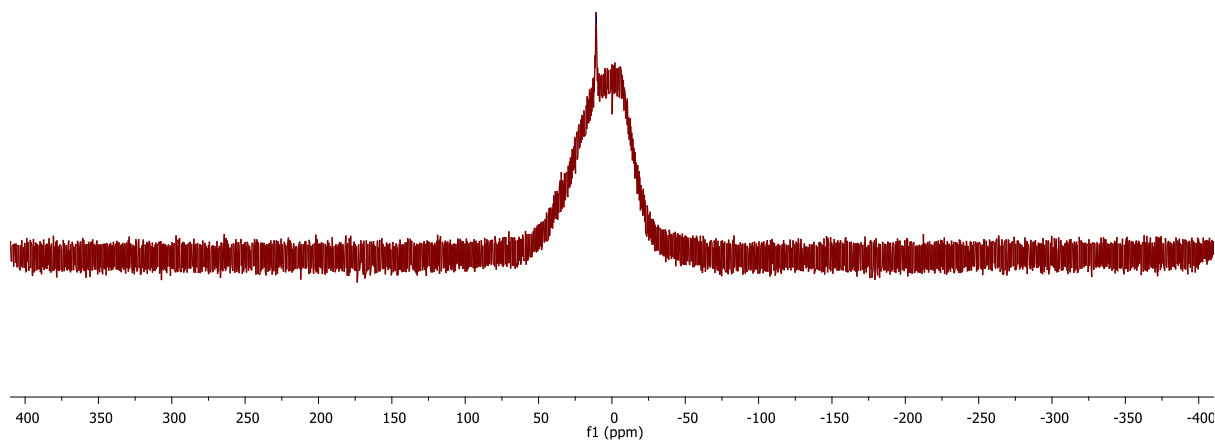


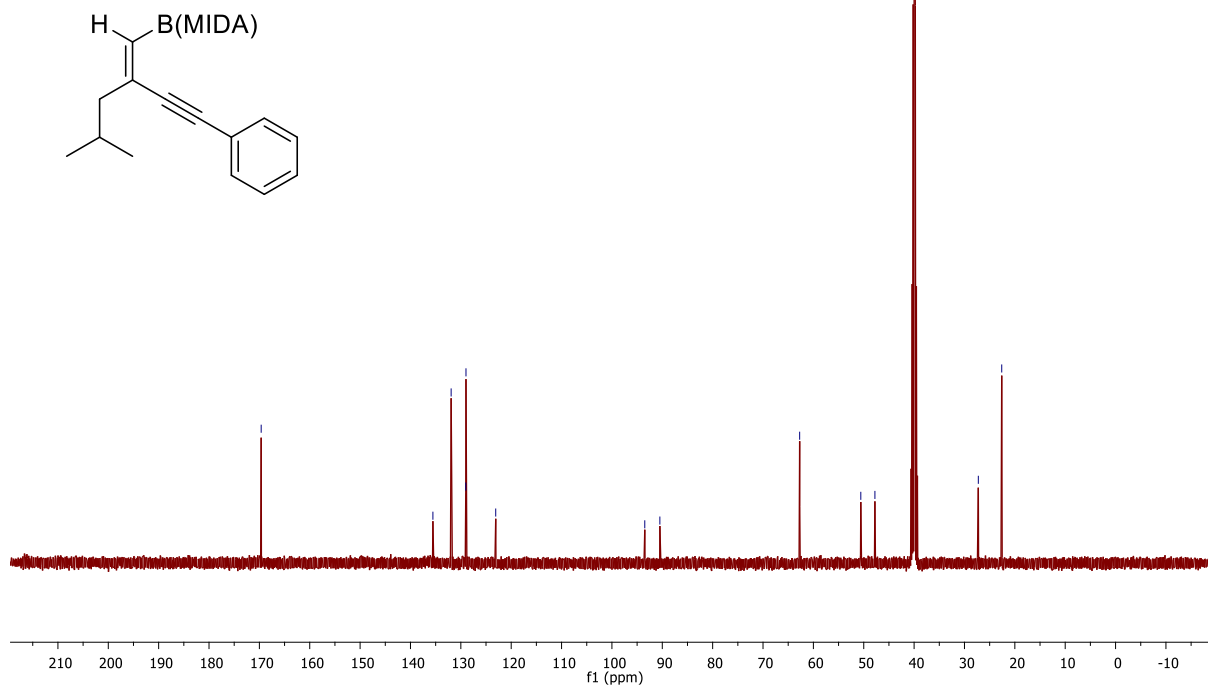
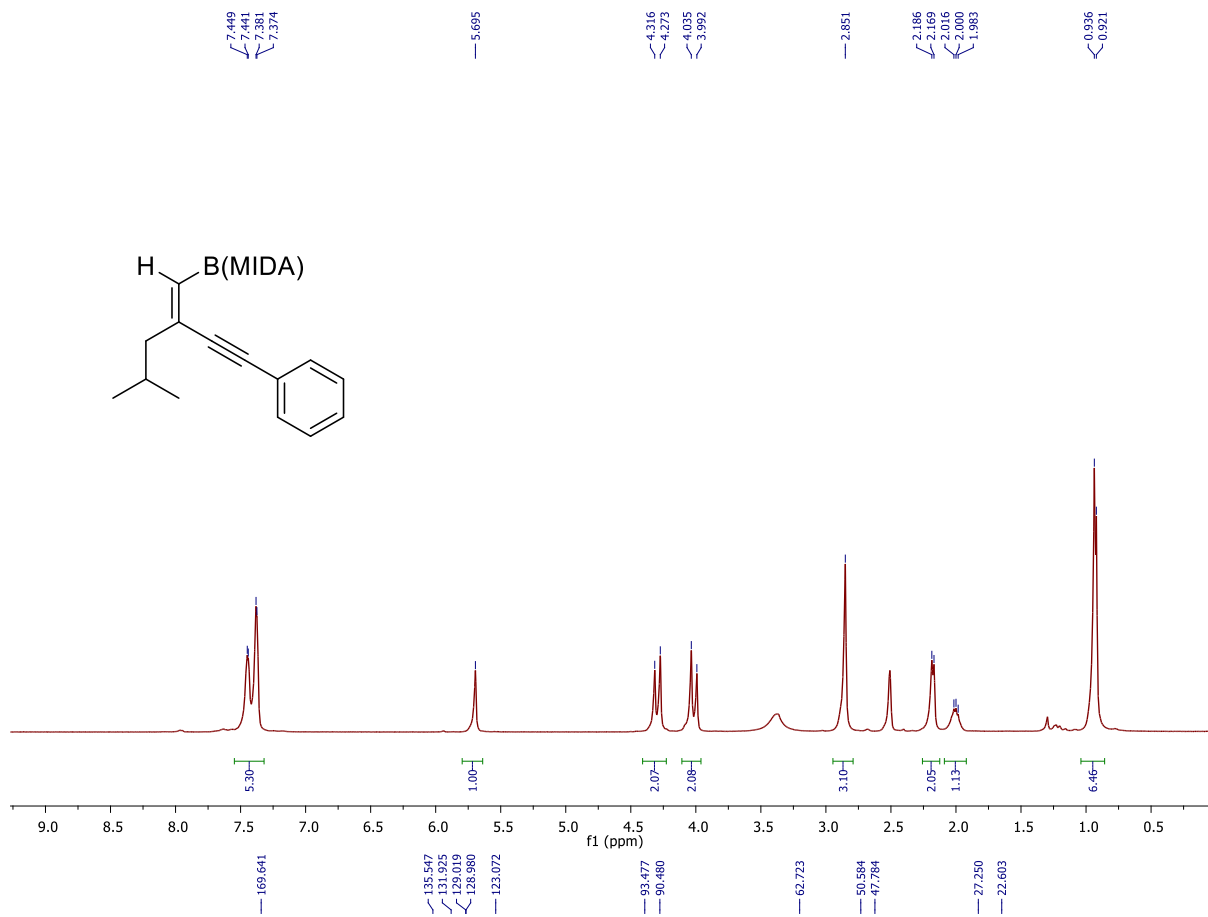


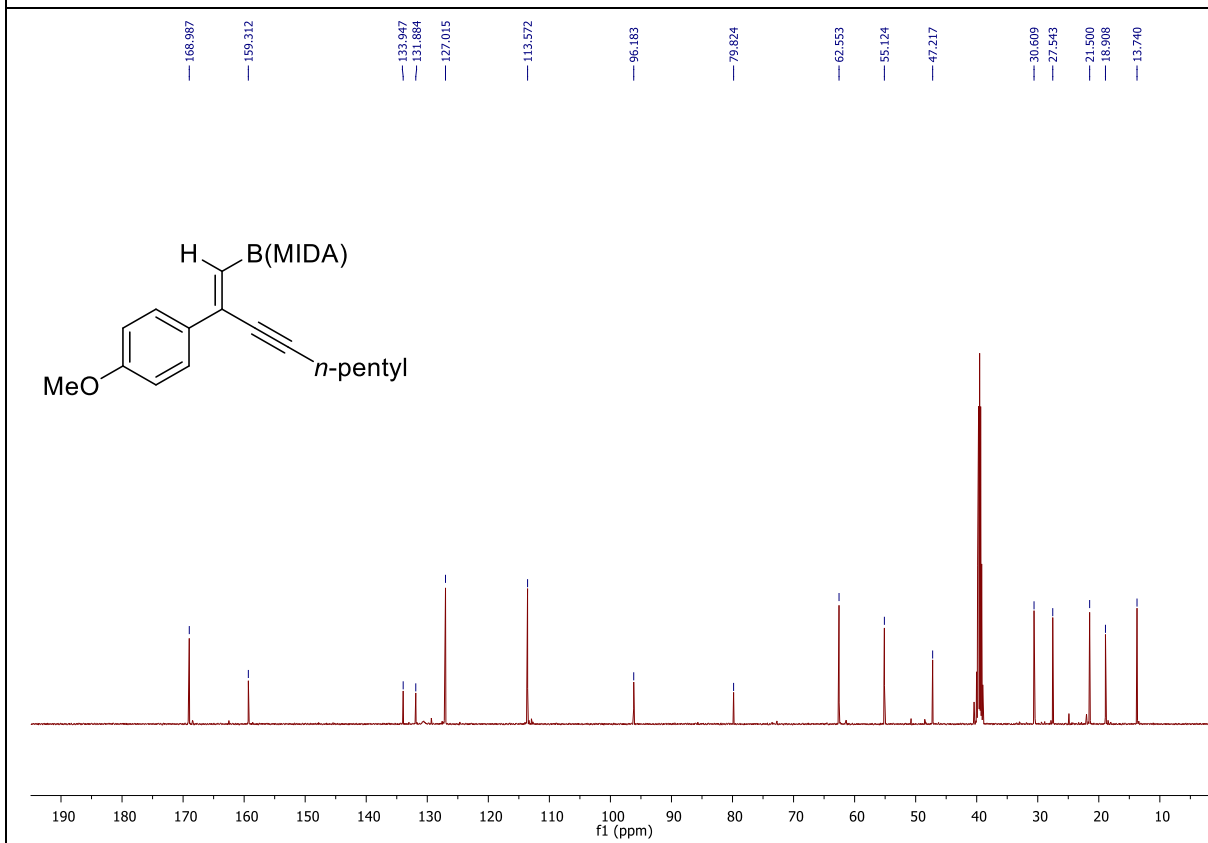
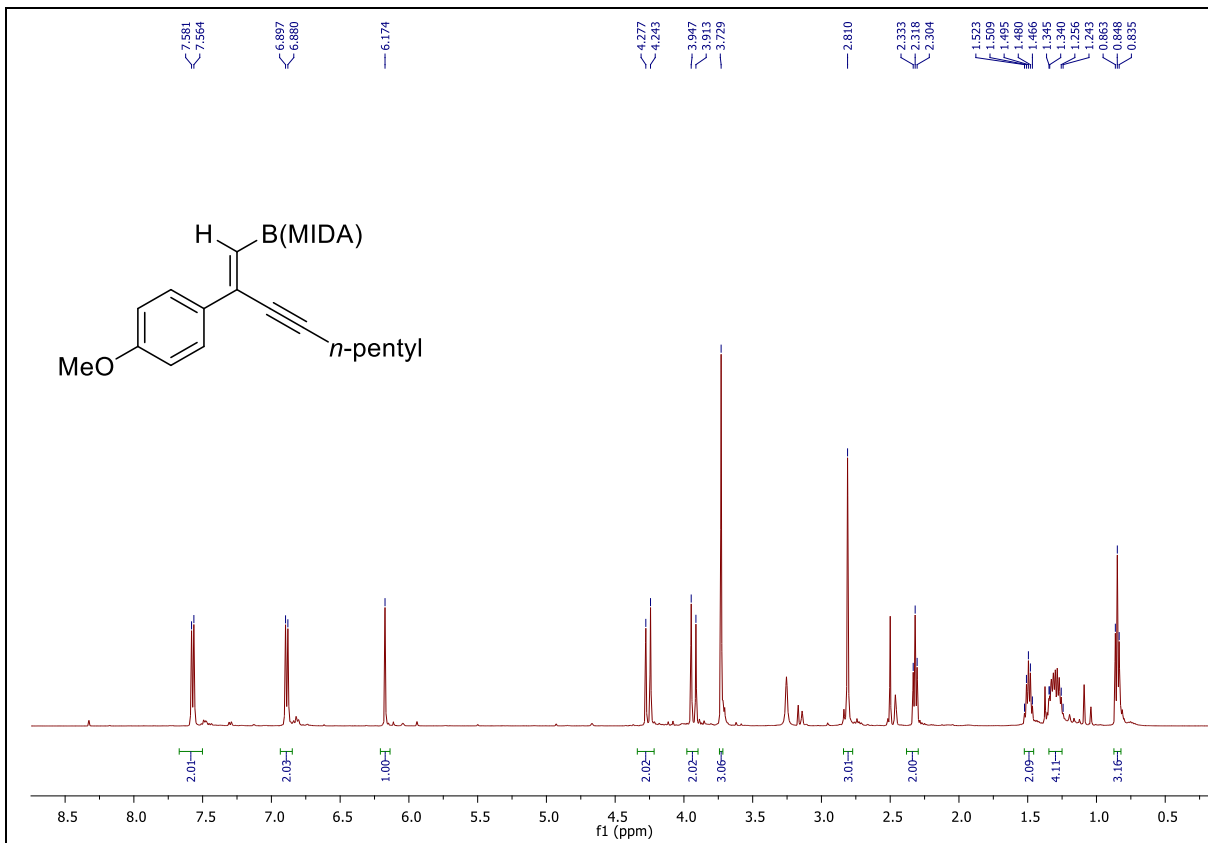


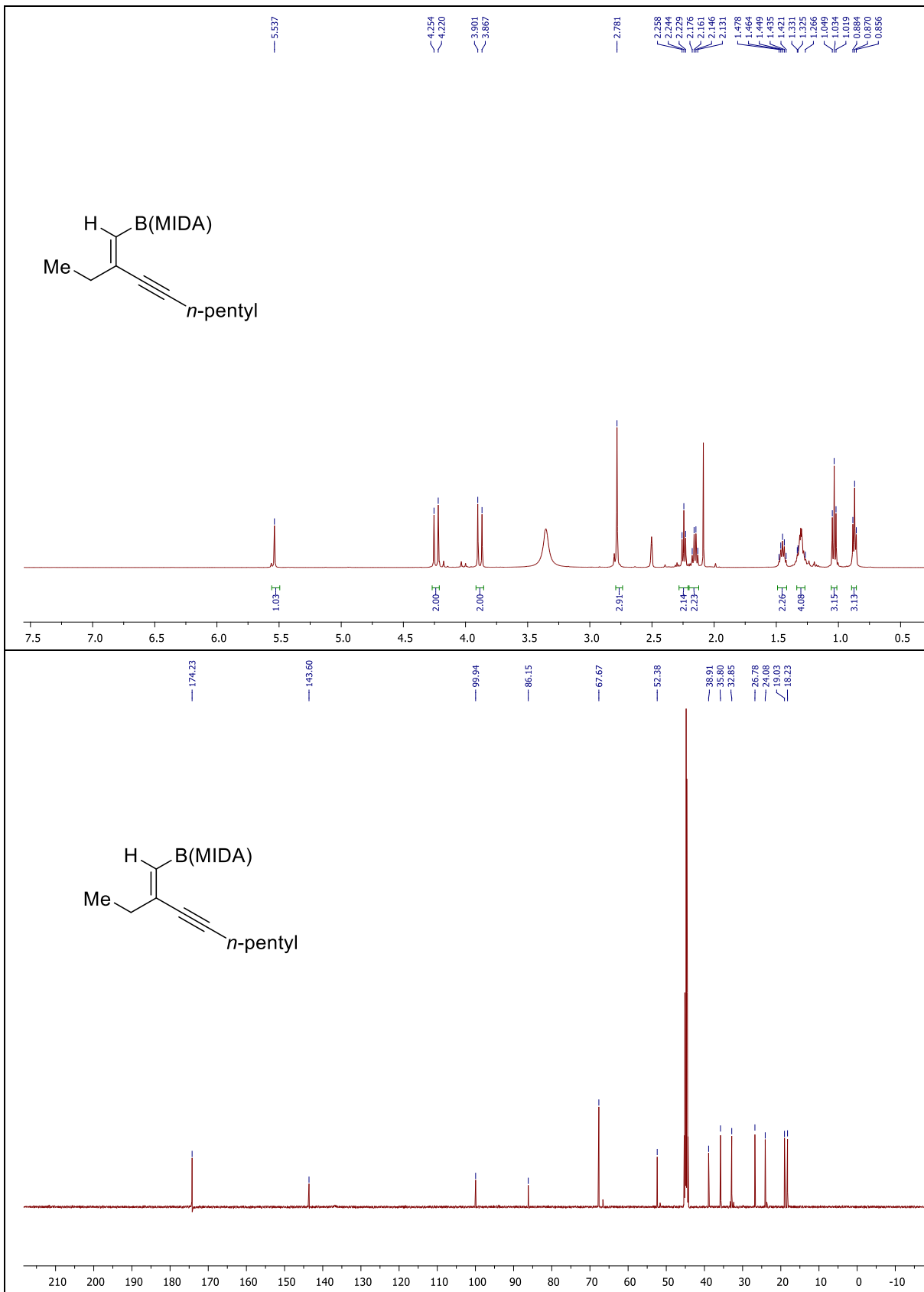


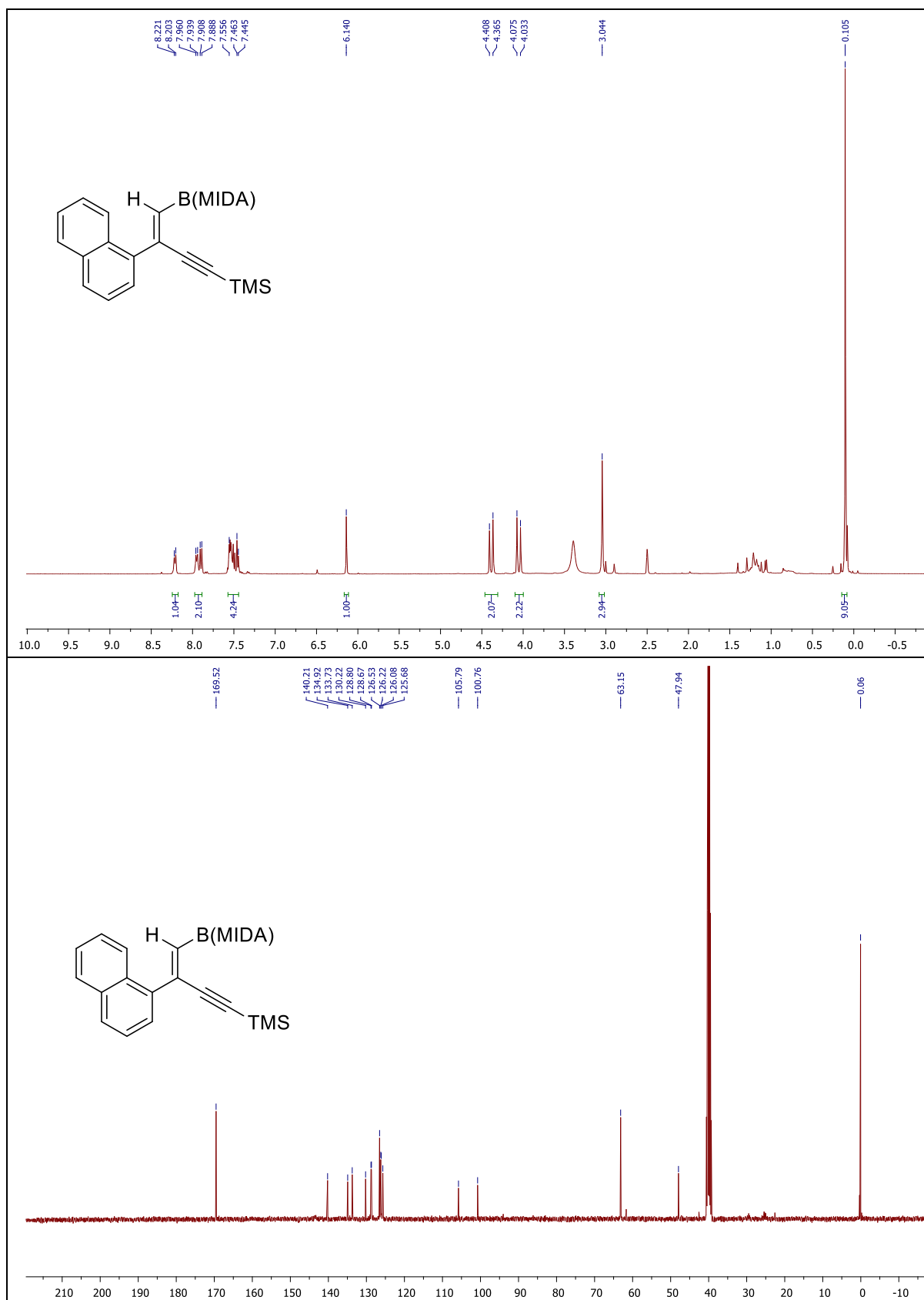
10.658

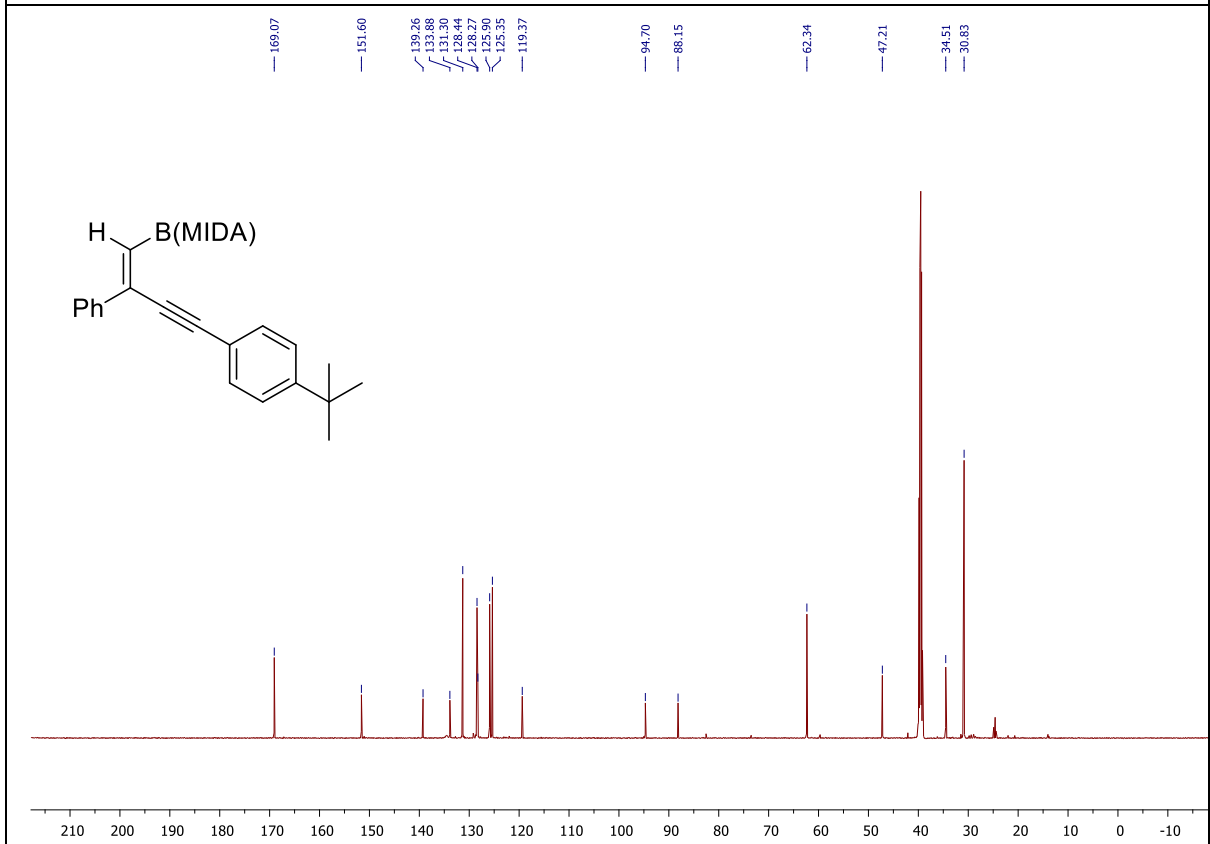
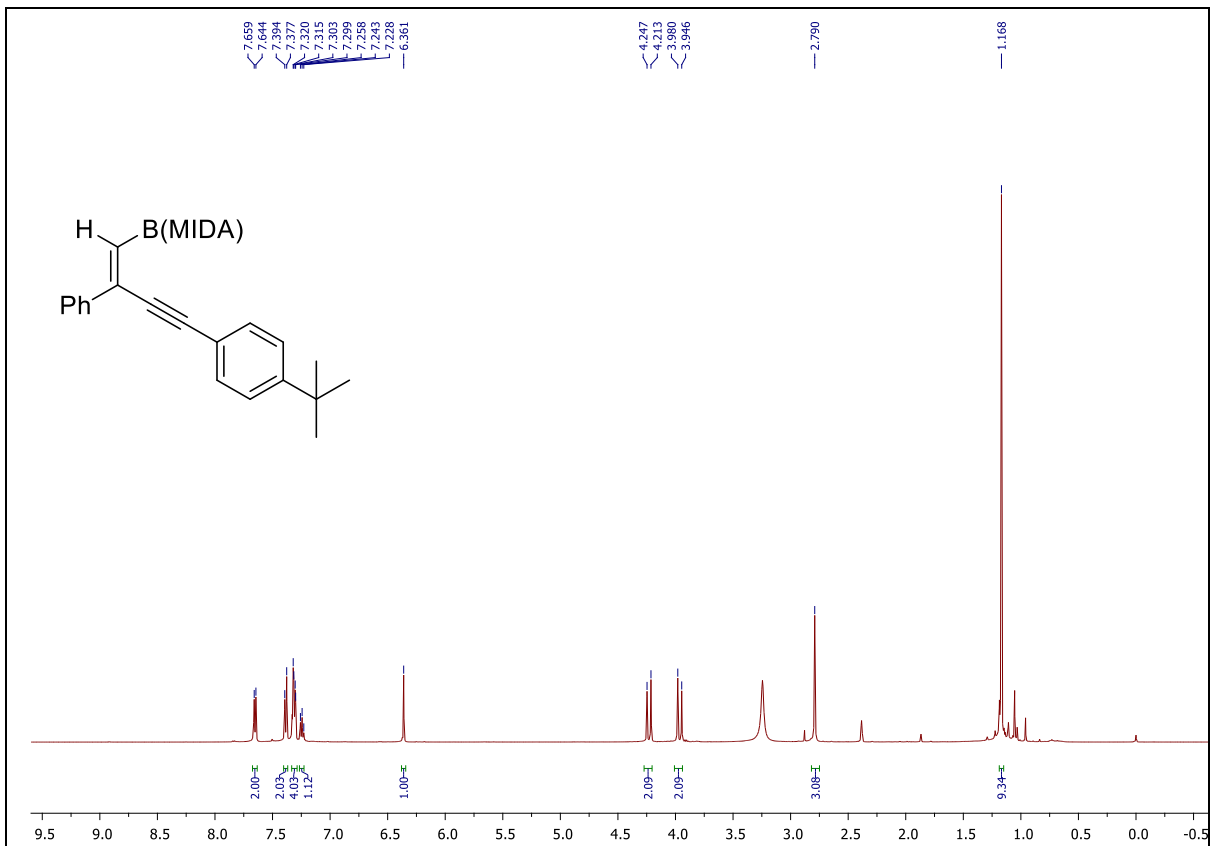


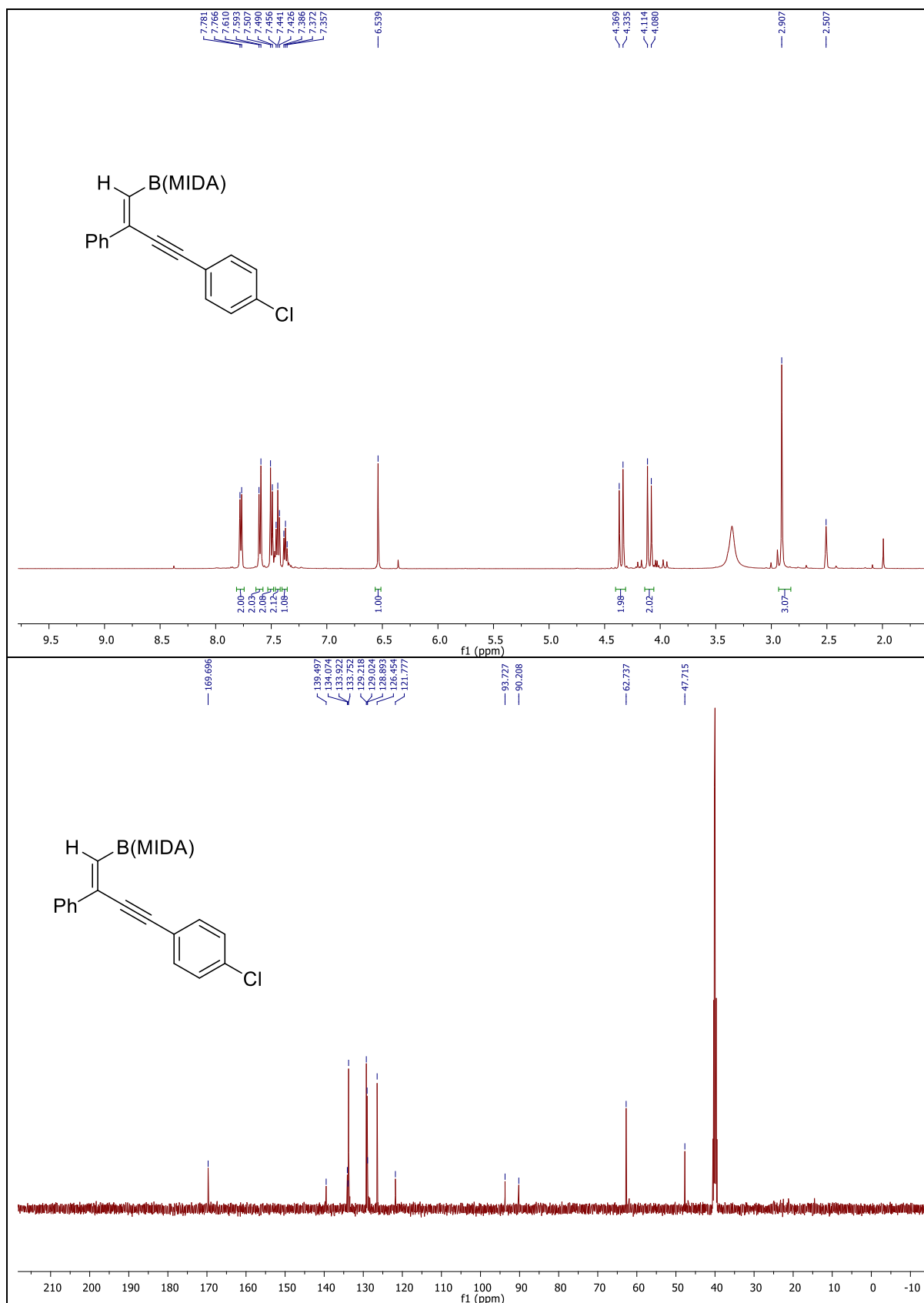


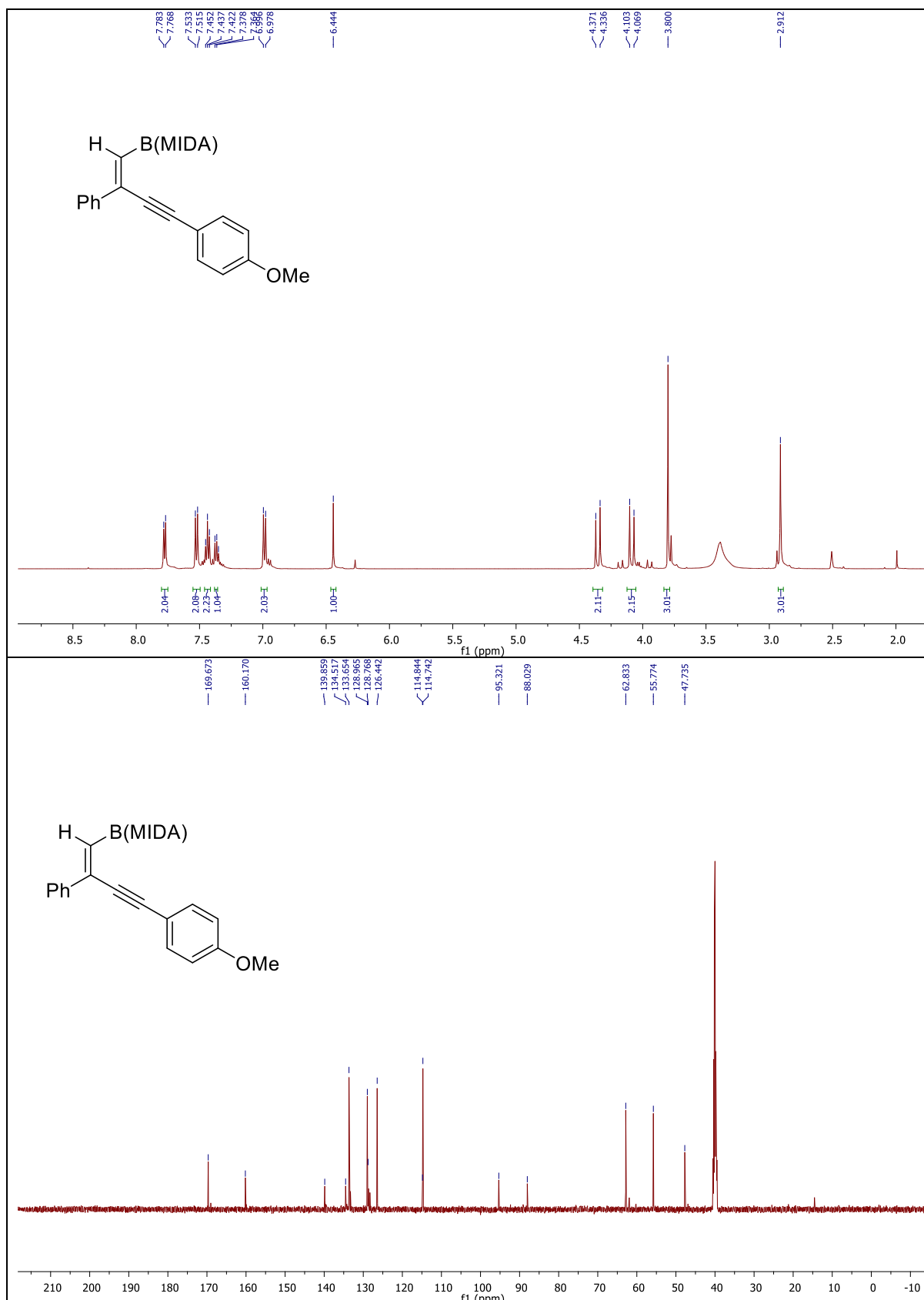


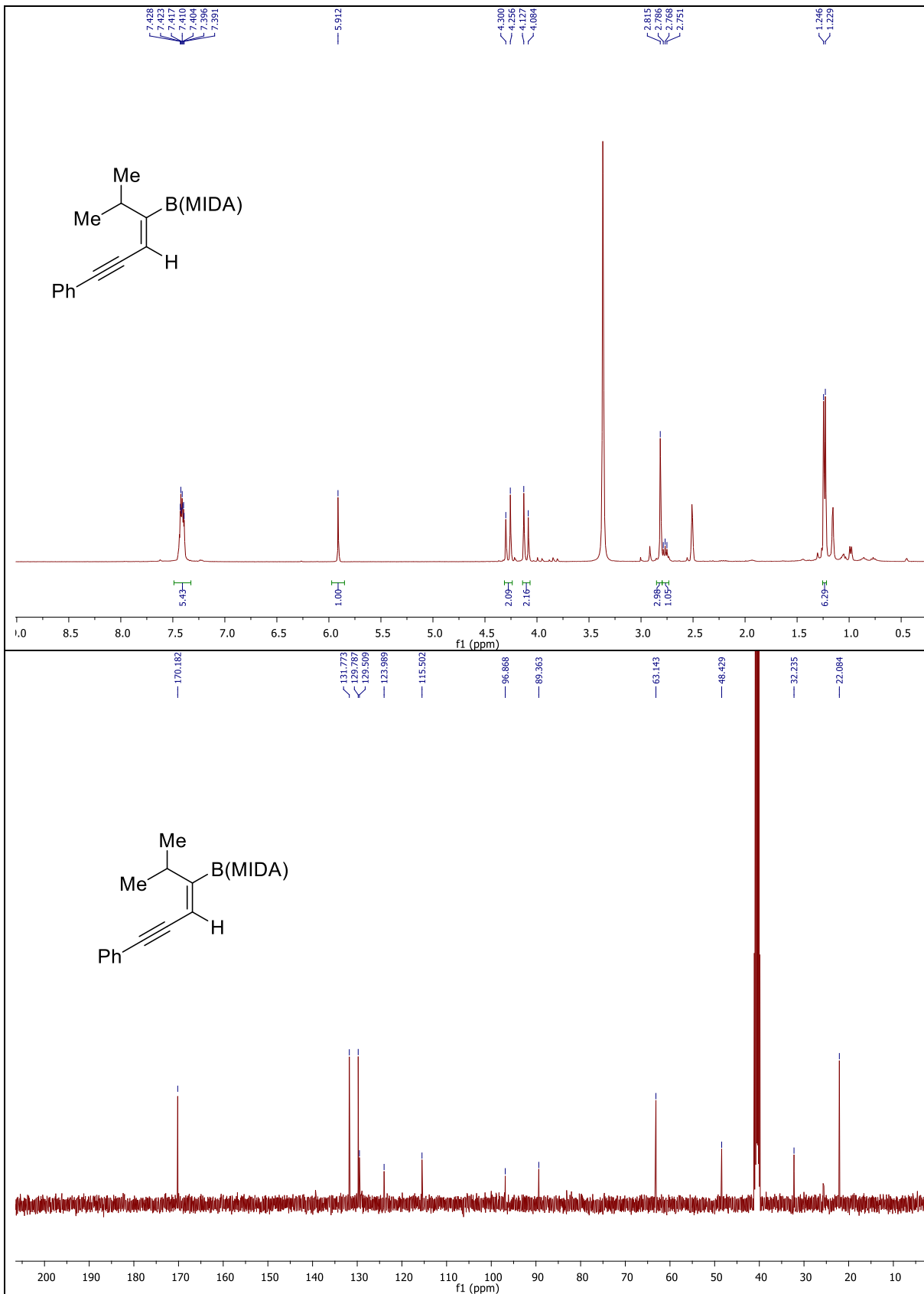


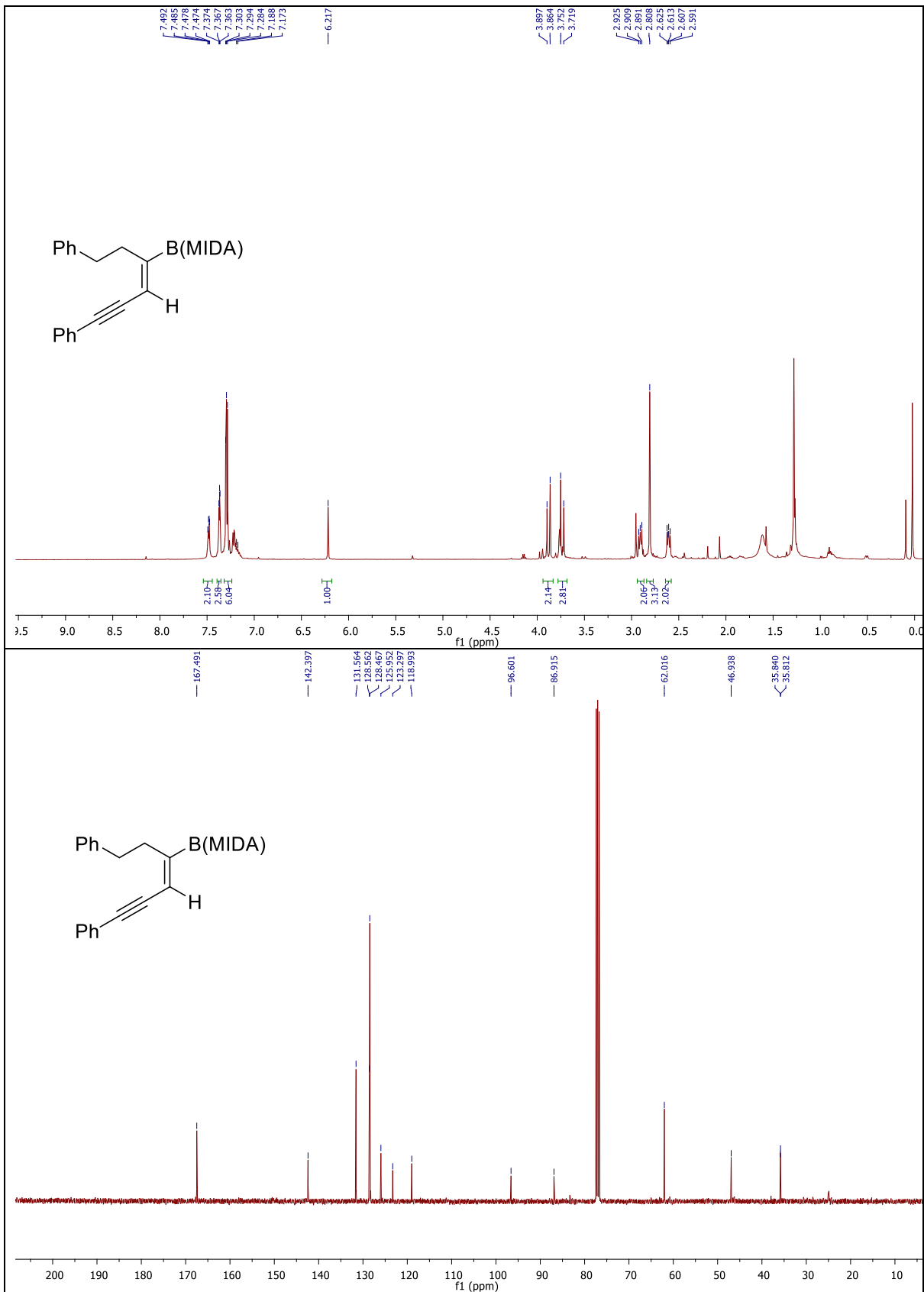


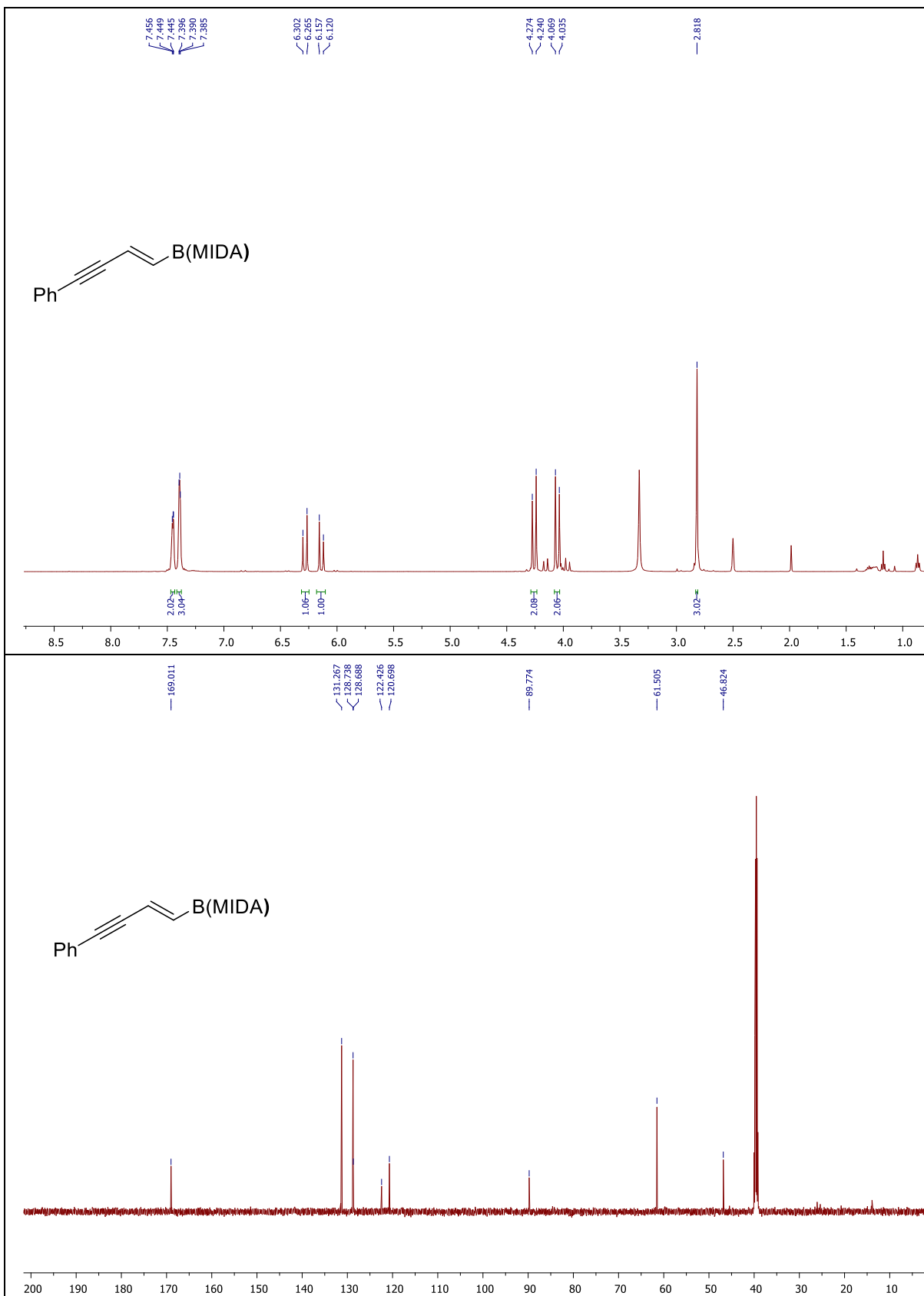


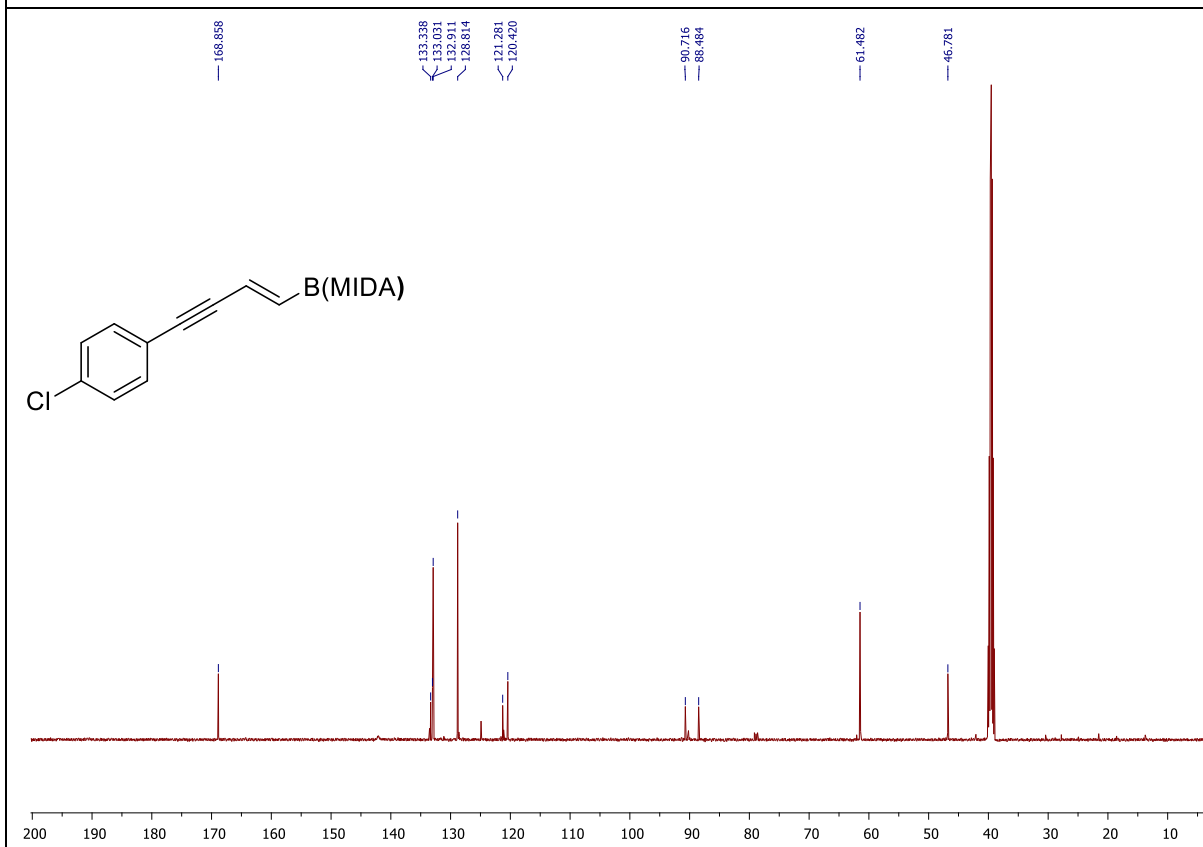
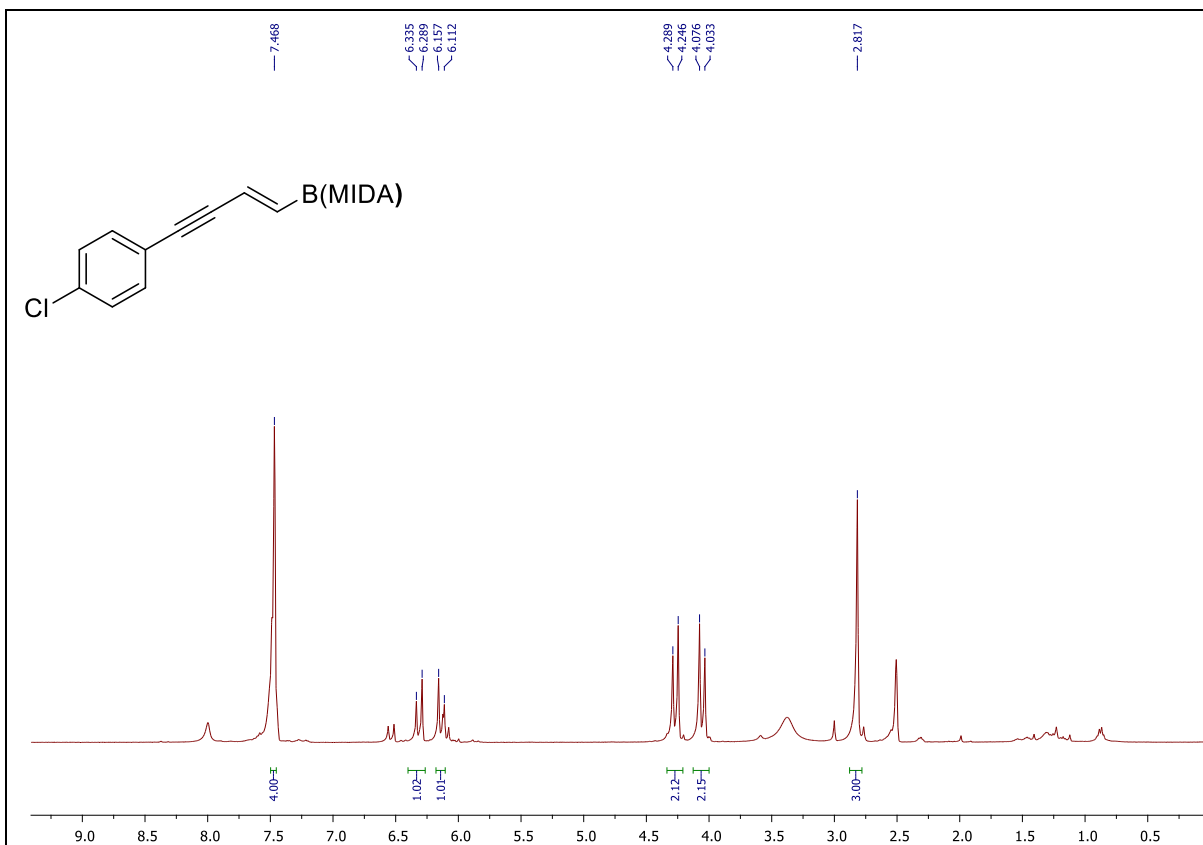


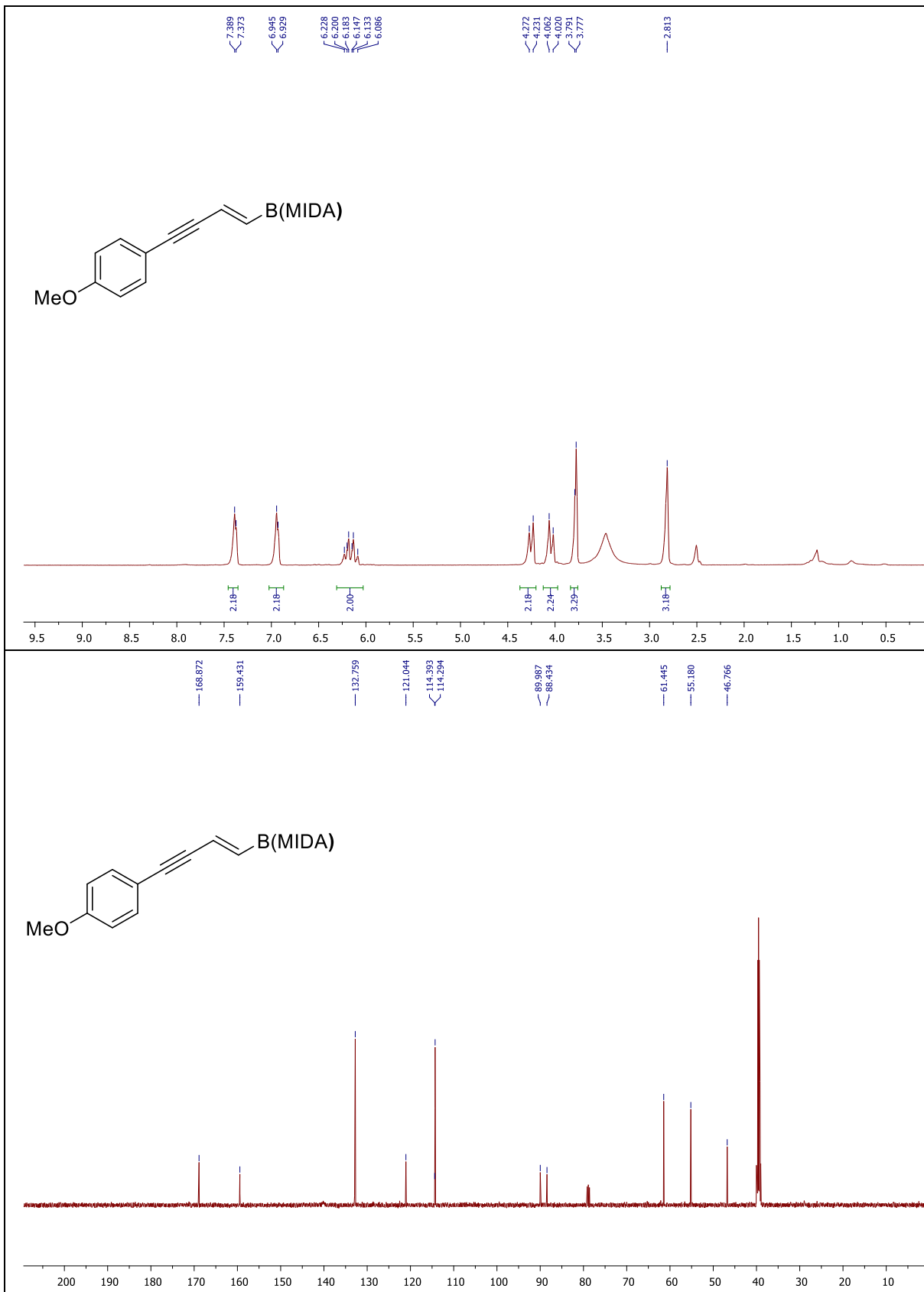


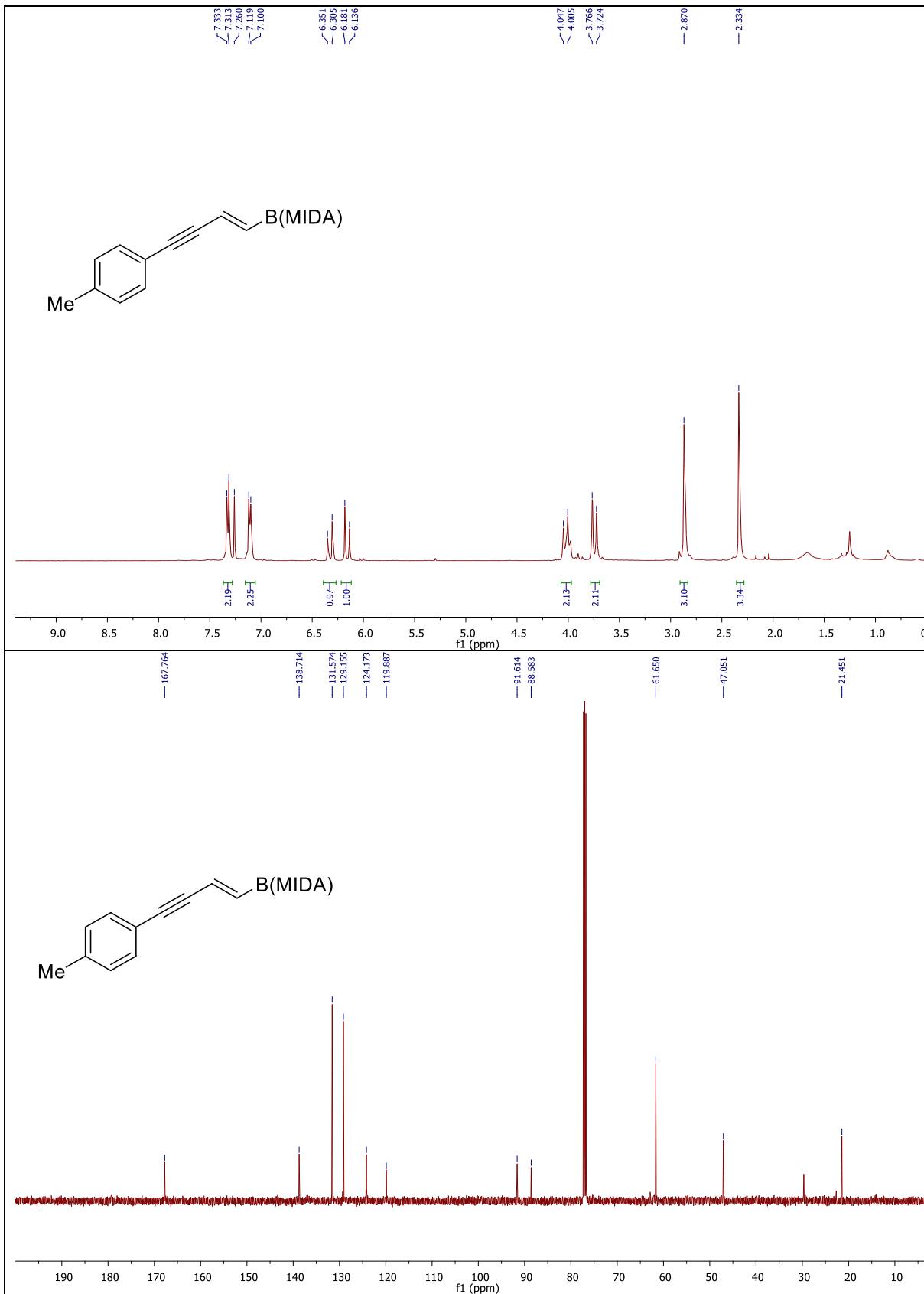


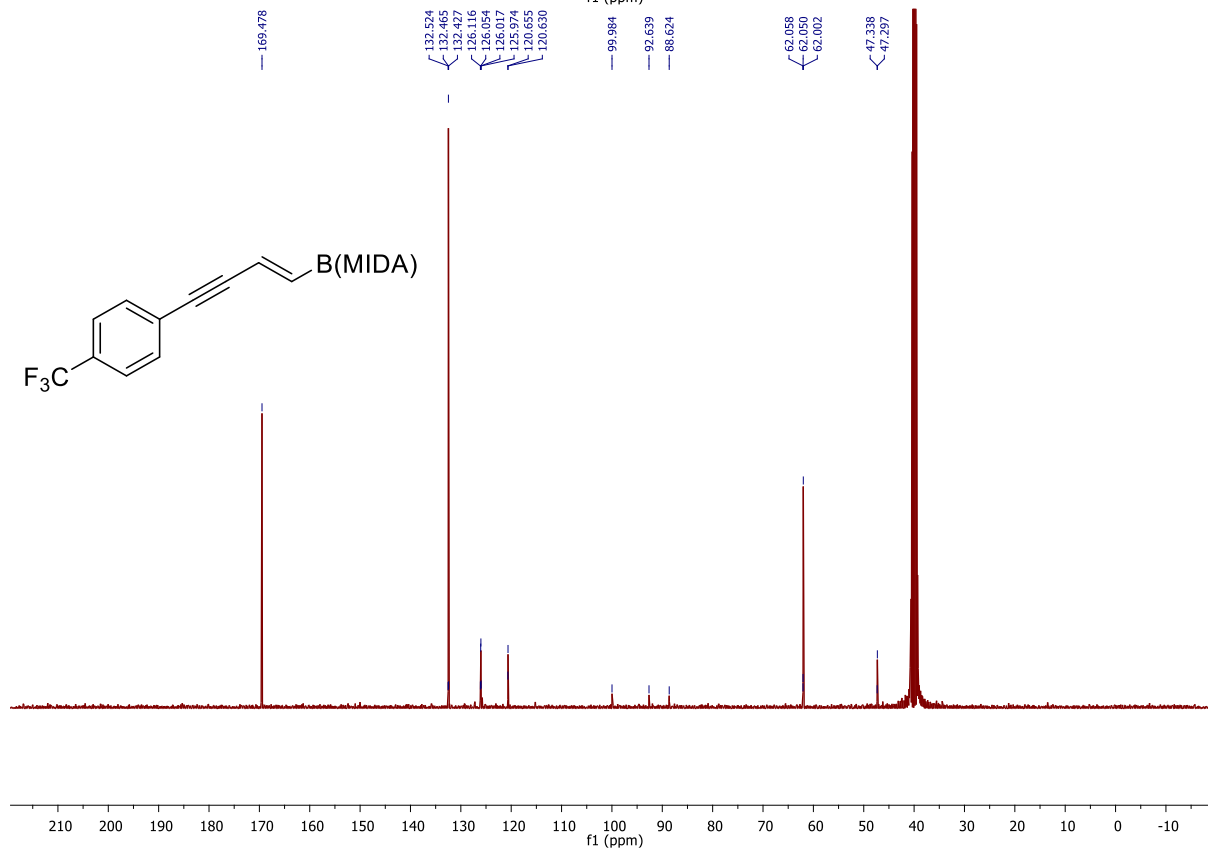
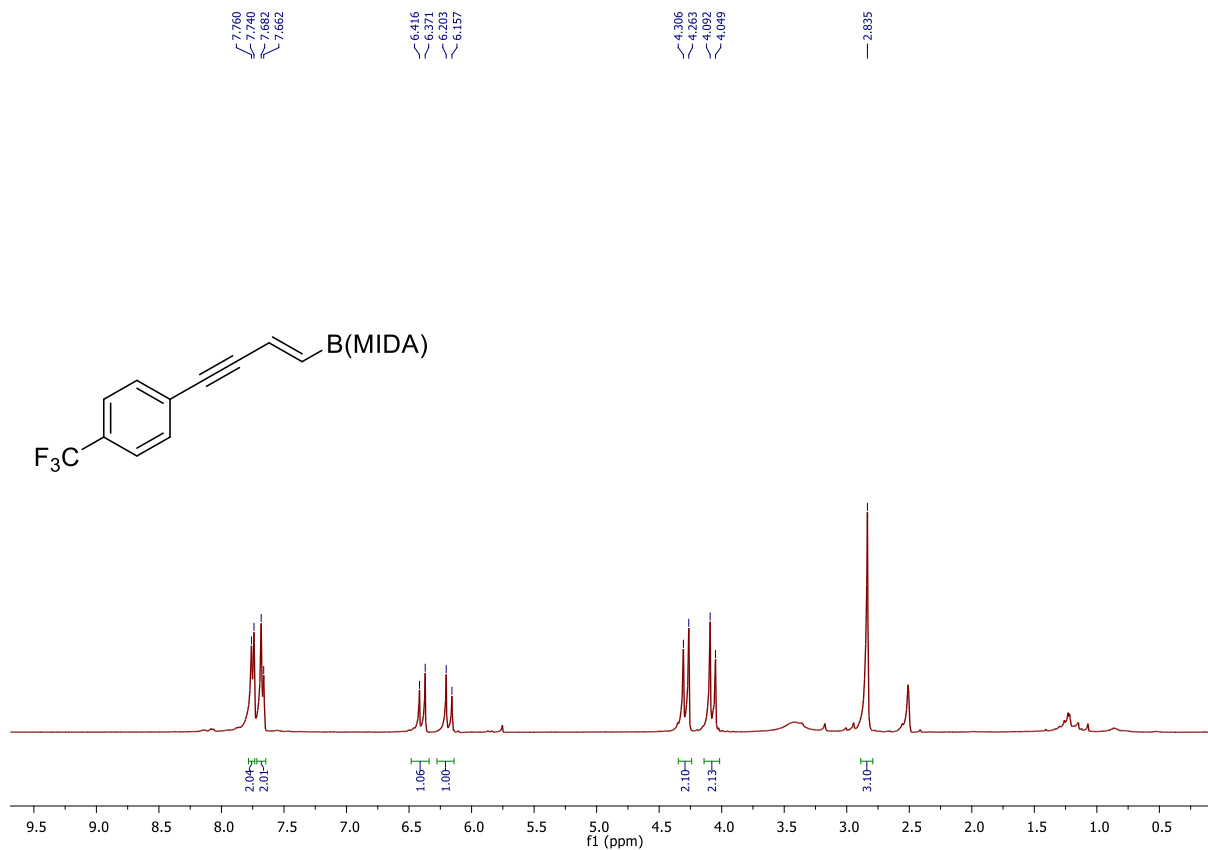


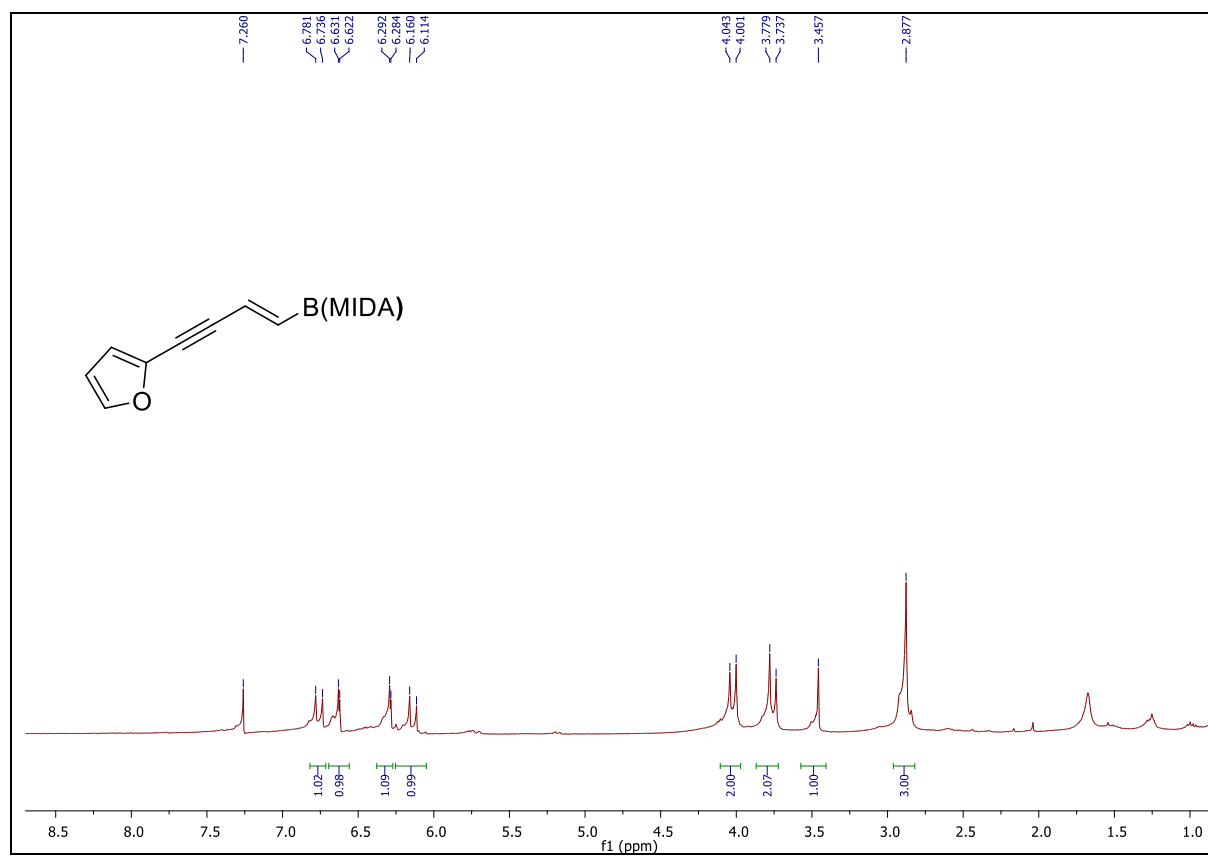
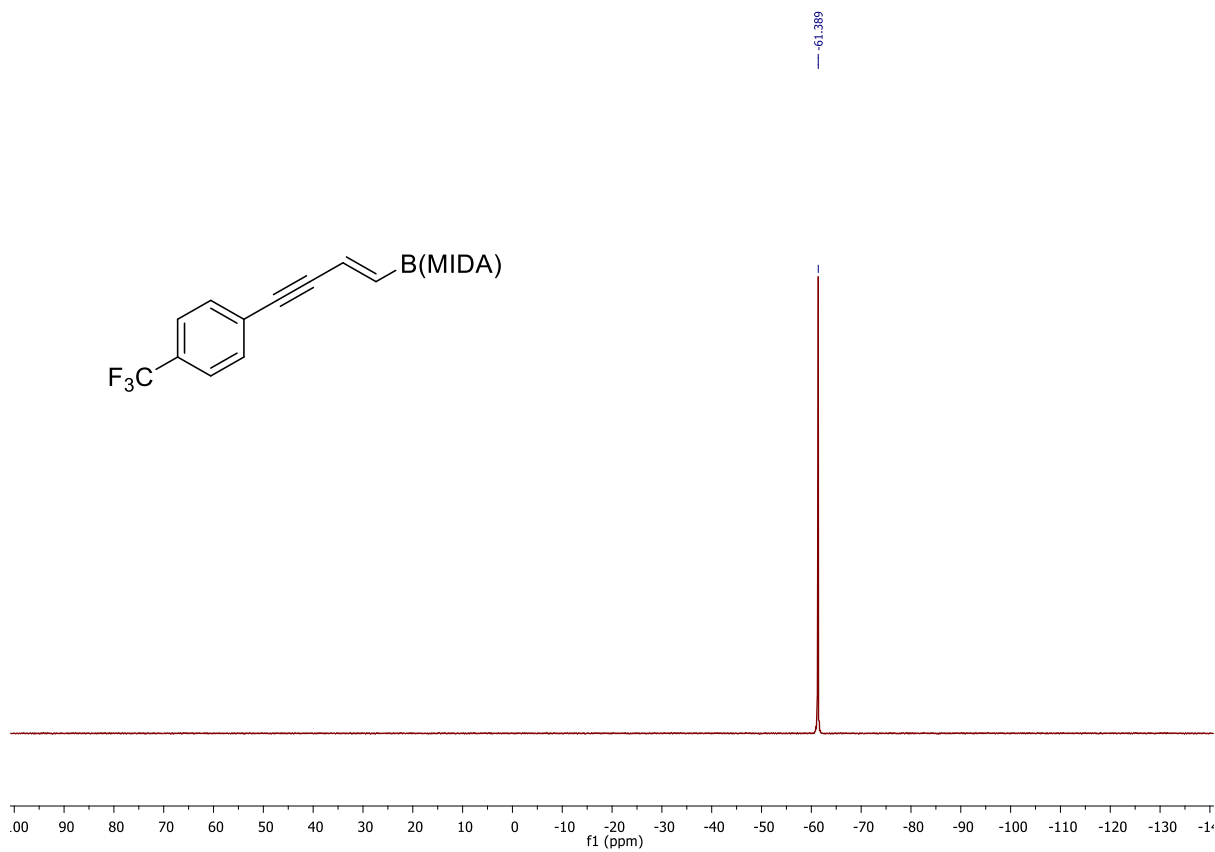


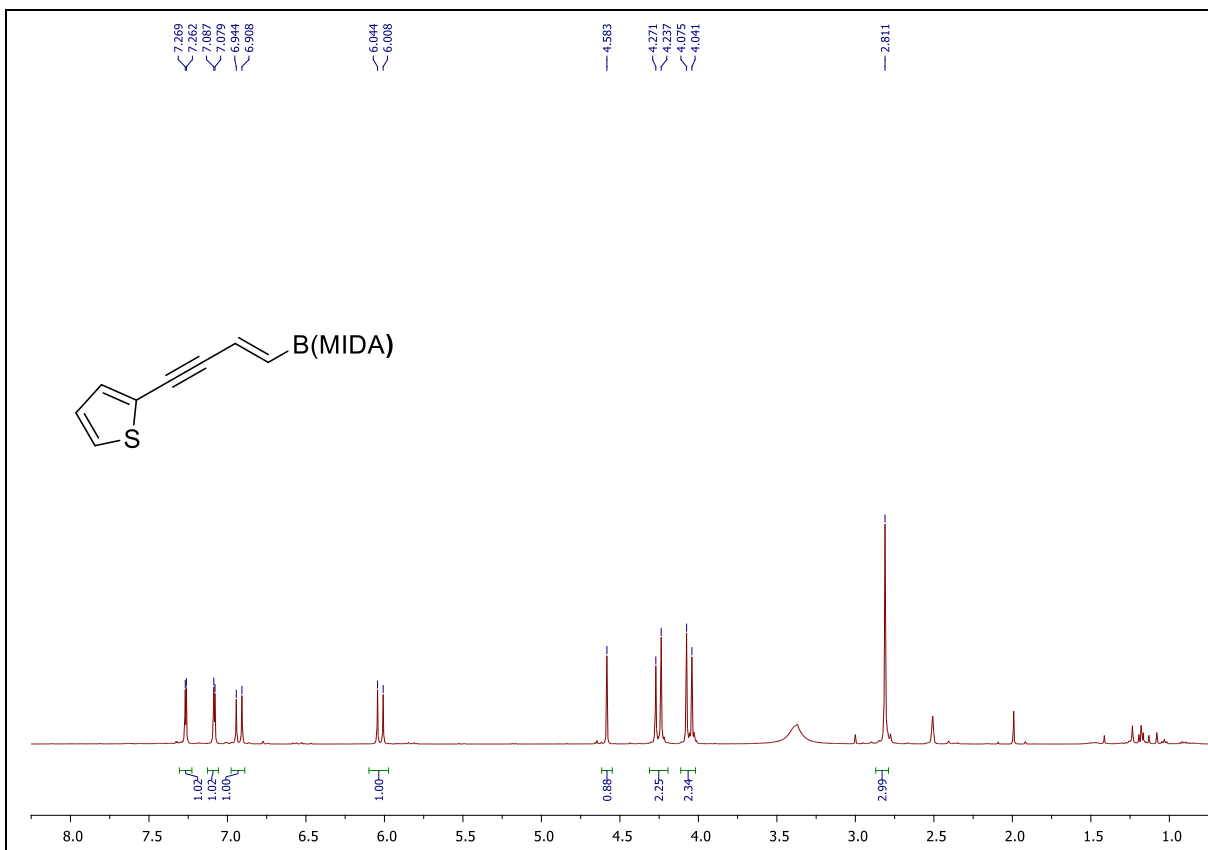
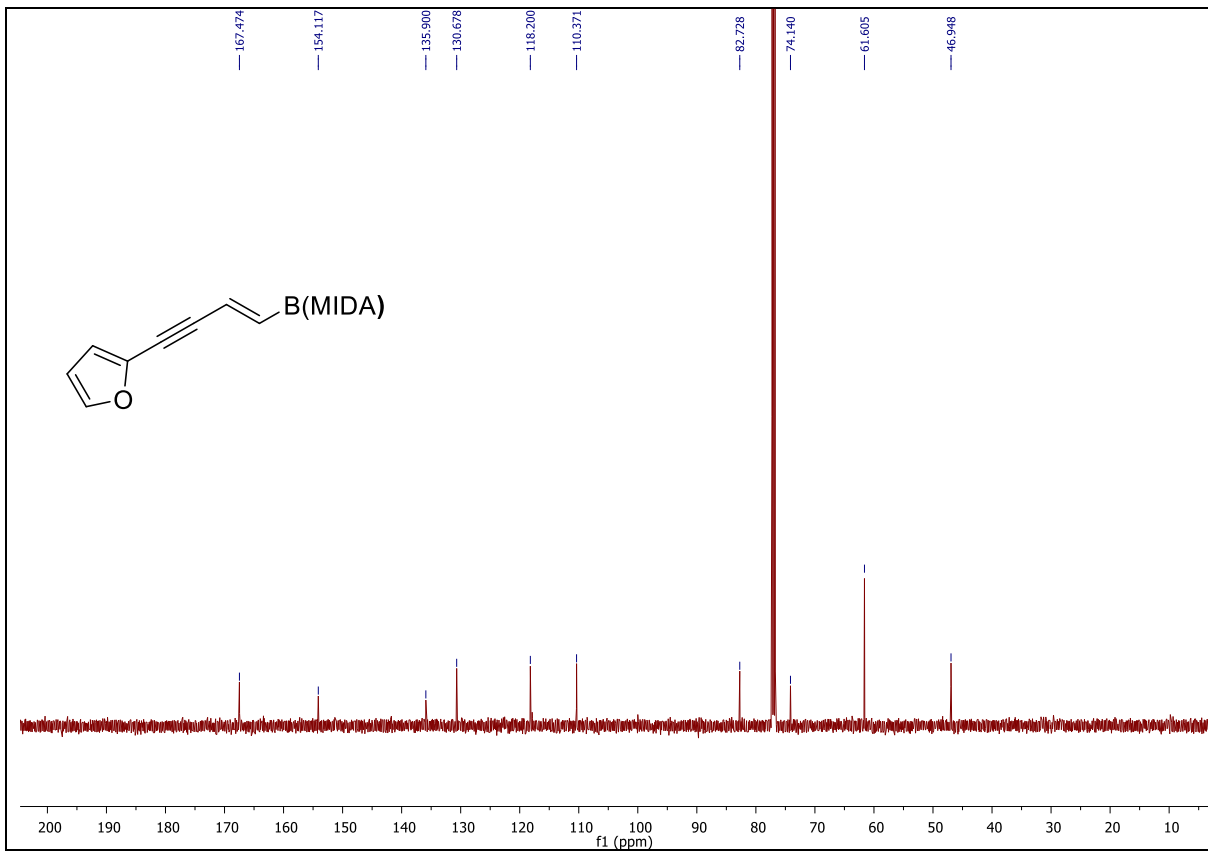


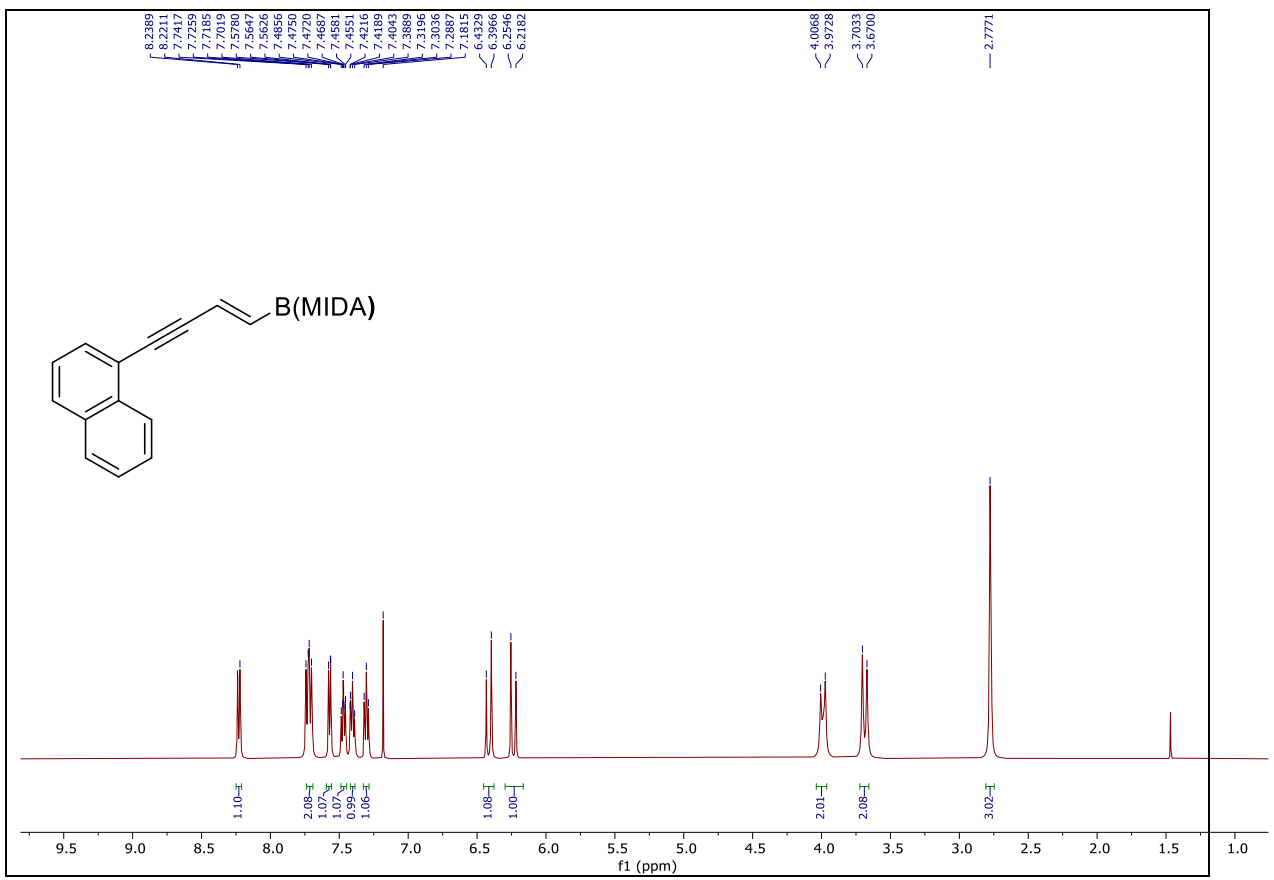
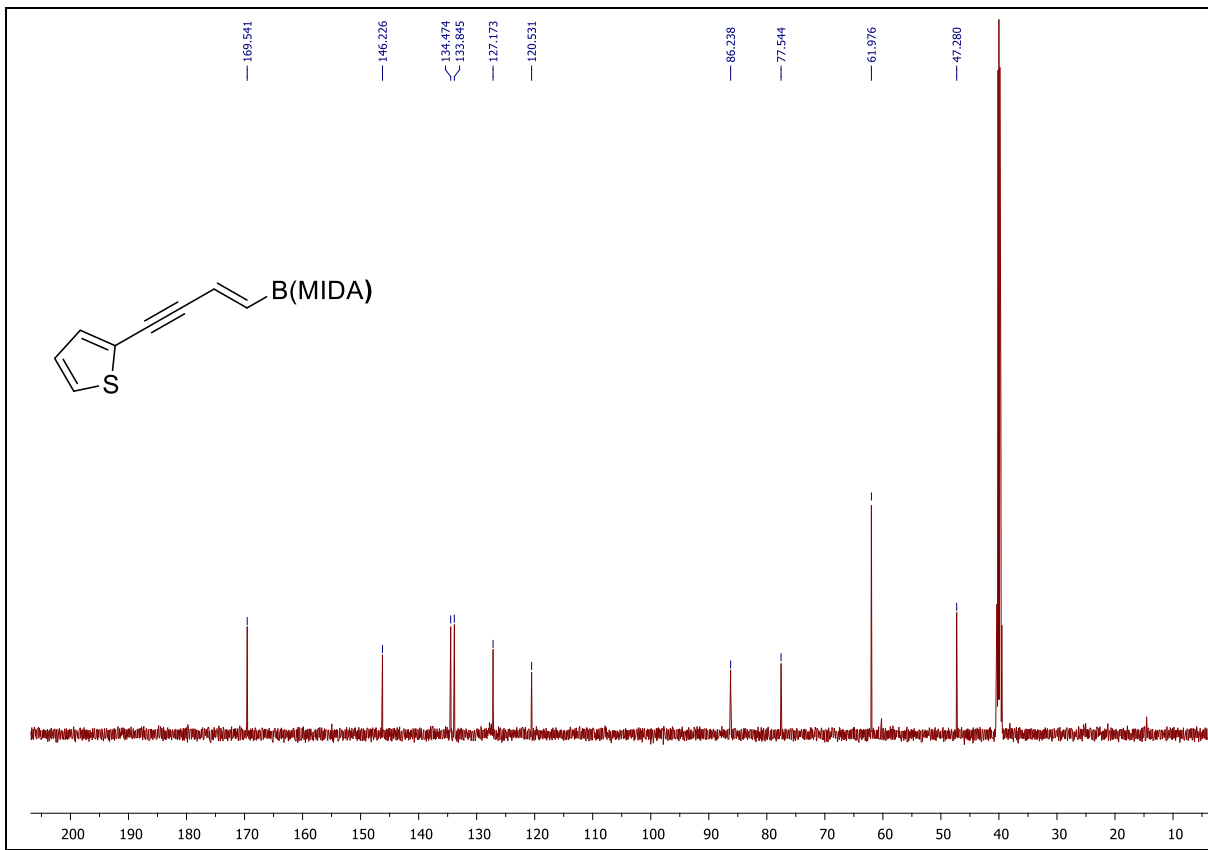


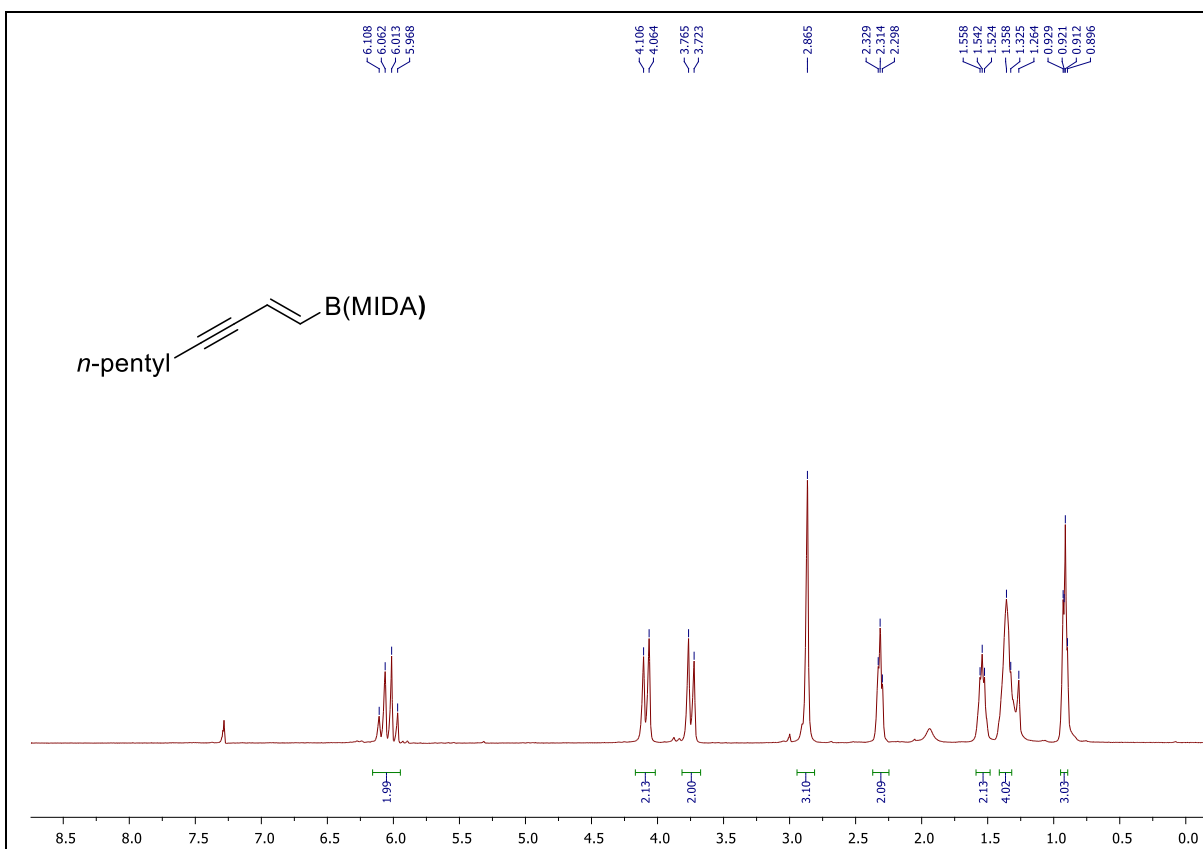
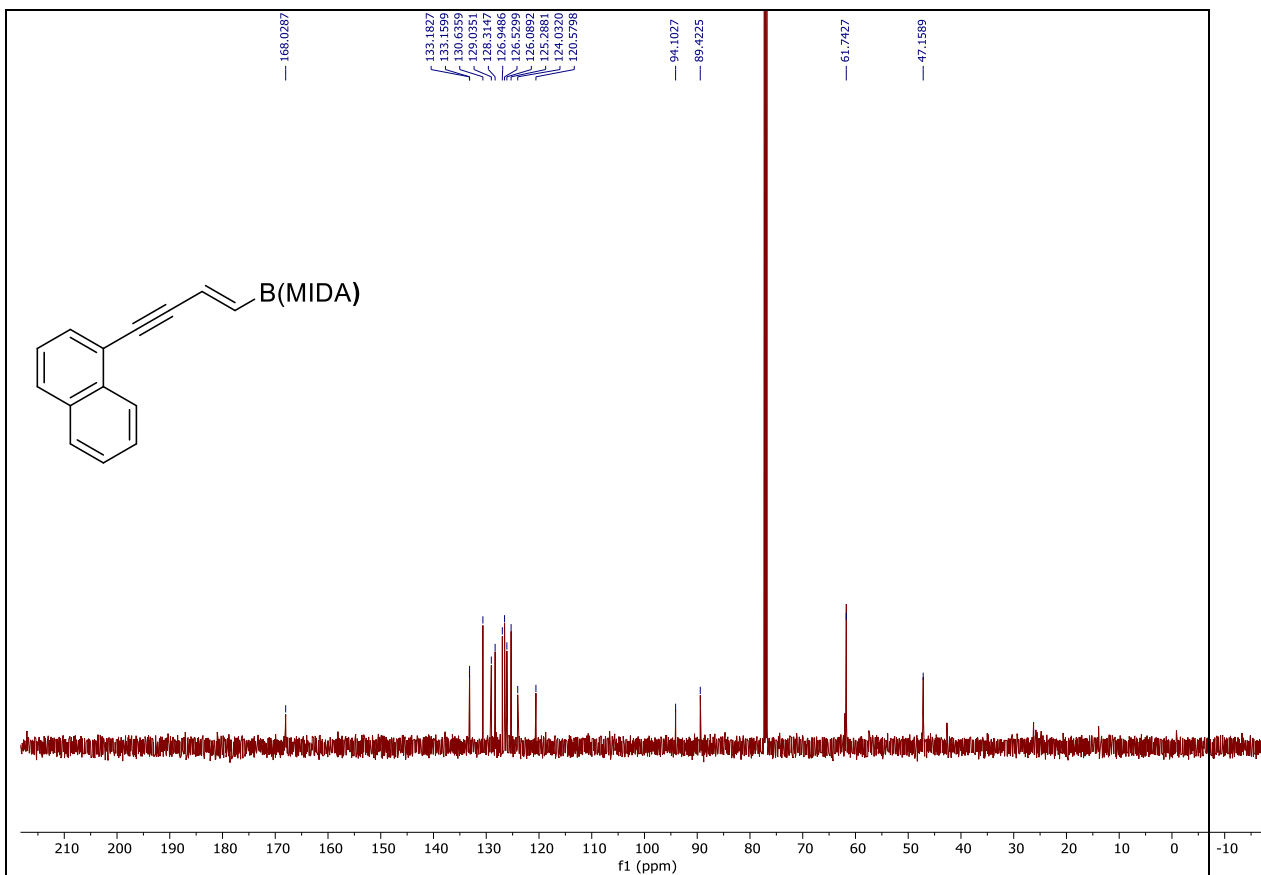


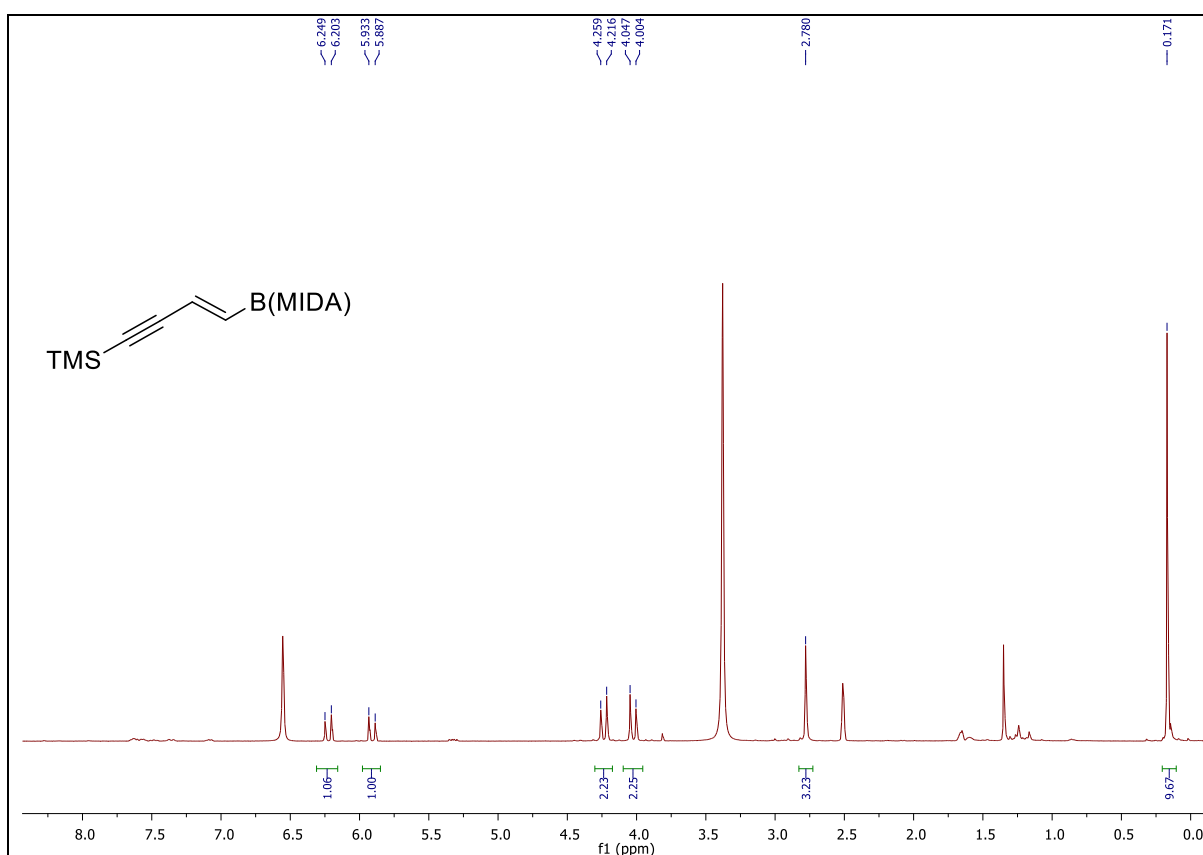
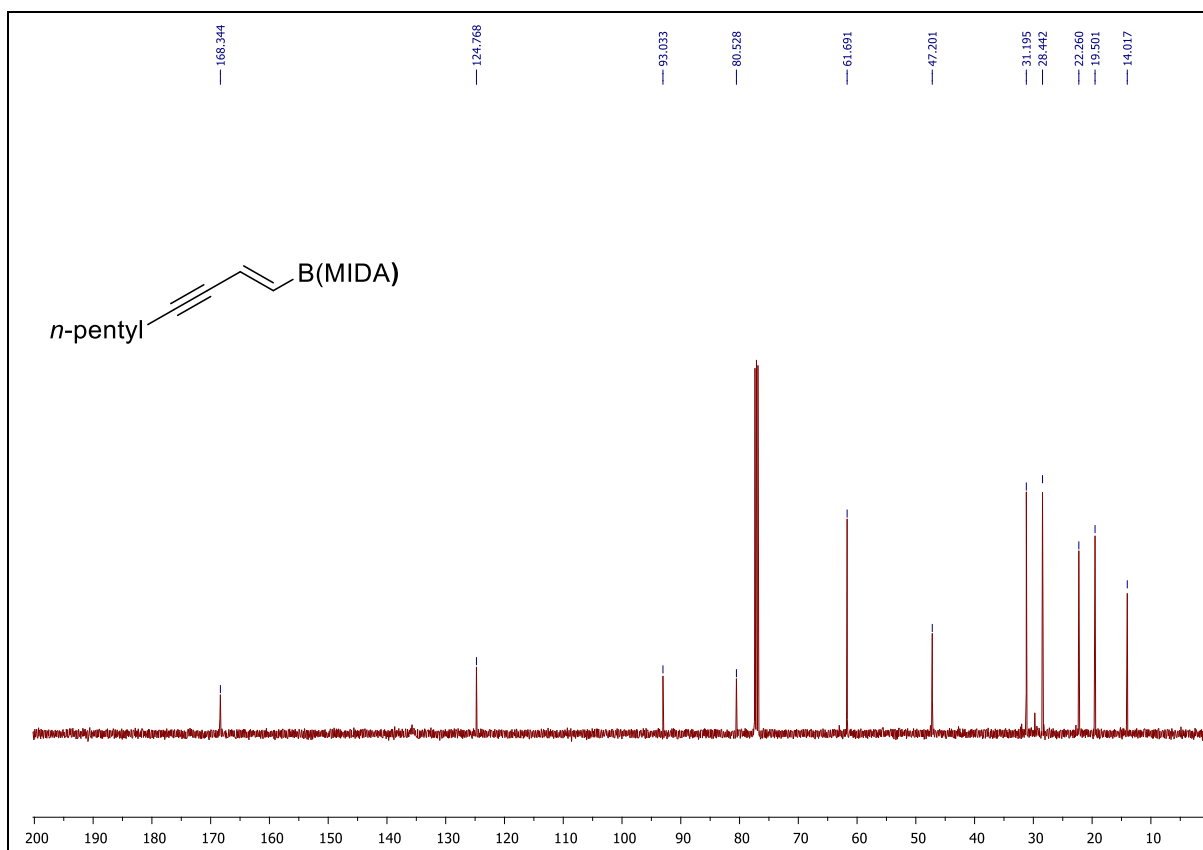


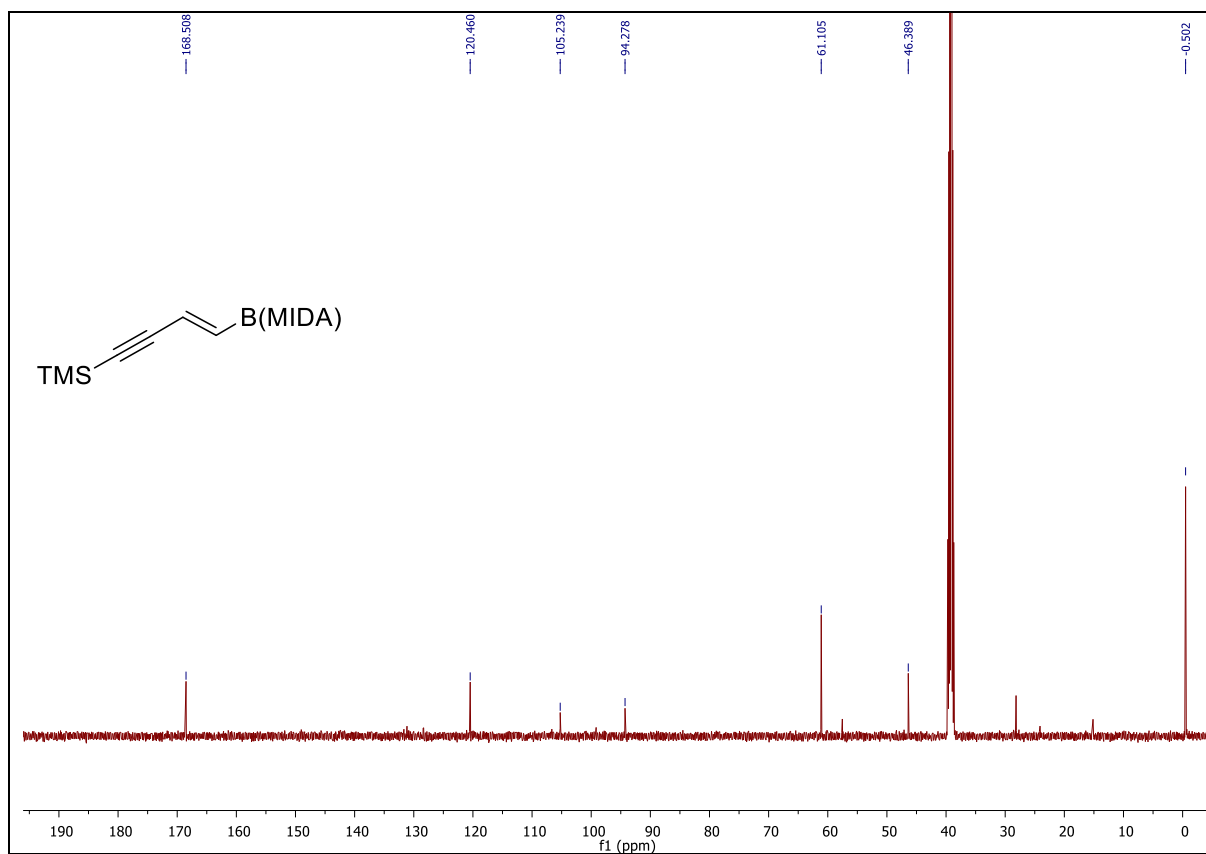


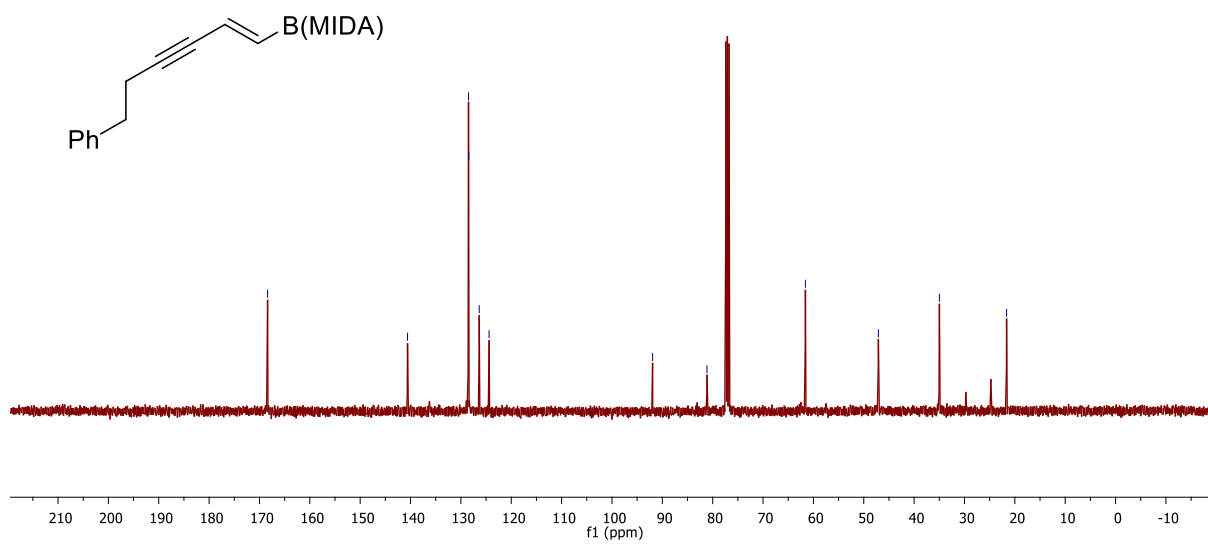
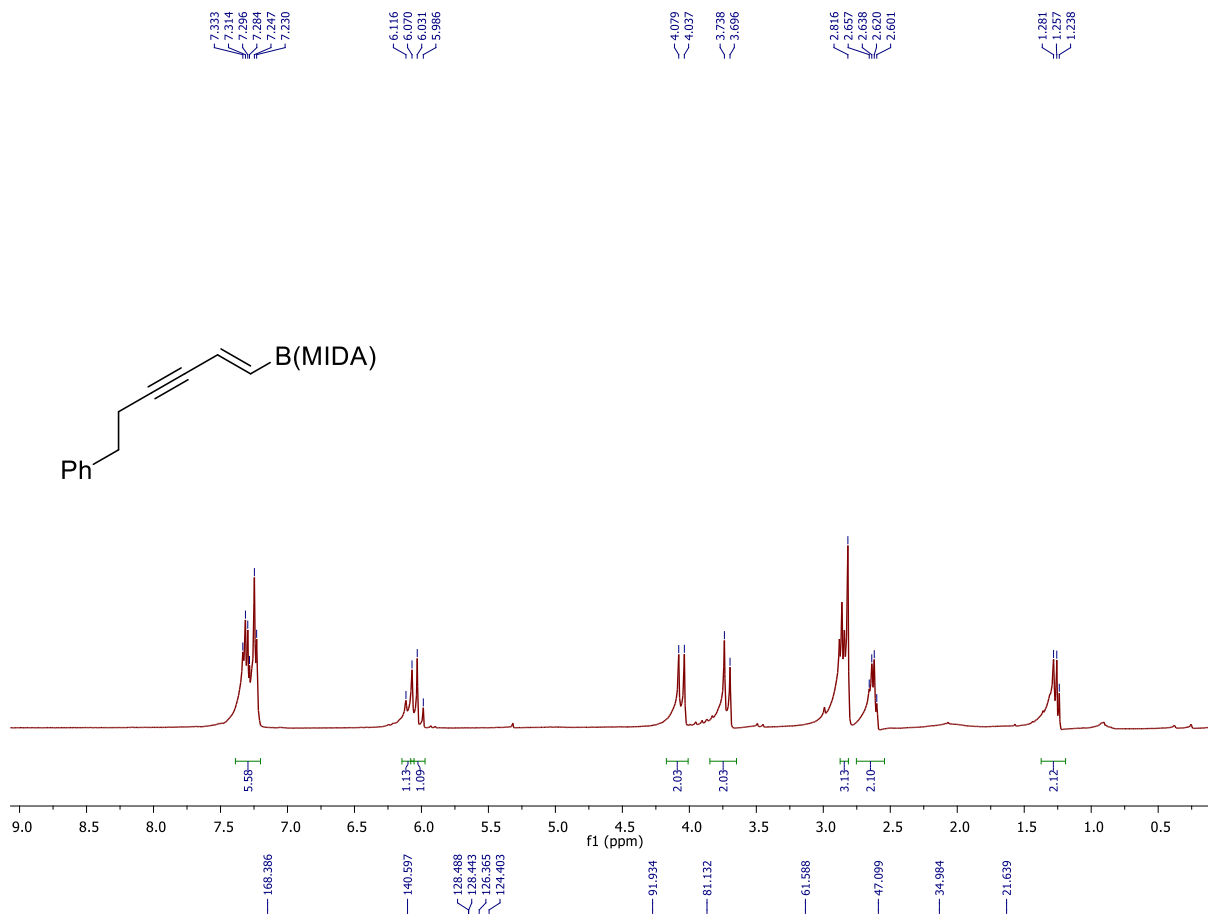


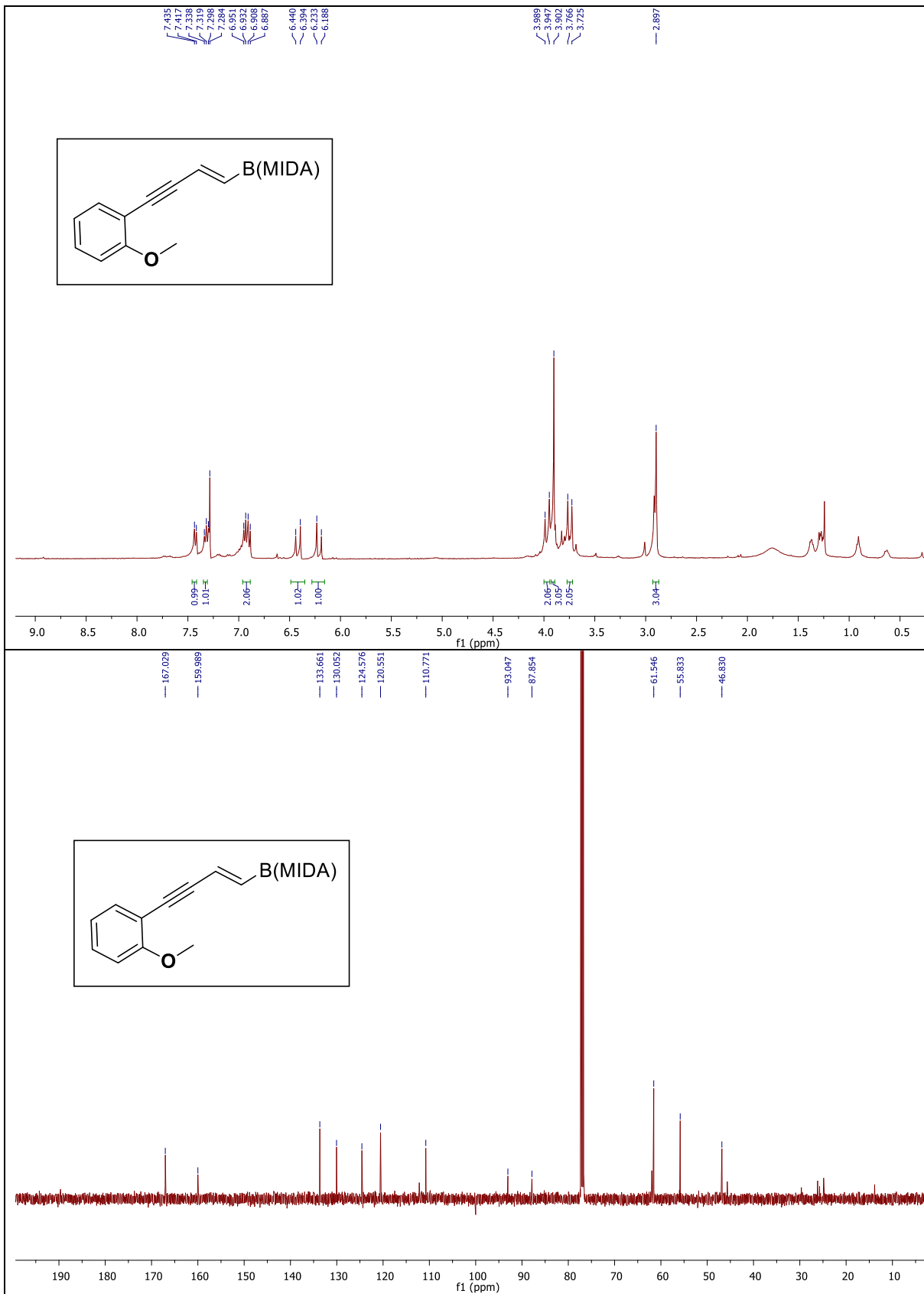


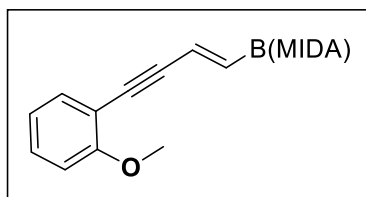




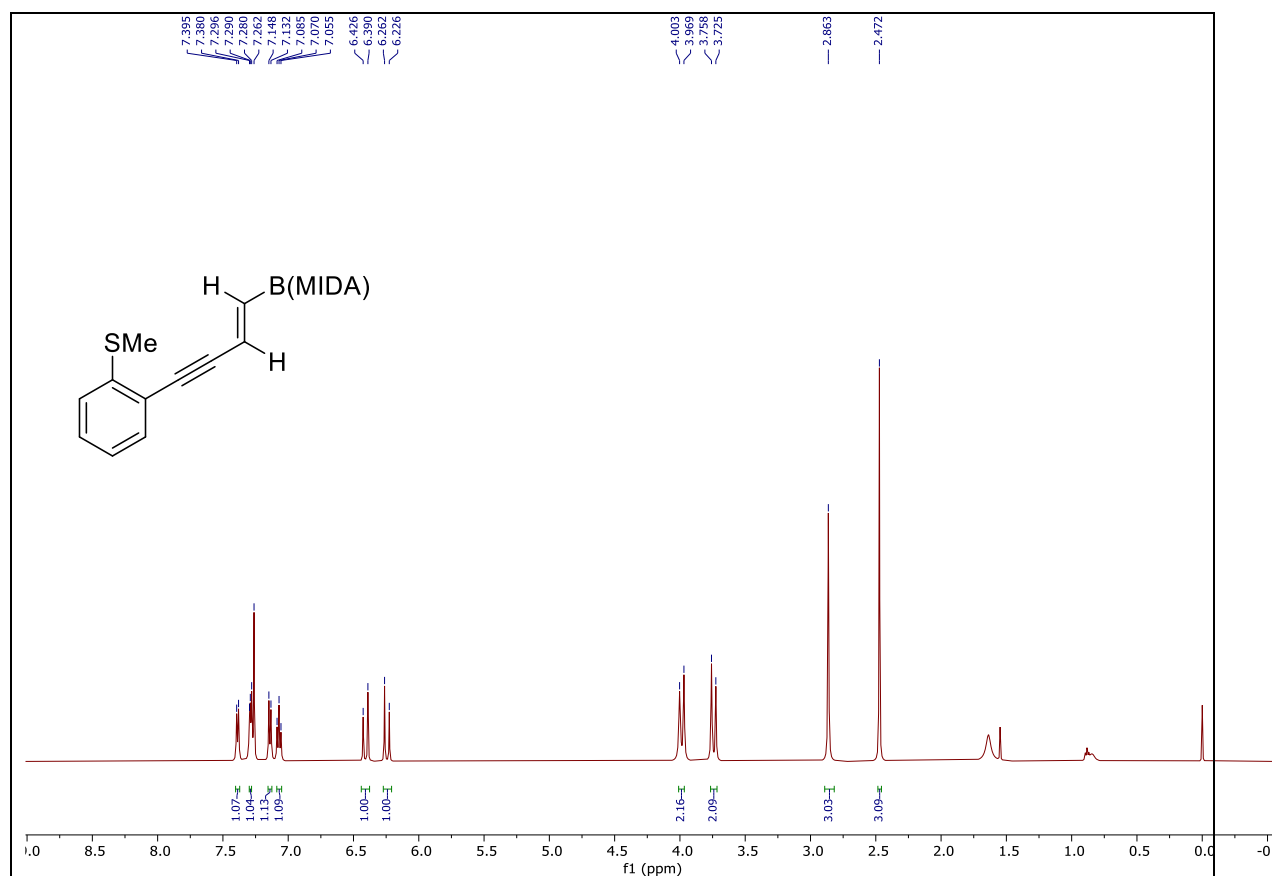
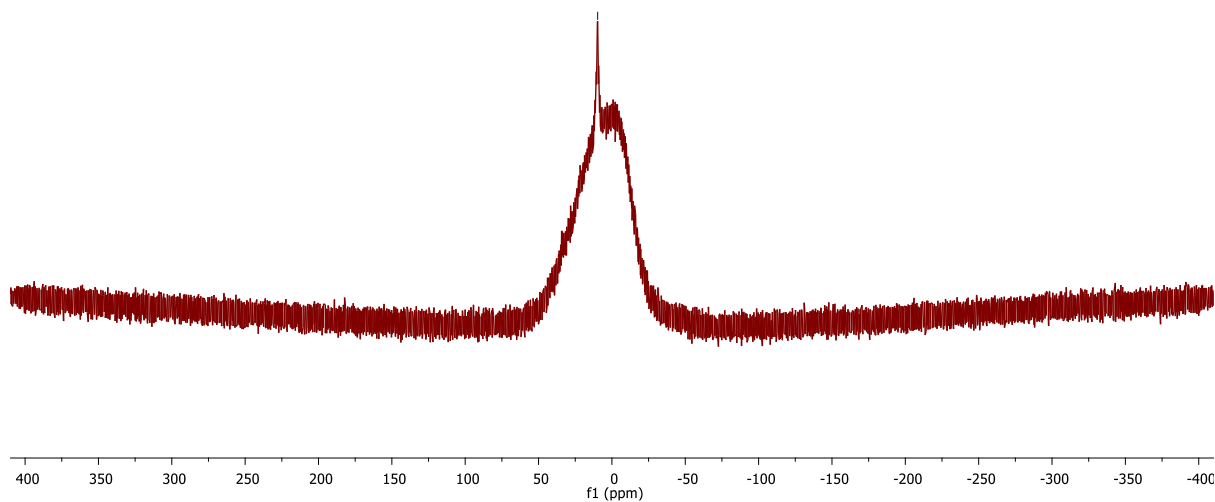


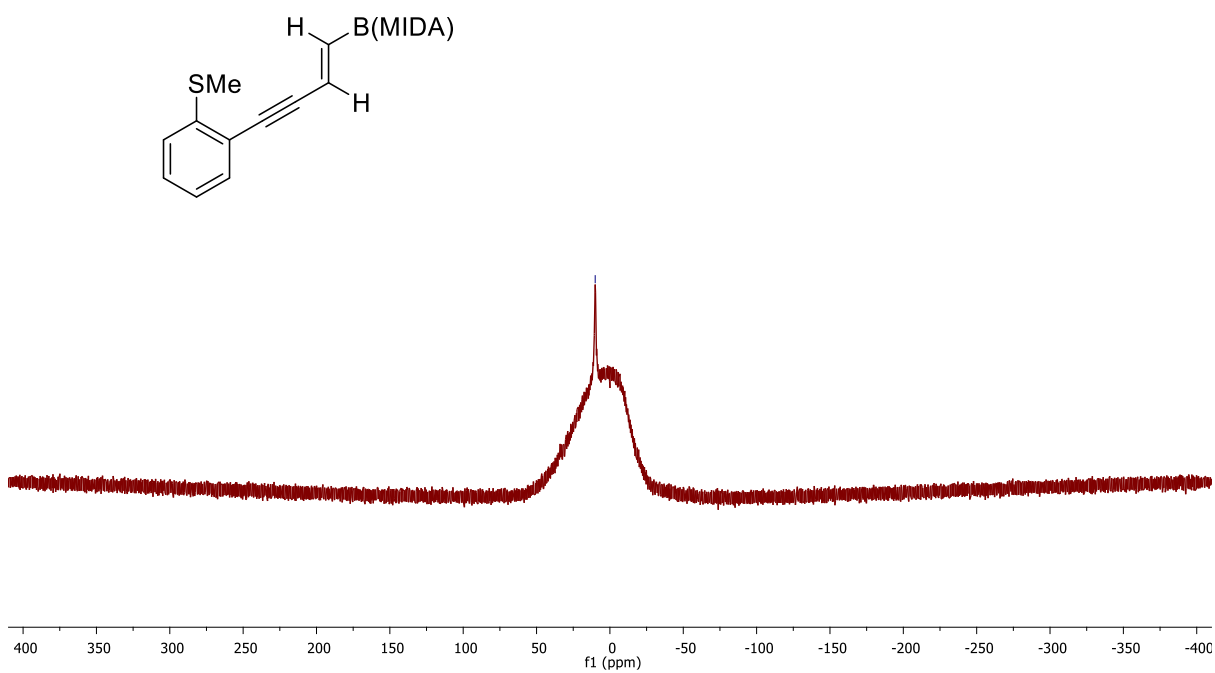
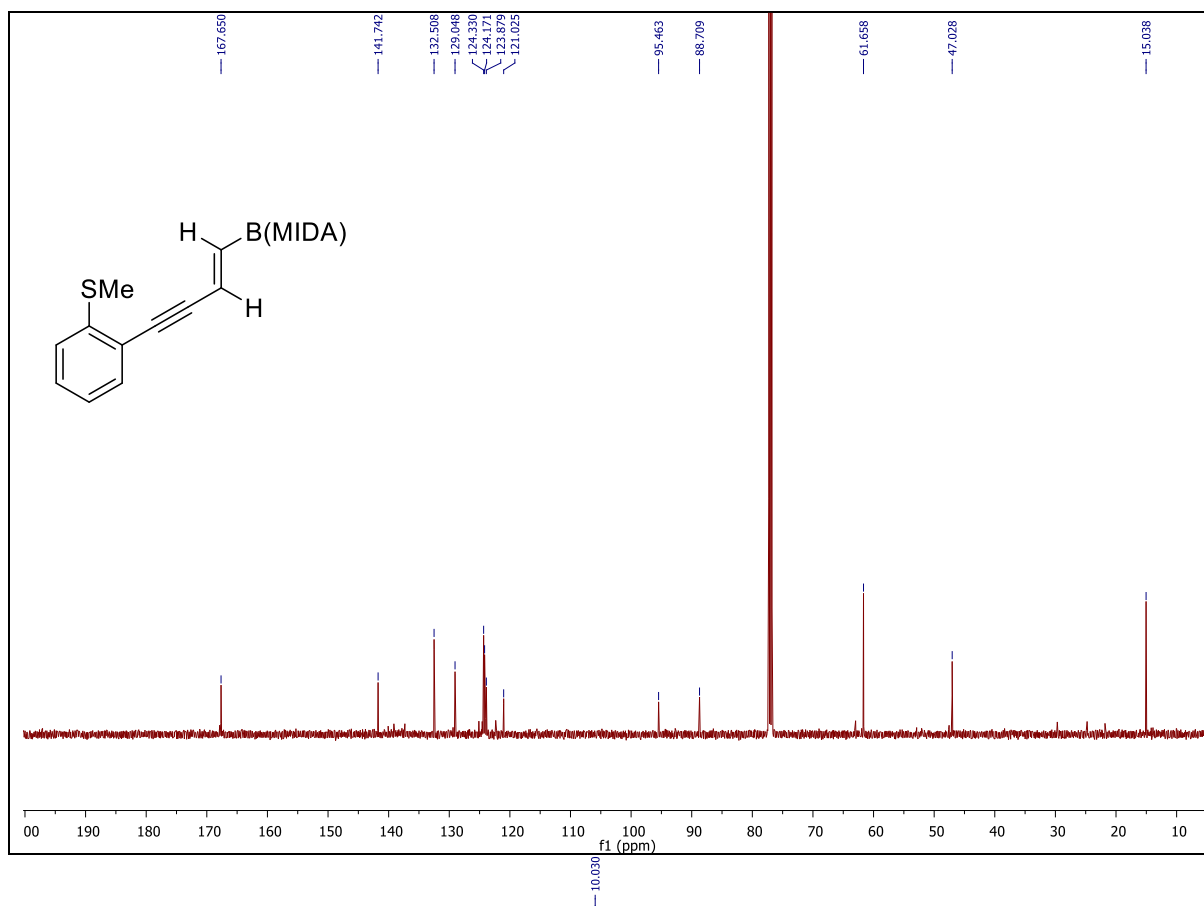


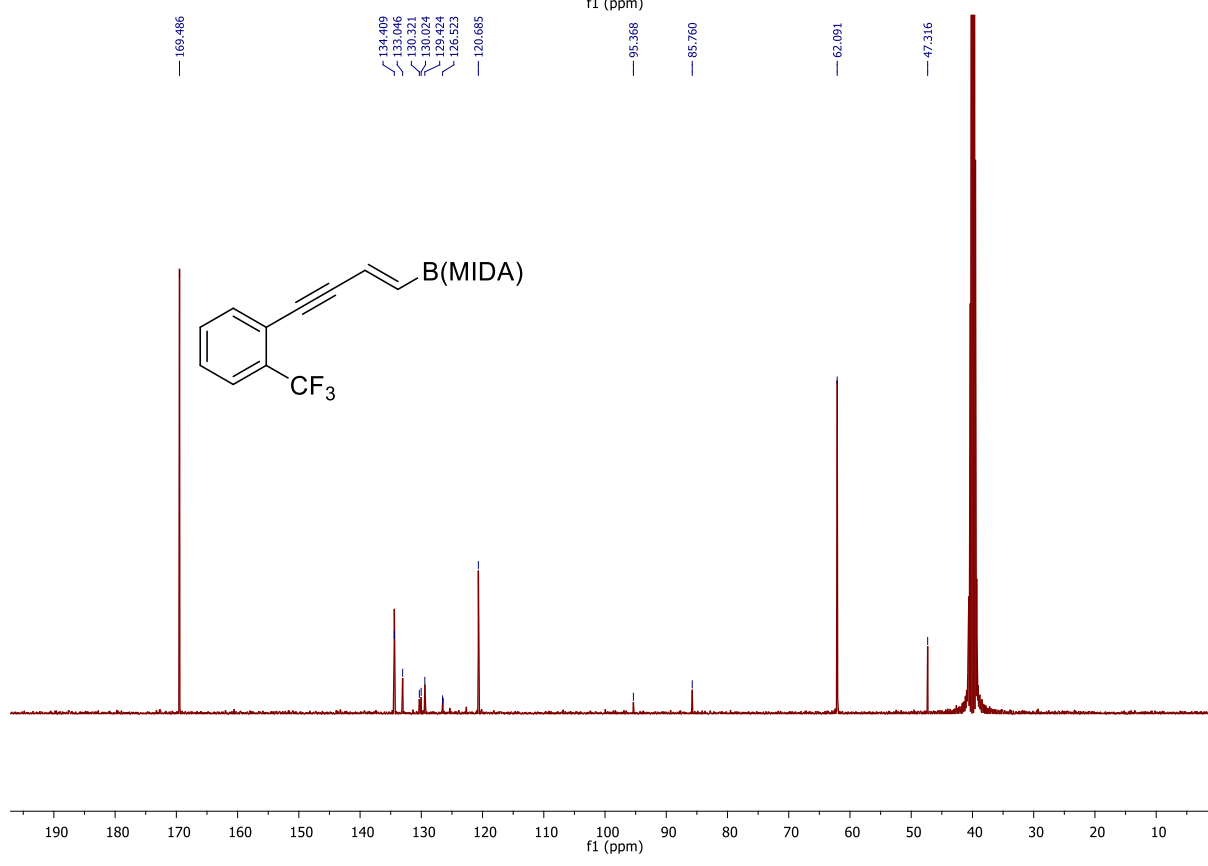
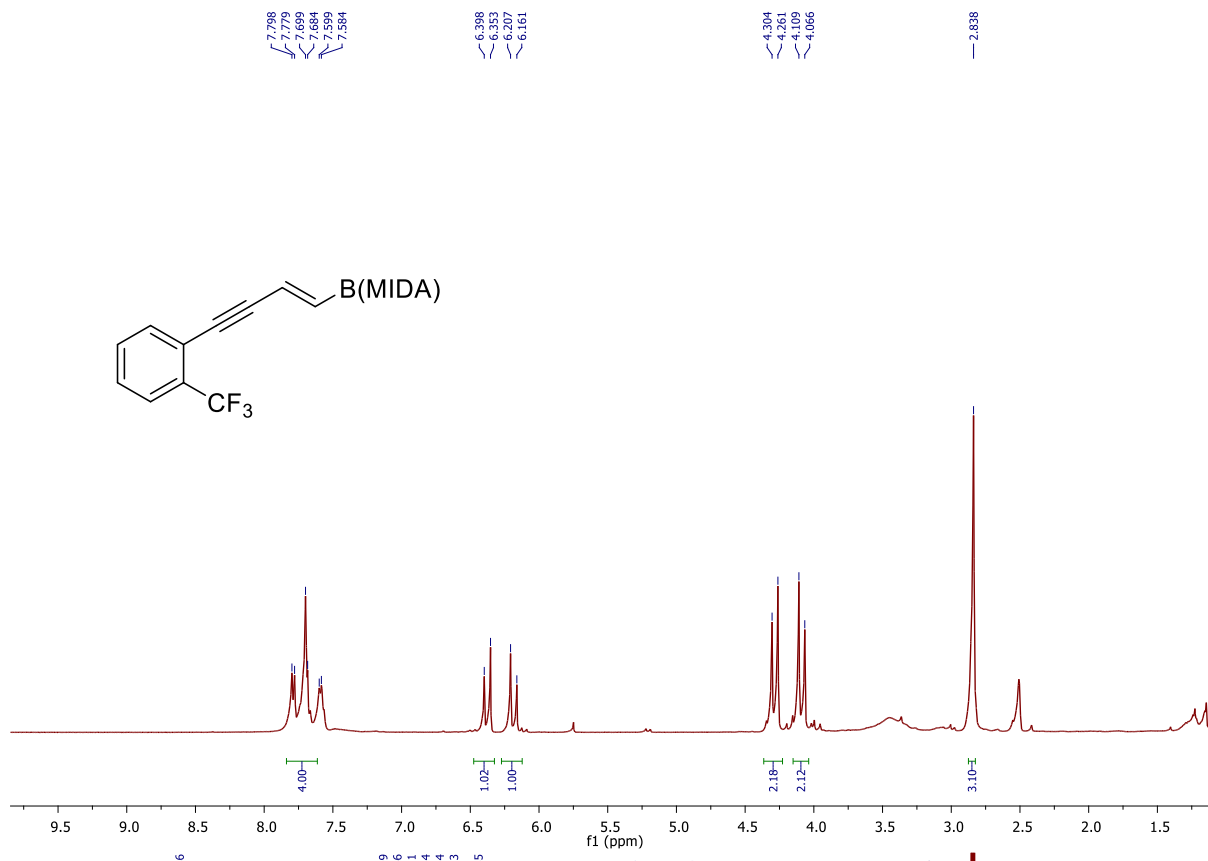


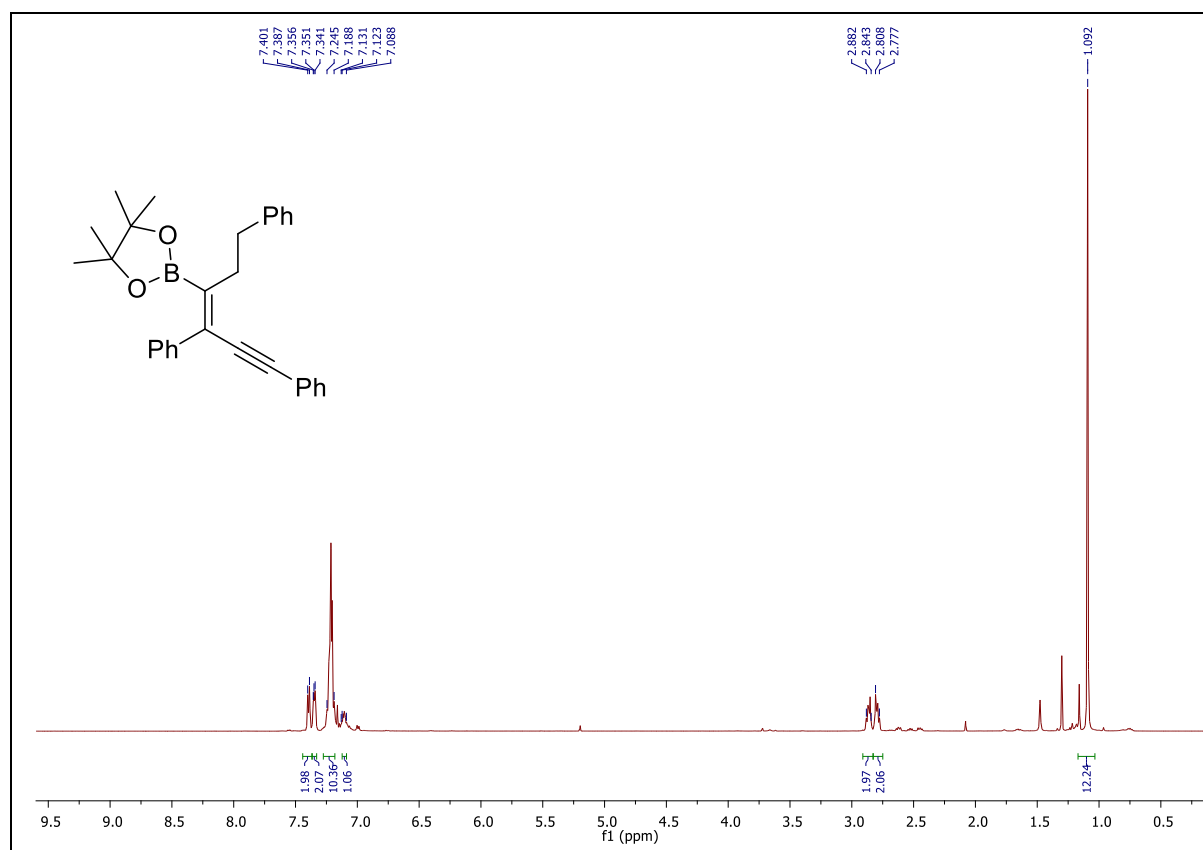
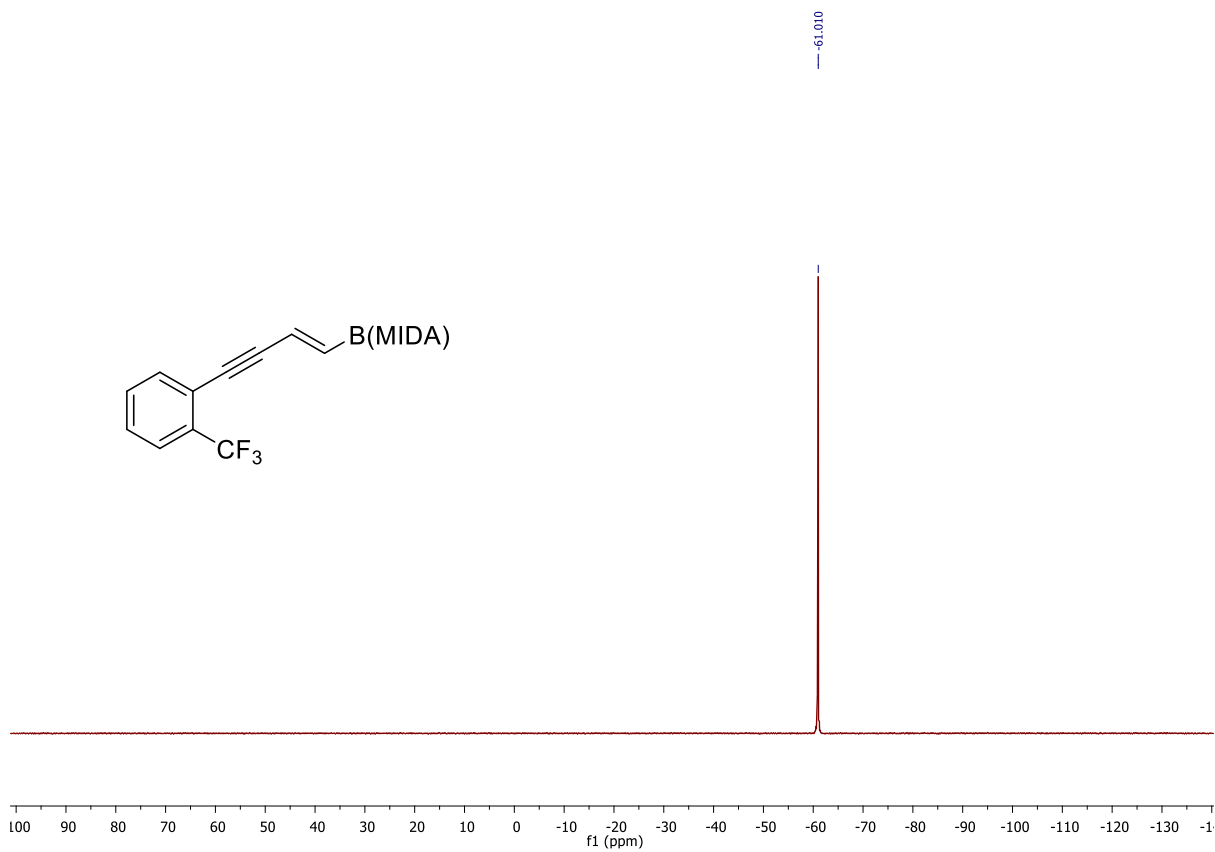


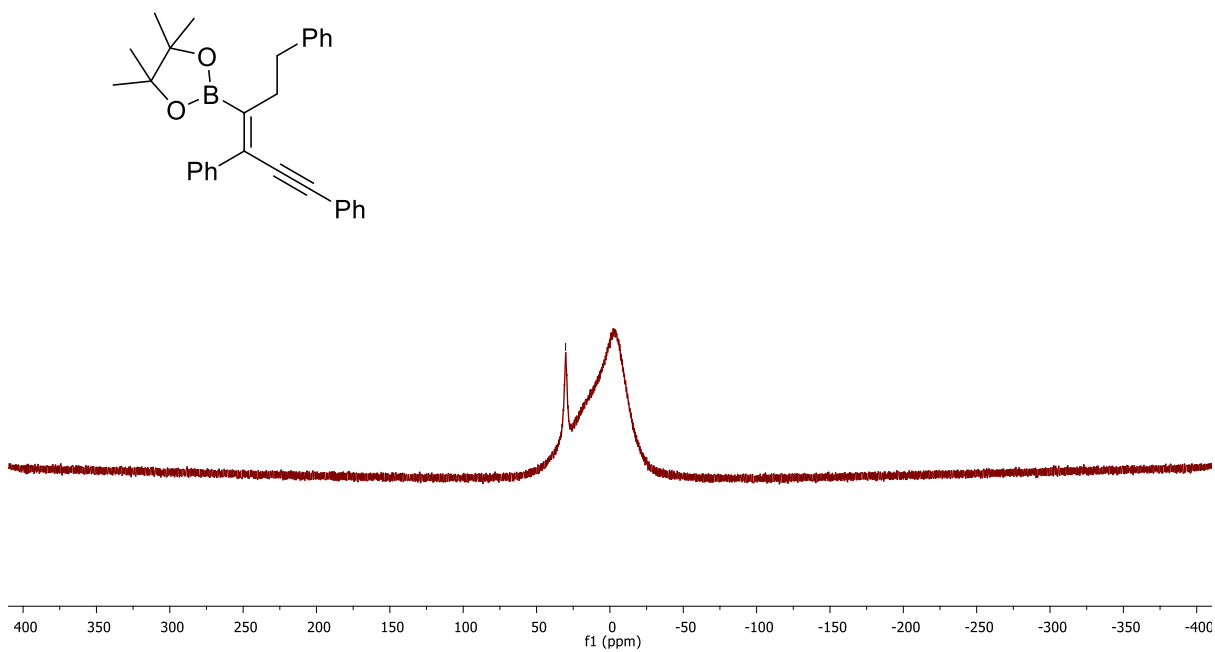
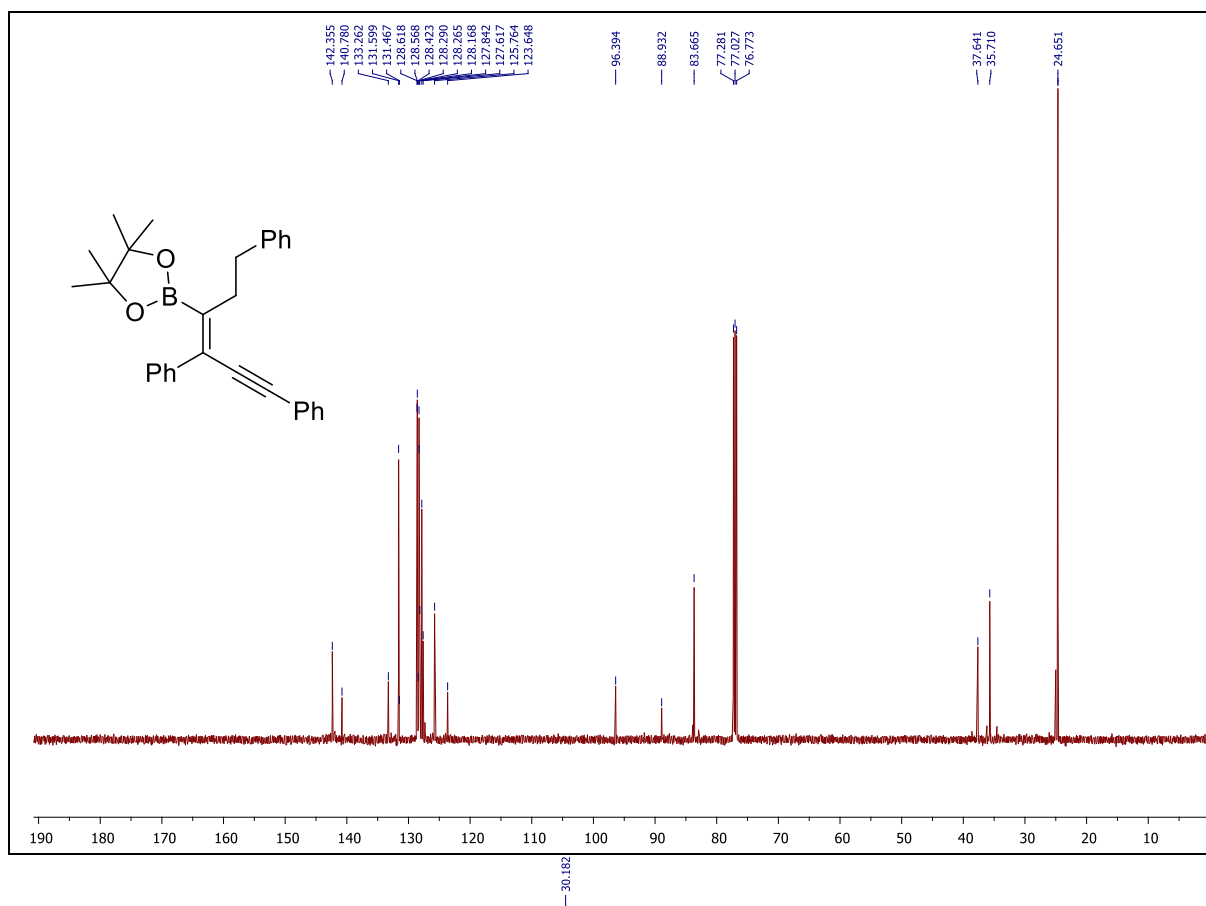
— 9.732

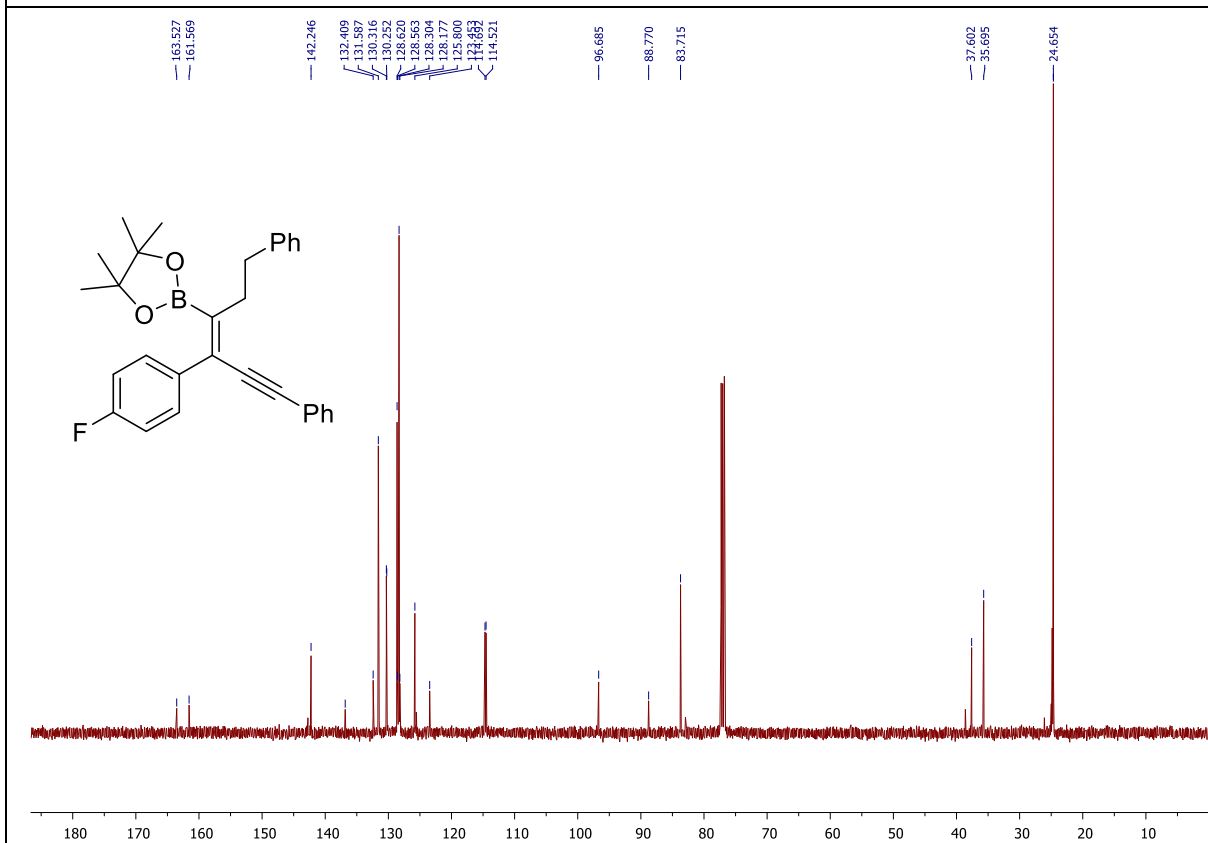
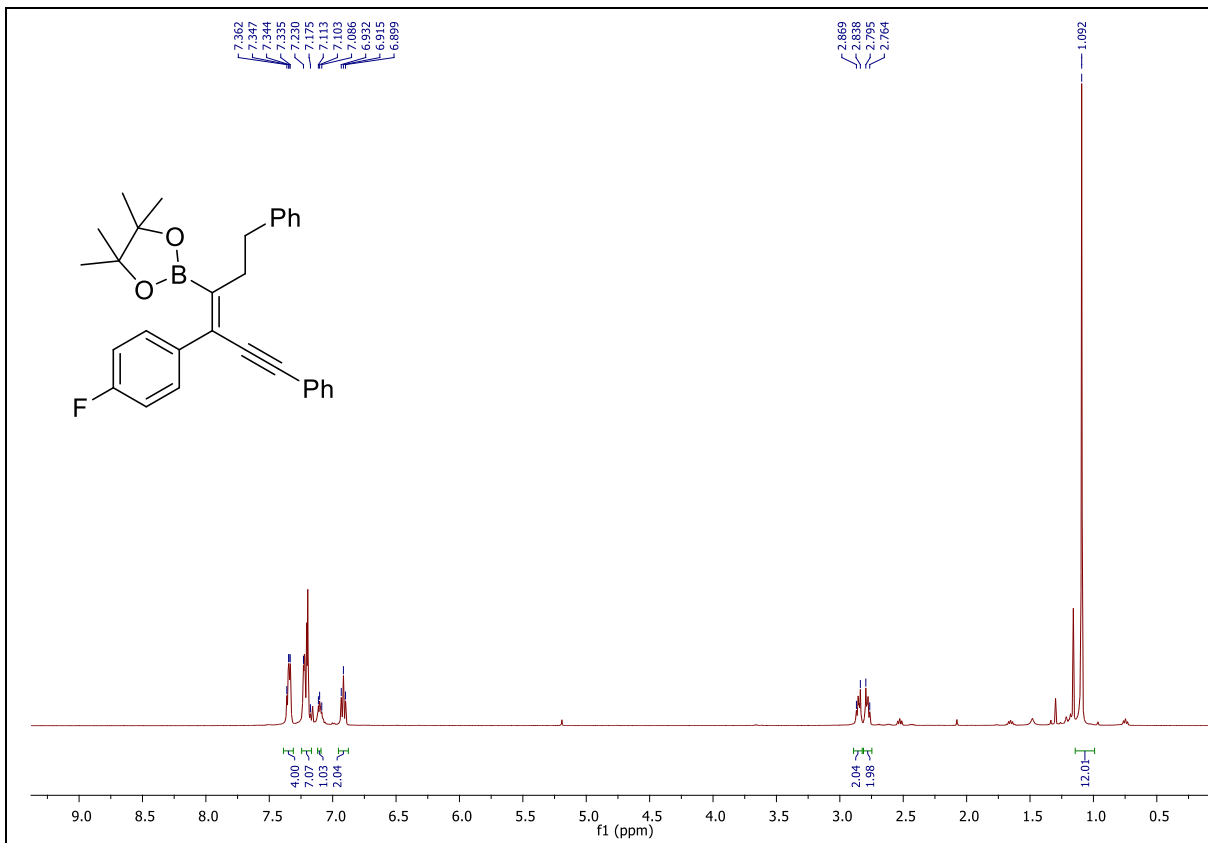


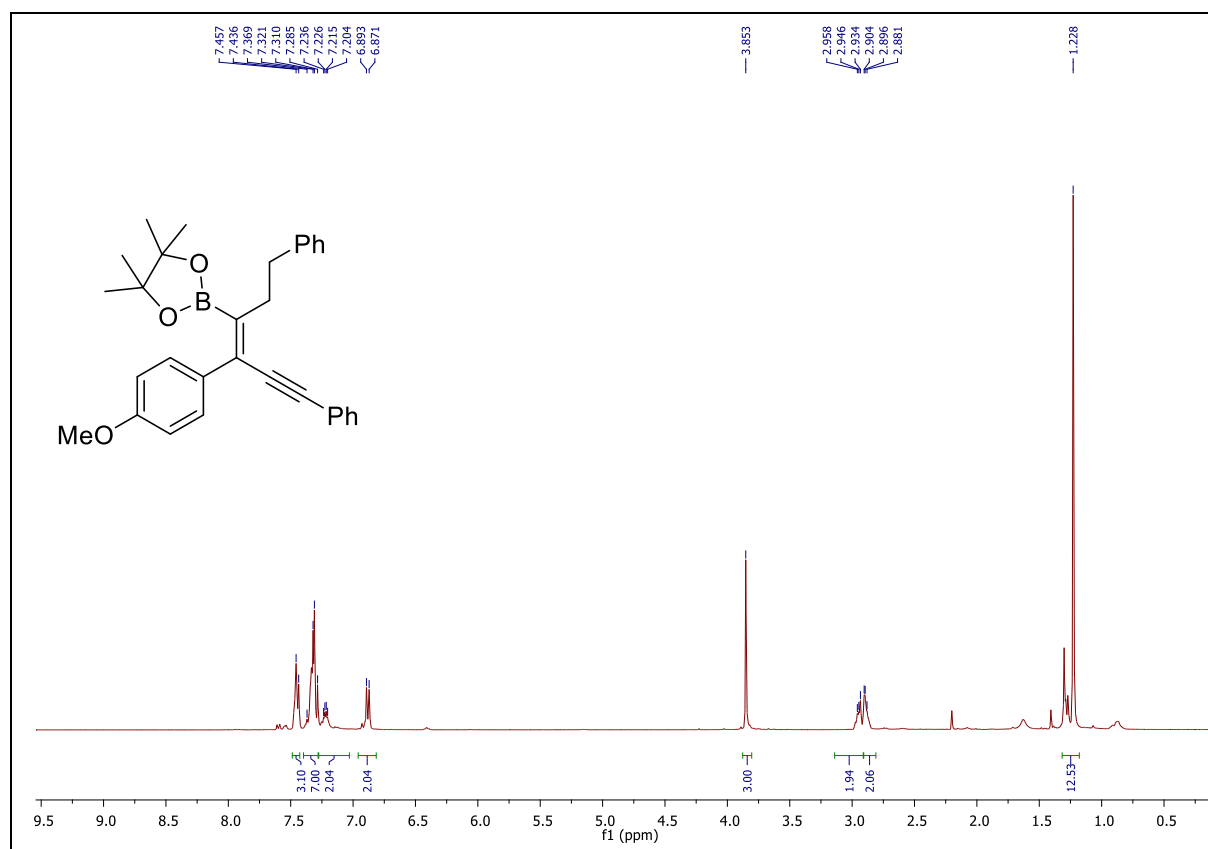
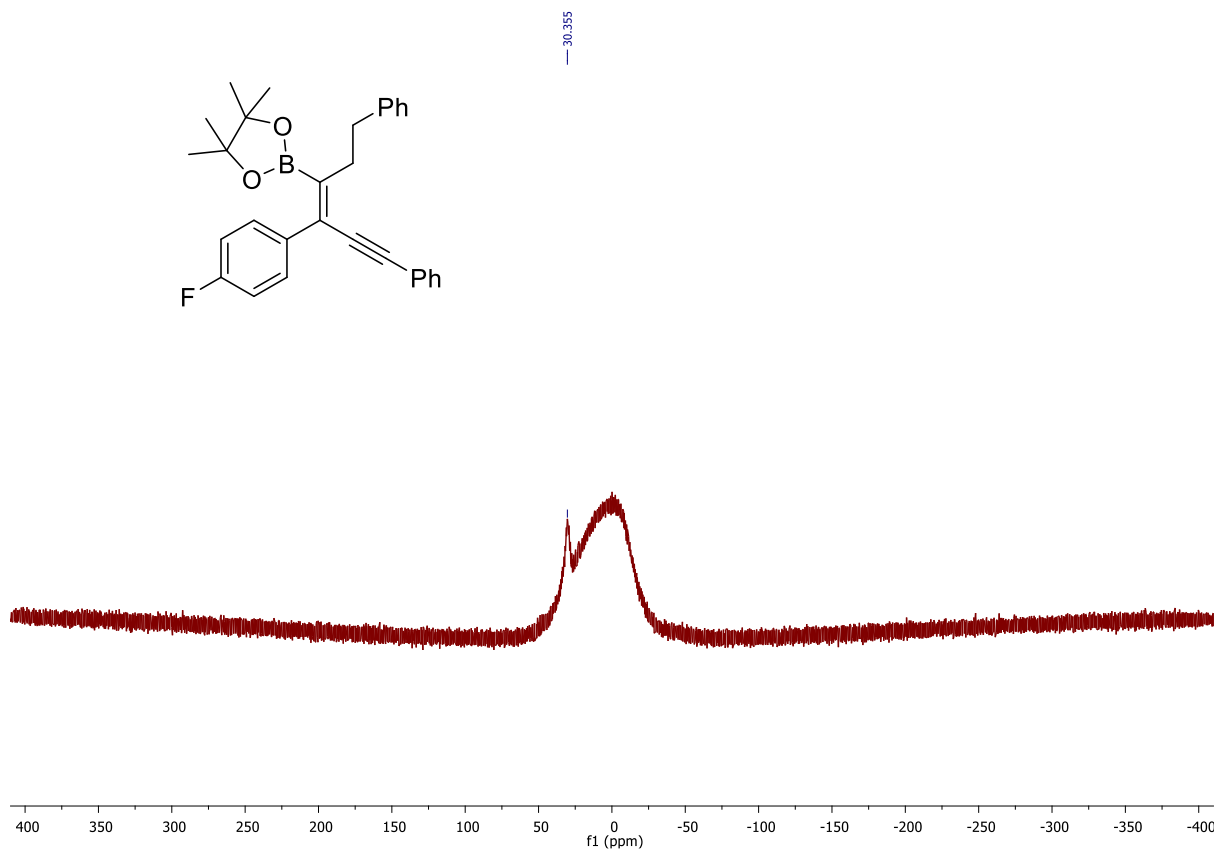


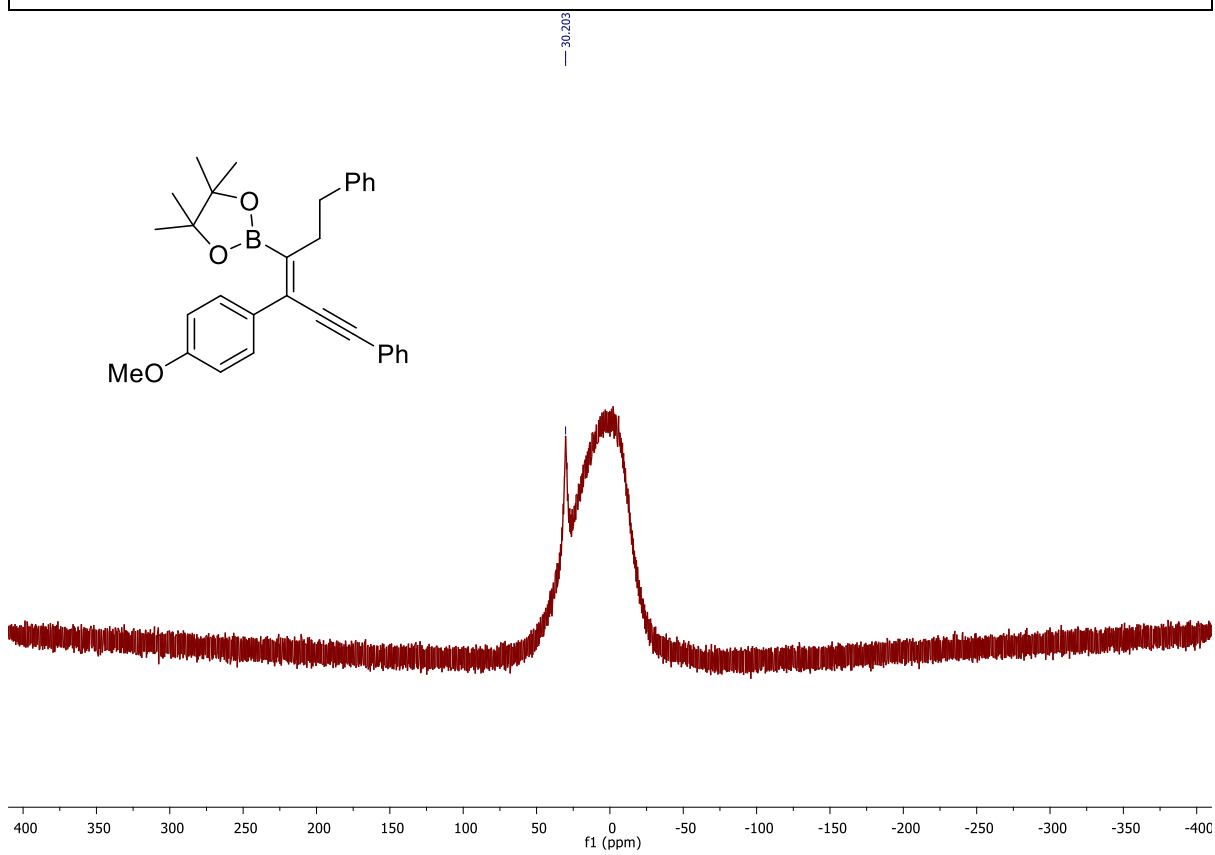
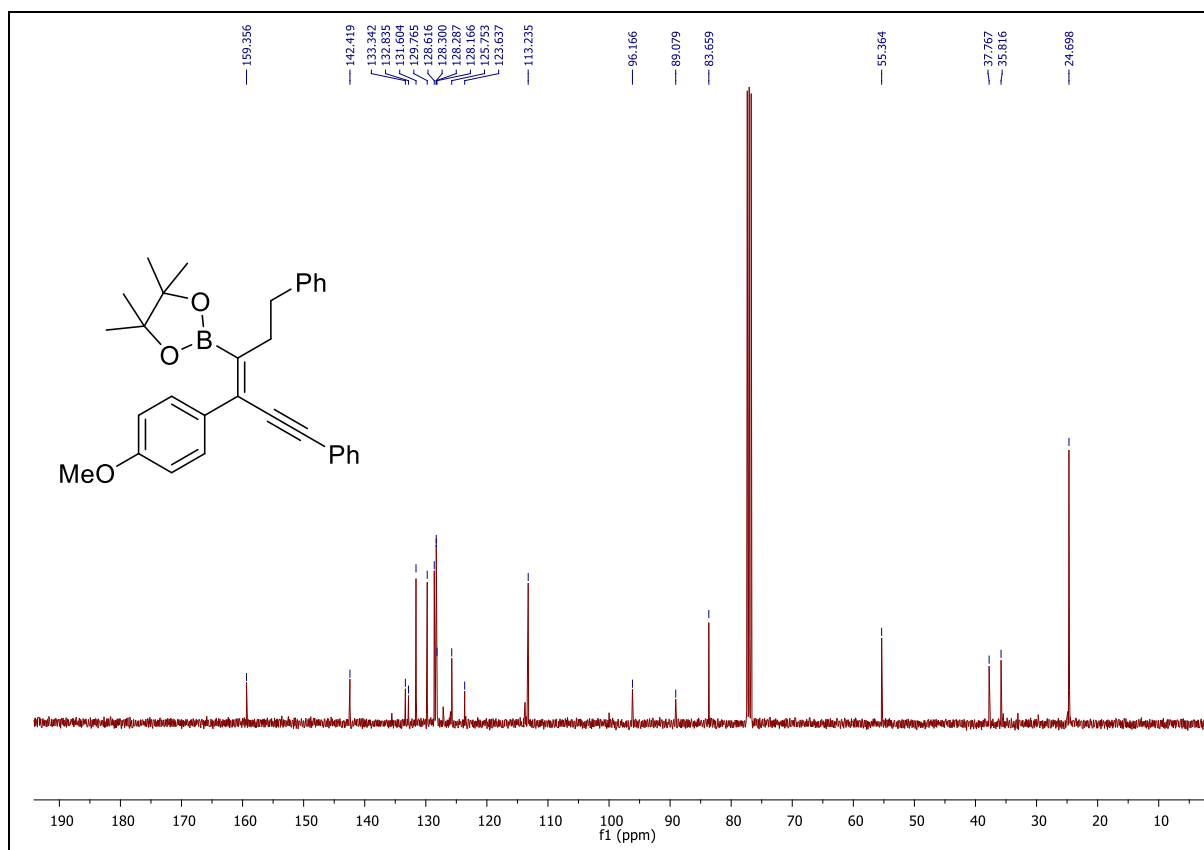


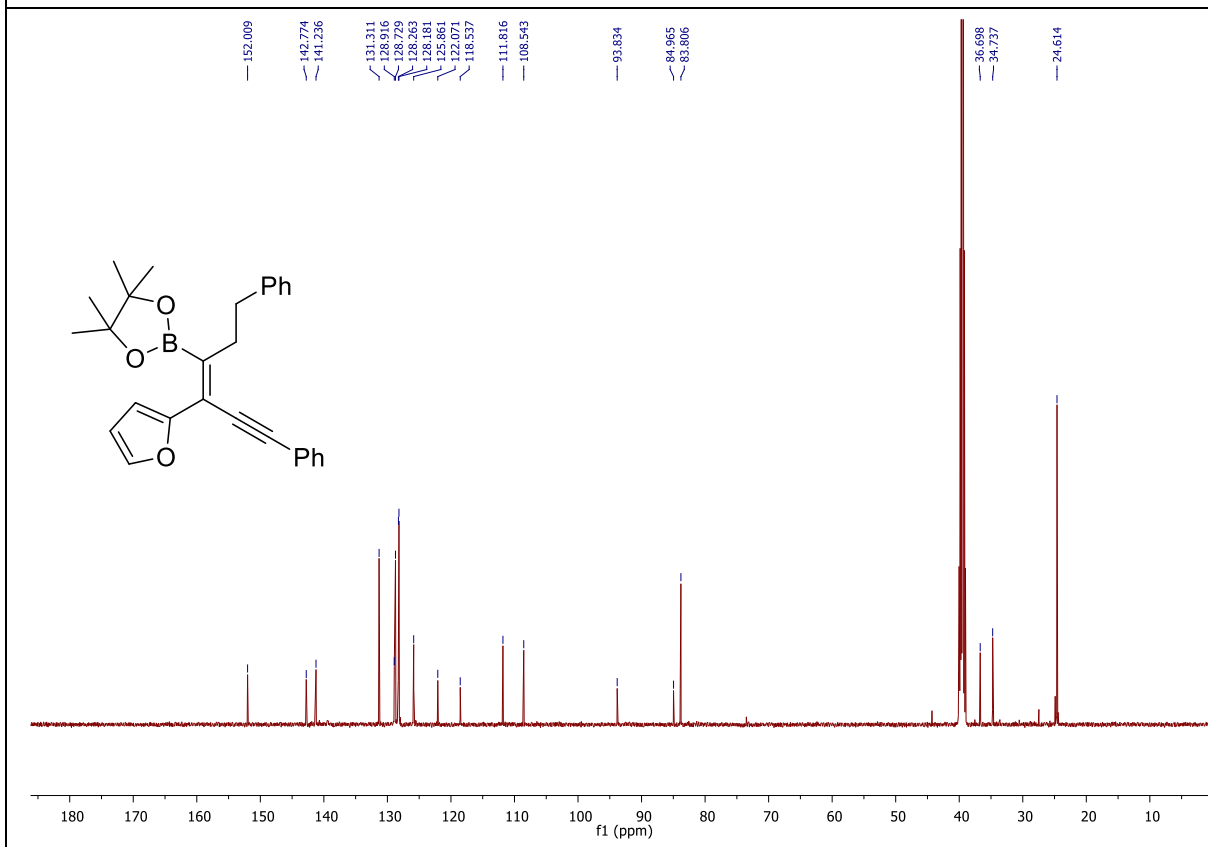
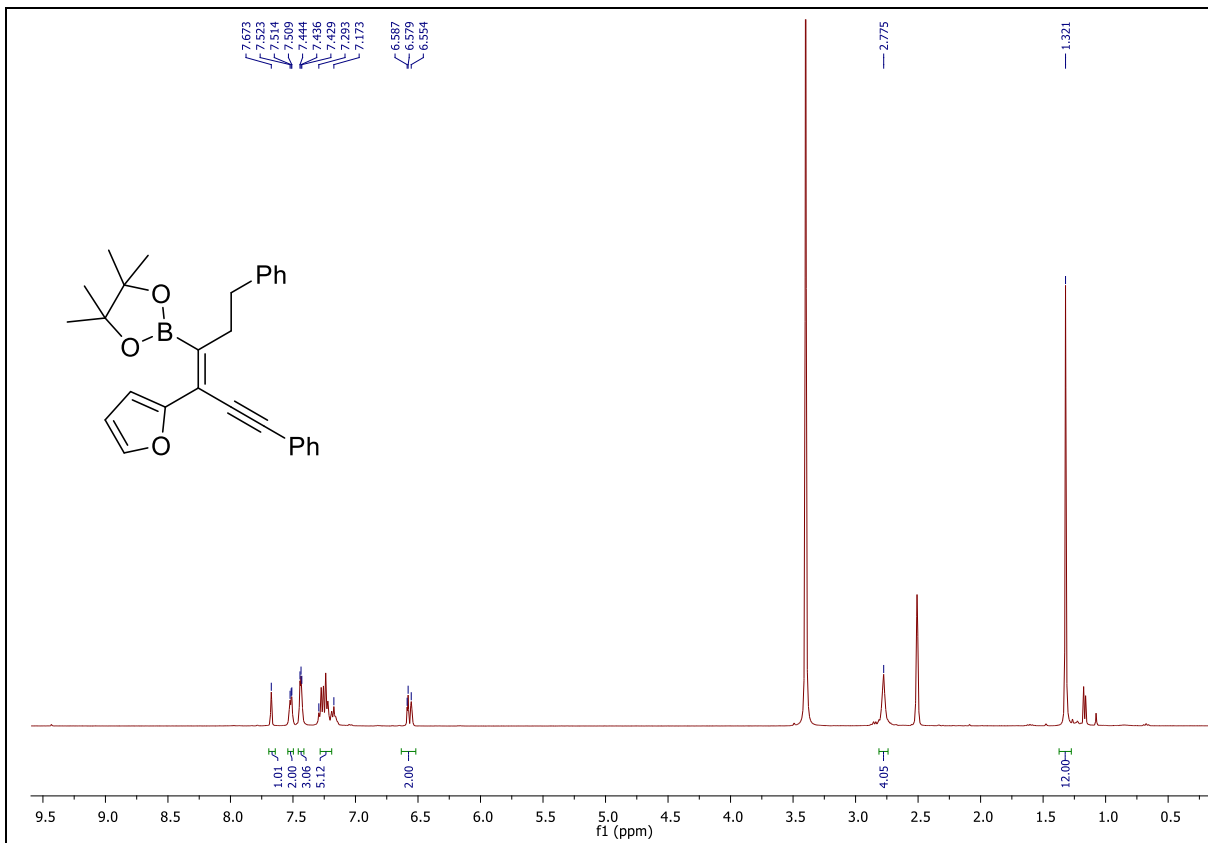


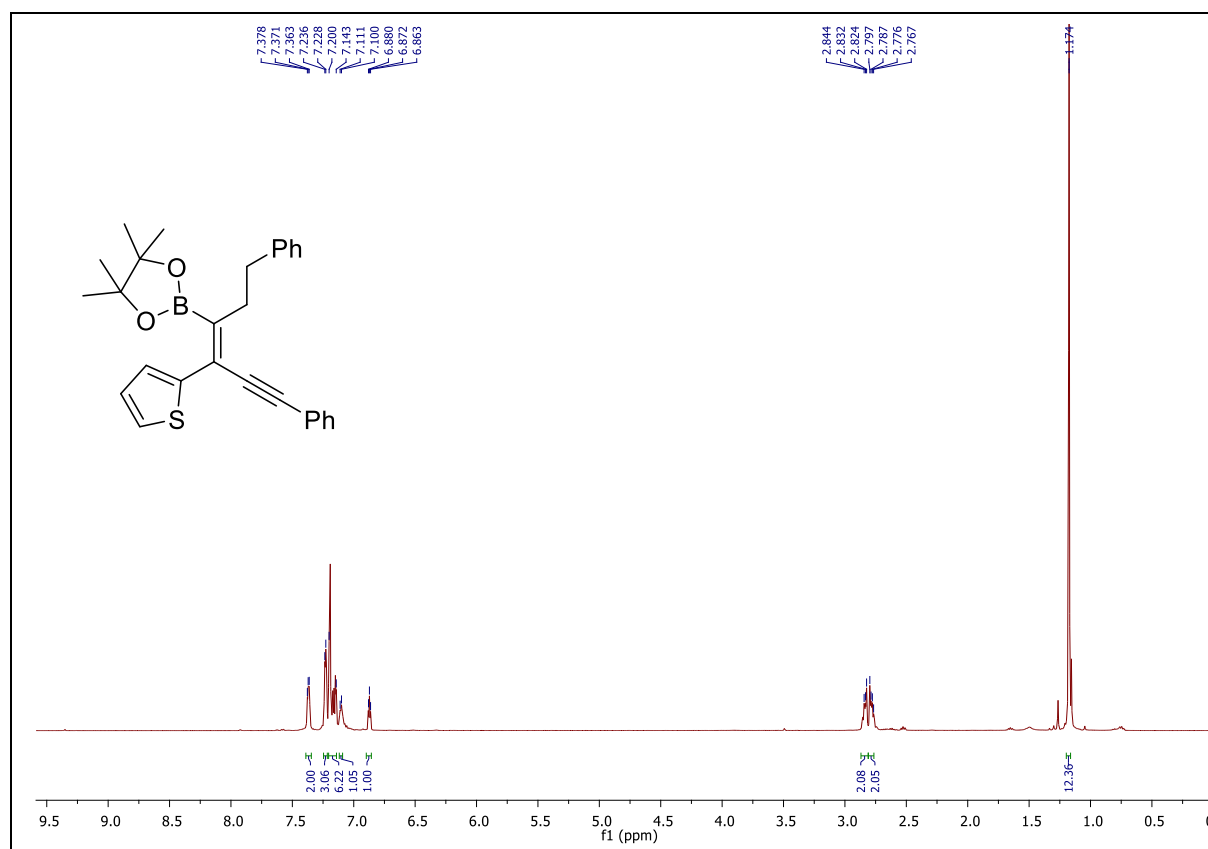
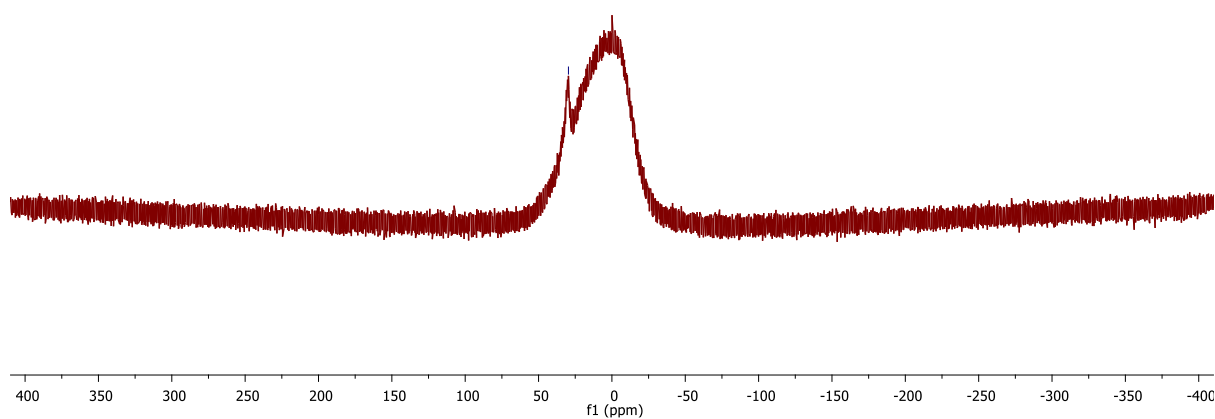
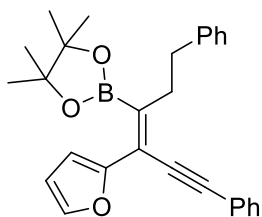


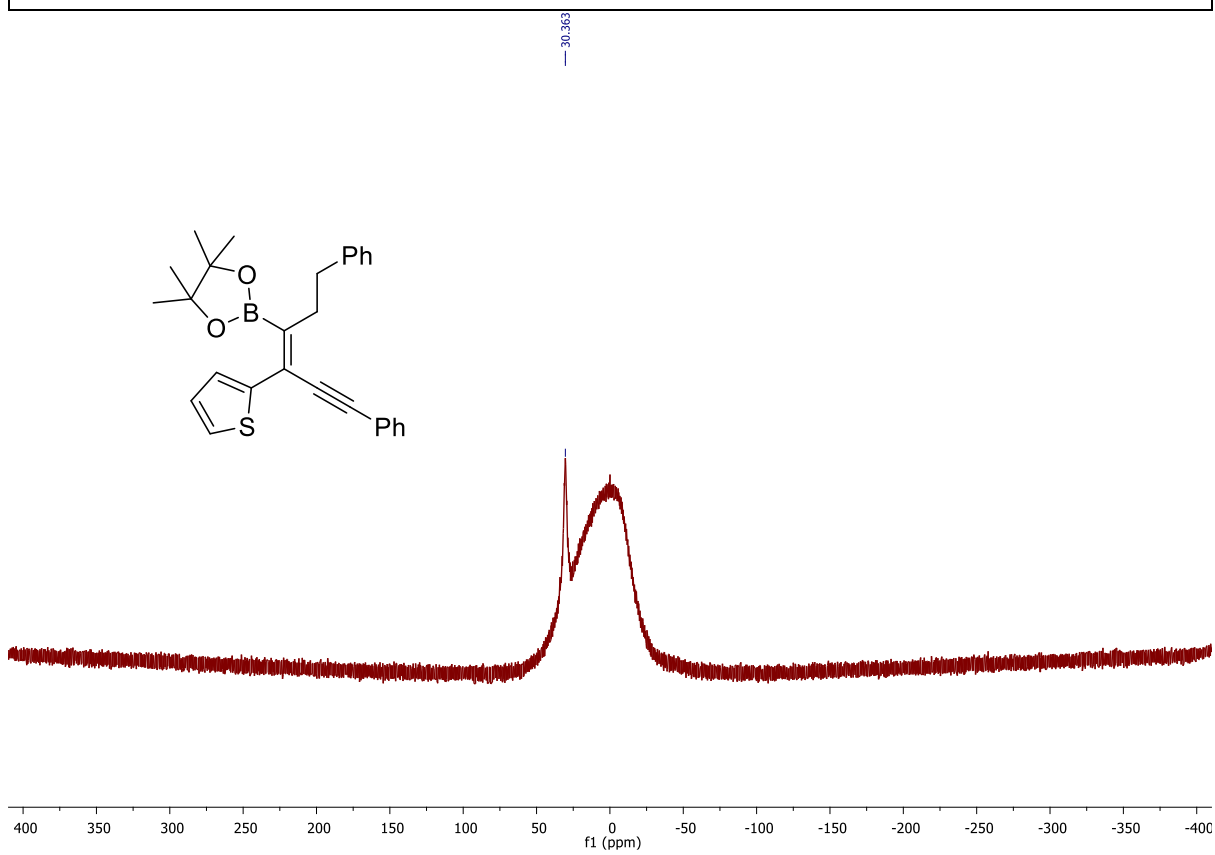
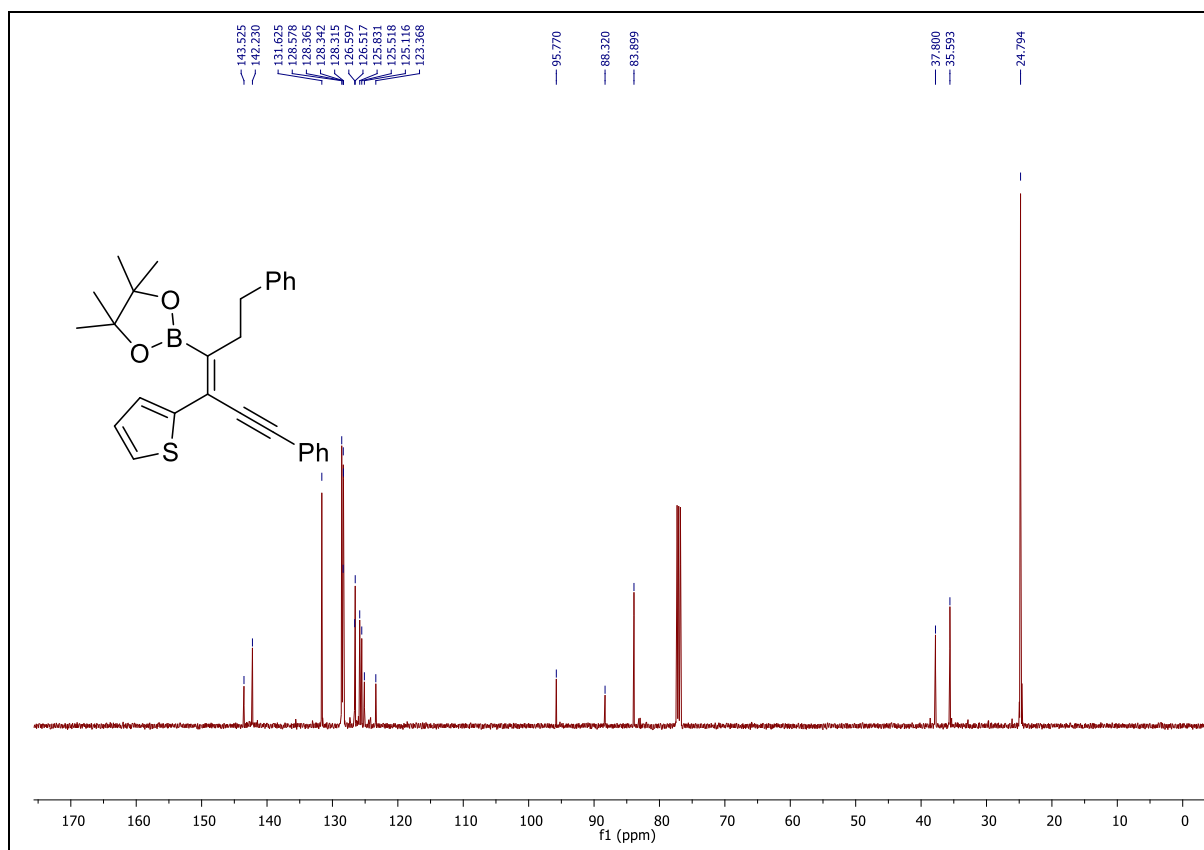


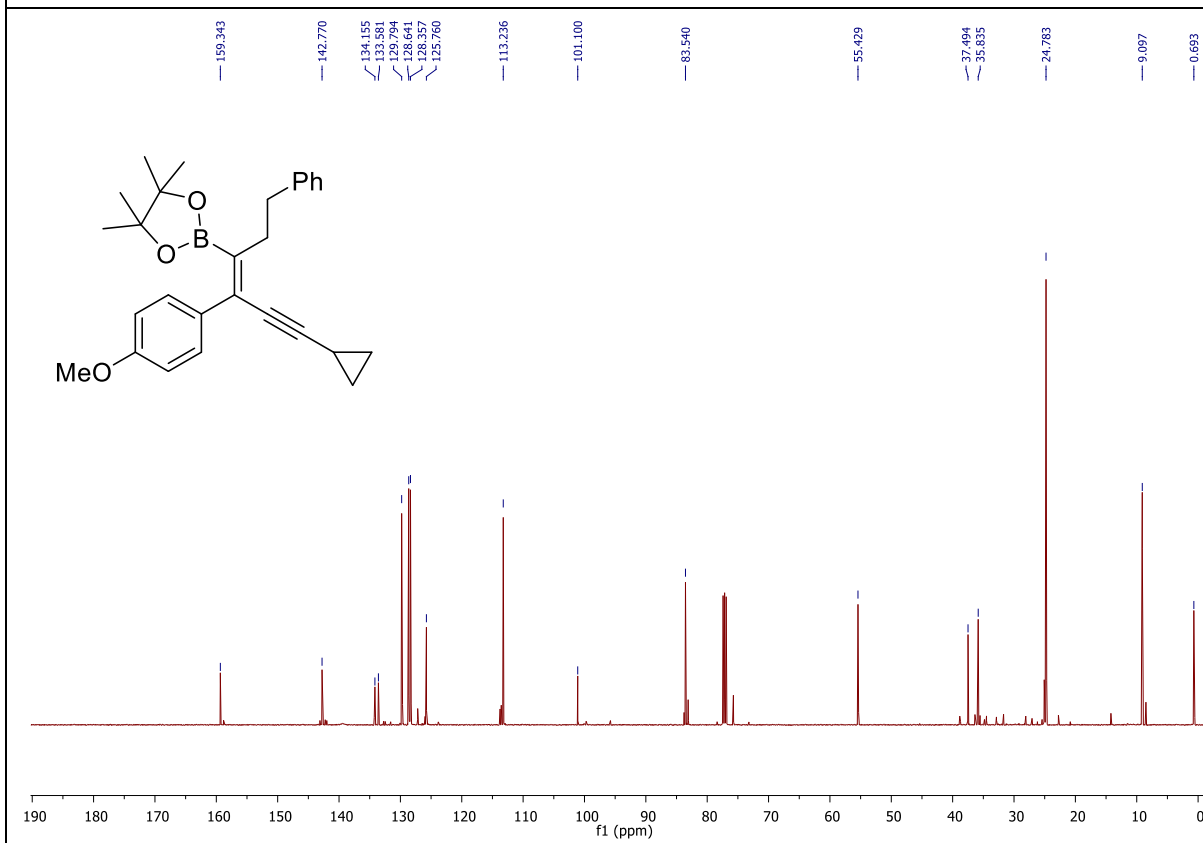
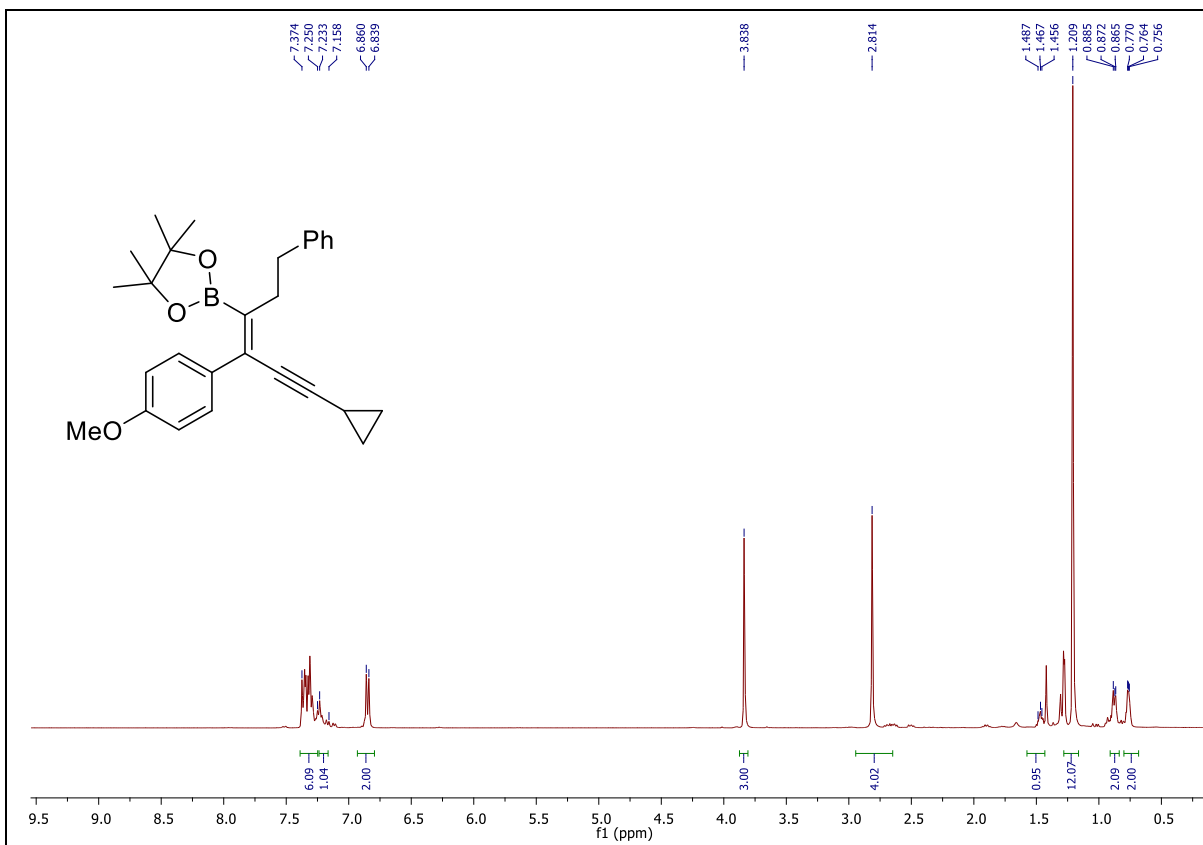


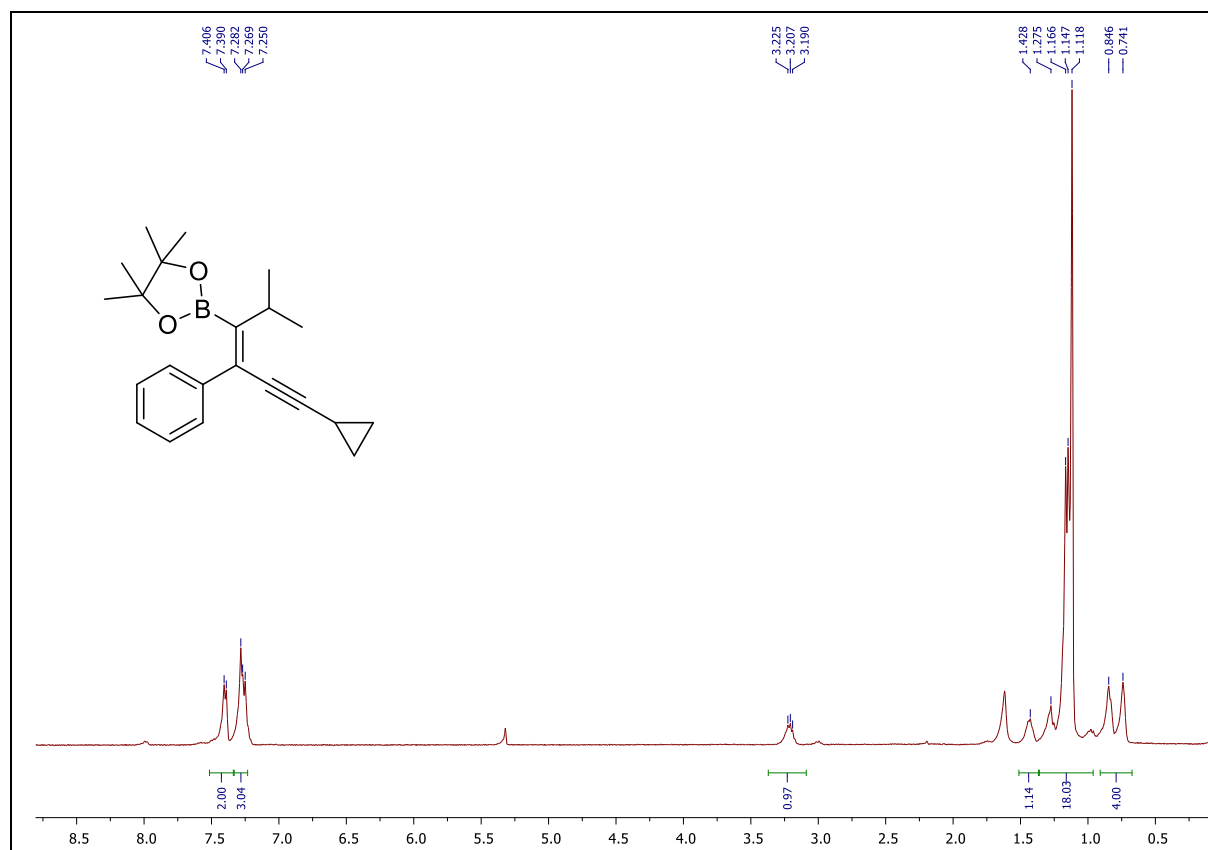
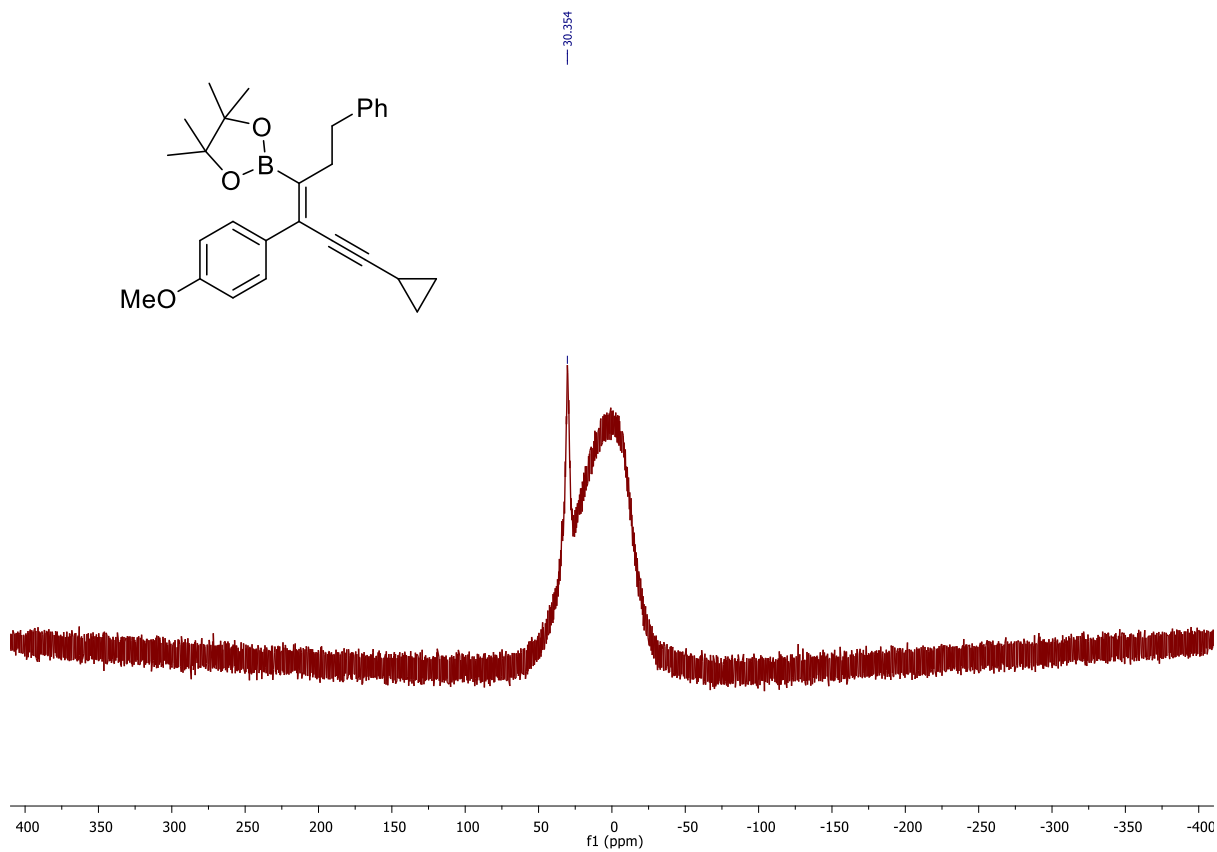


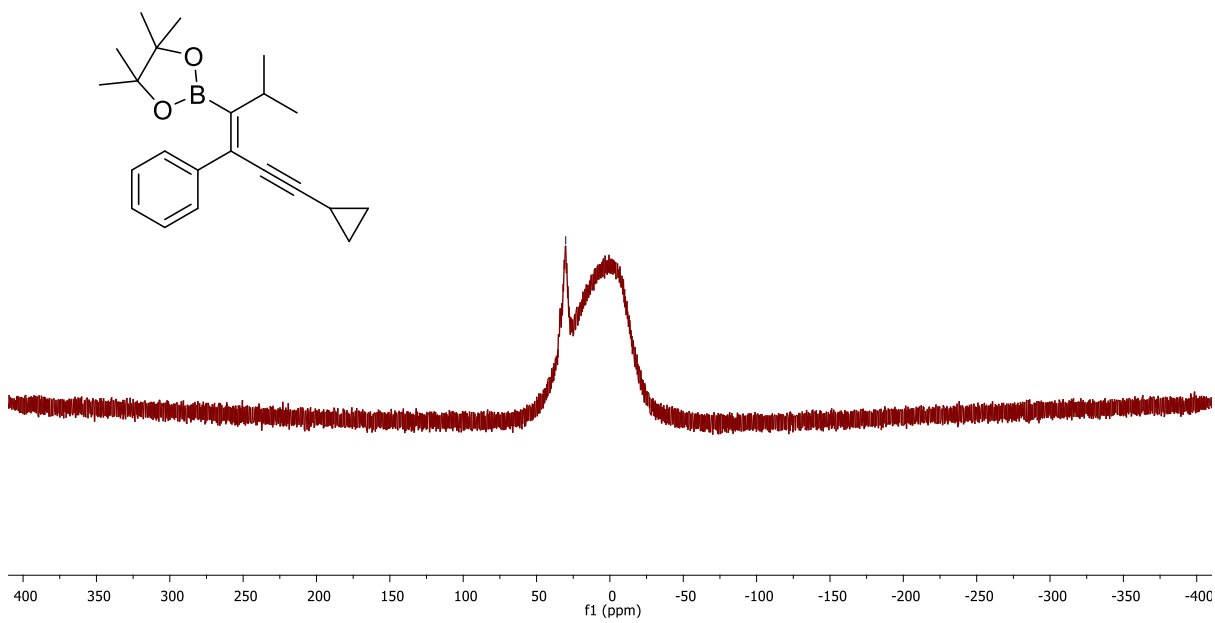
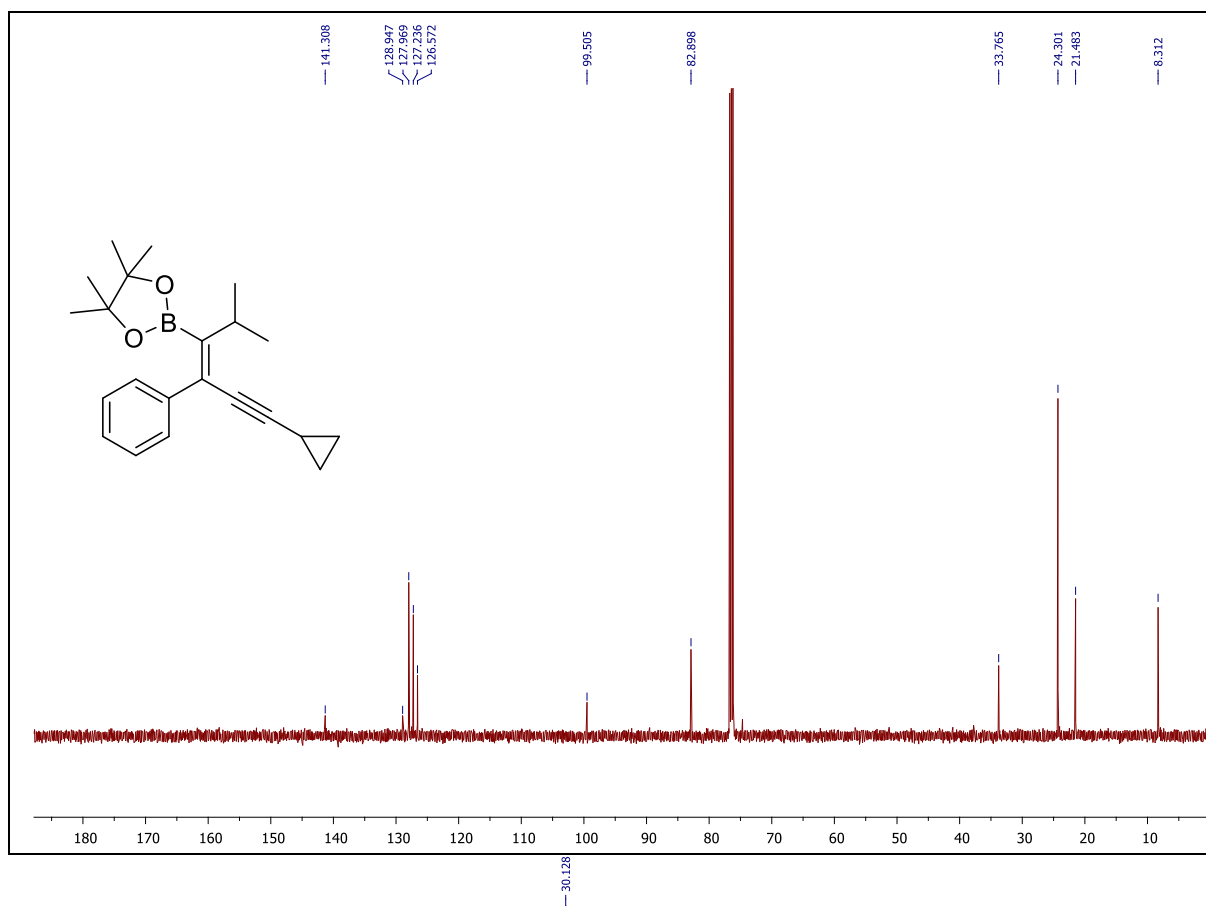


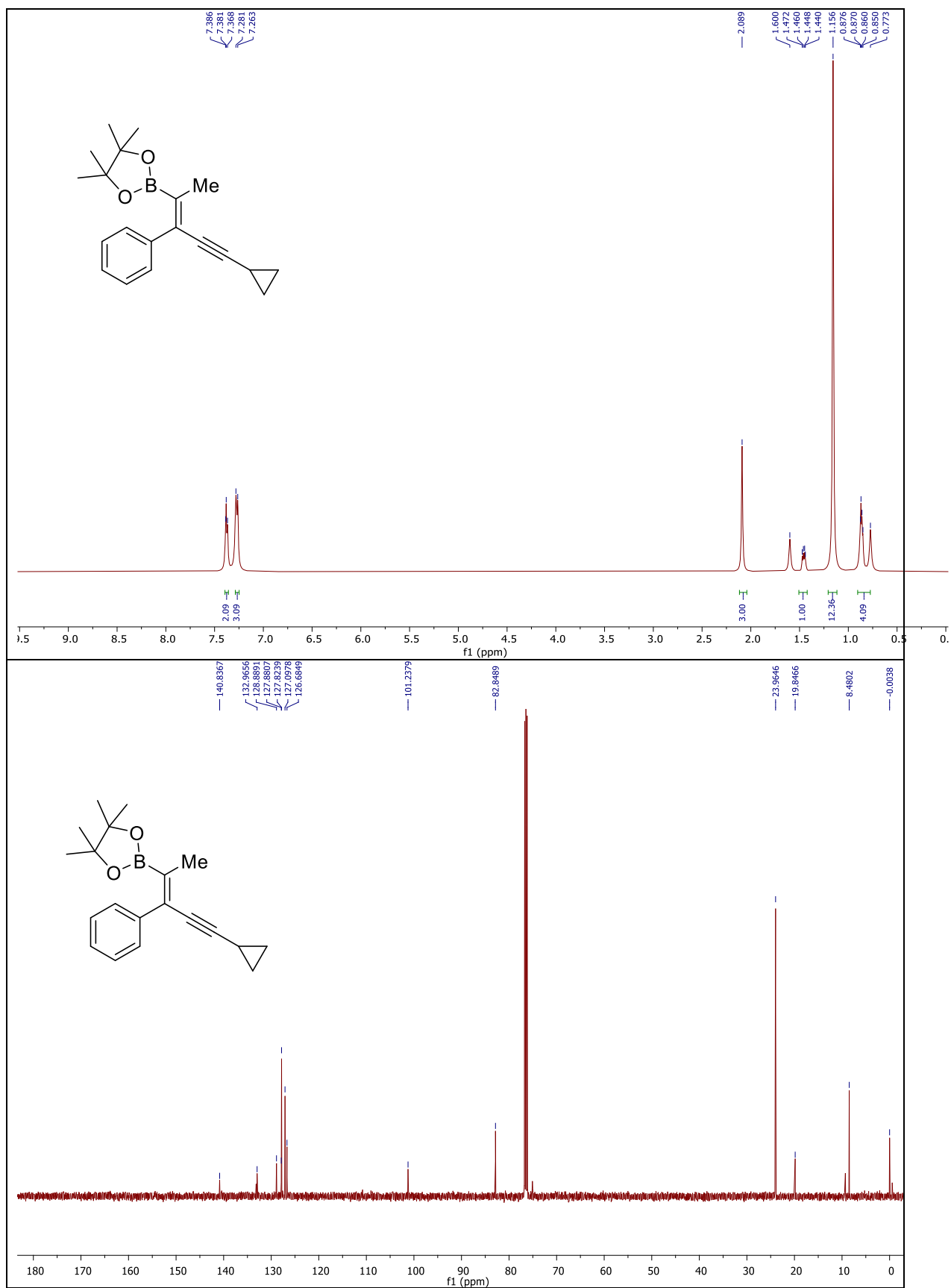


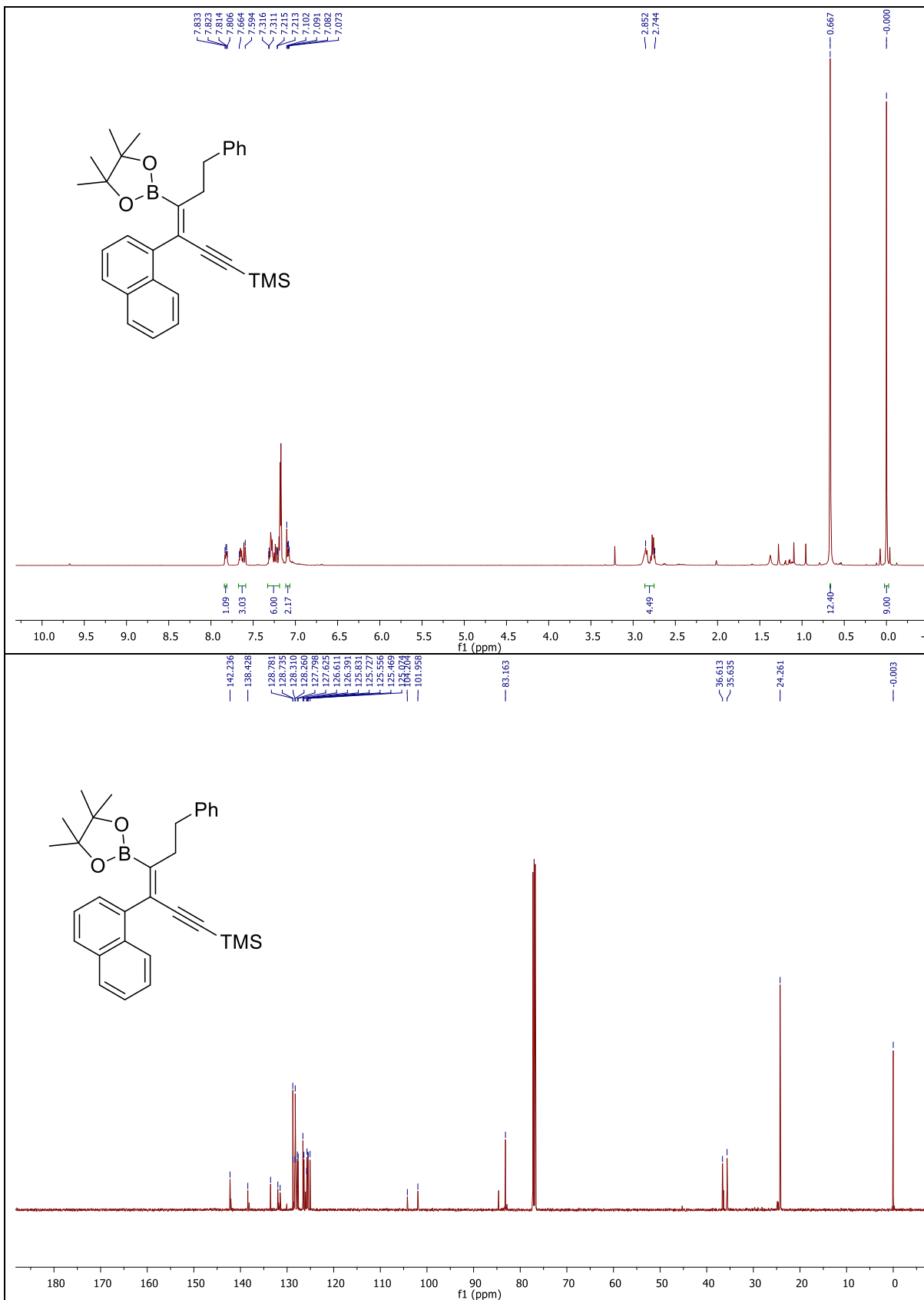


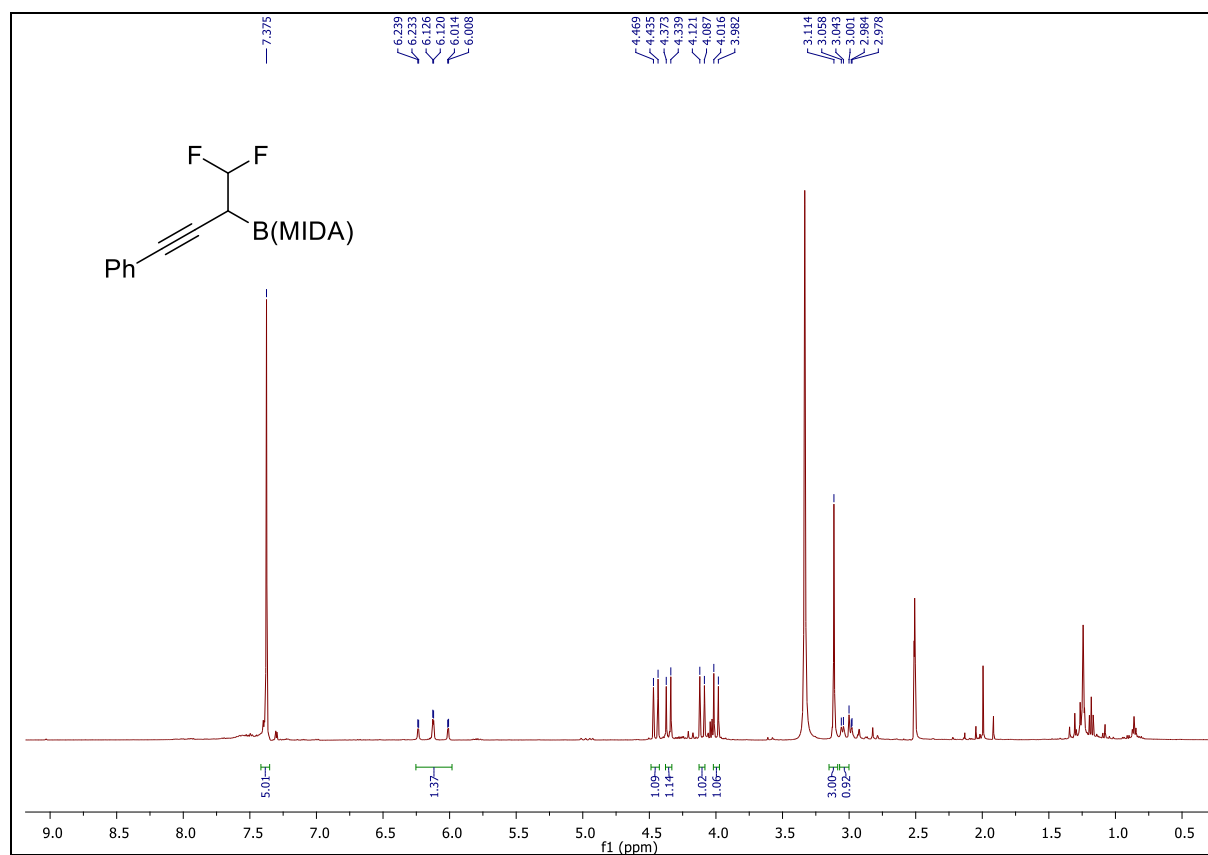
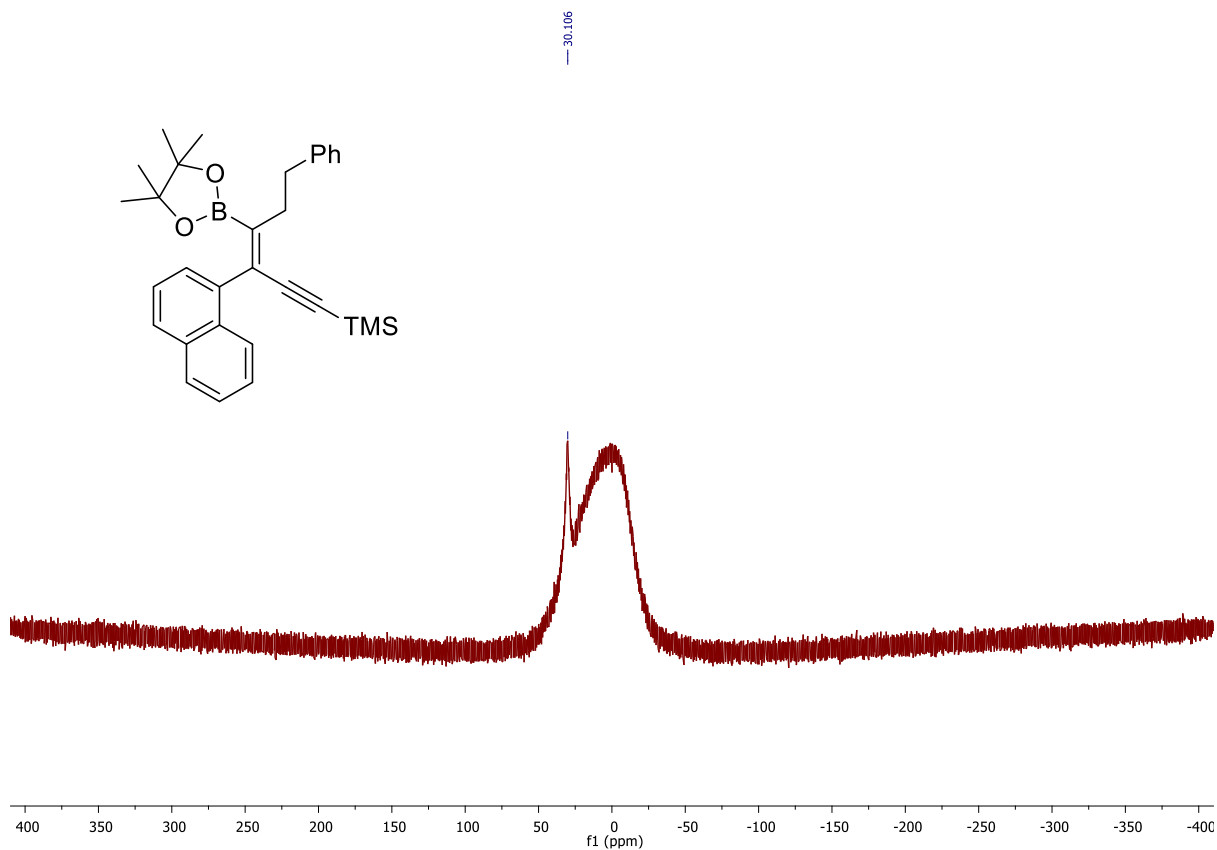


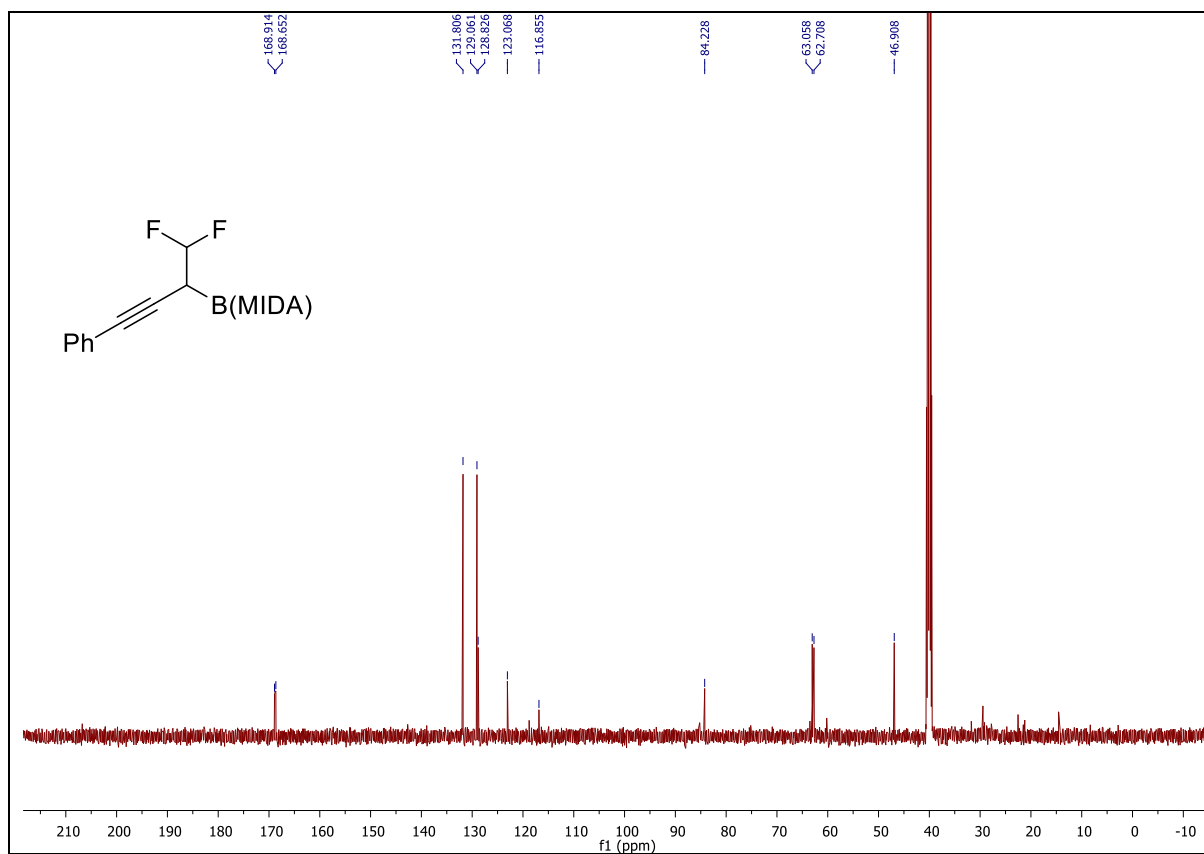


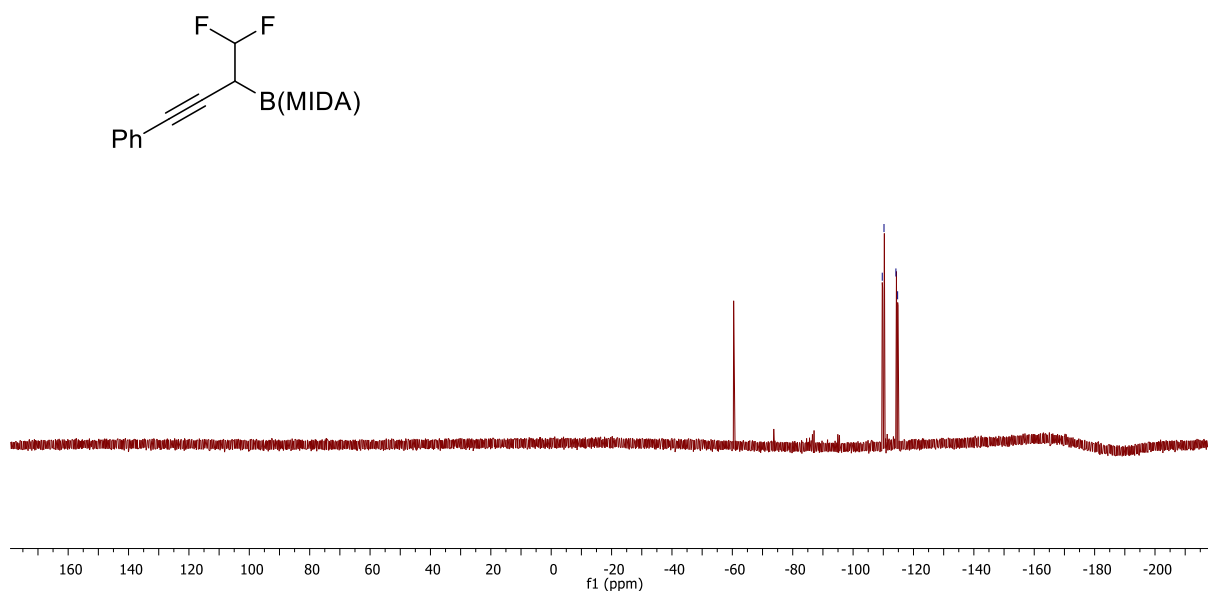
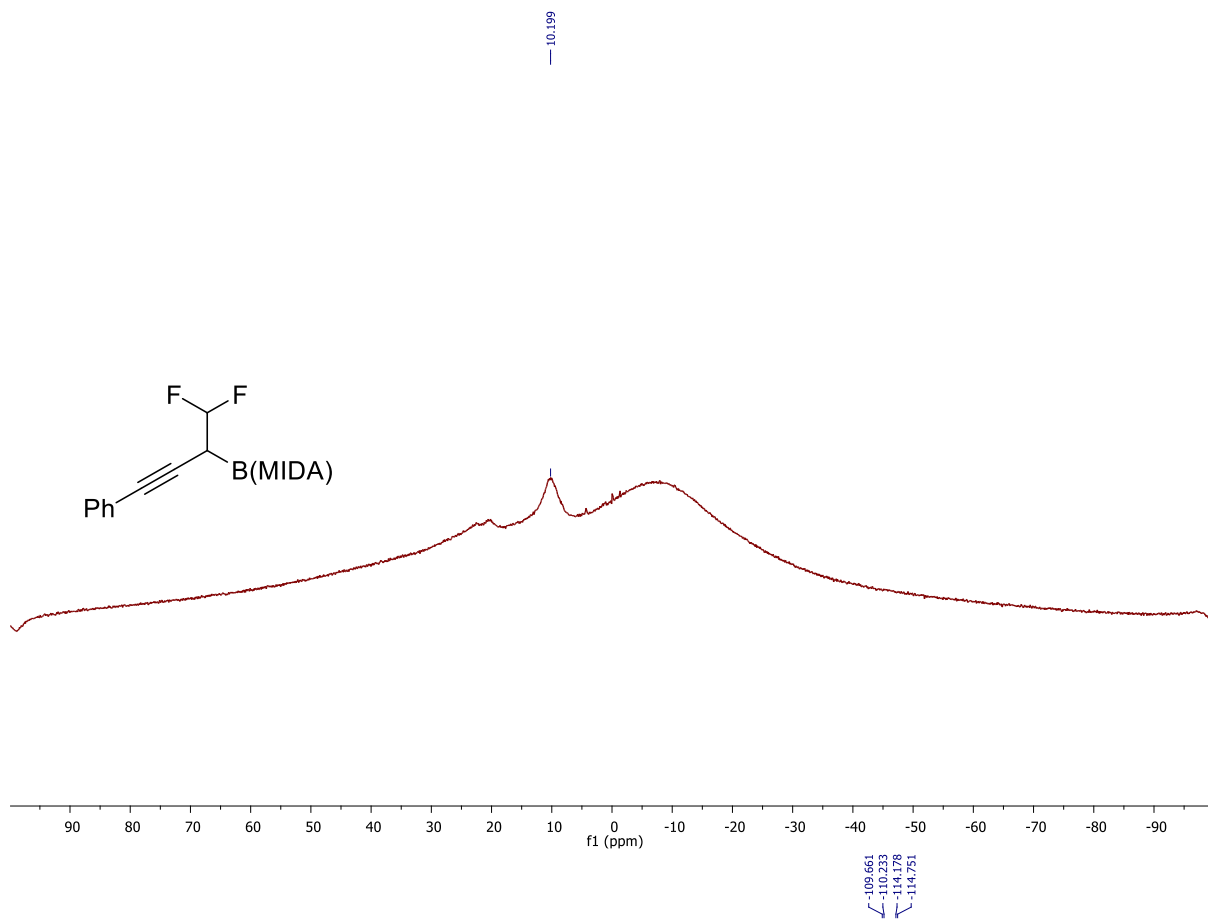


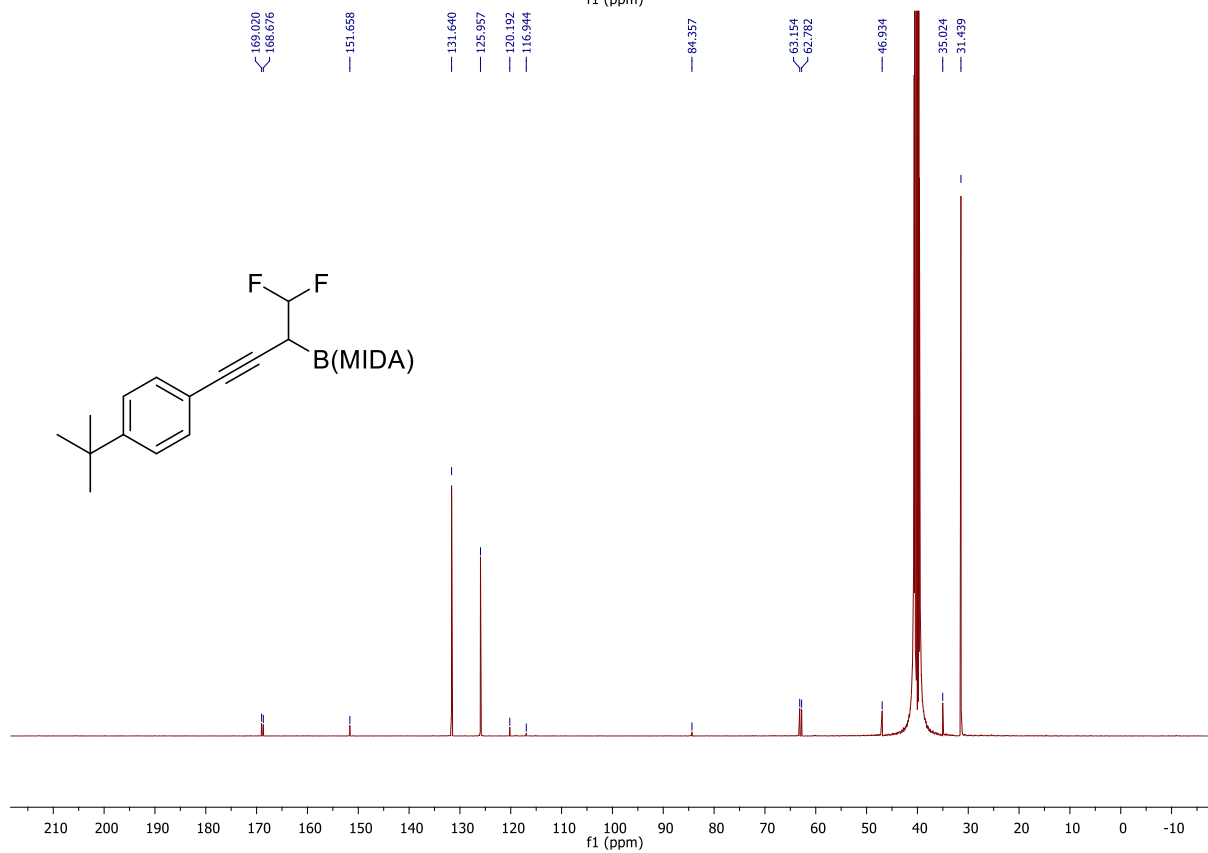
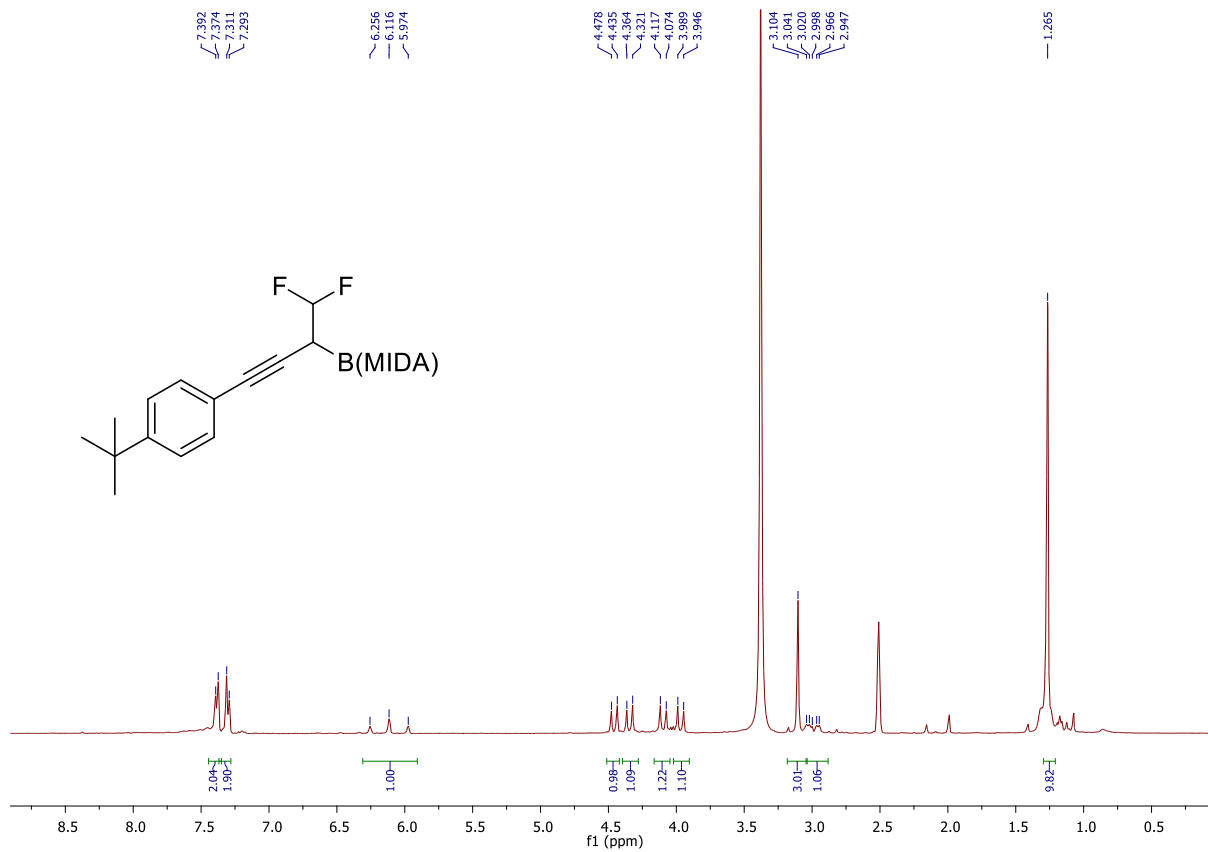


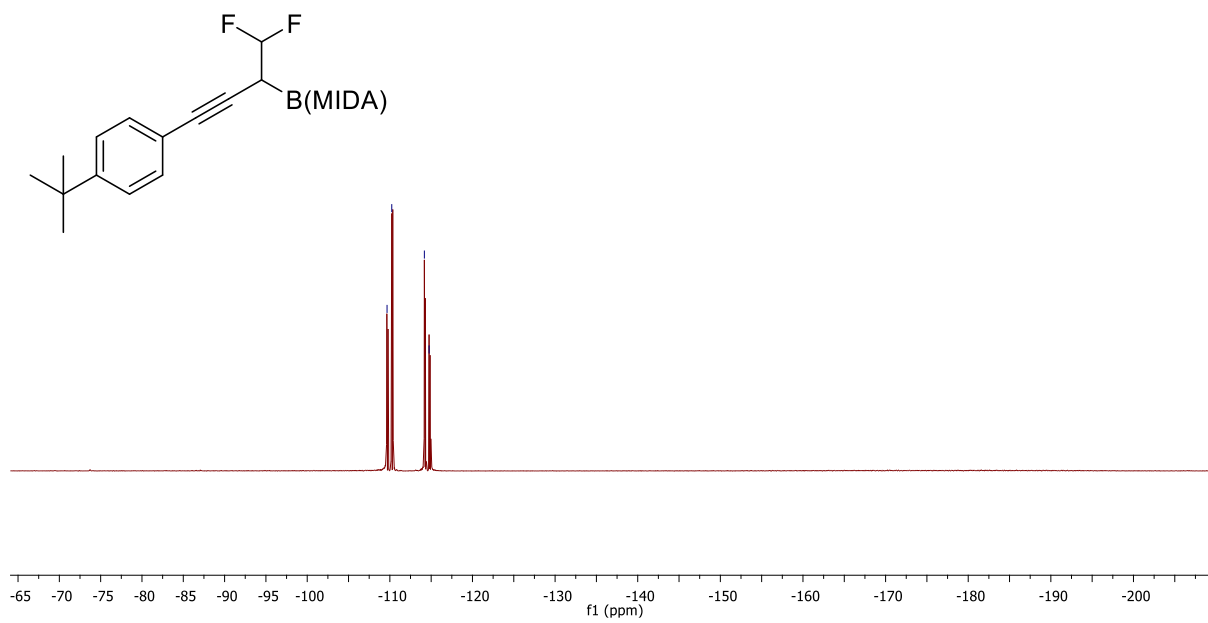
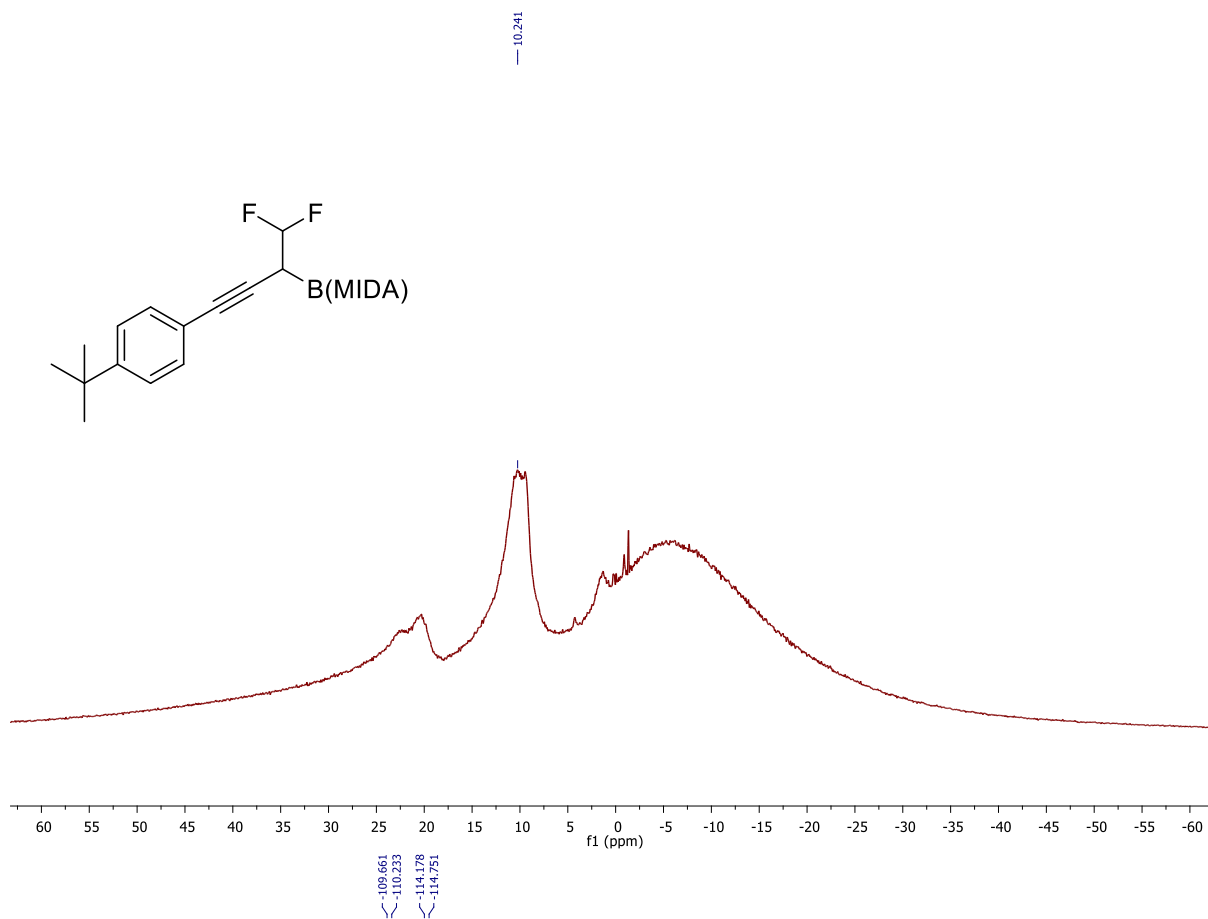


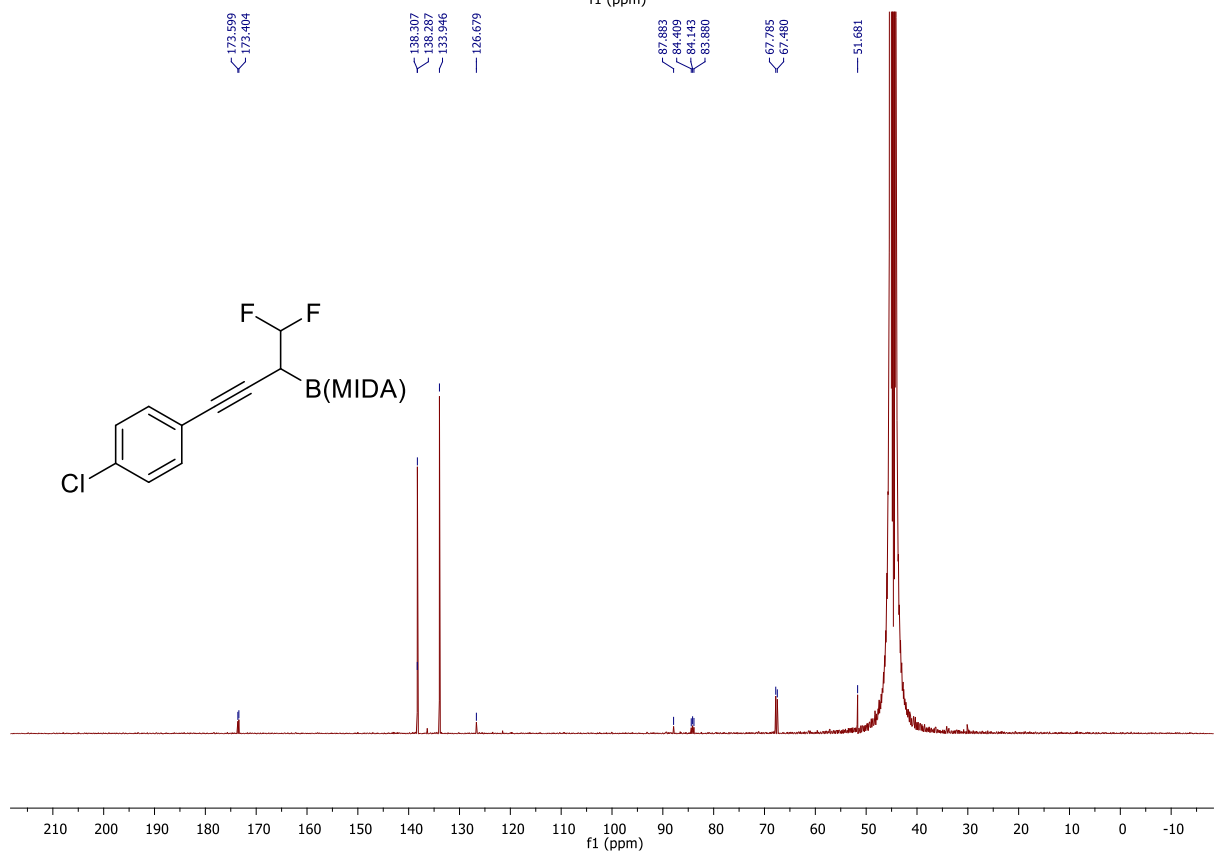
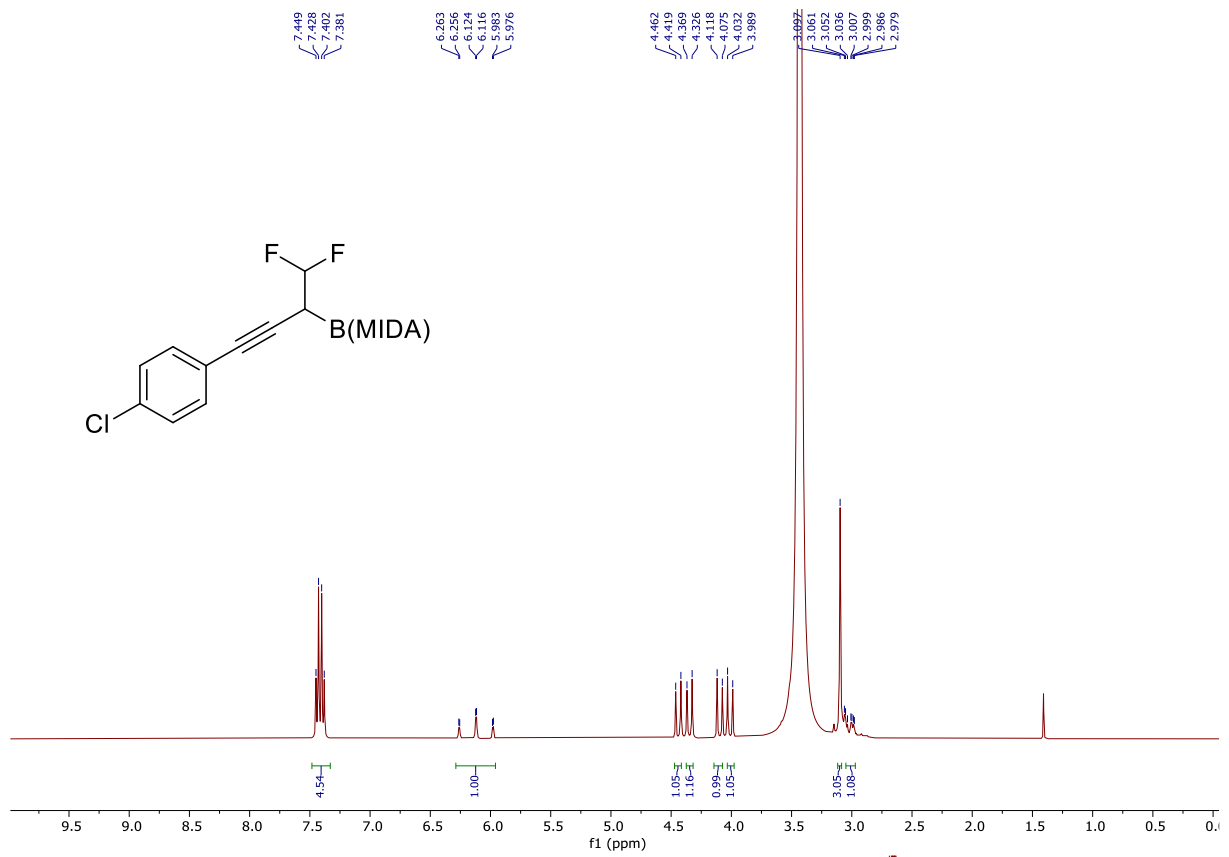


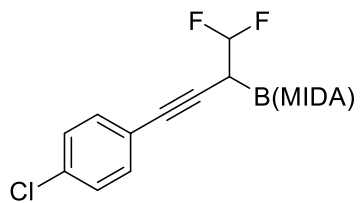




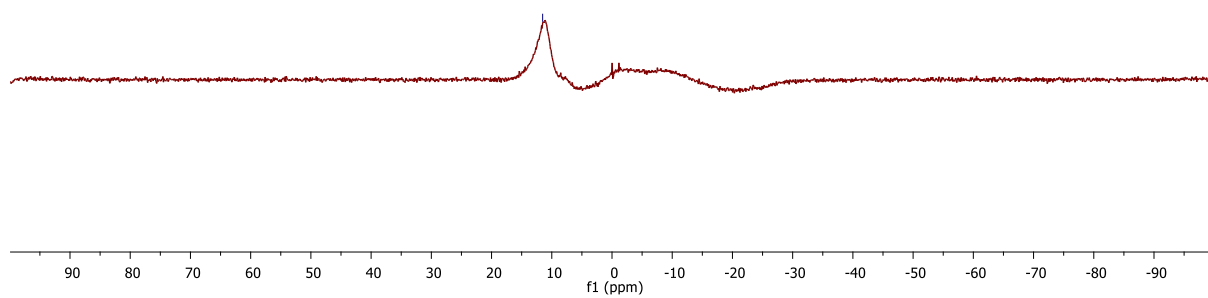




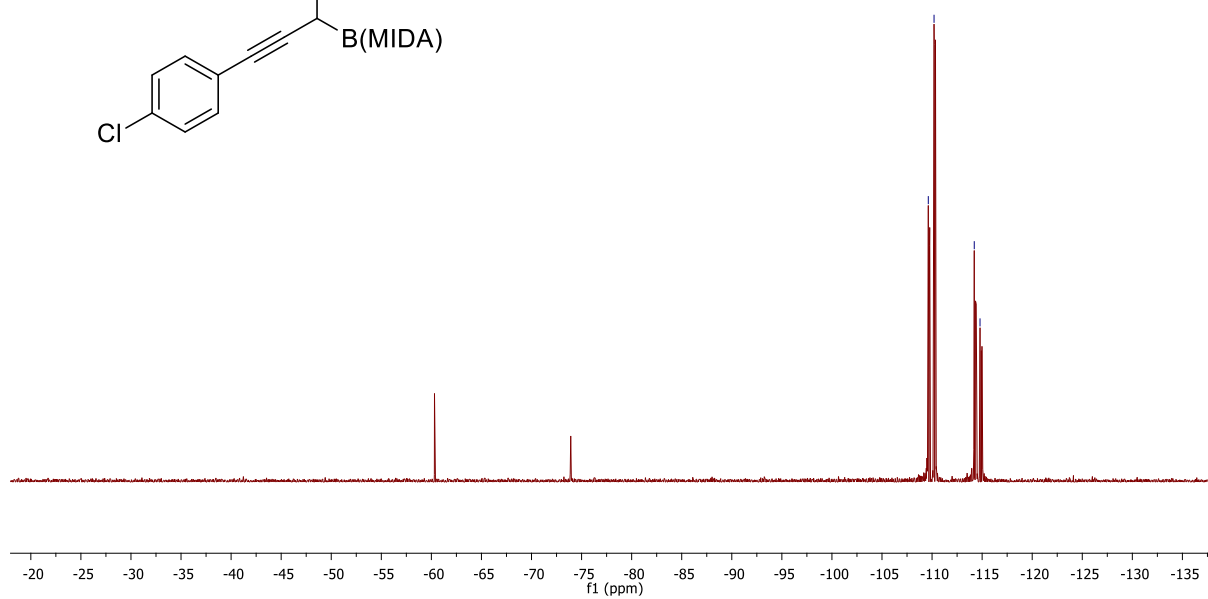
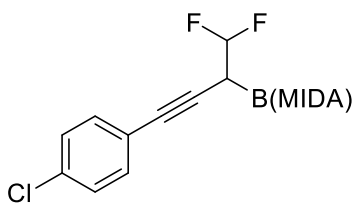


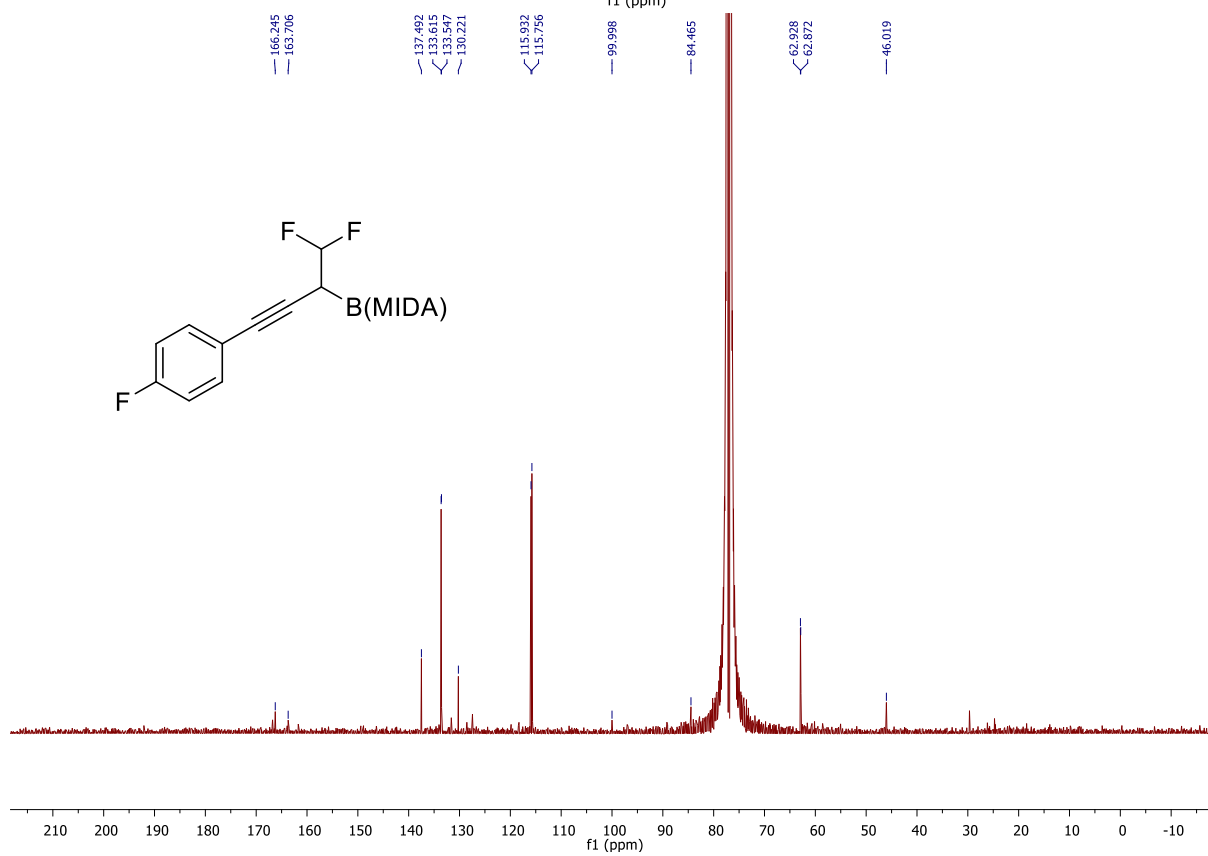
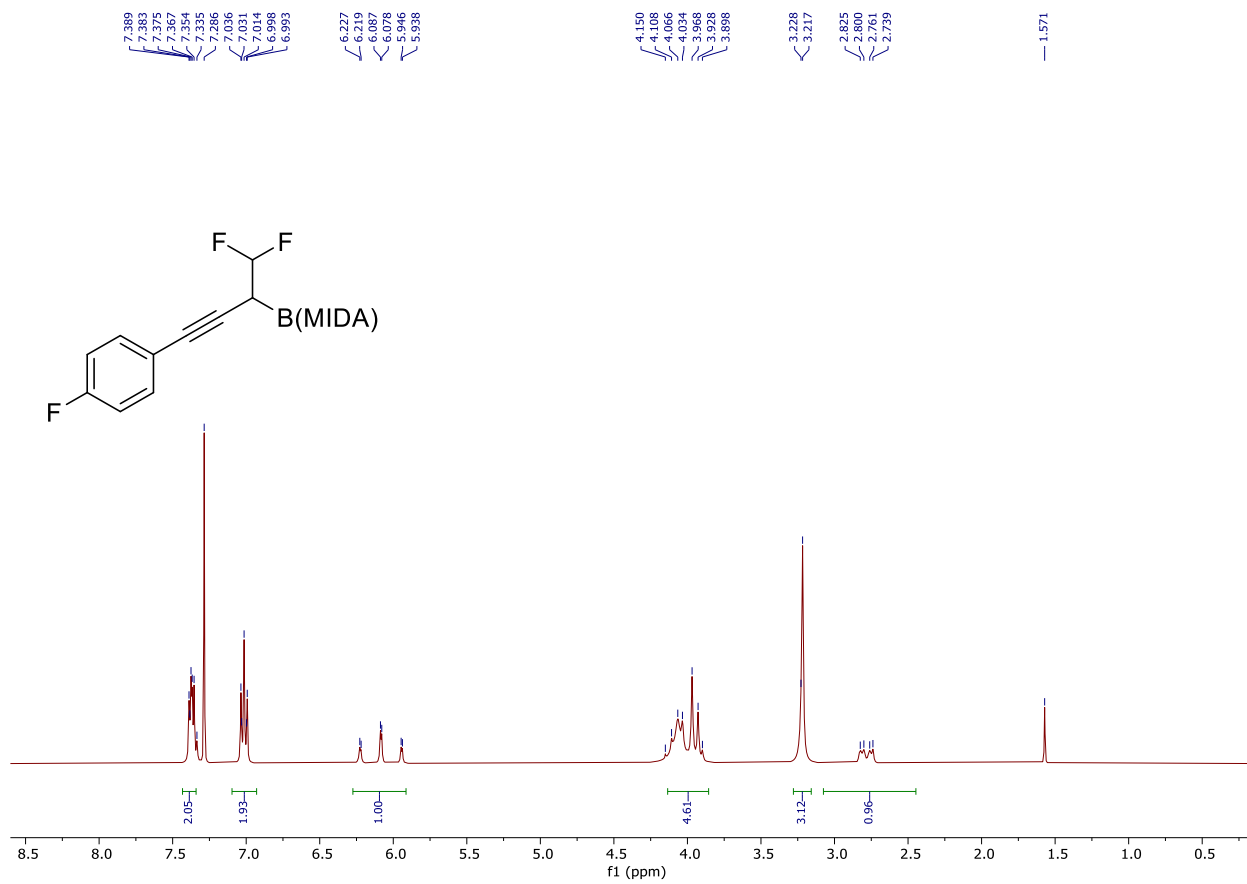


11.518

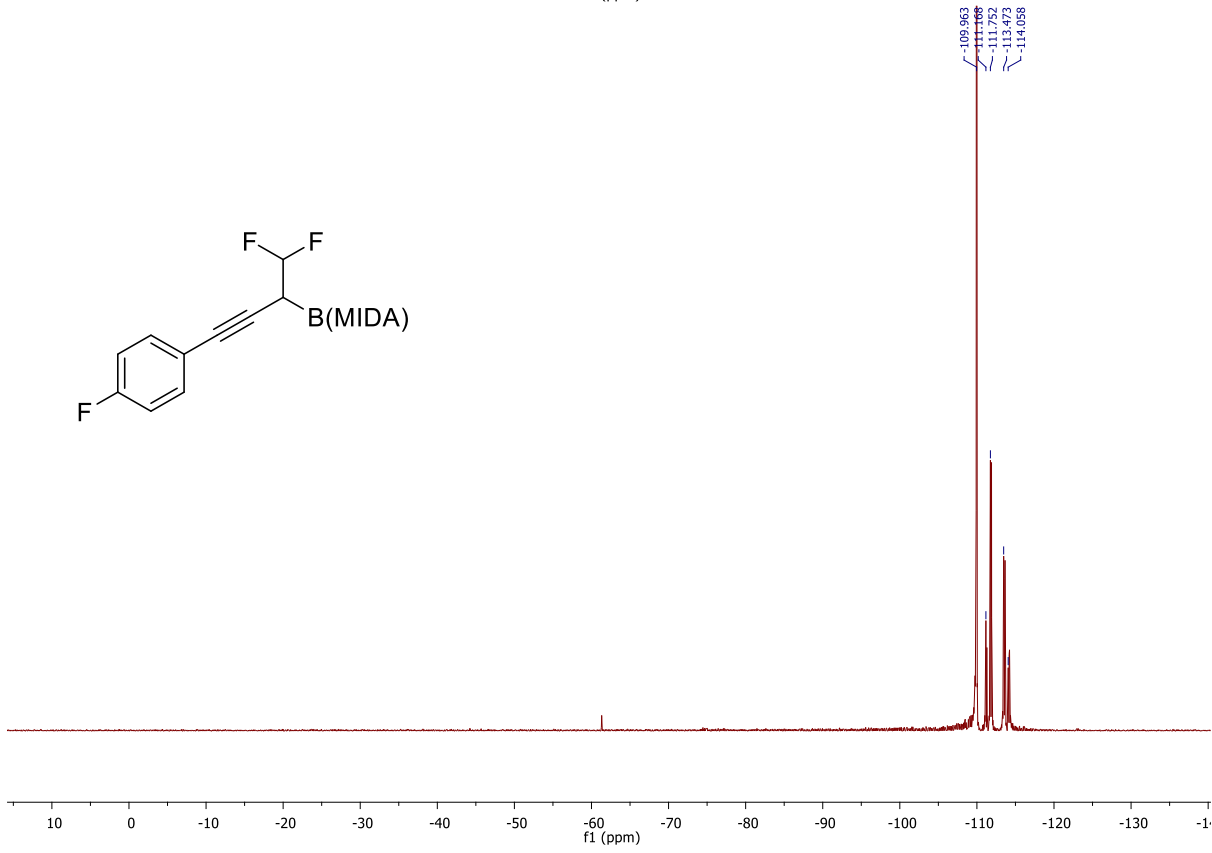
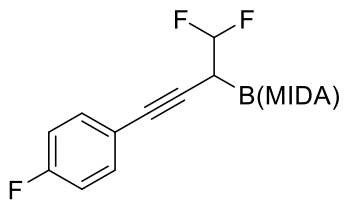
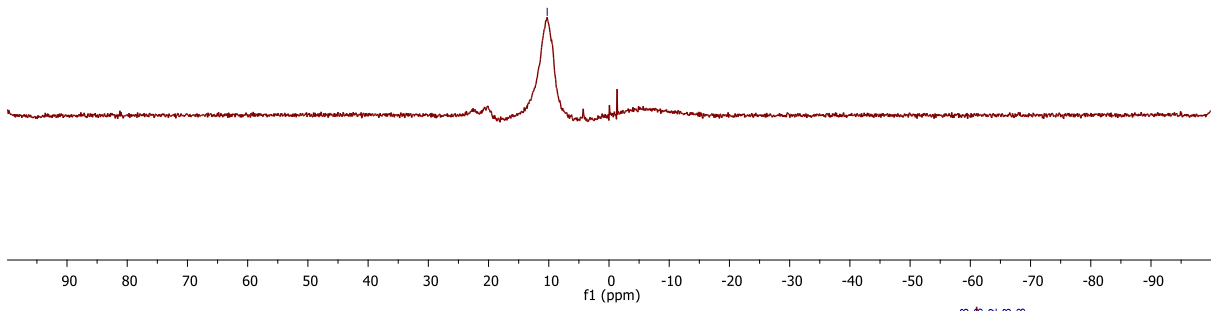
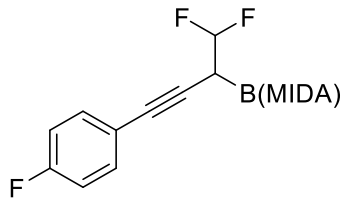


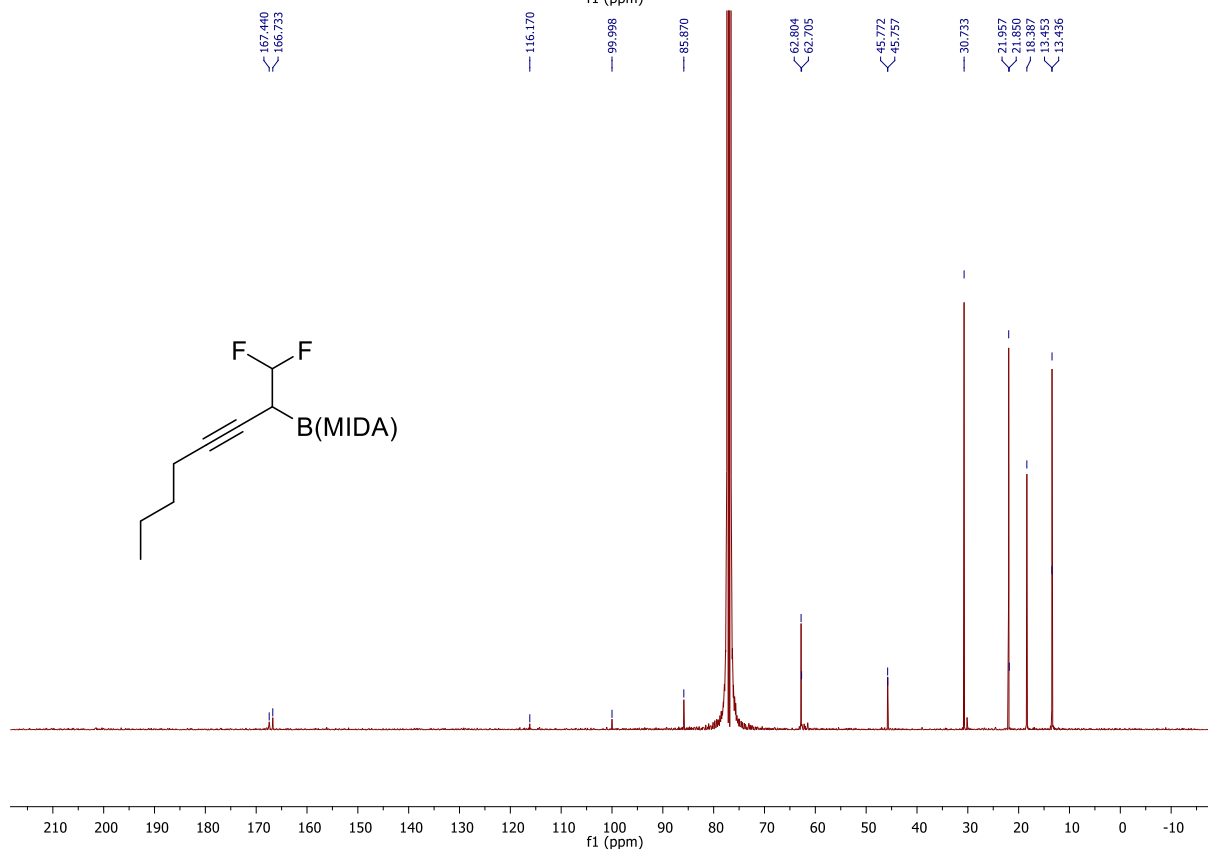
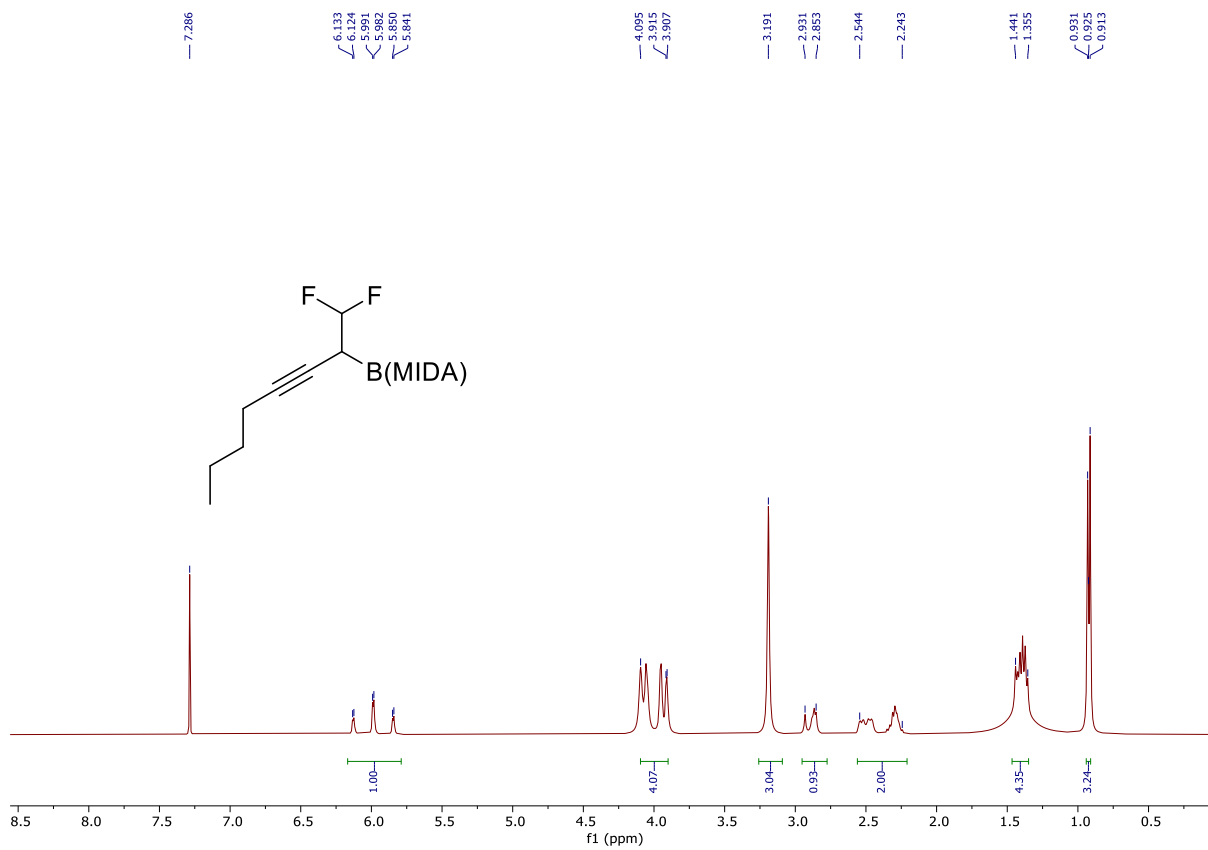
109.624
110.198
114.214
114.790

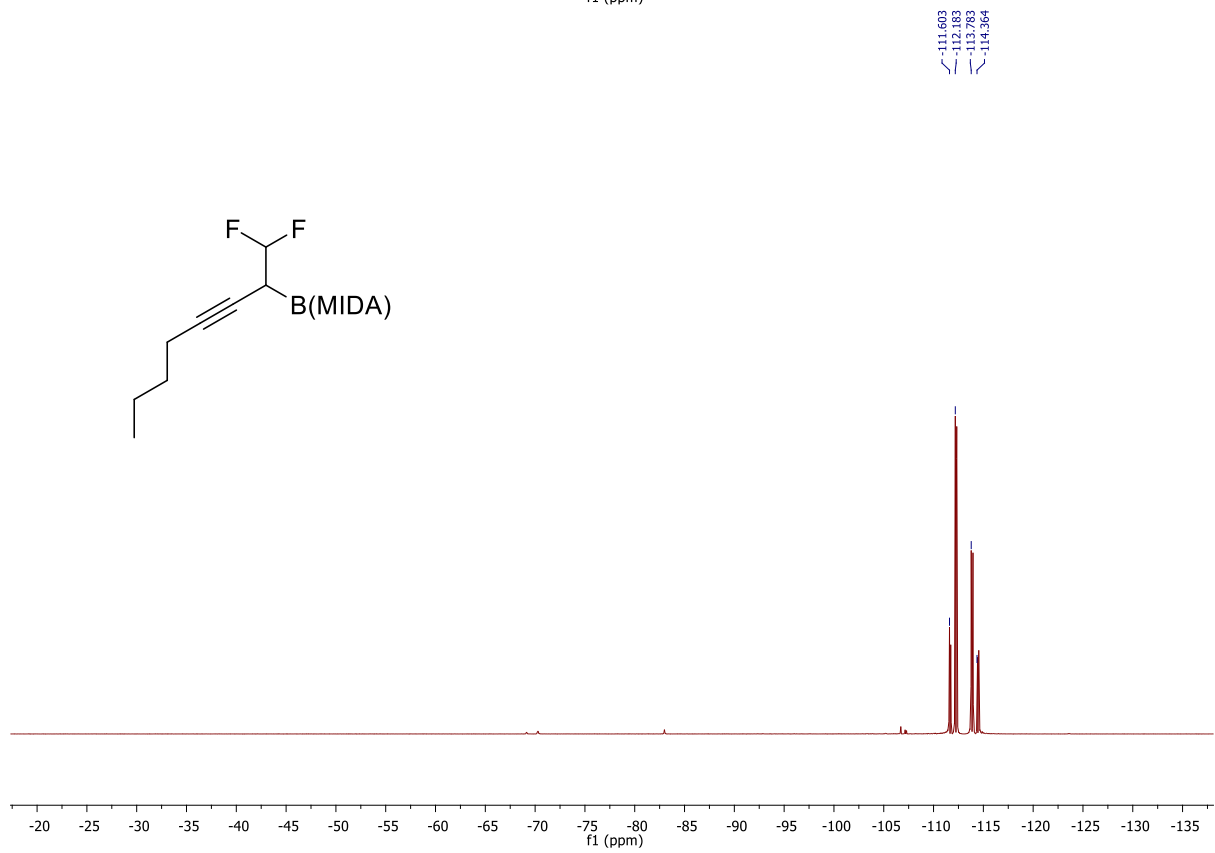
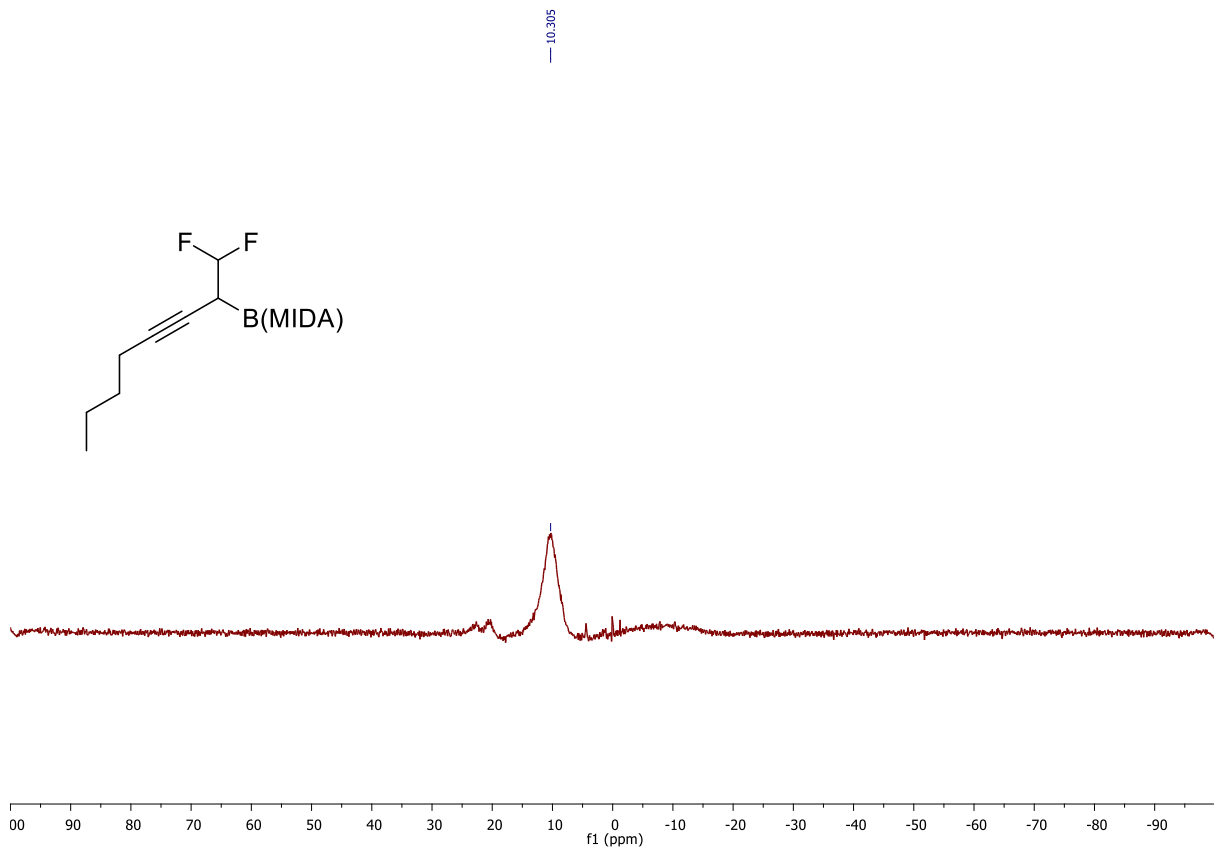


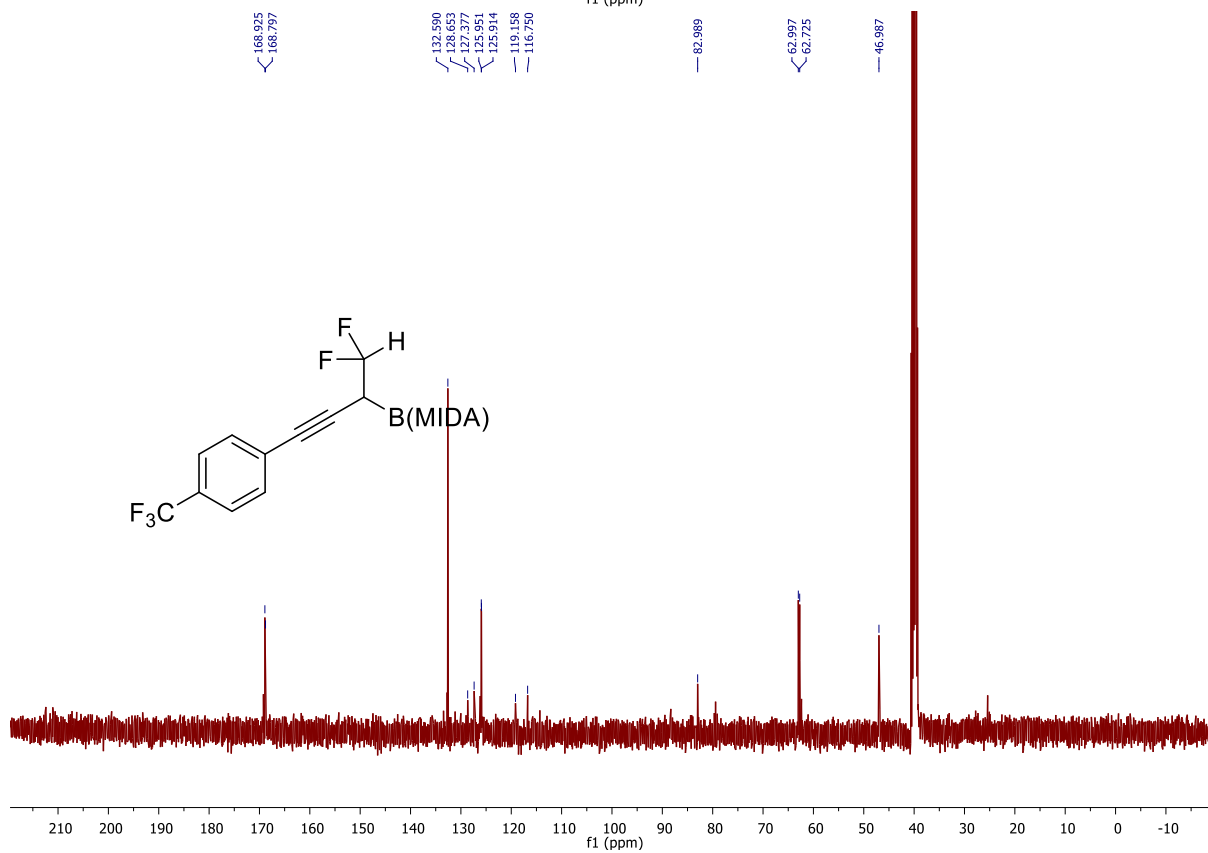
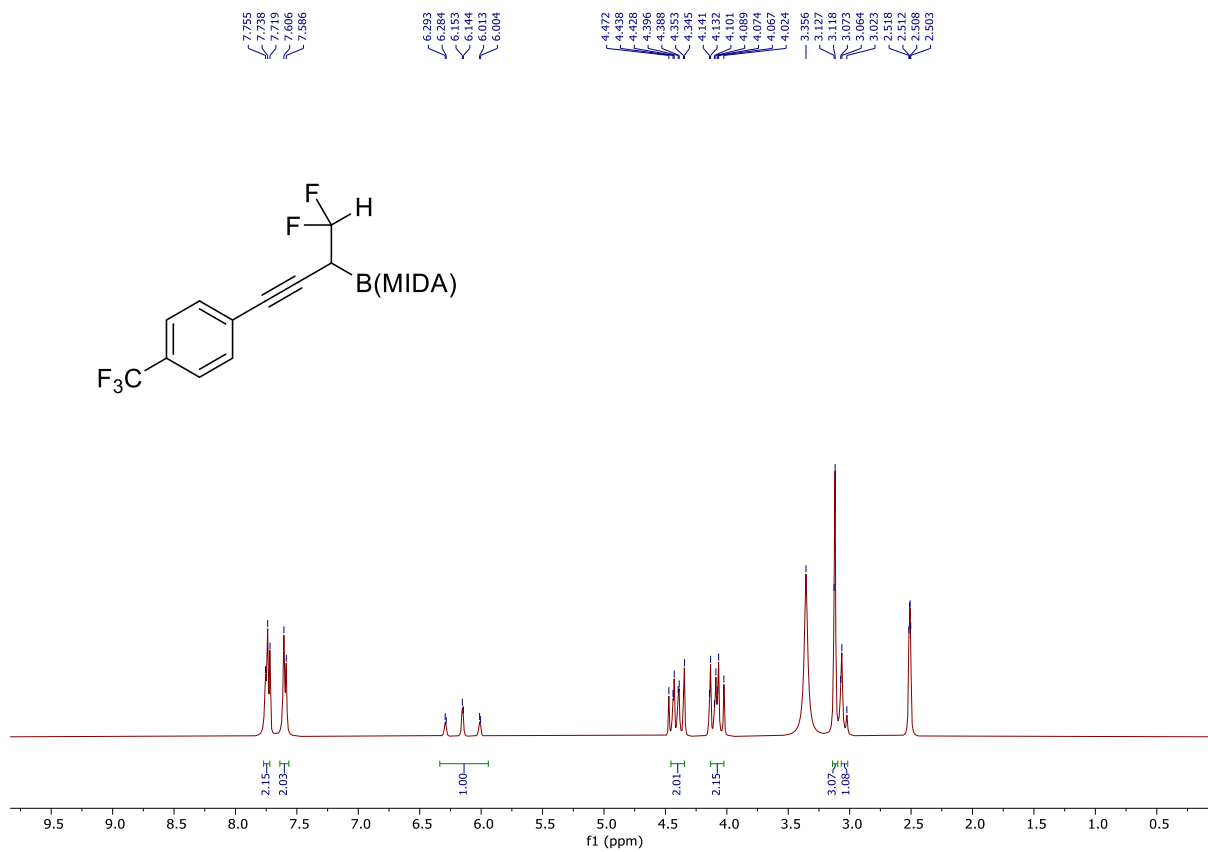


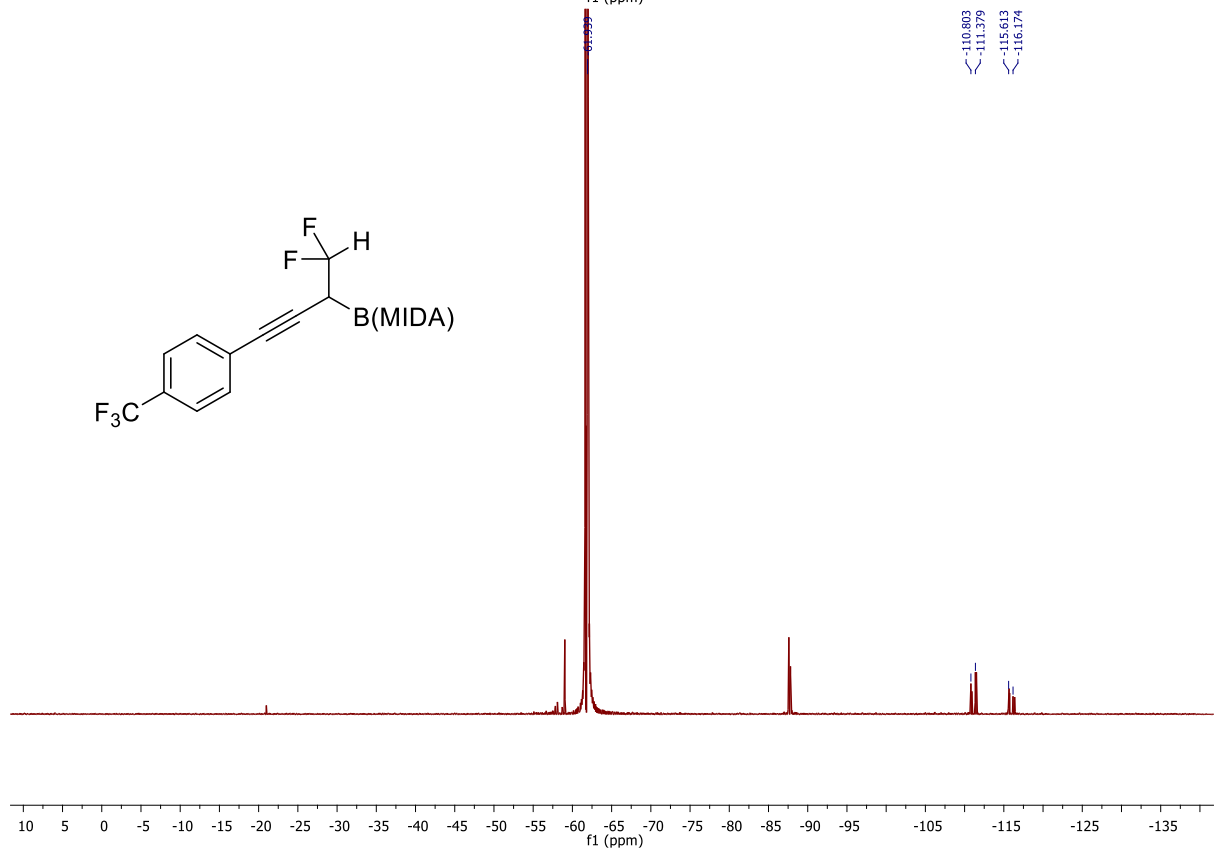
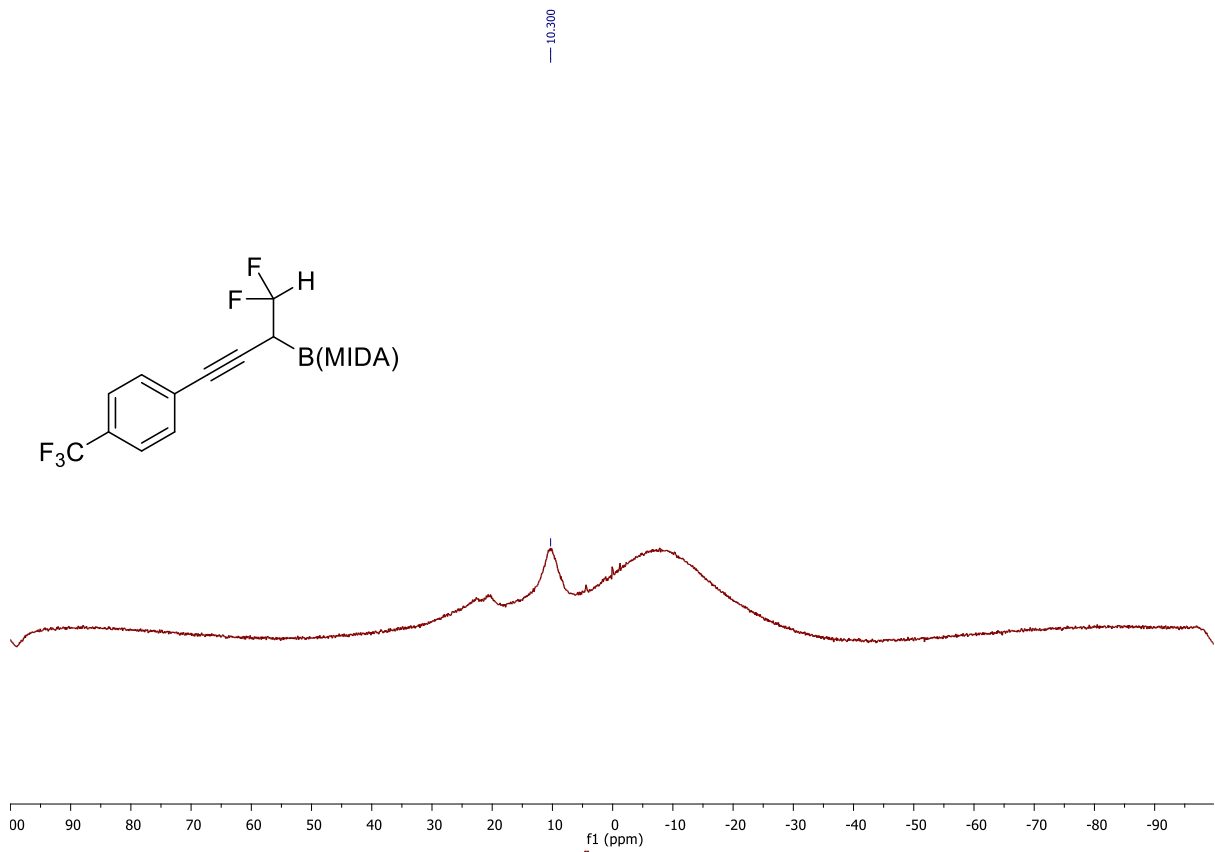
192.61

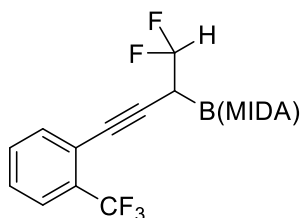
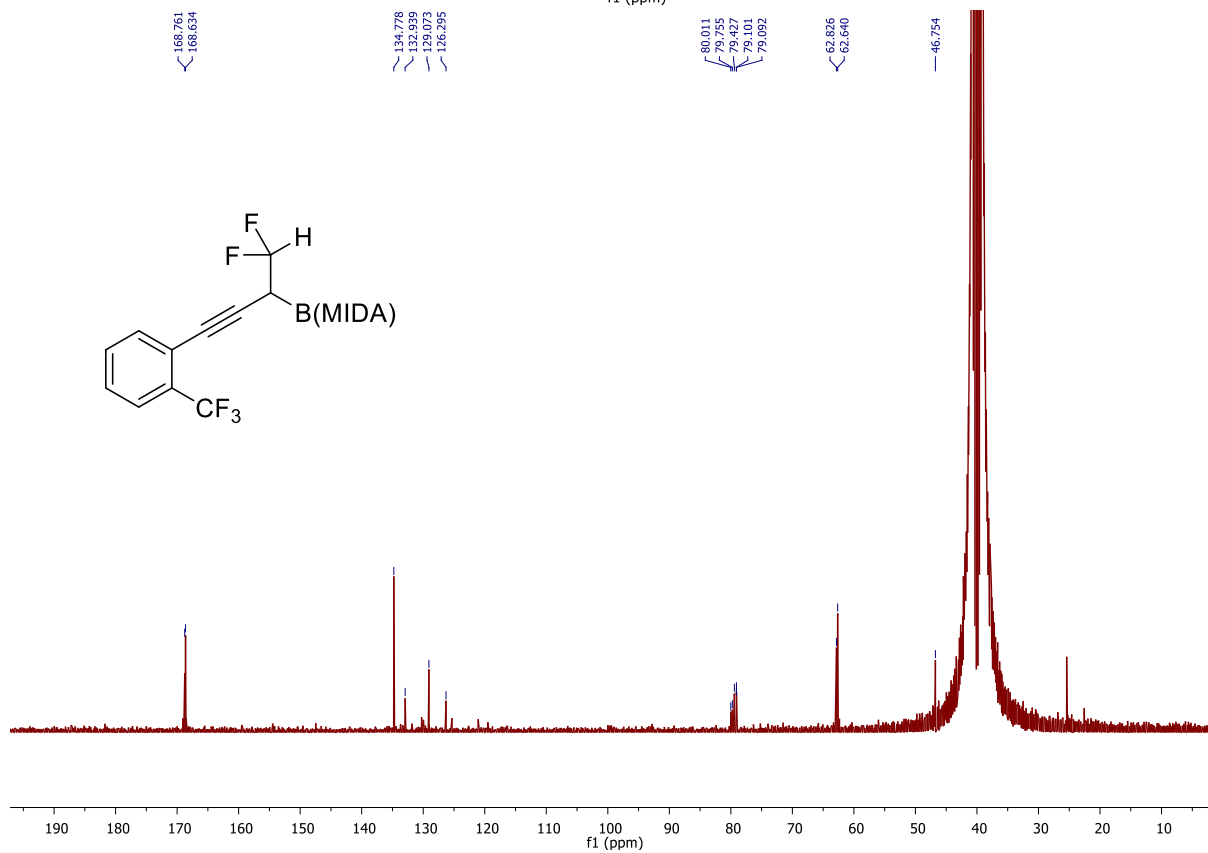
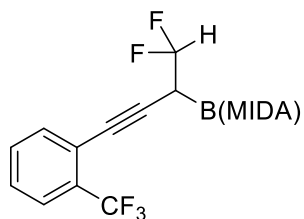
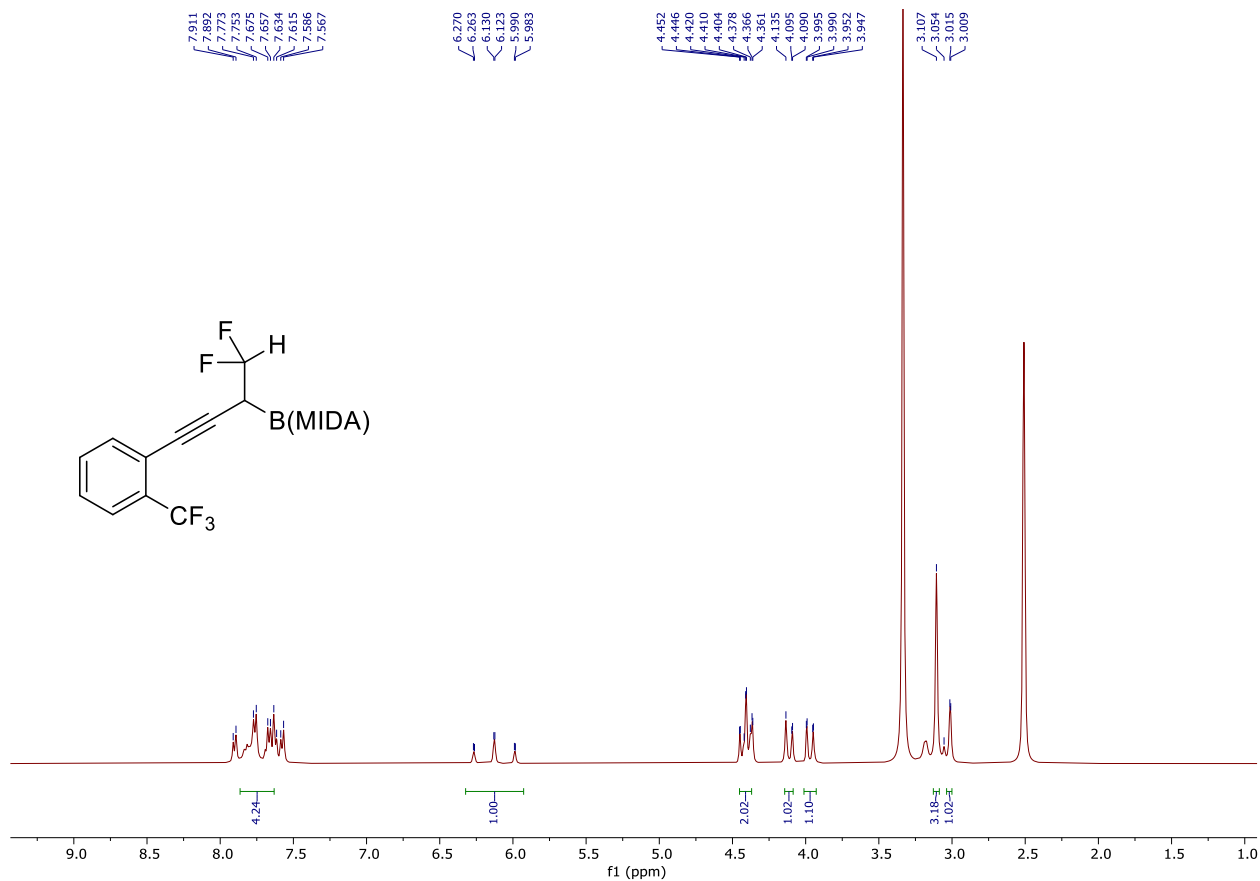


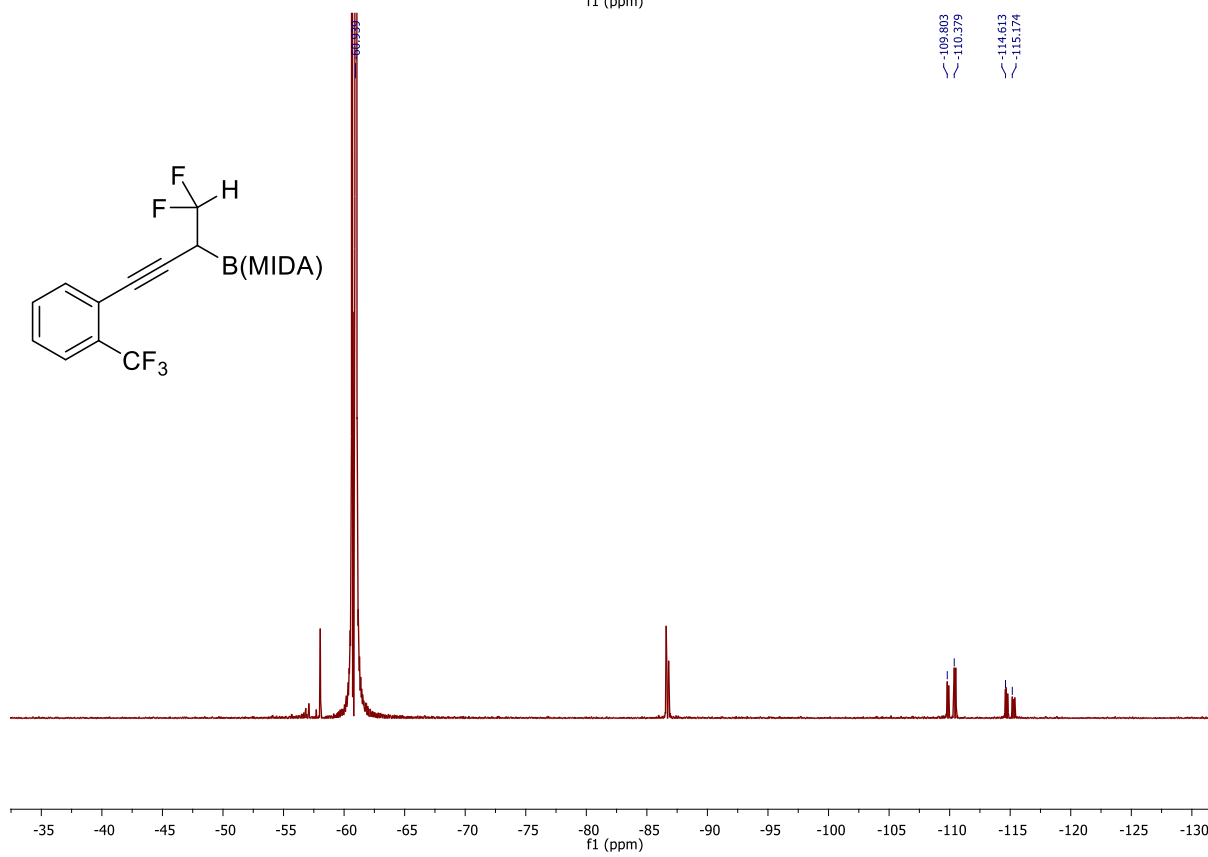
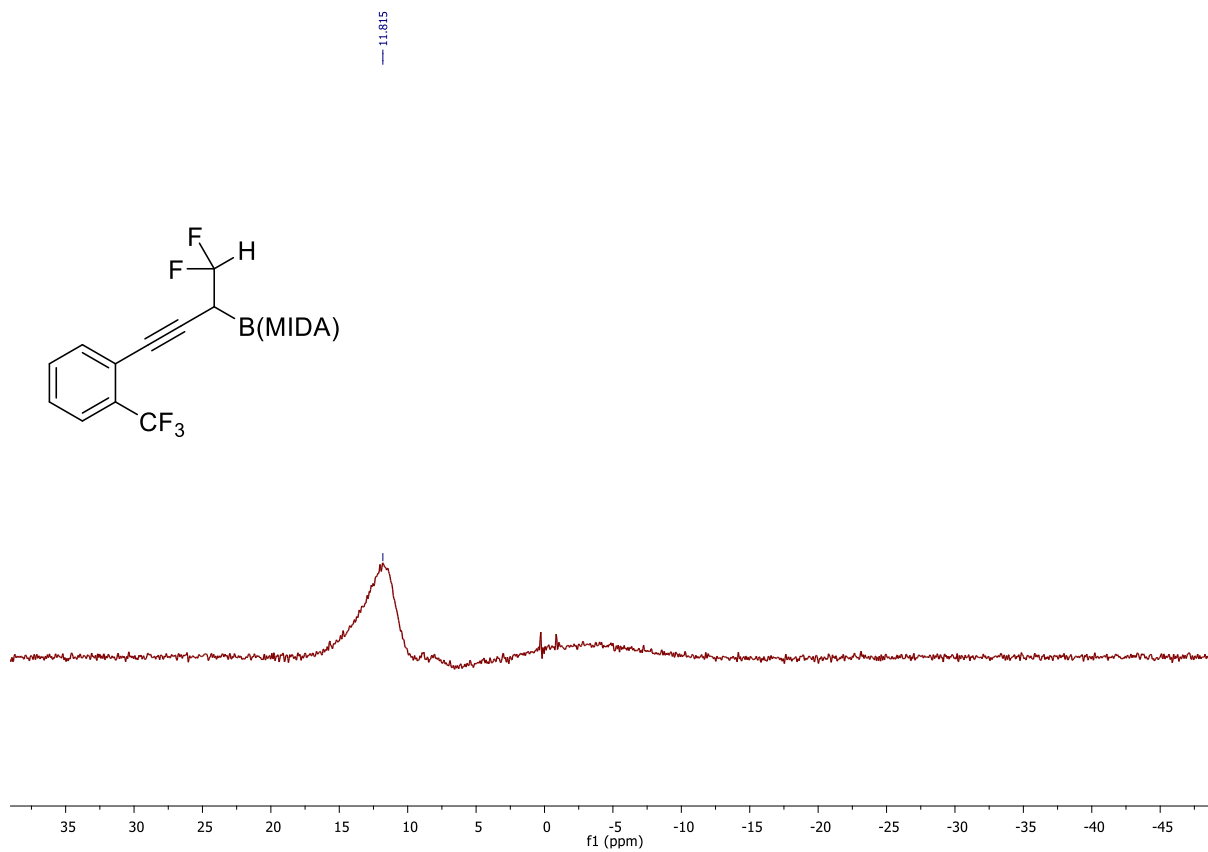


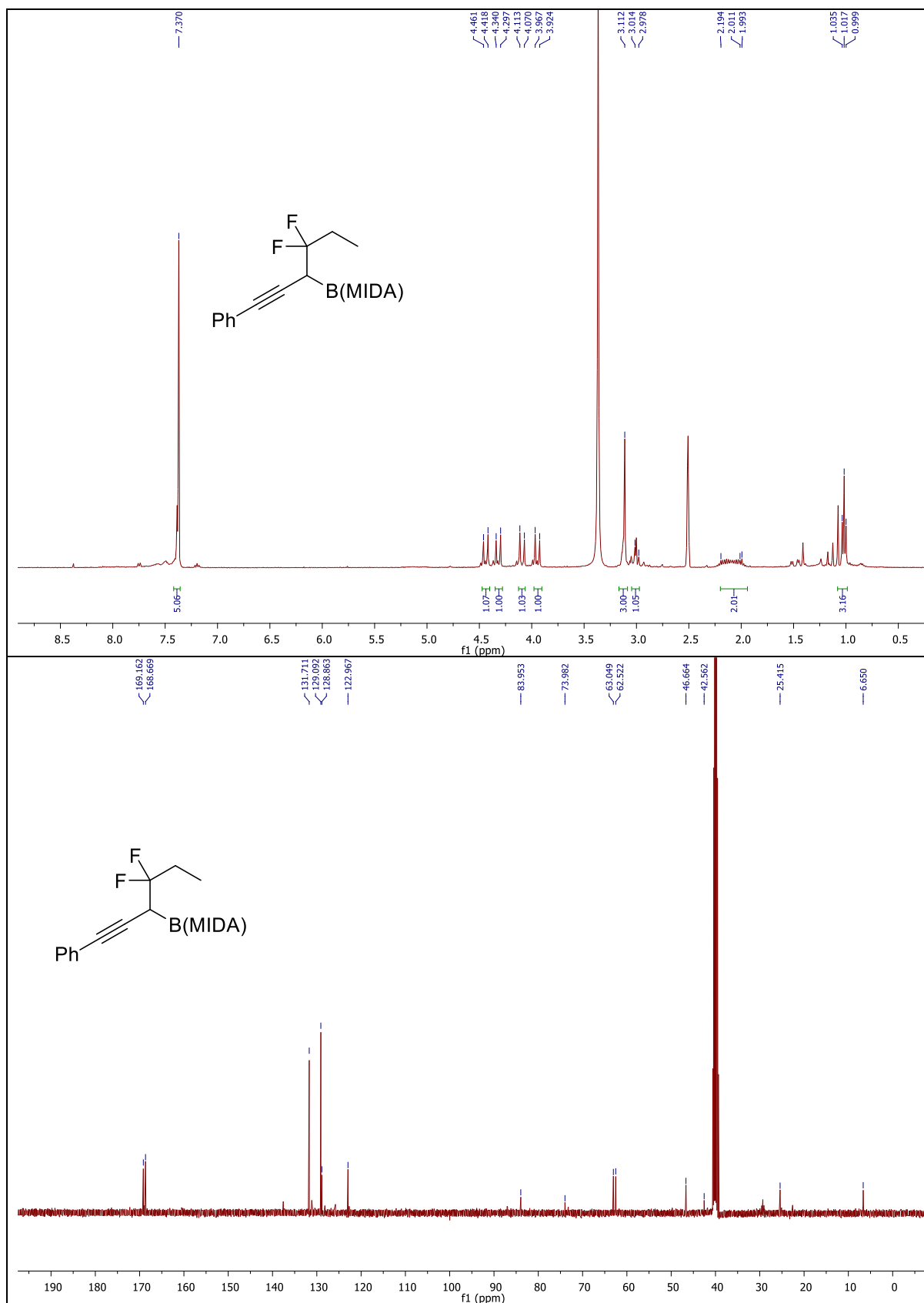


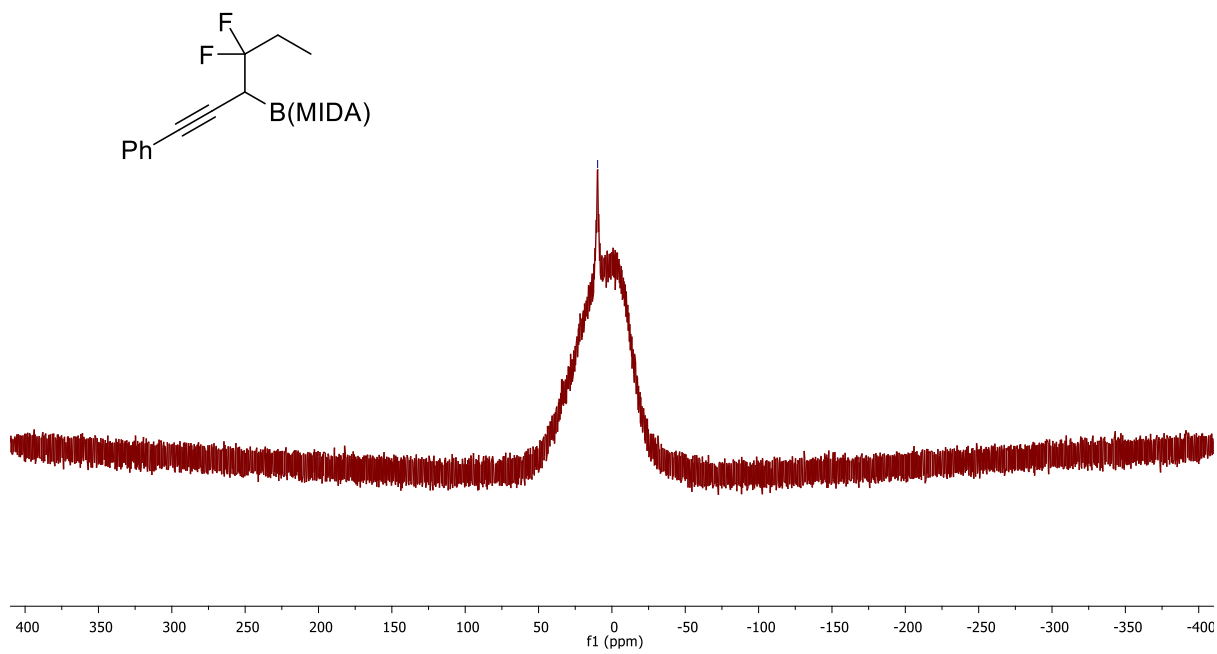
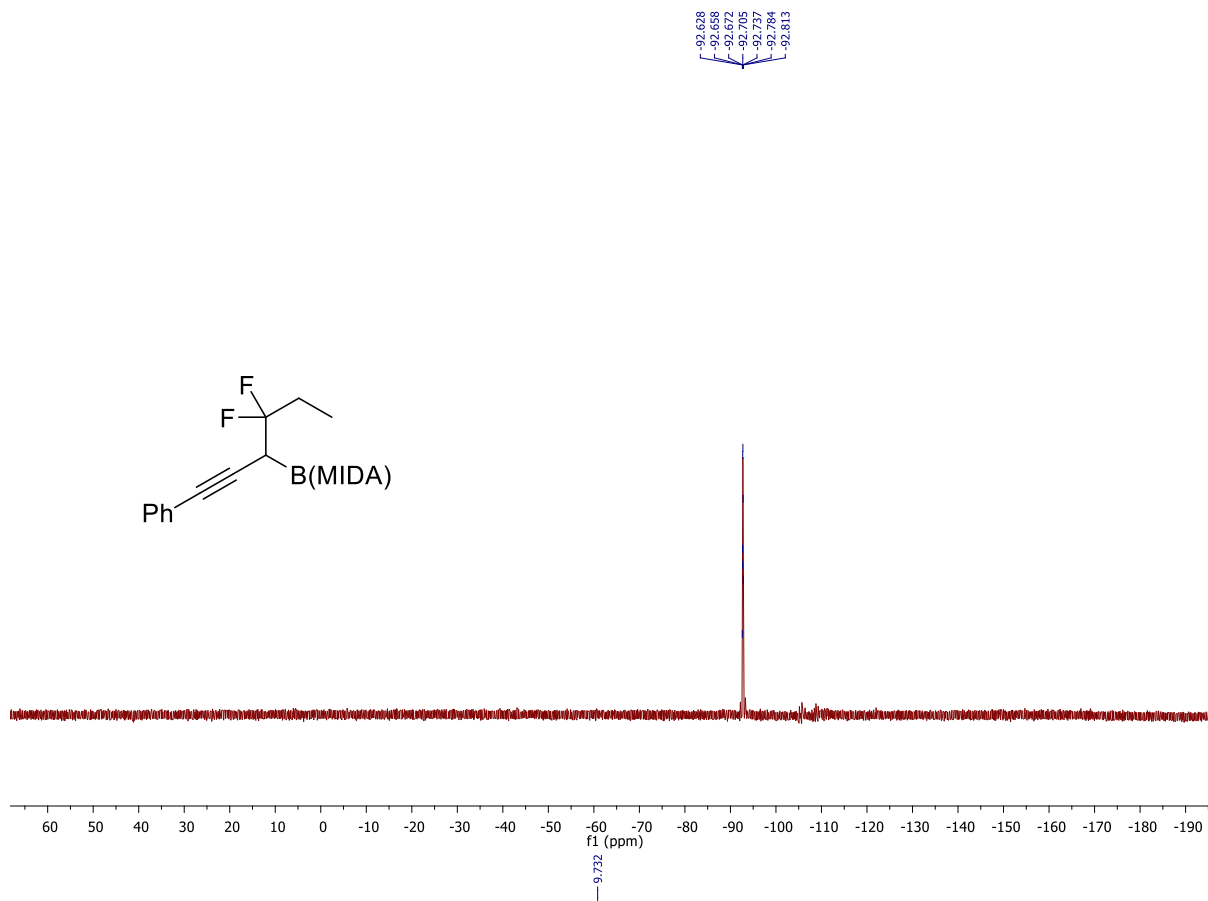


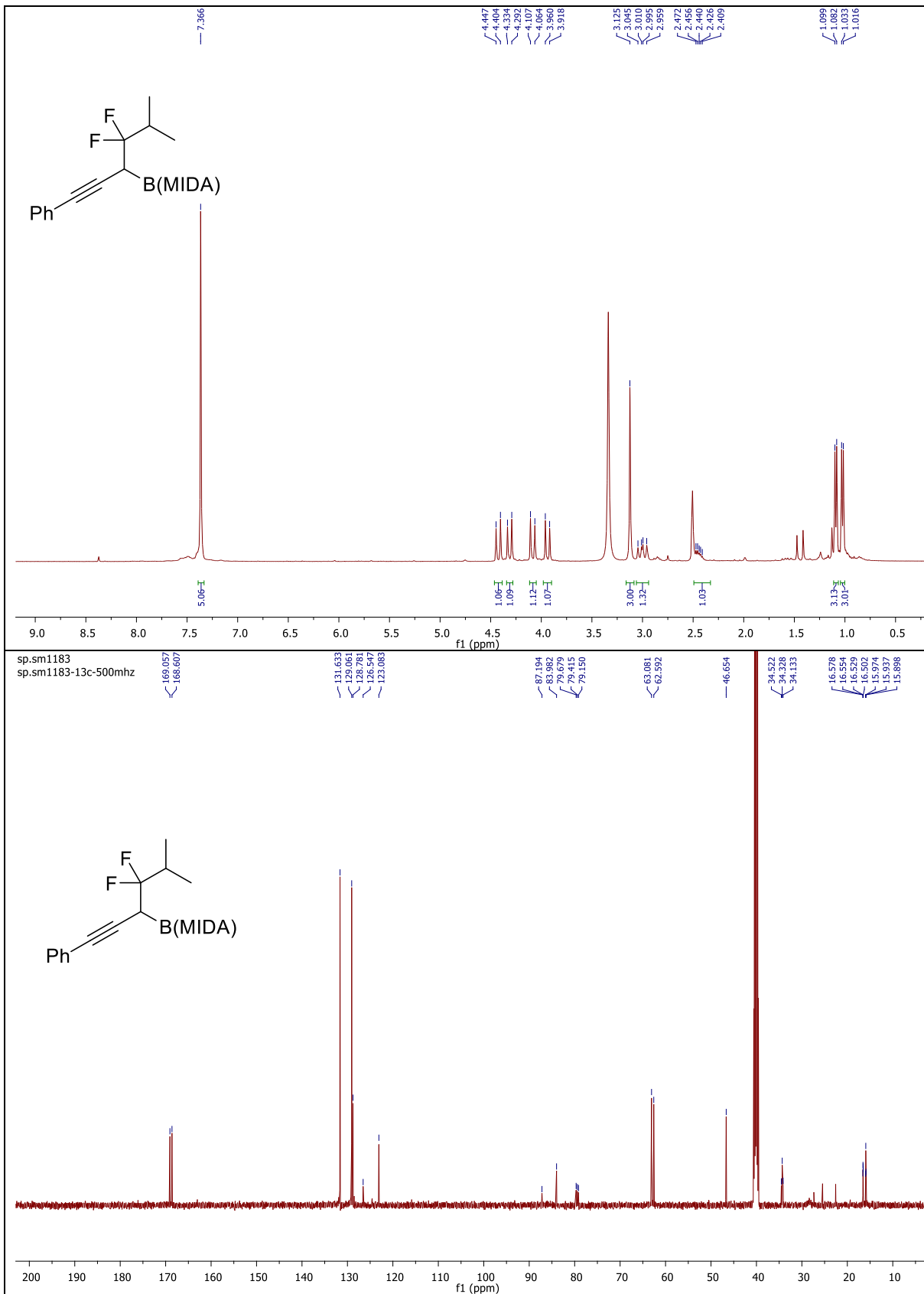


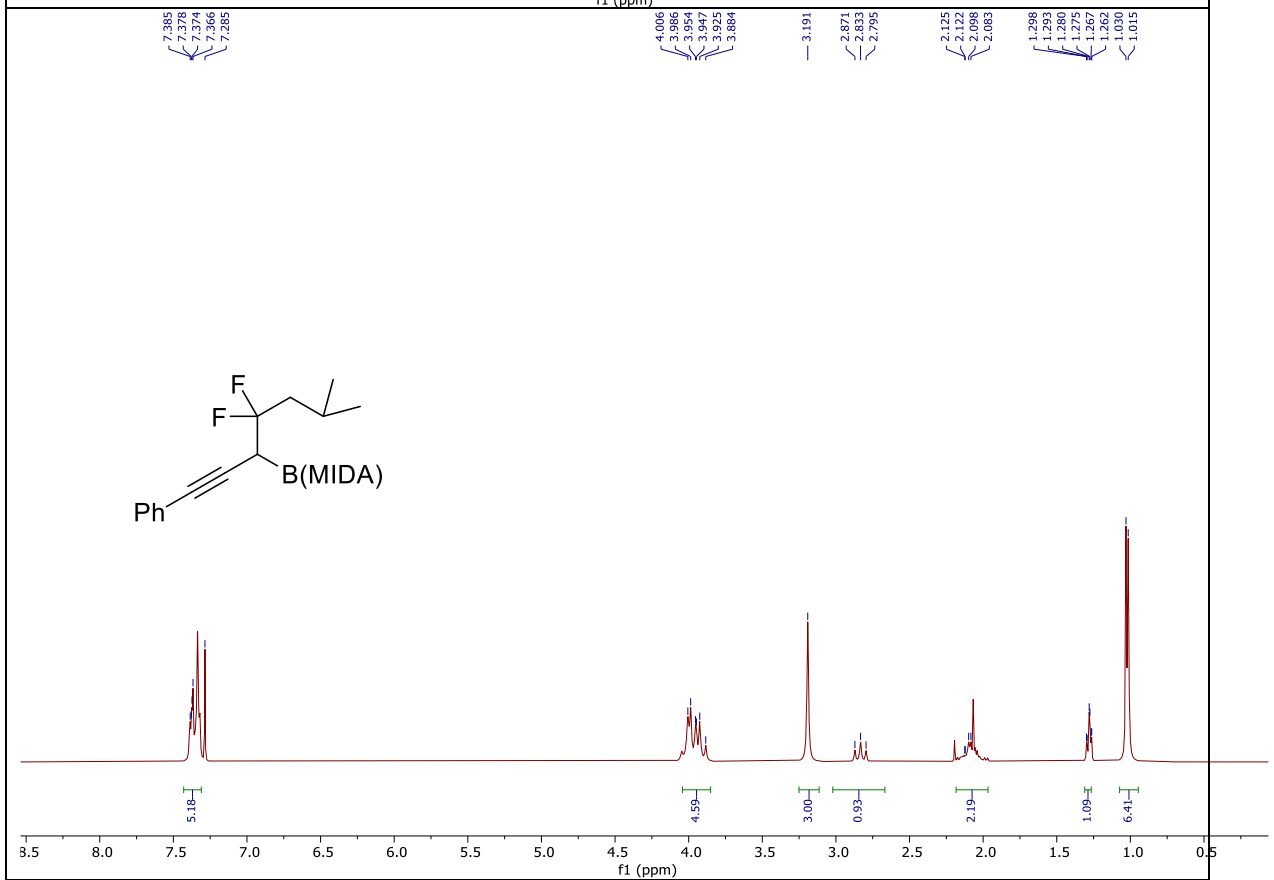
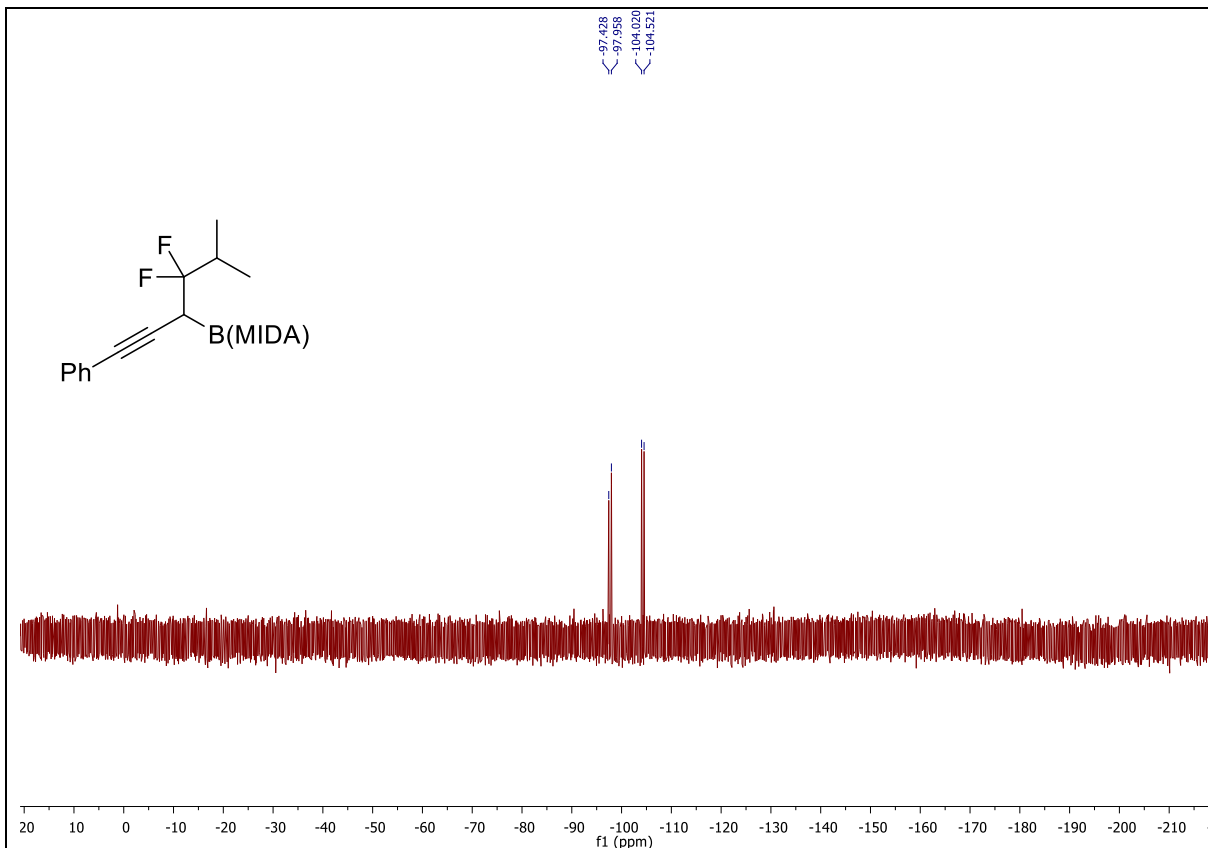


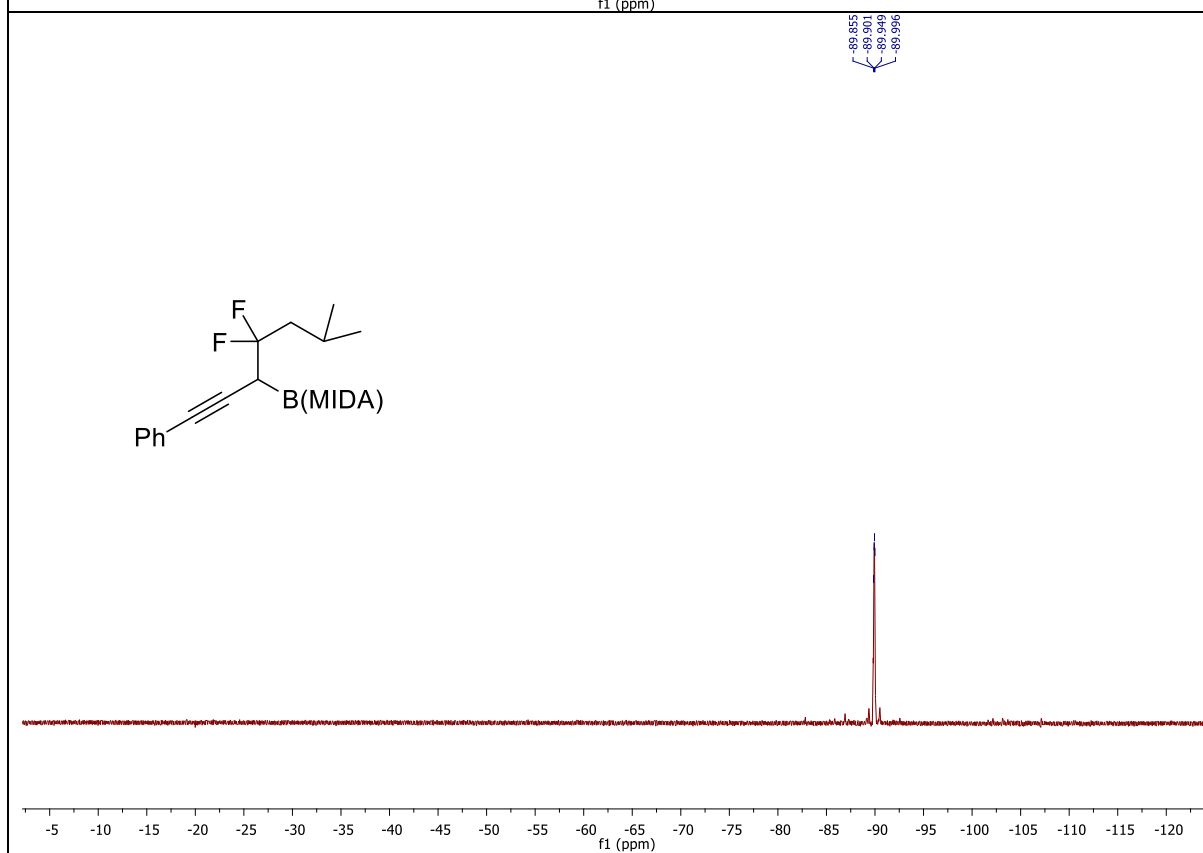
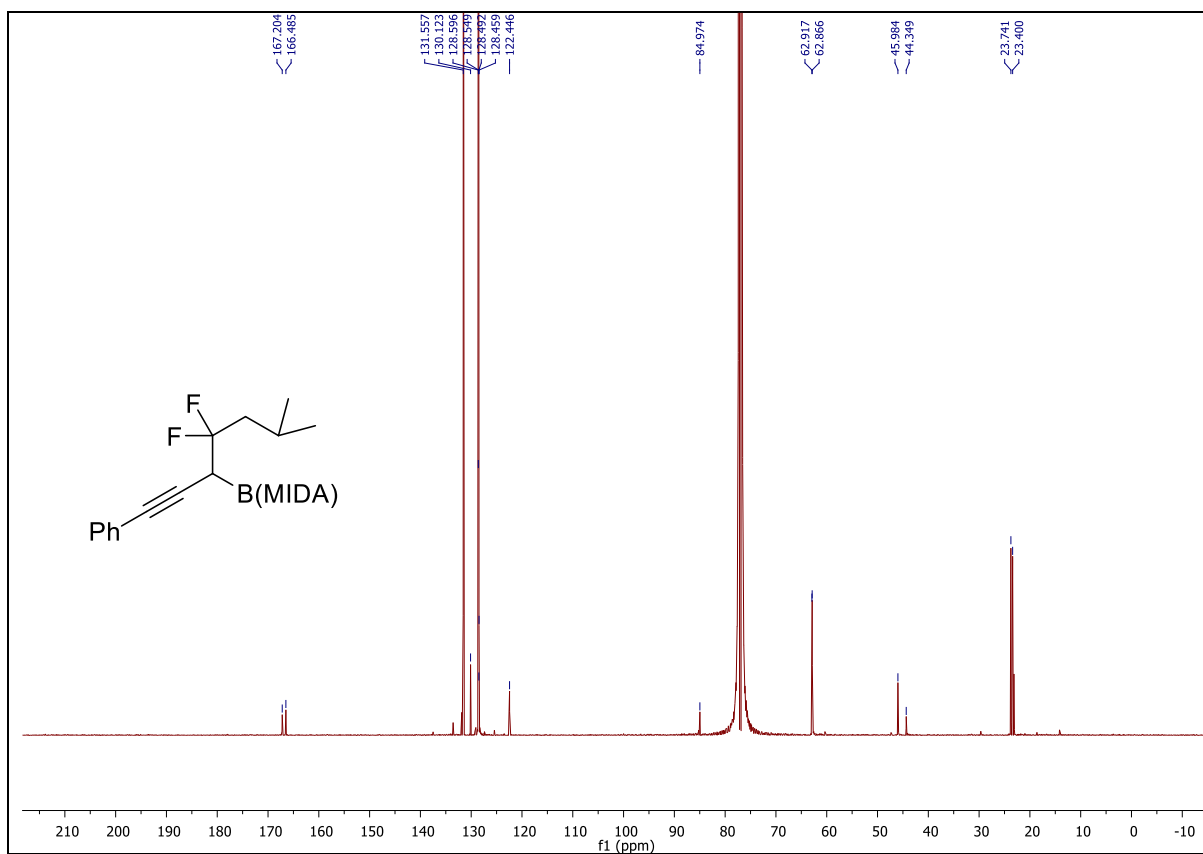


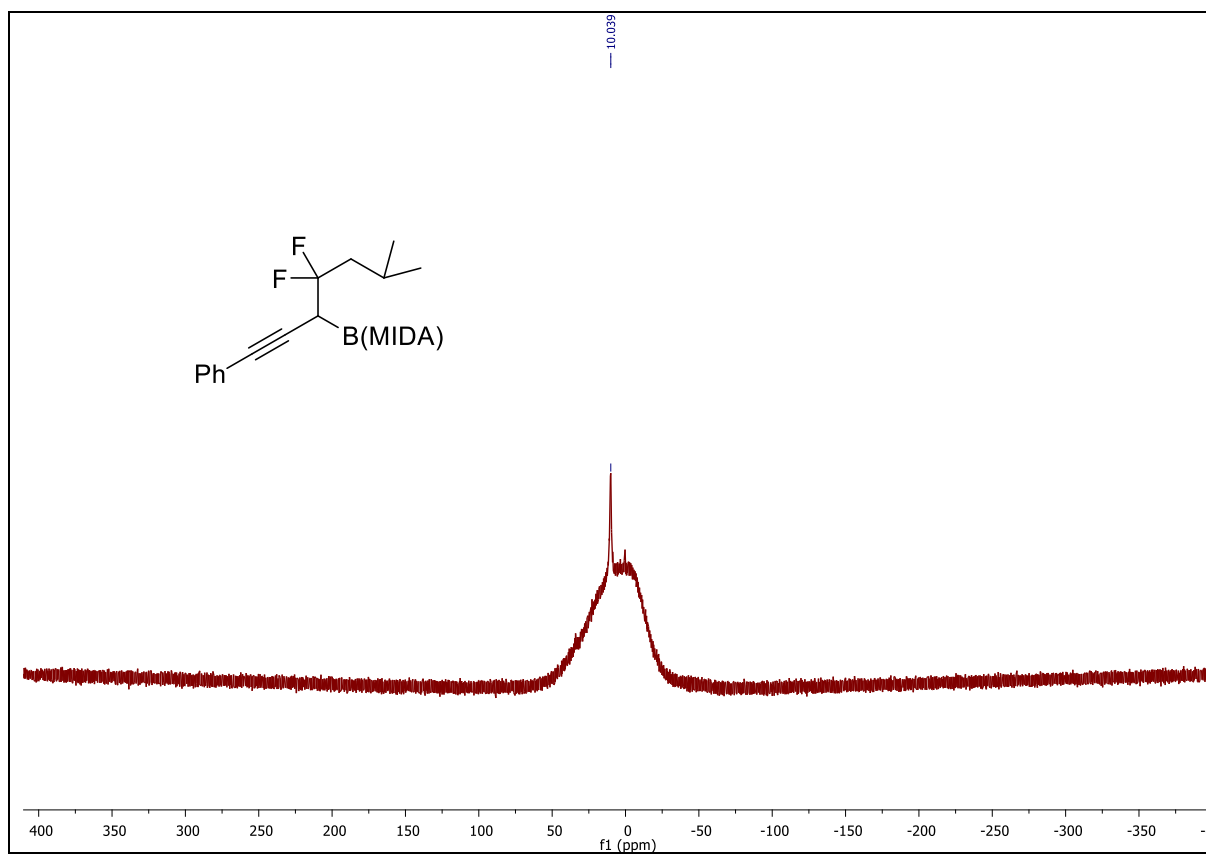


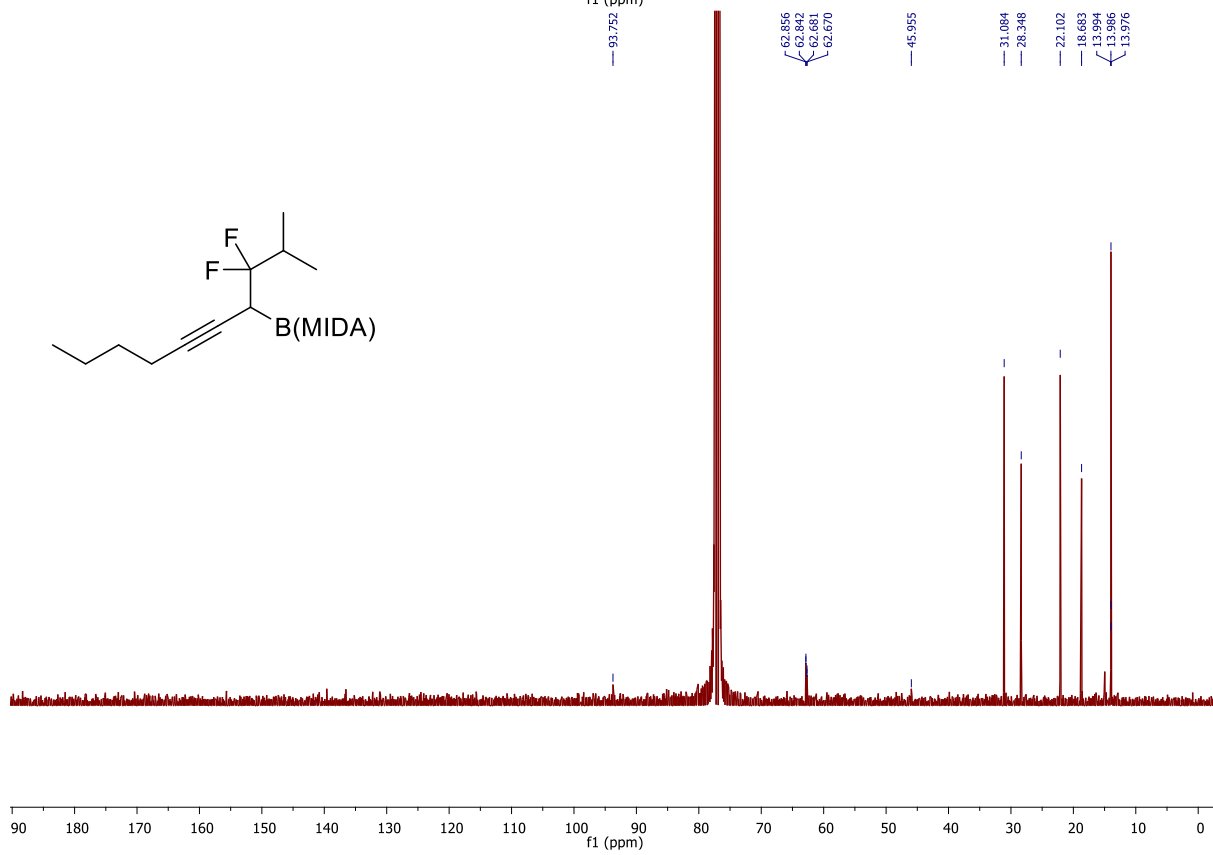
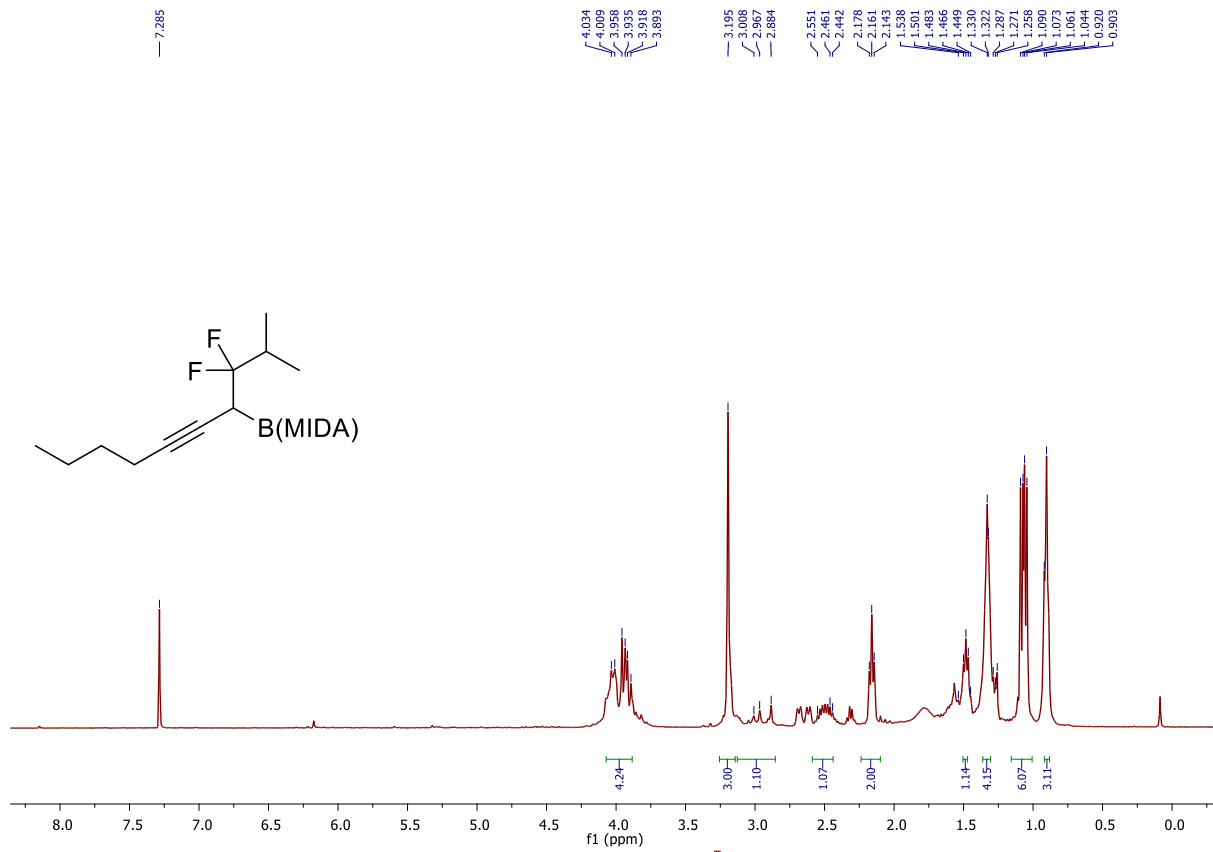


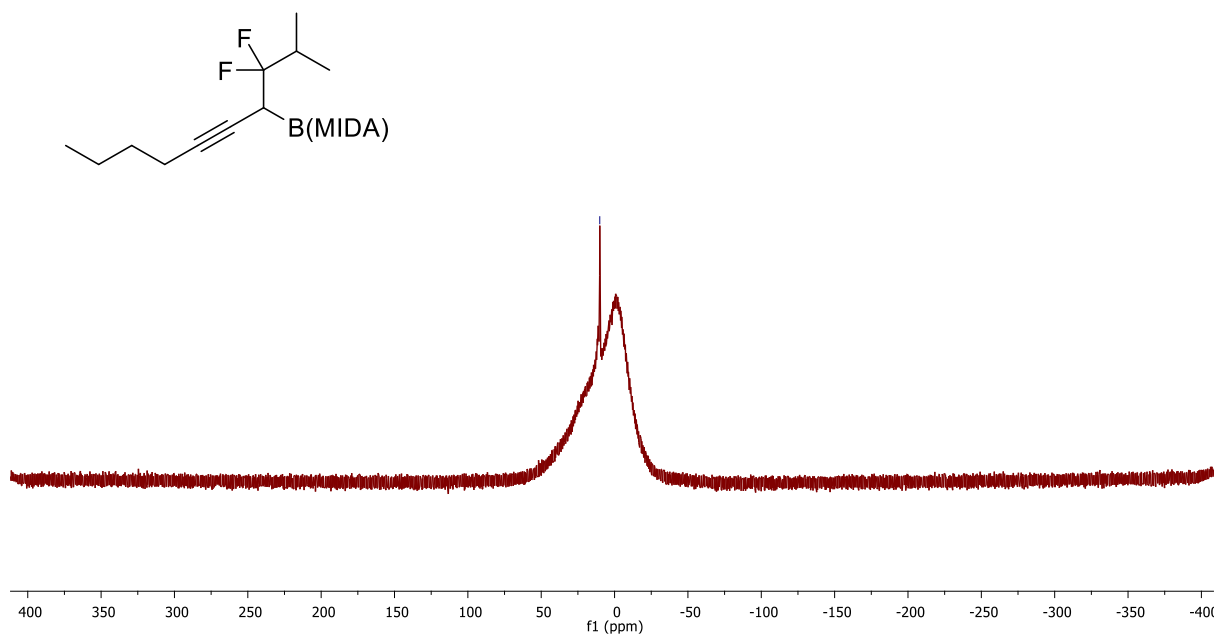
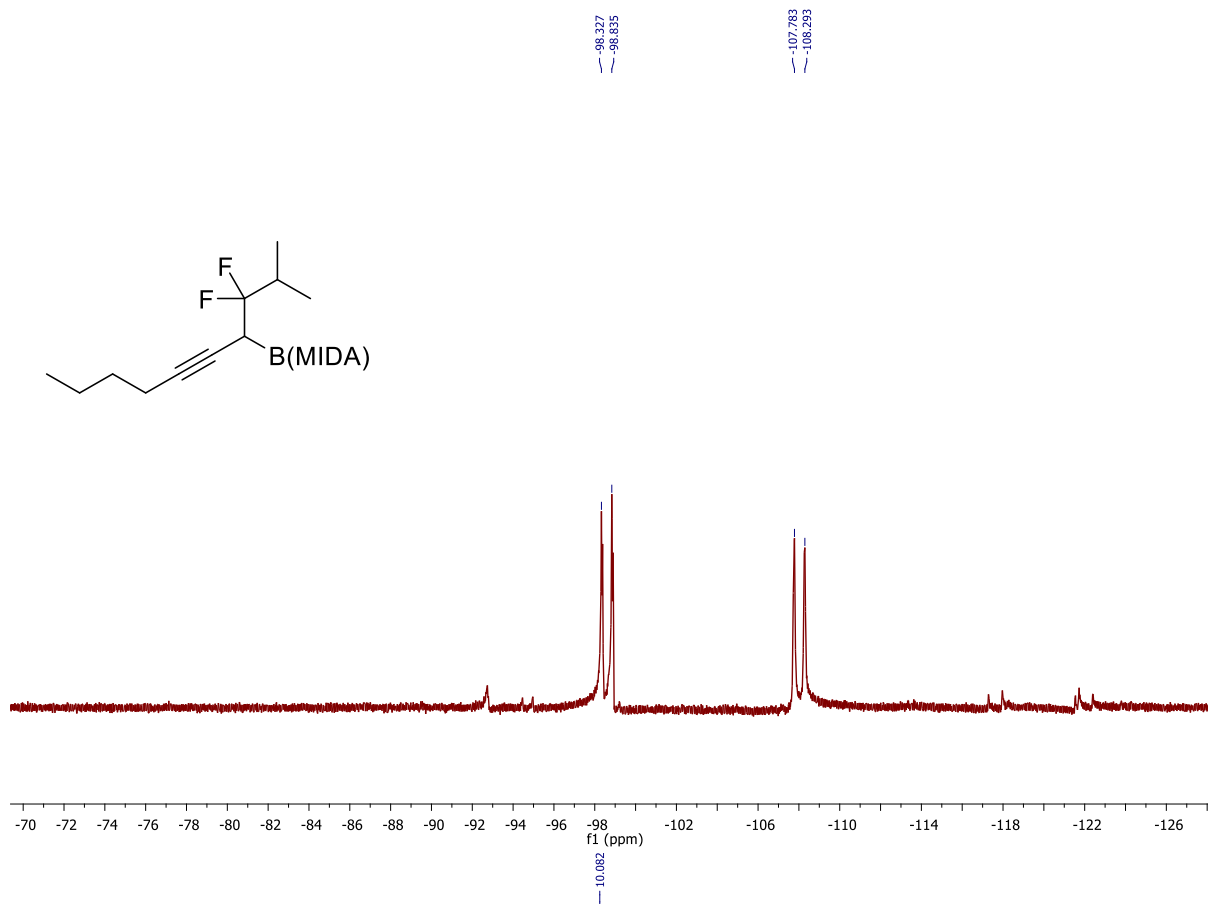


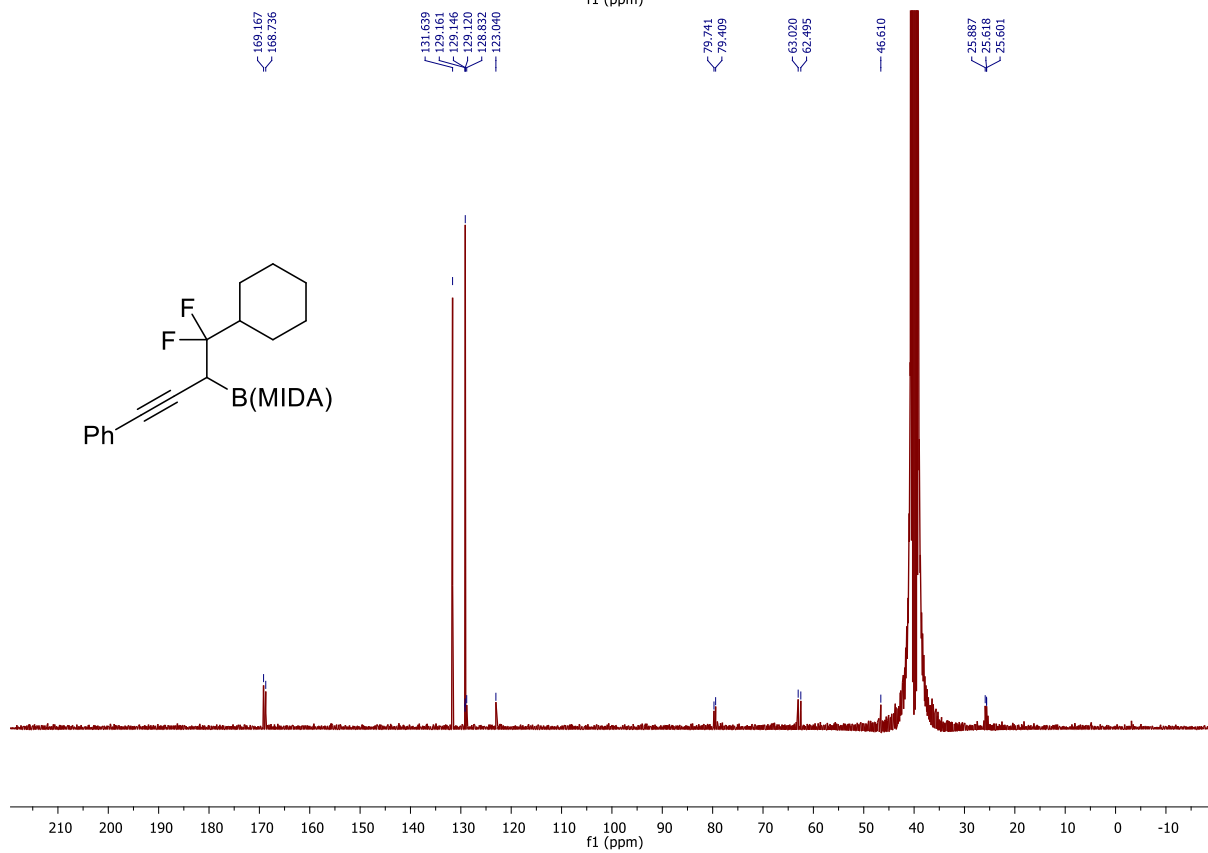
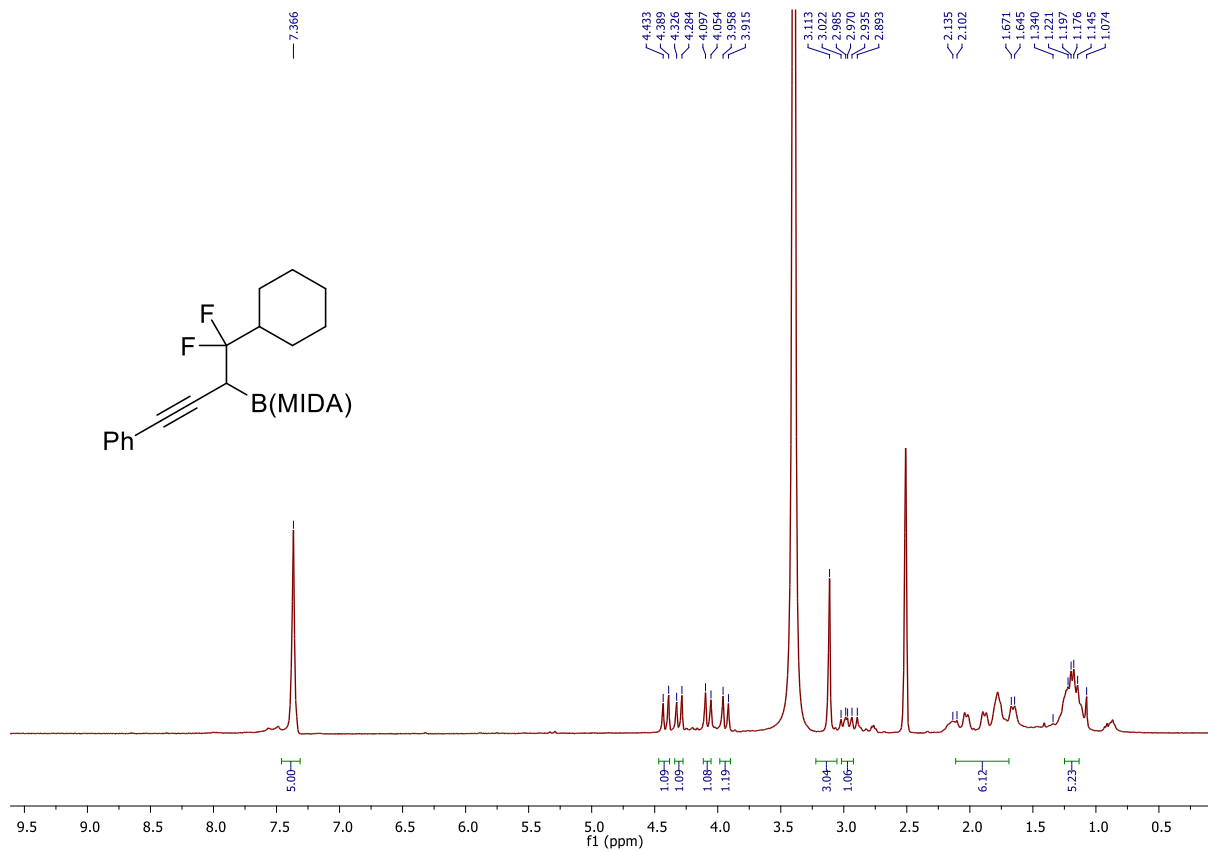


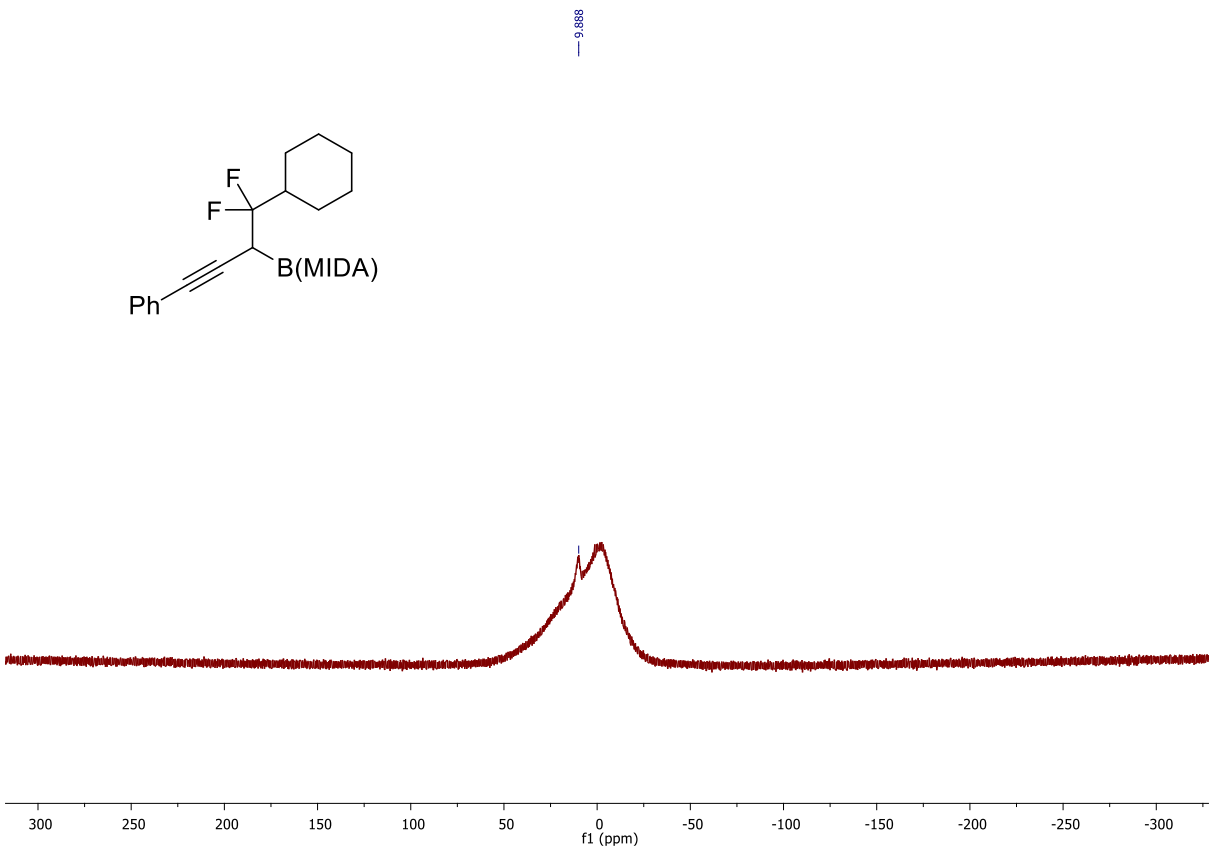
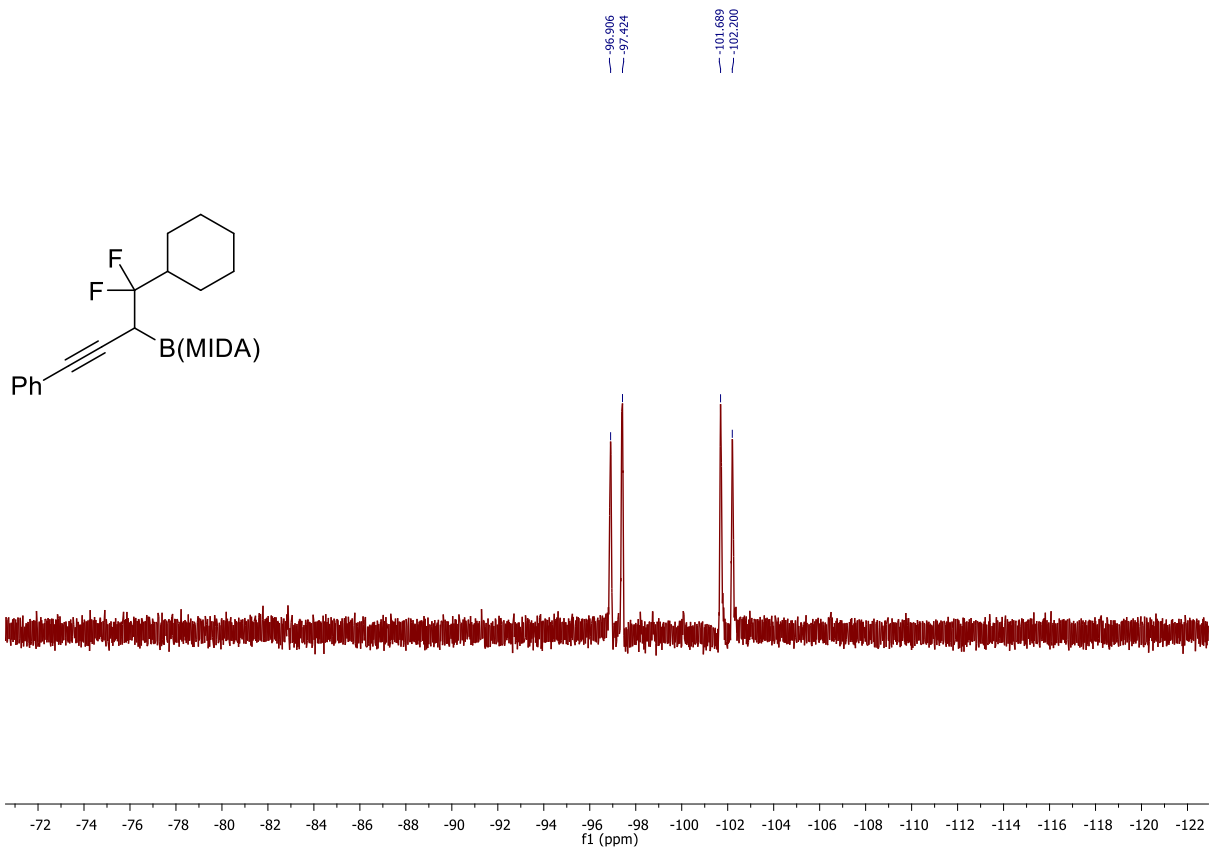


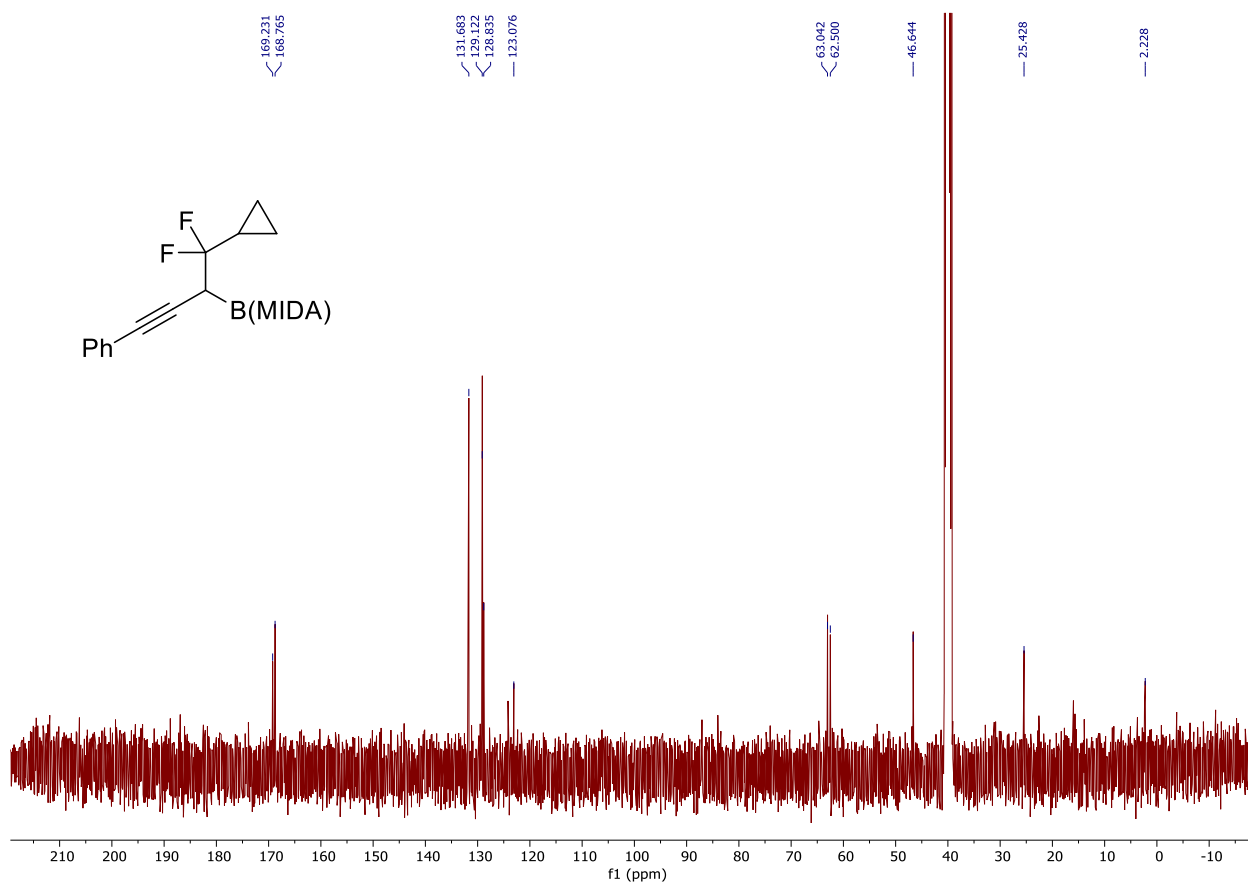
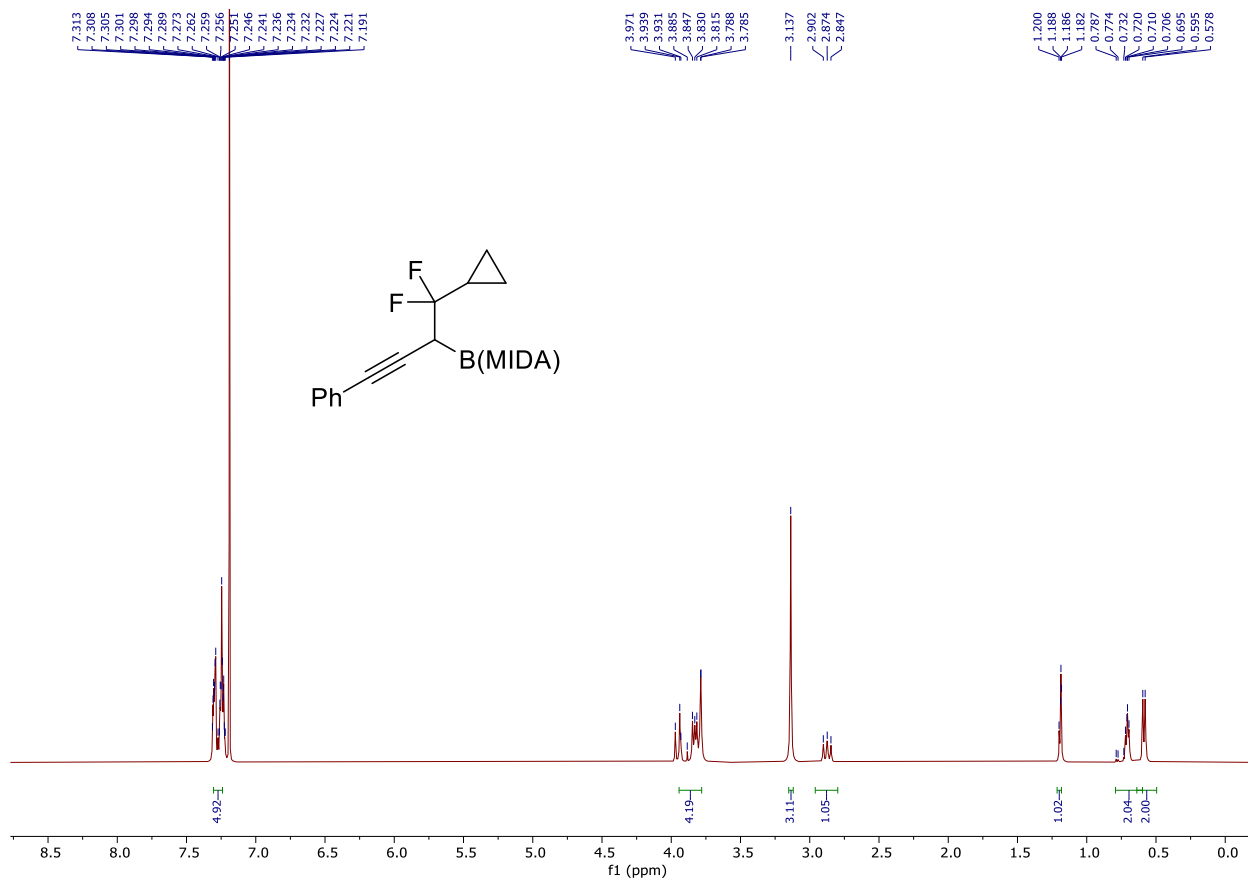


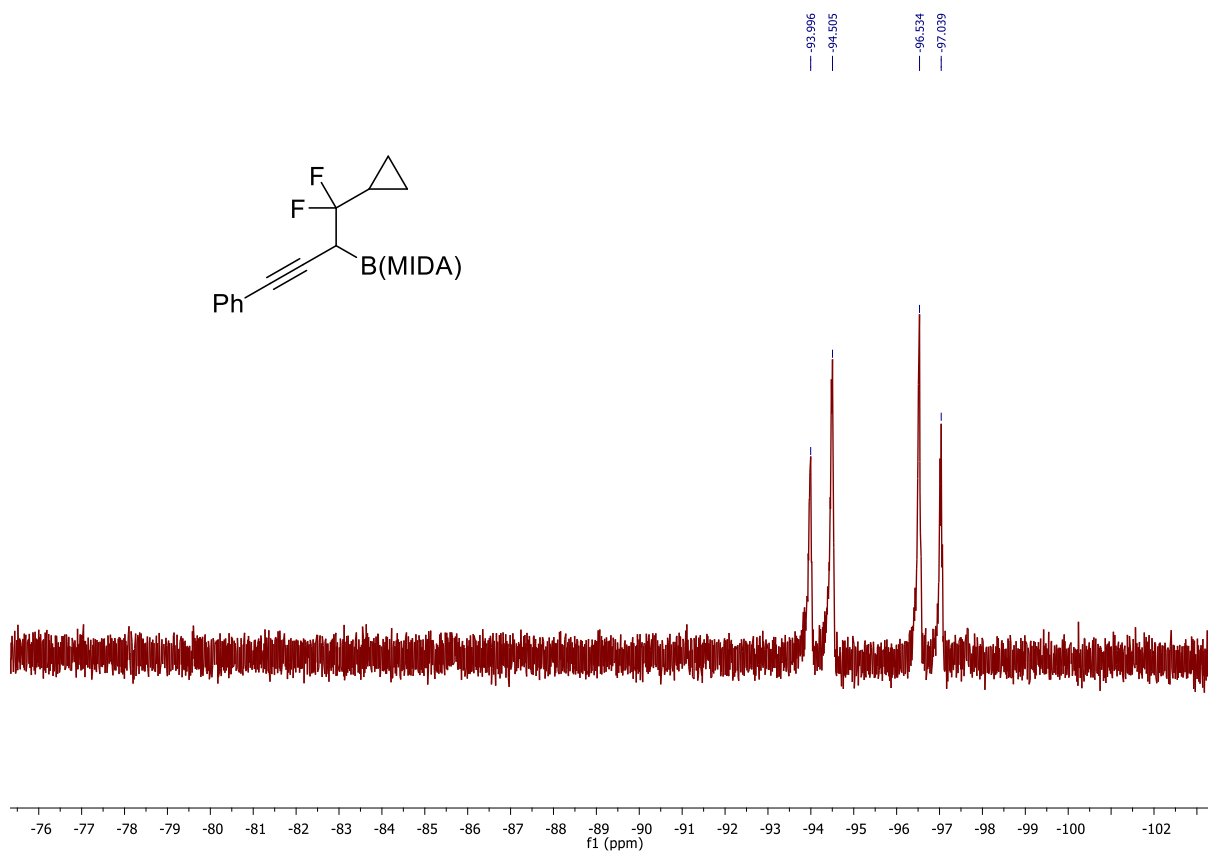
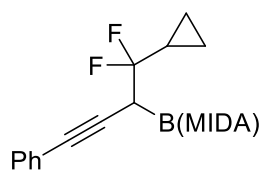


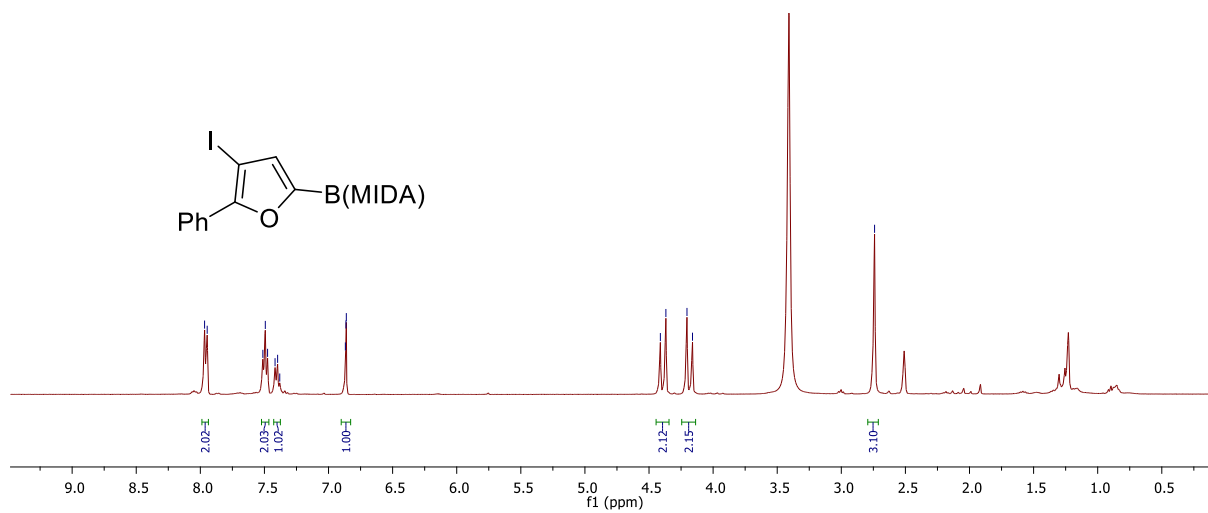
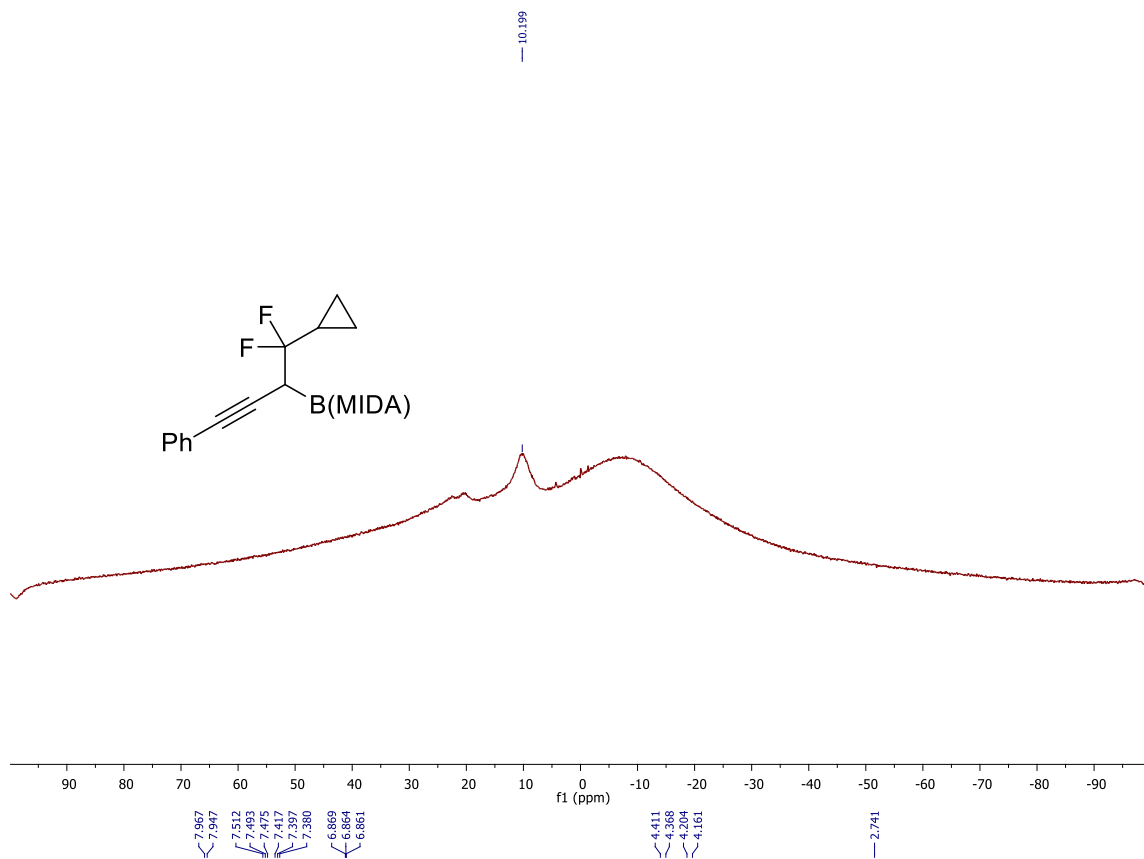


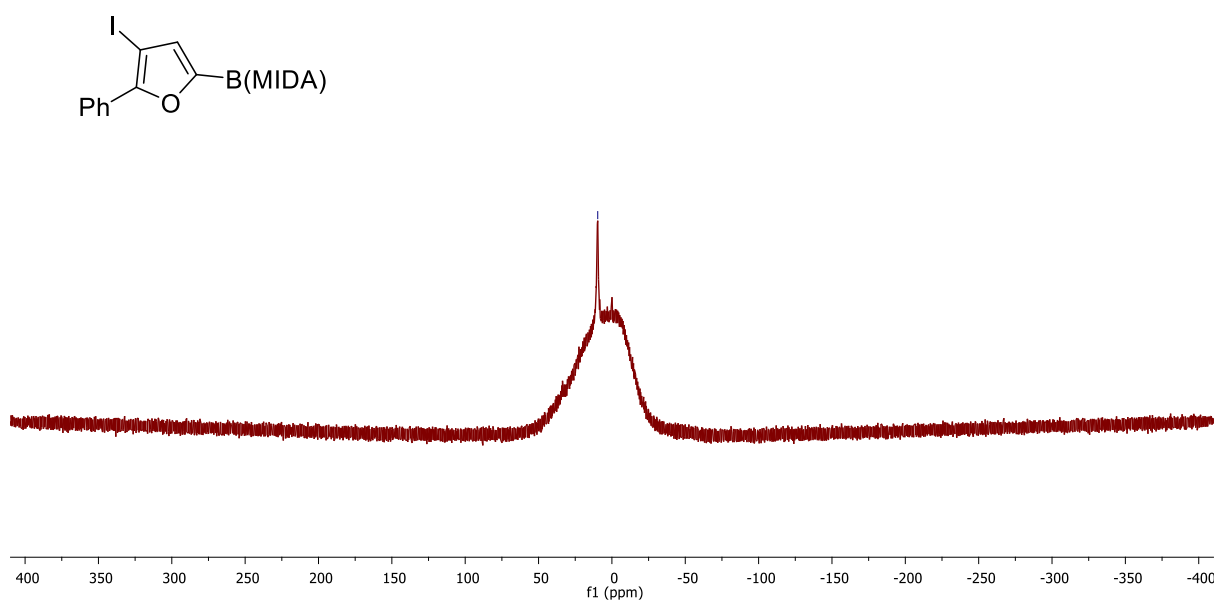
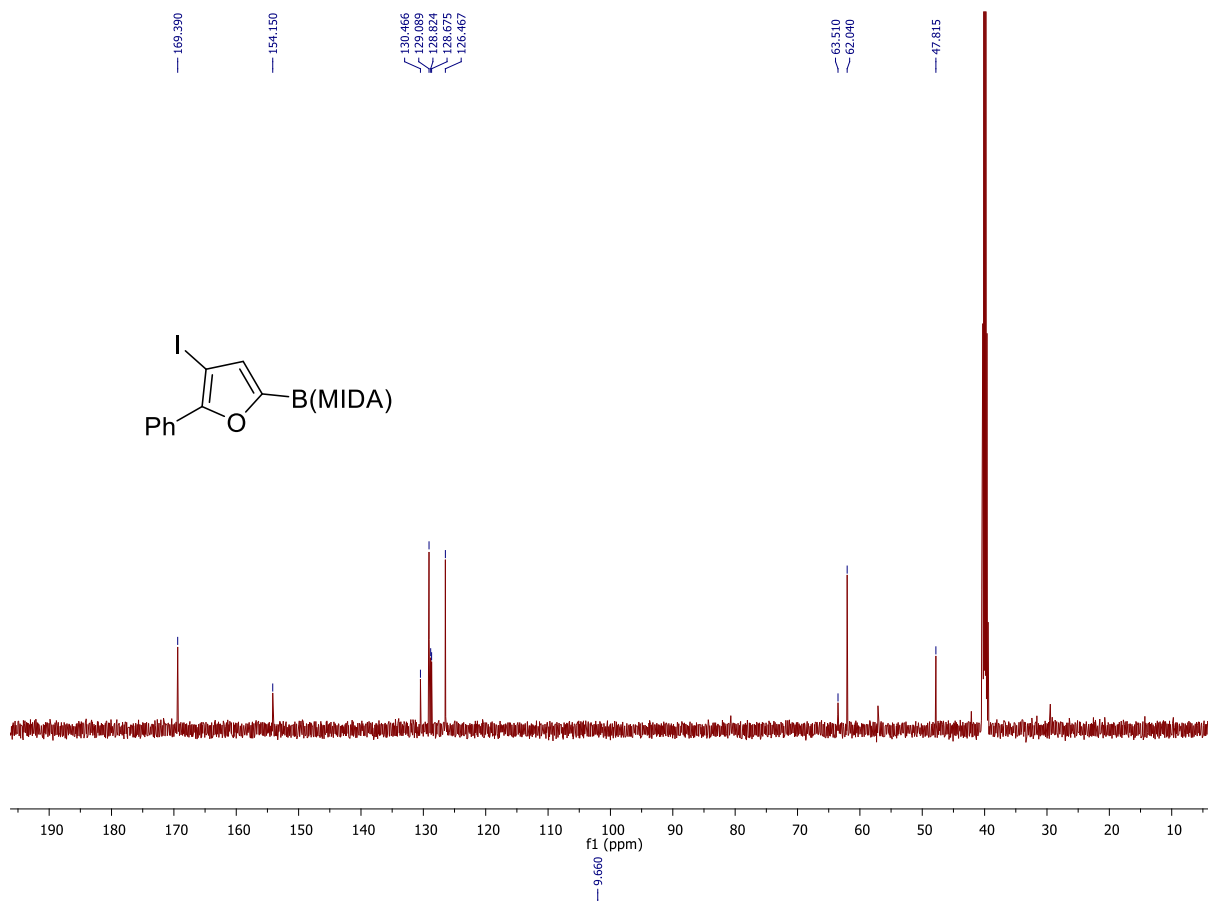


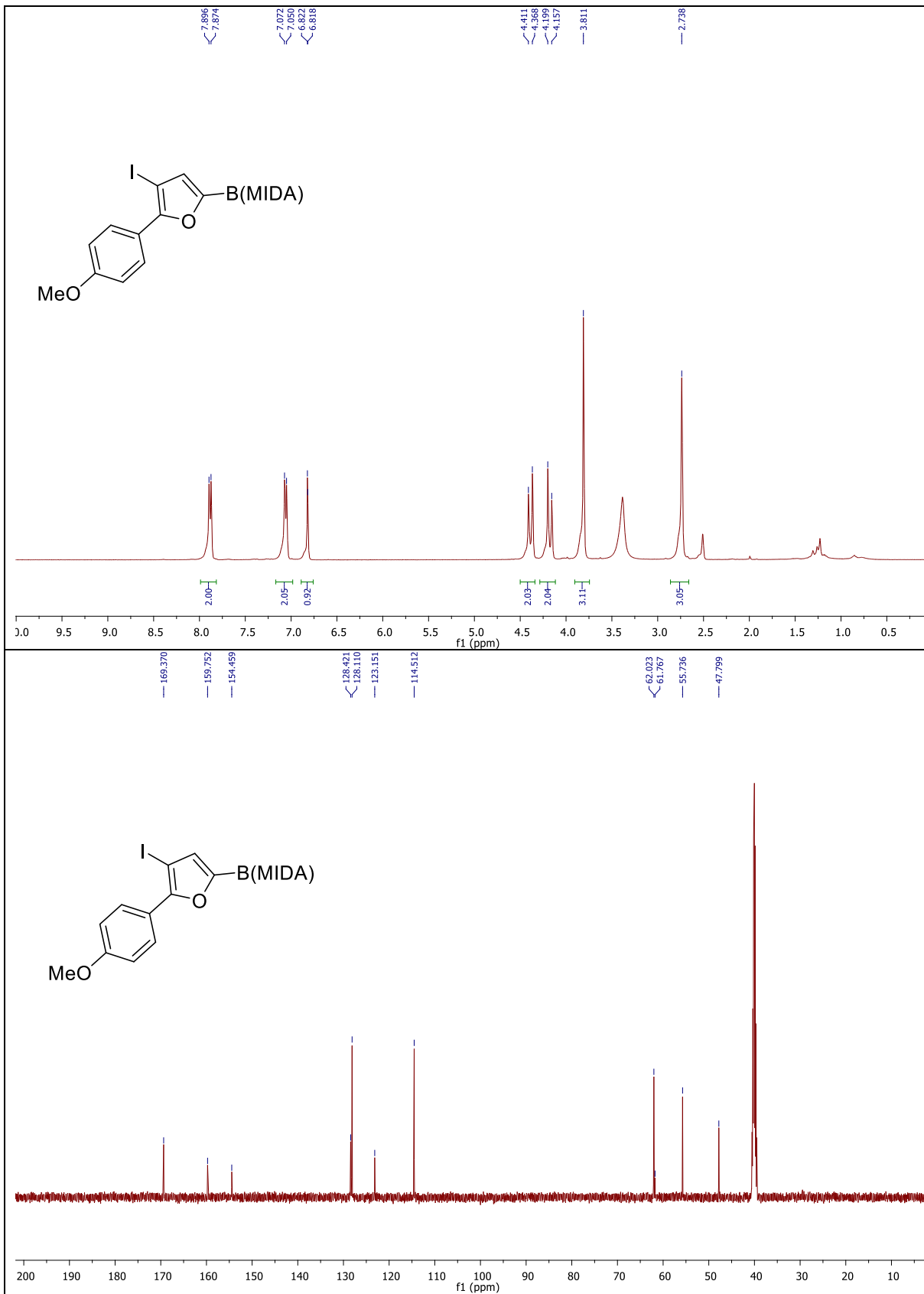


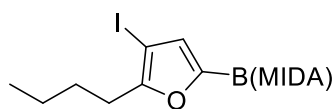
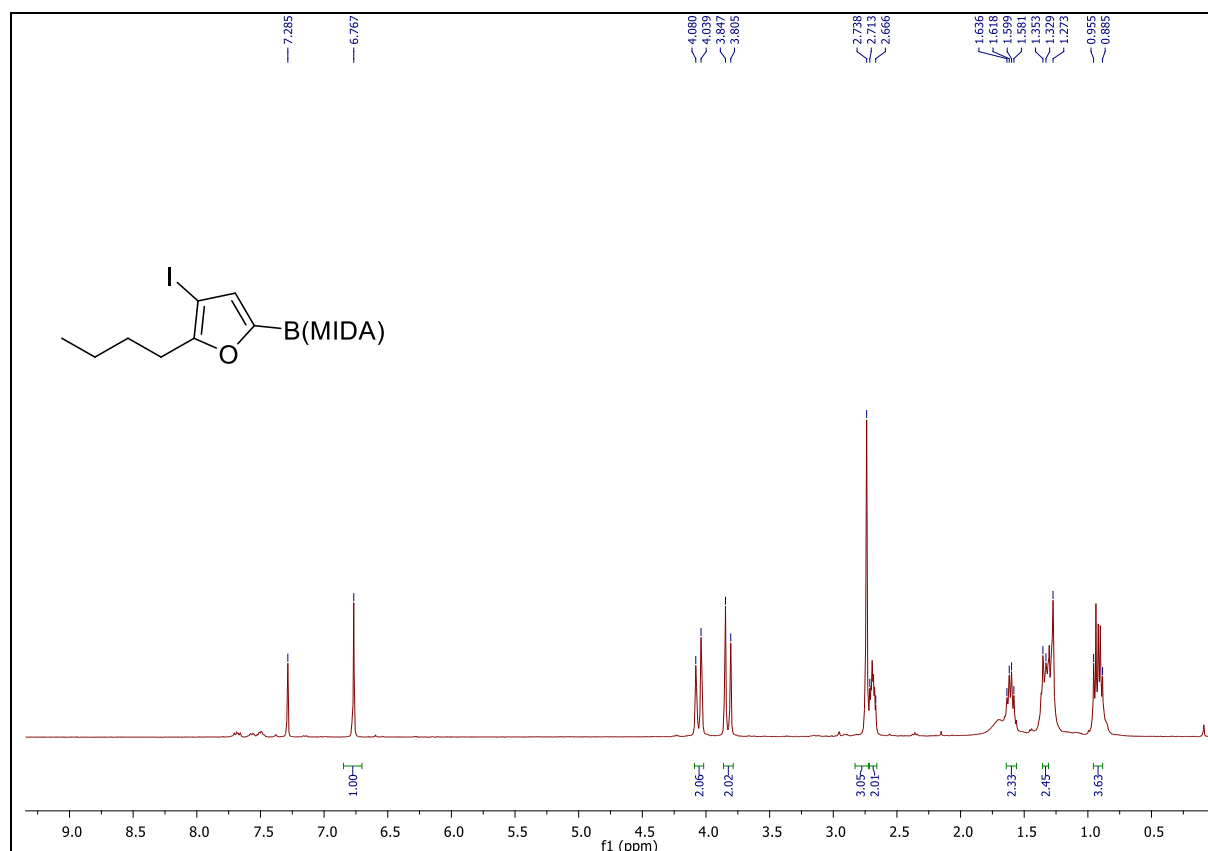
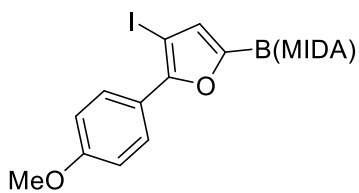
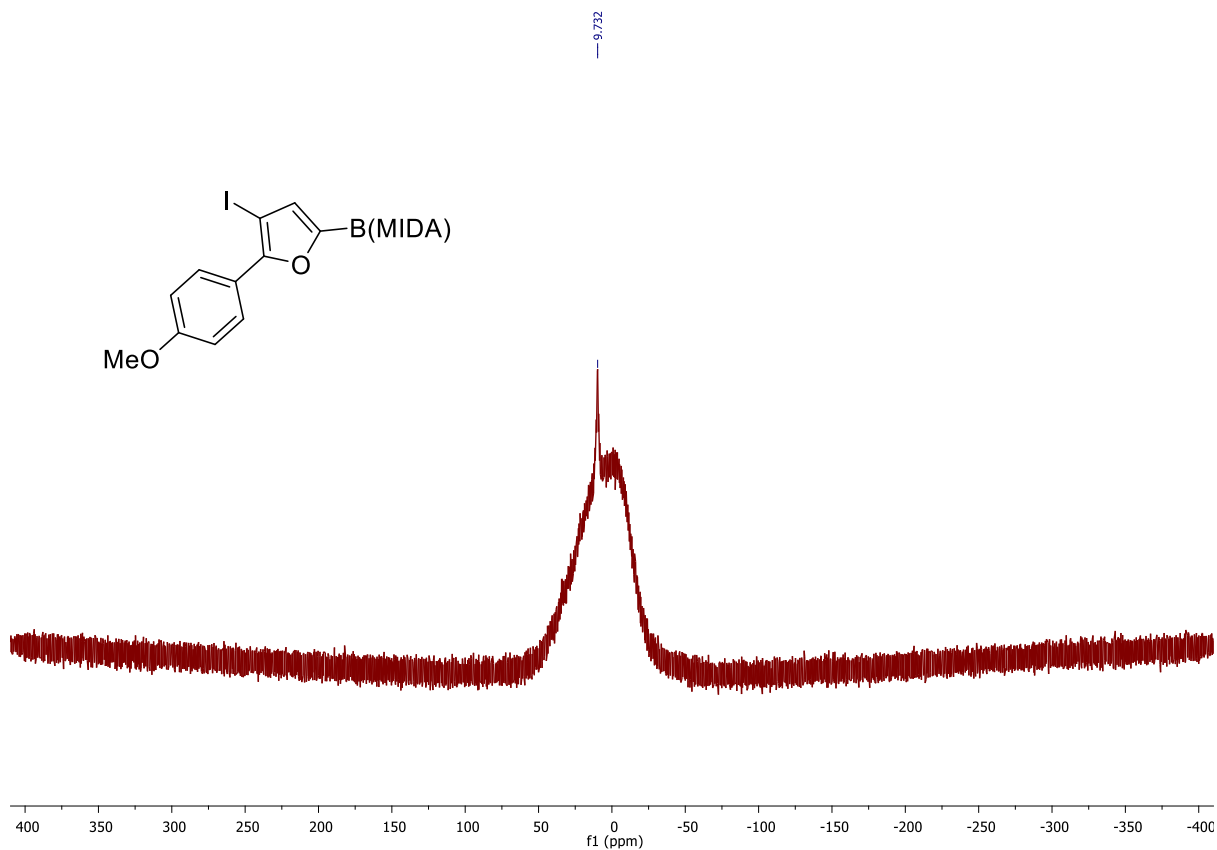


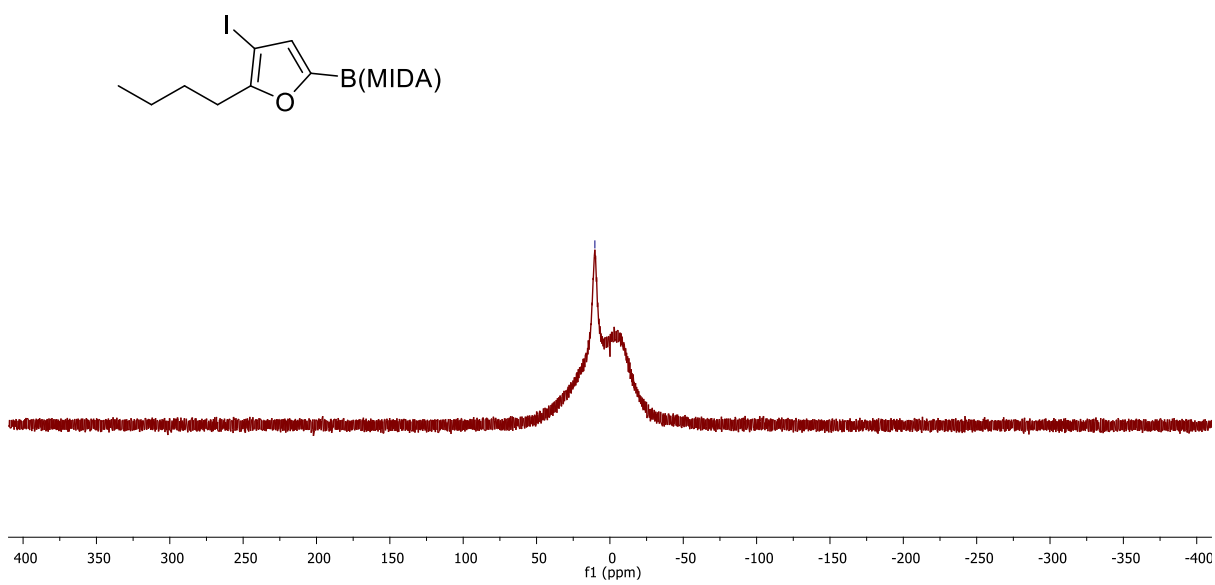
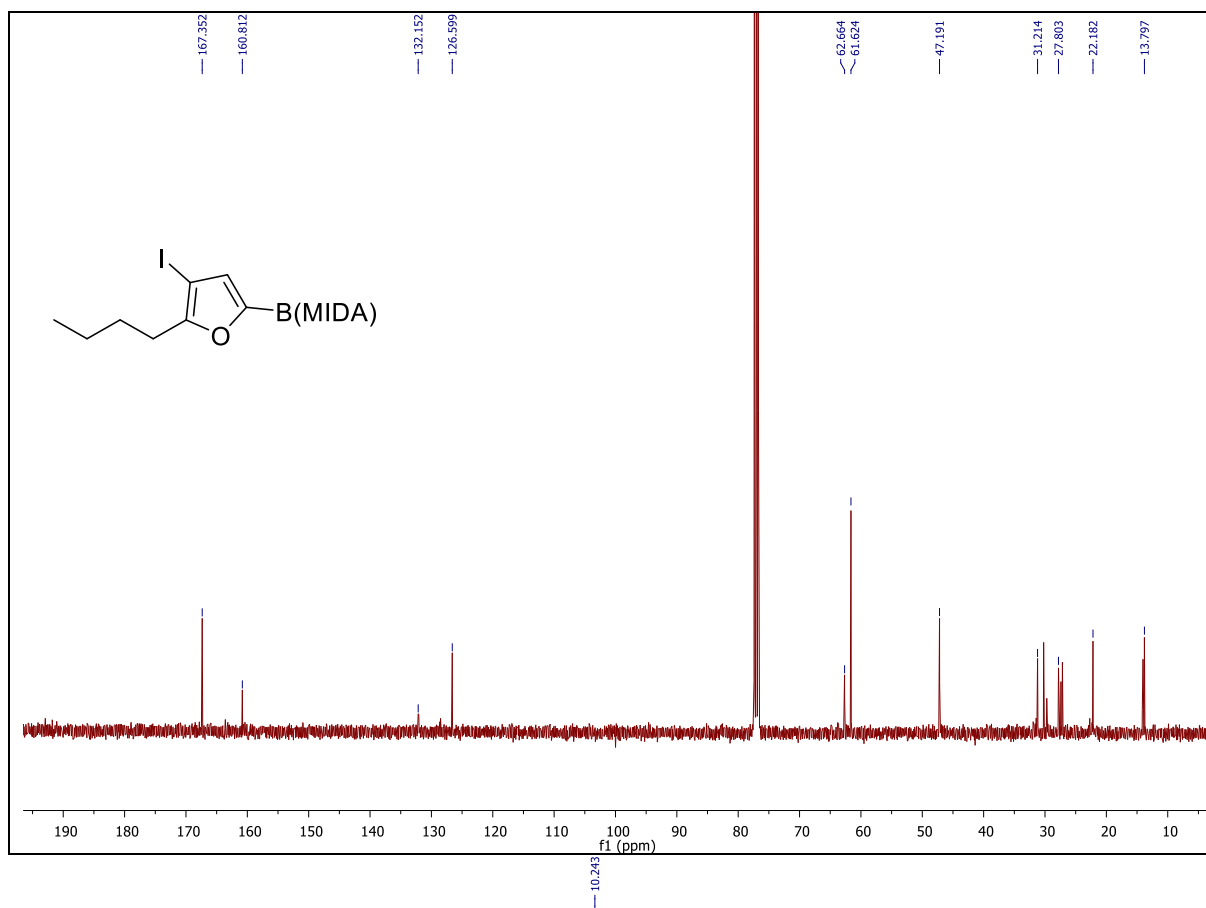


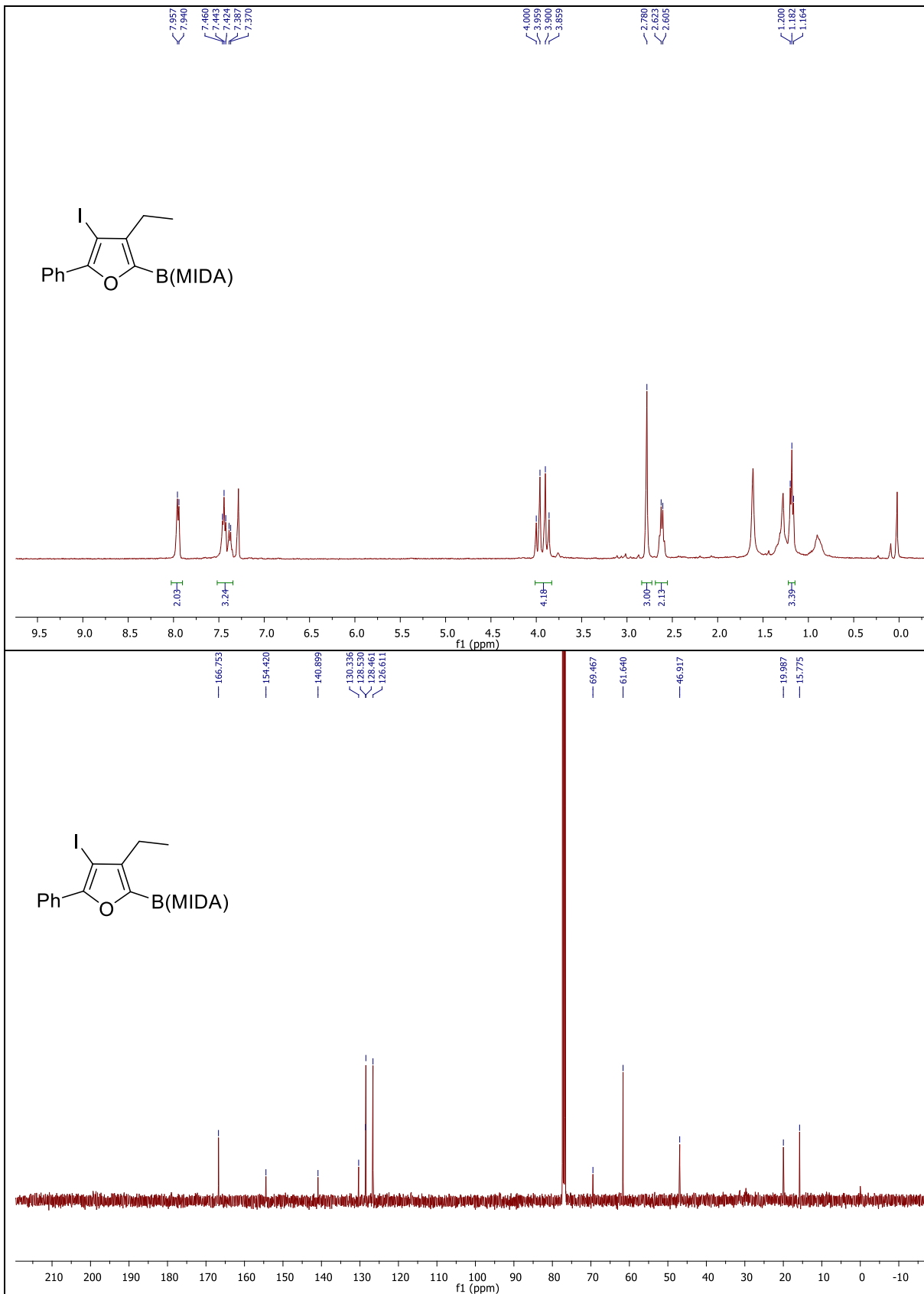


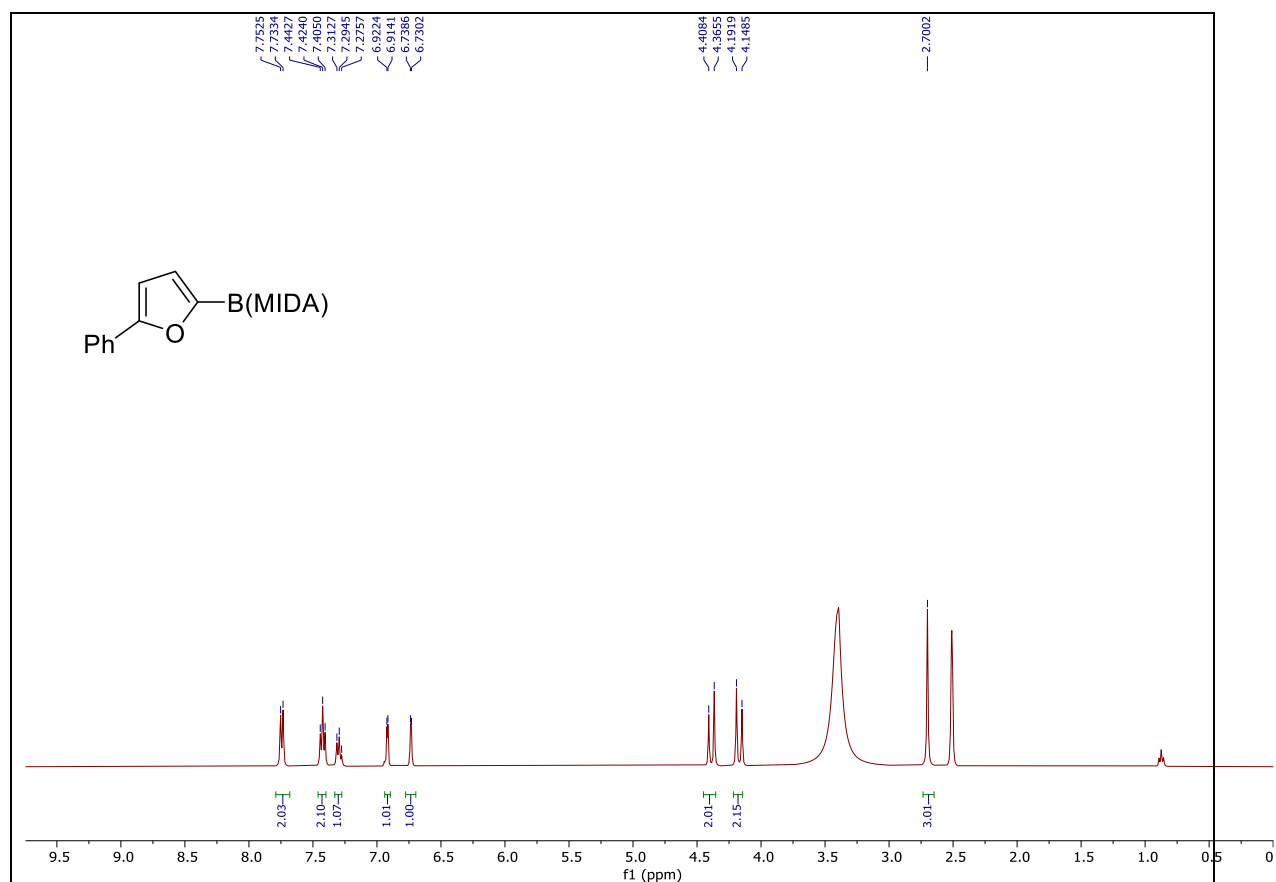
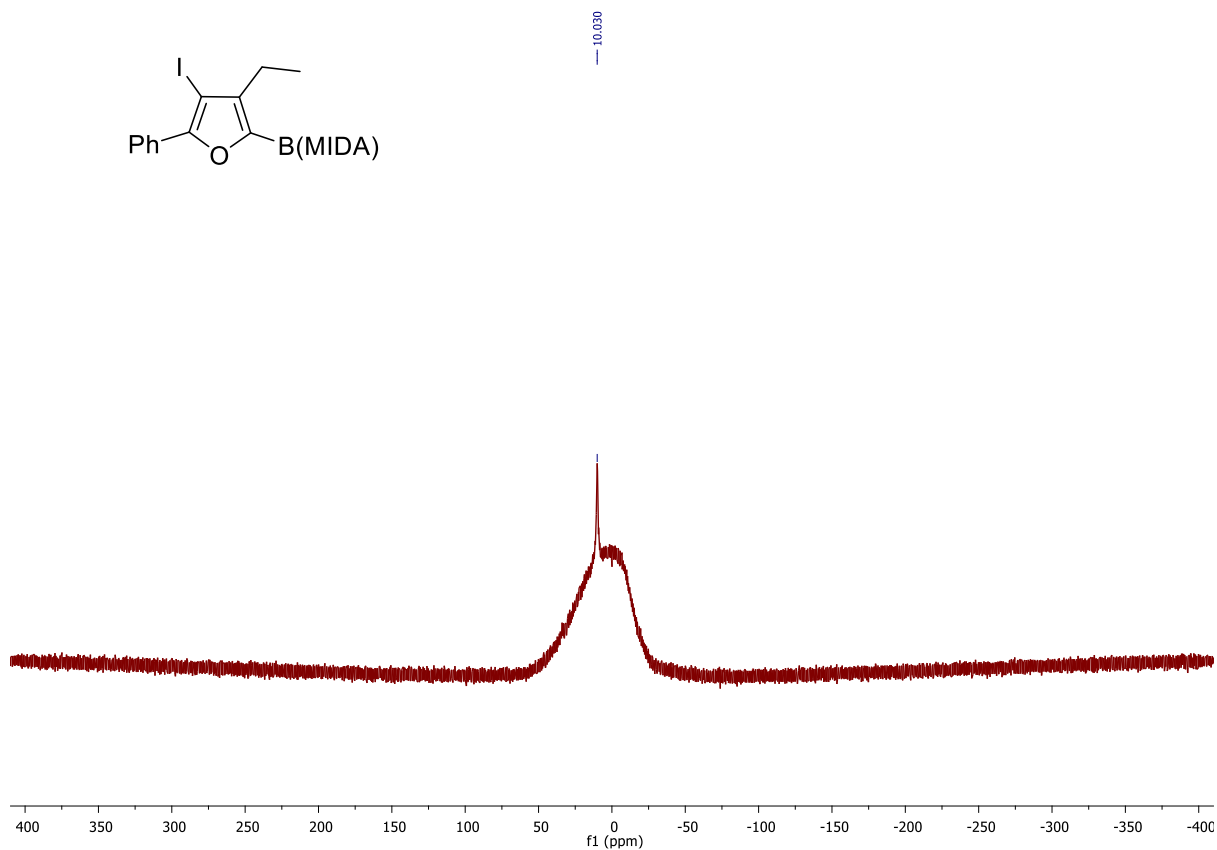
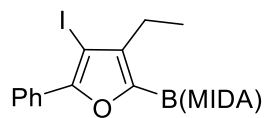


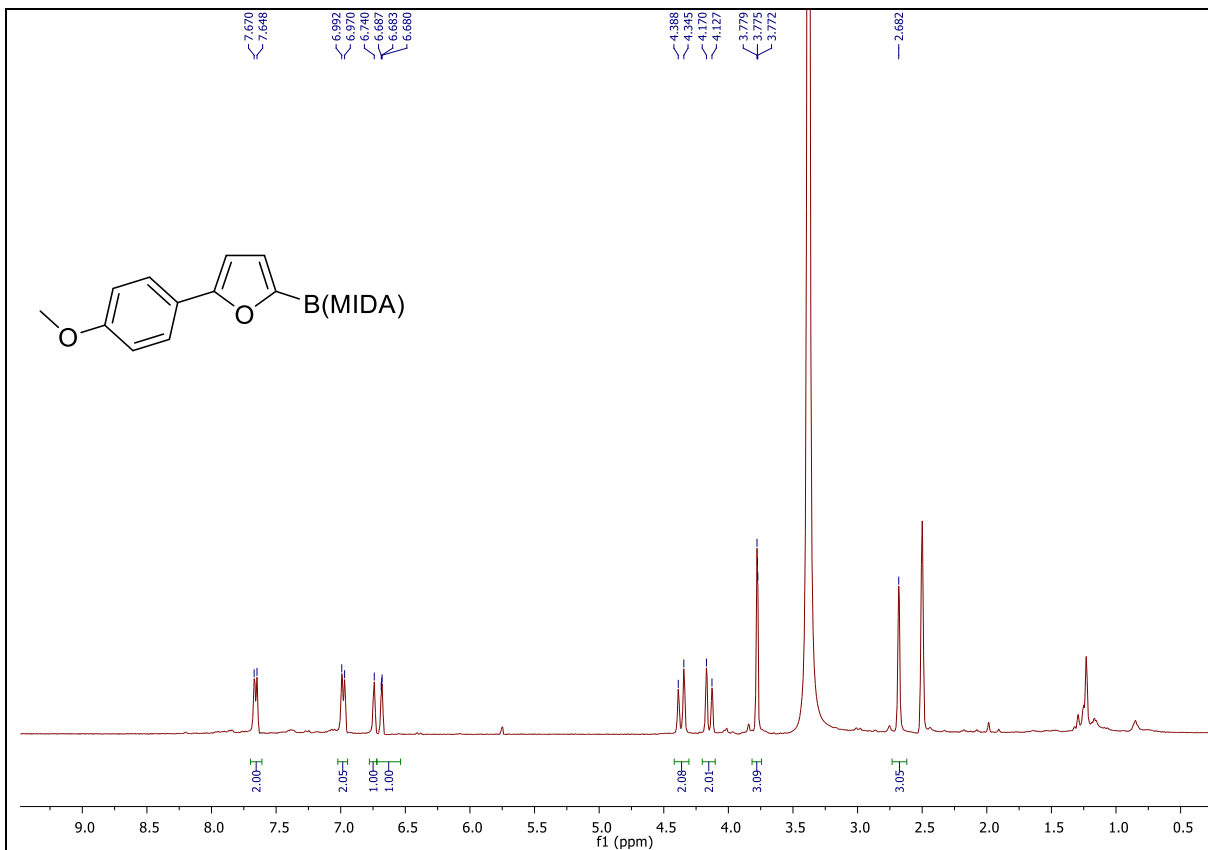
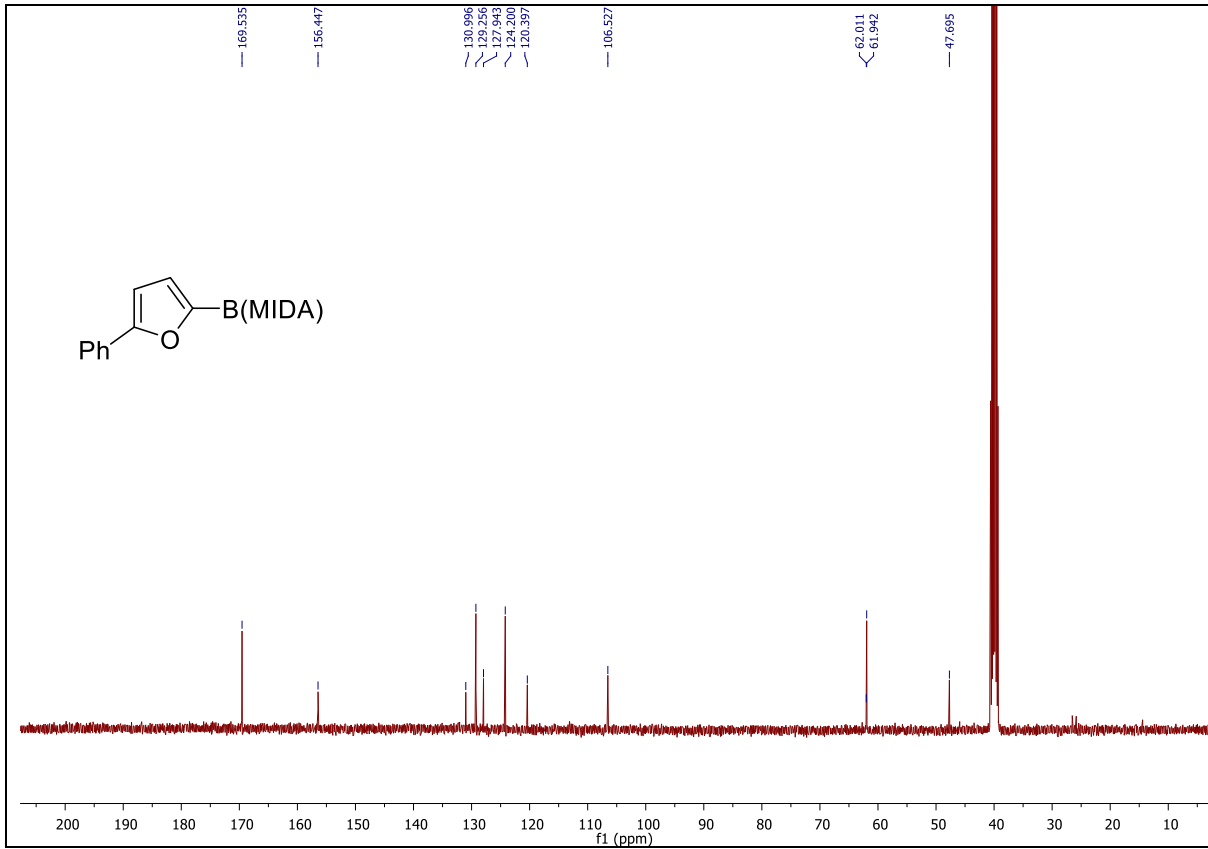


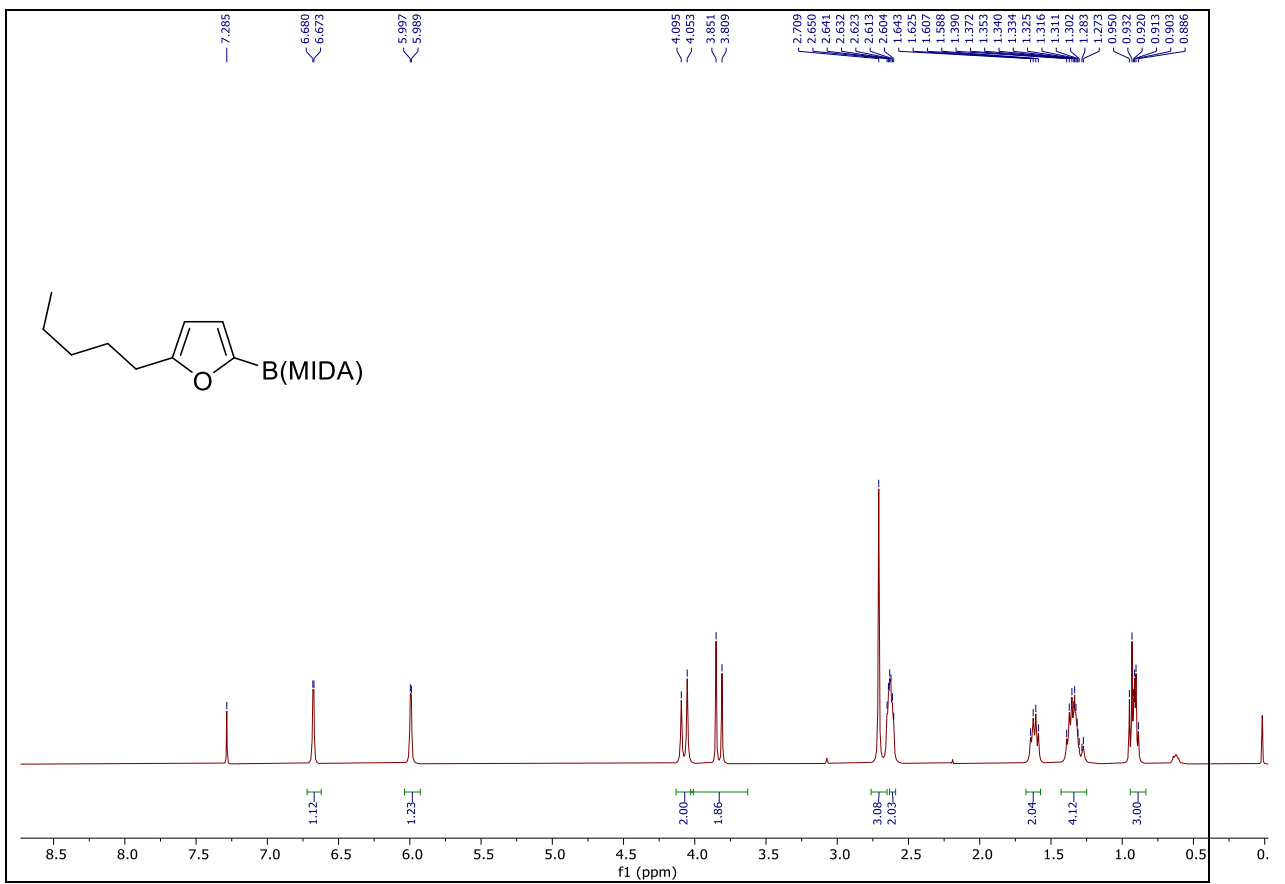
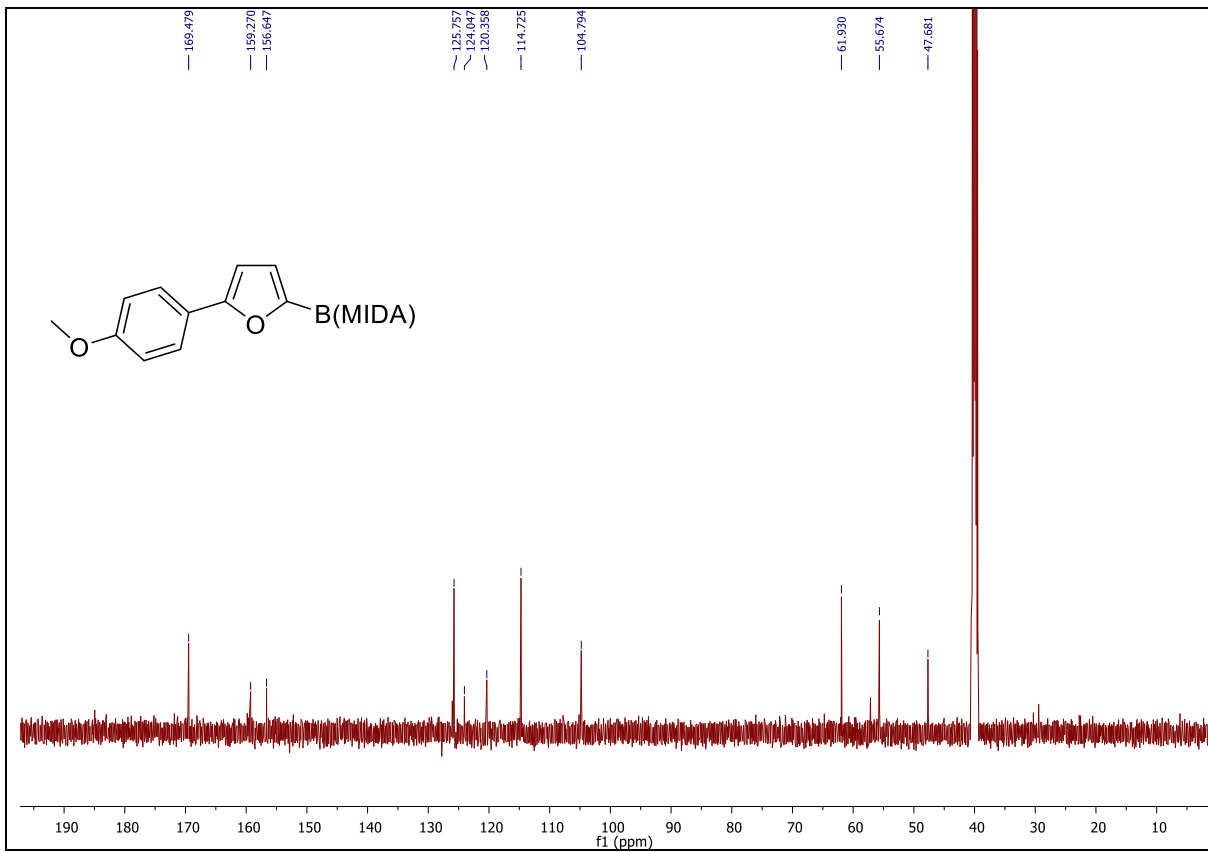


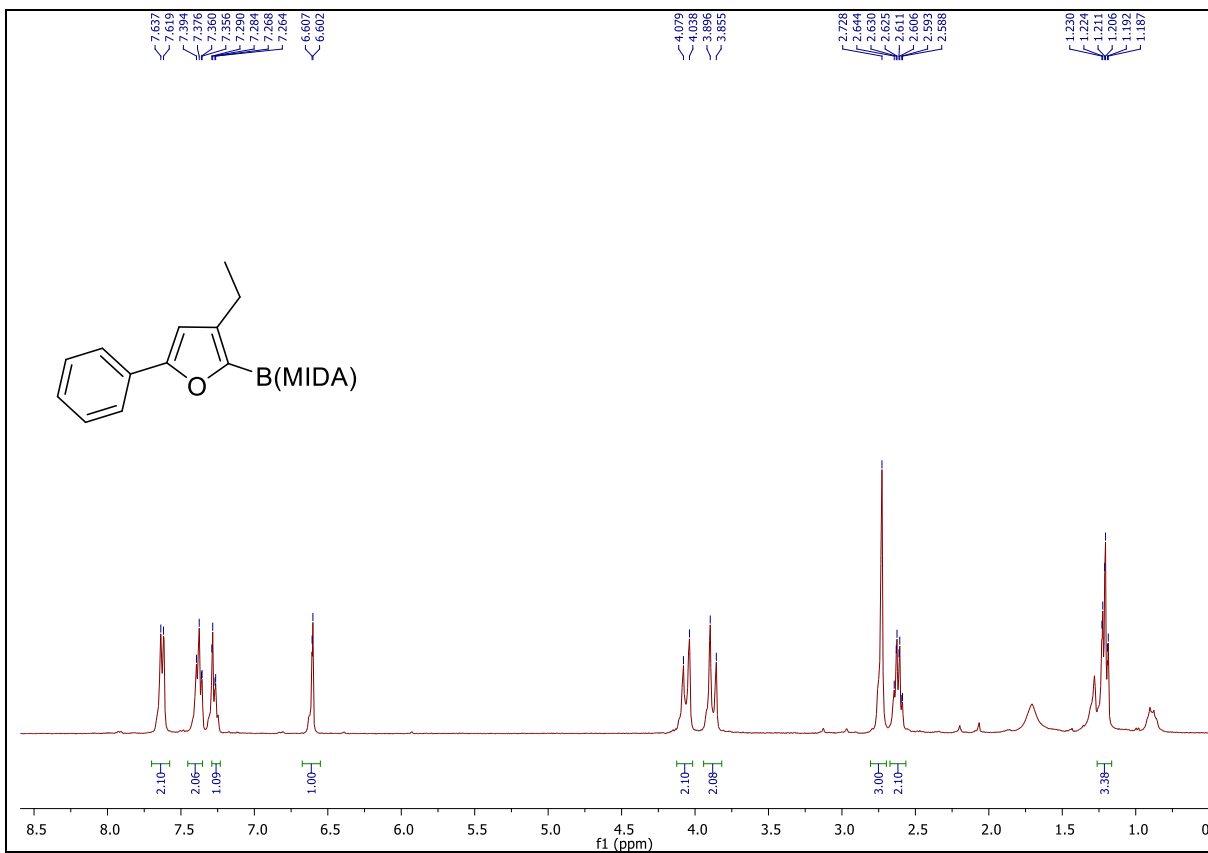
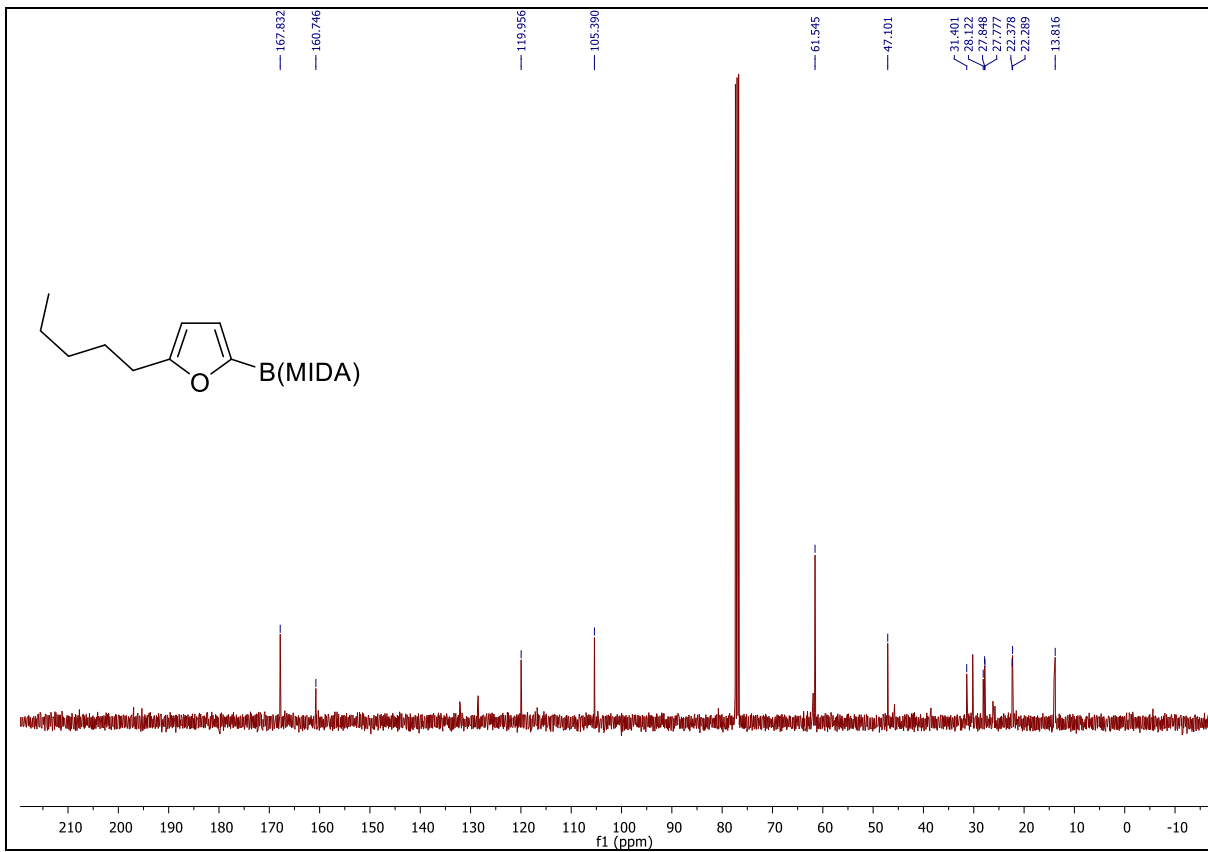


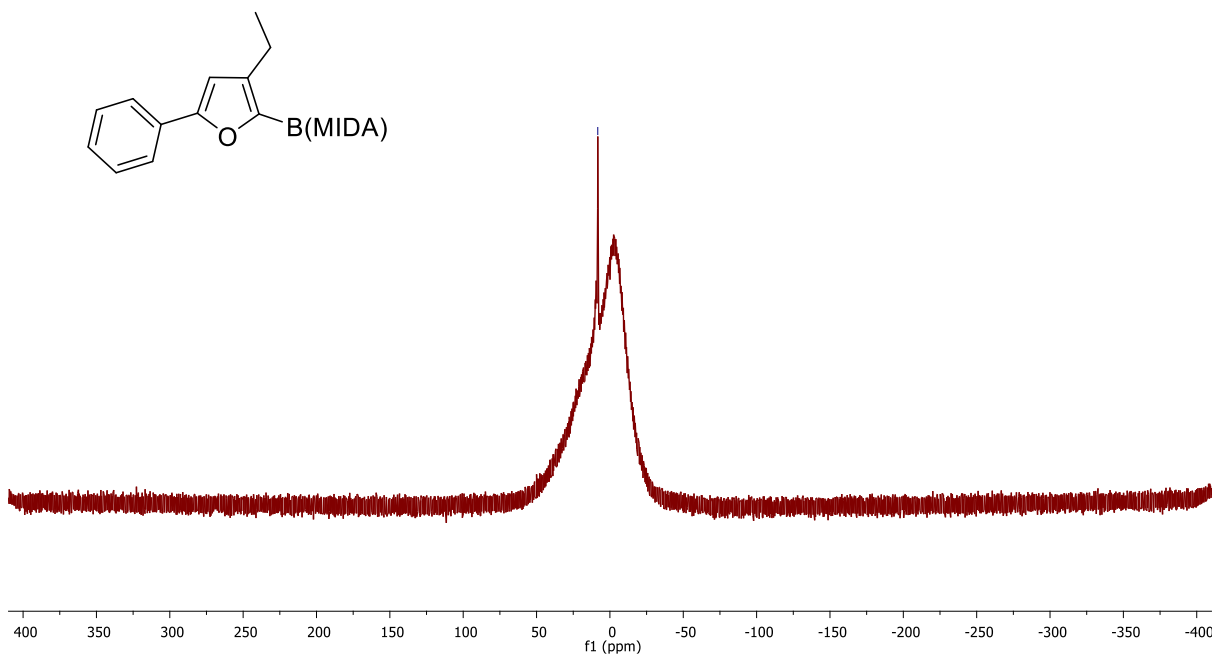
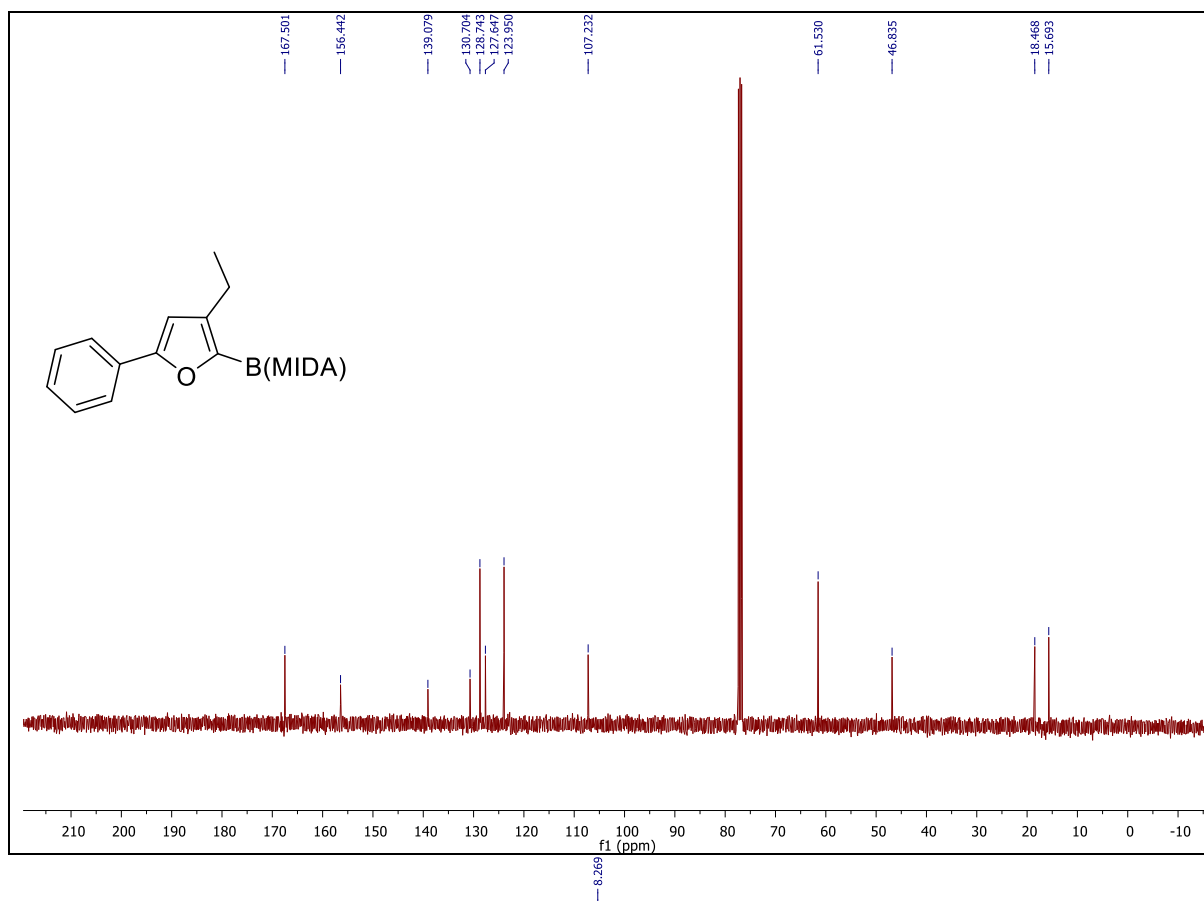


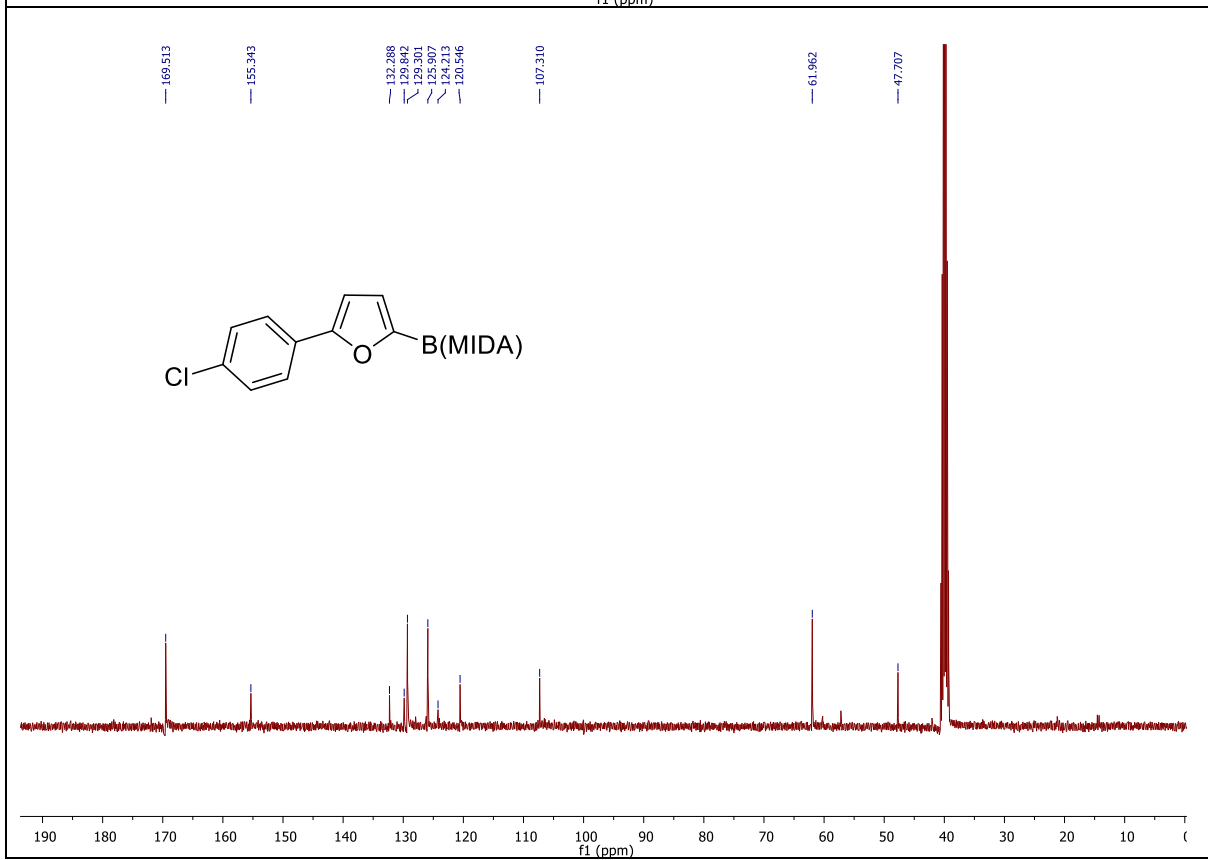
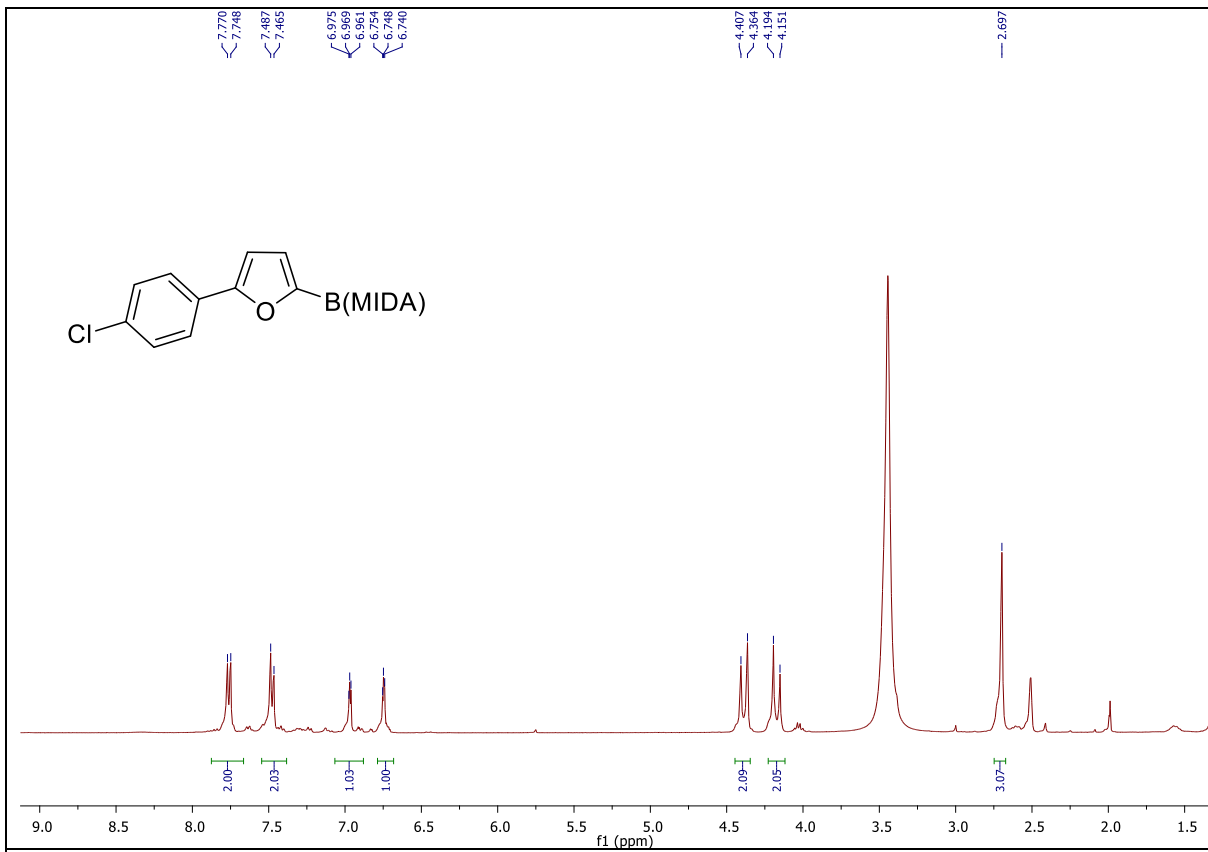


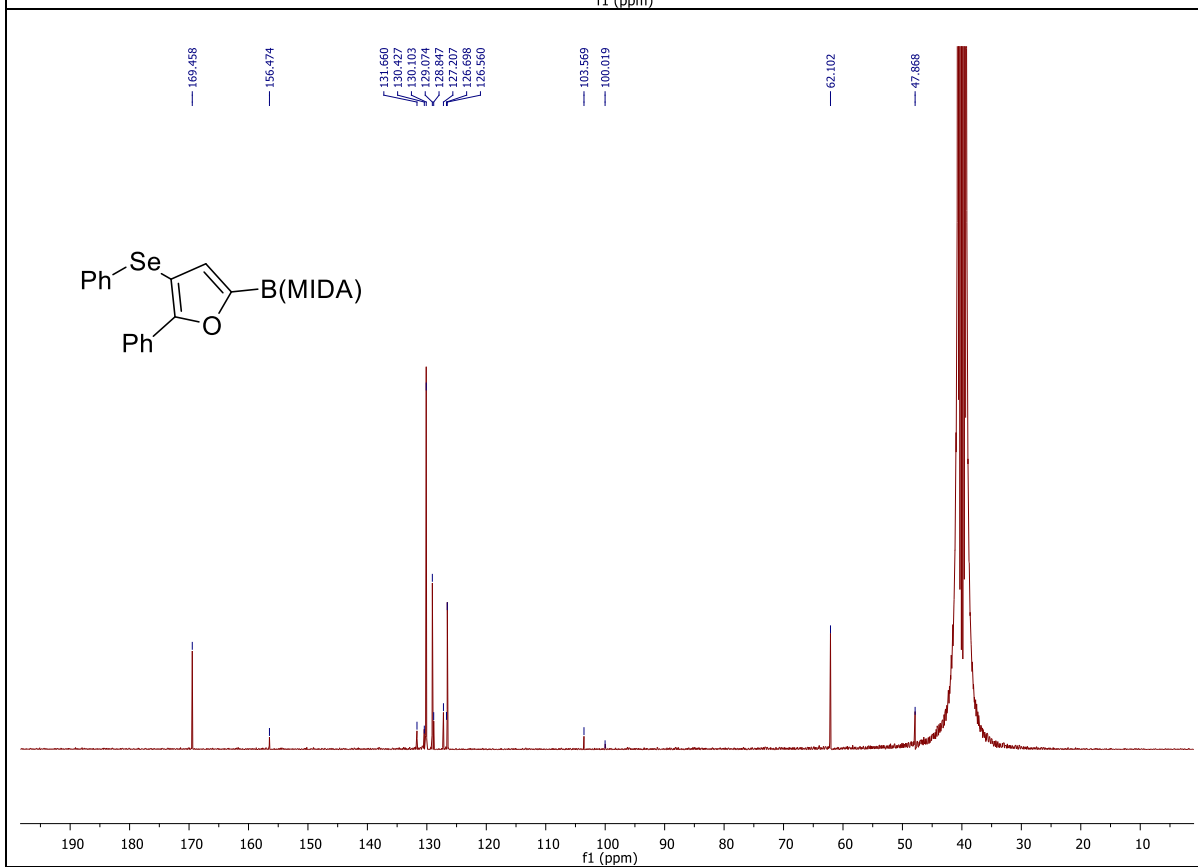
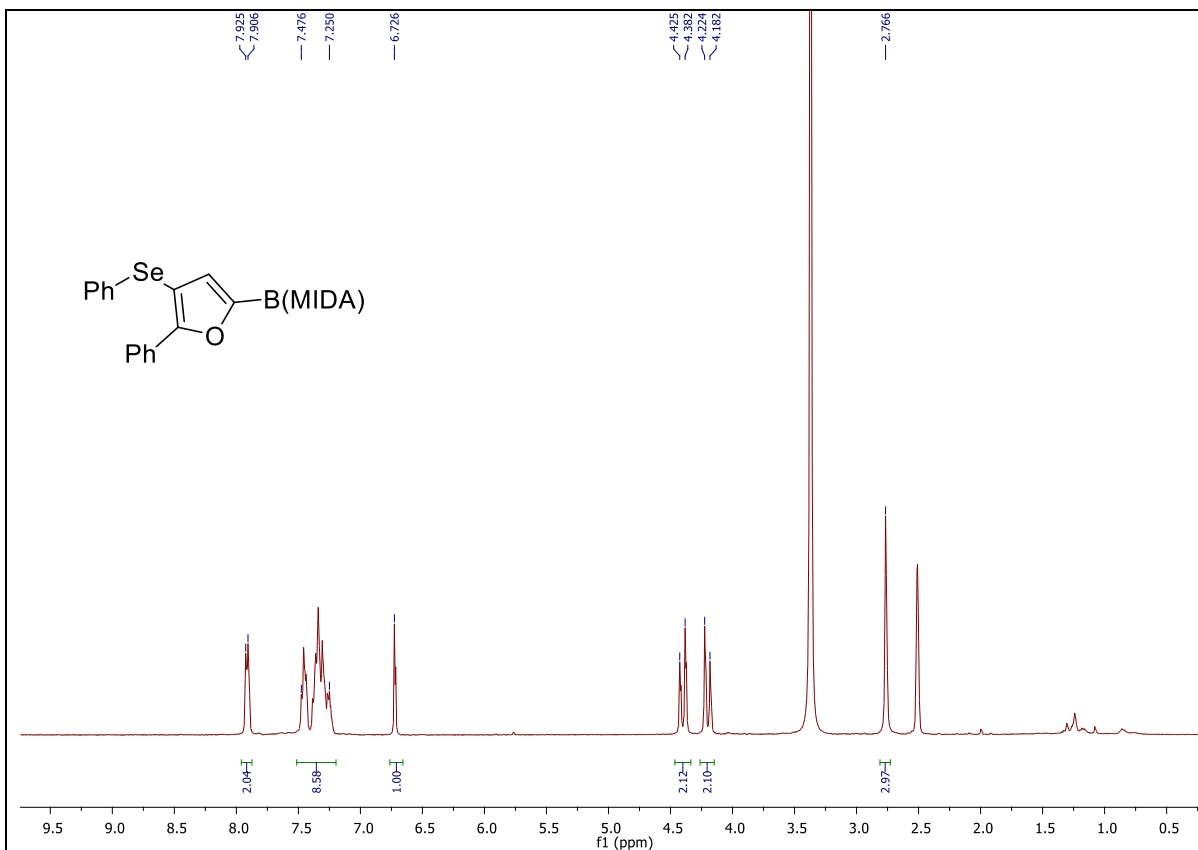


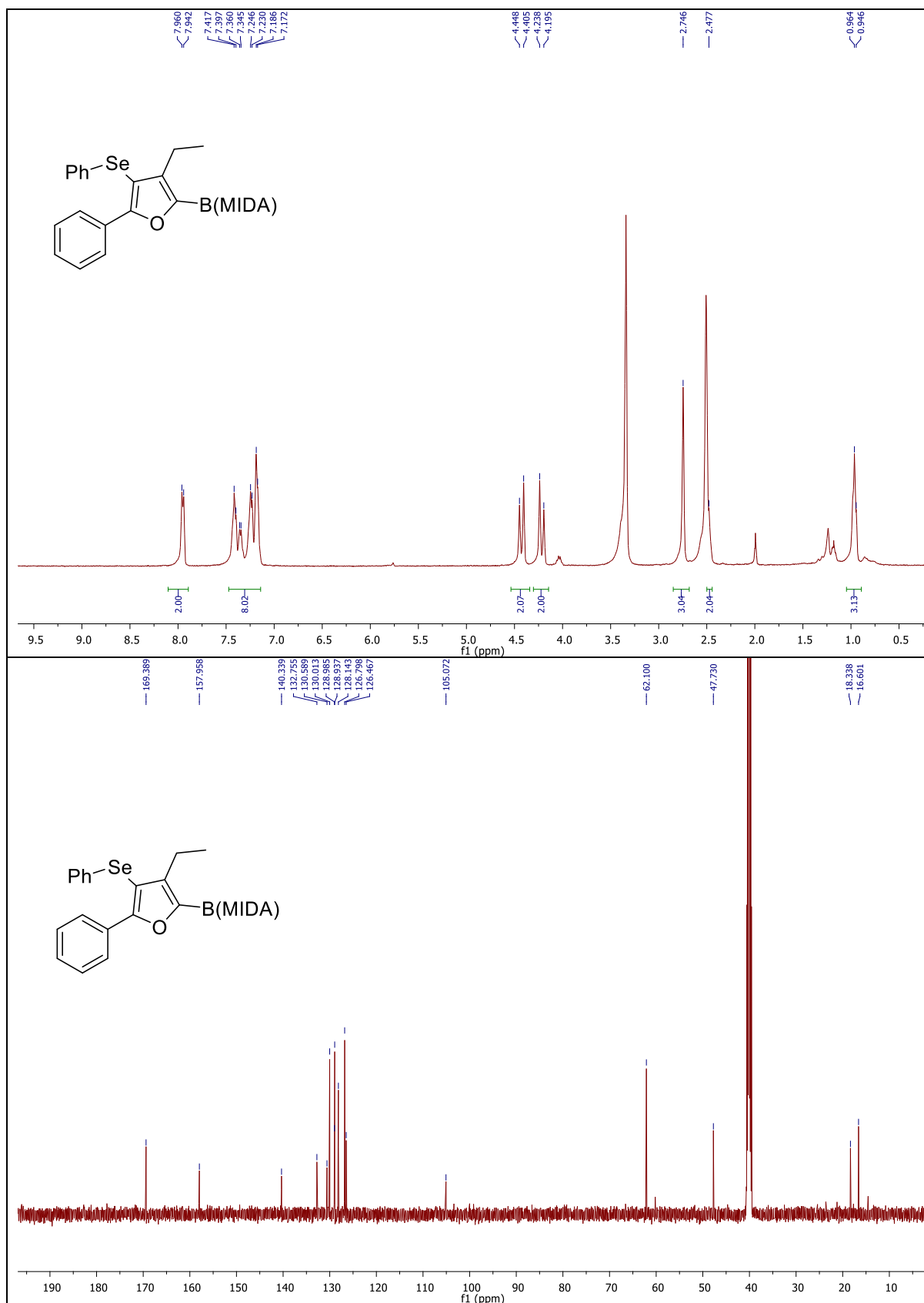


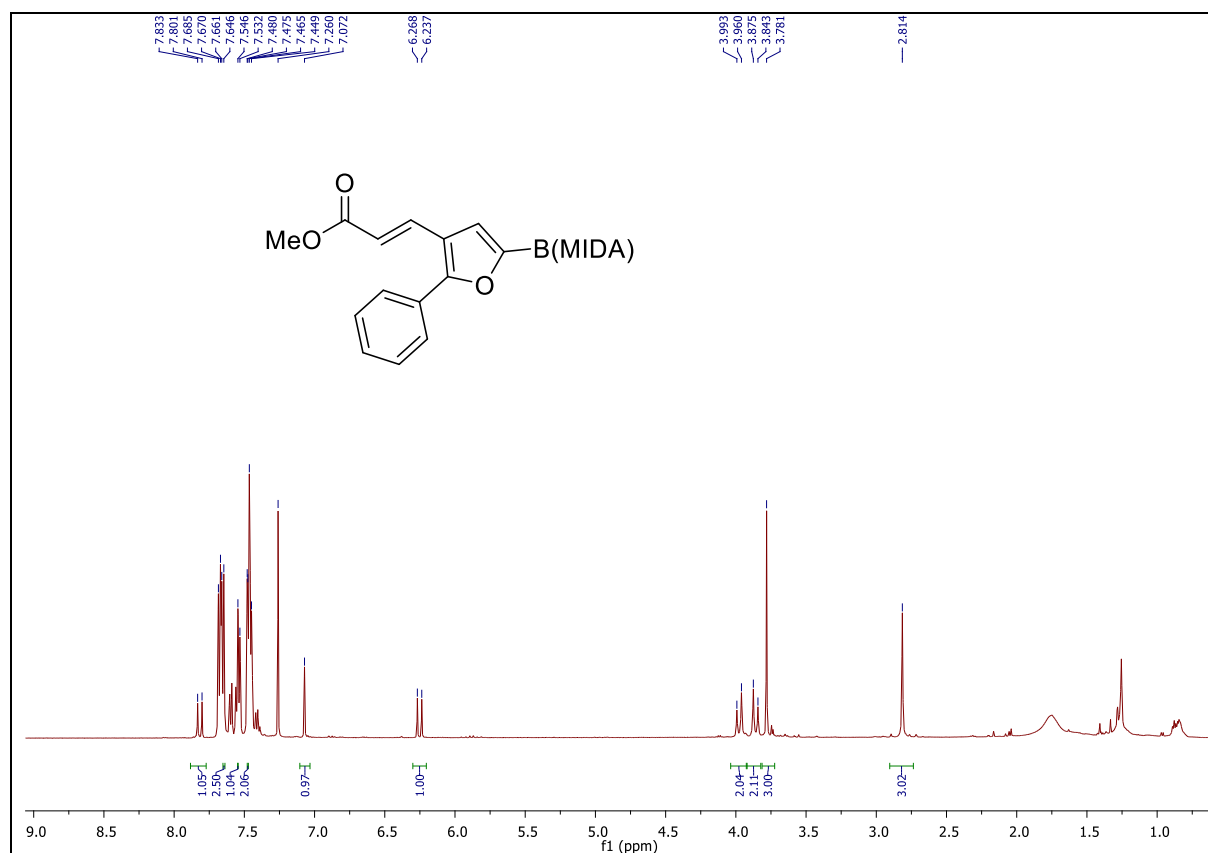
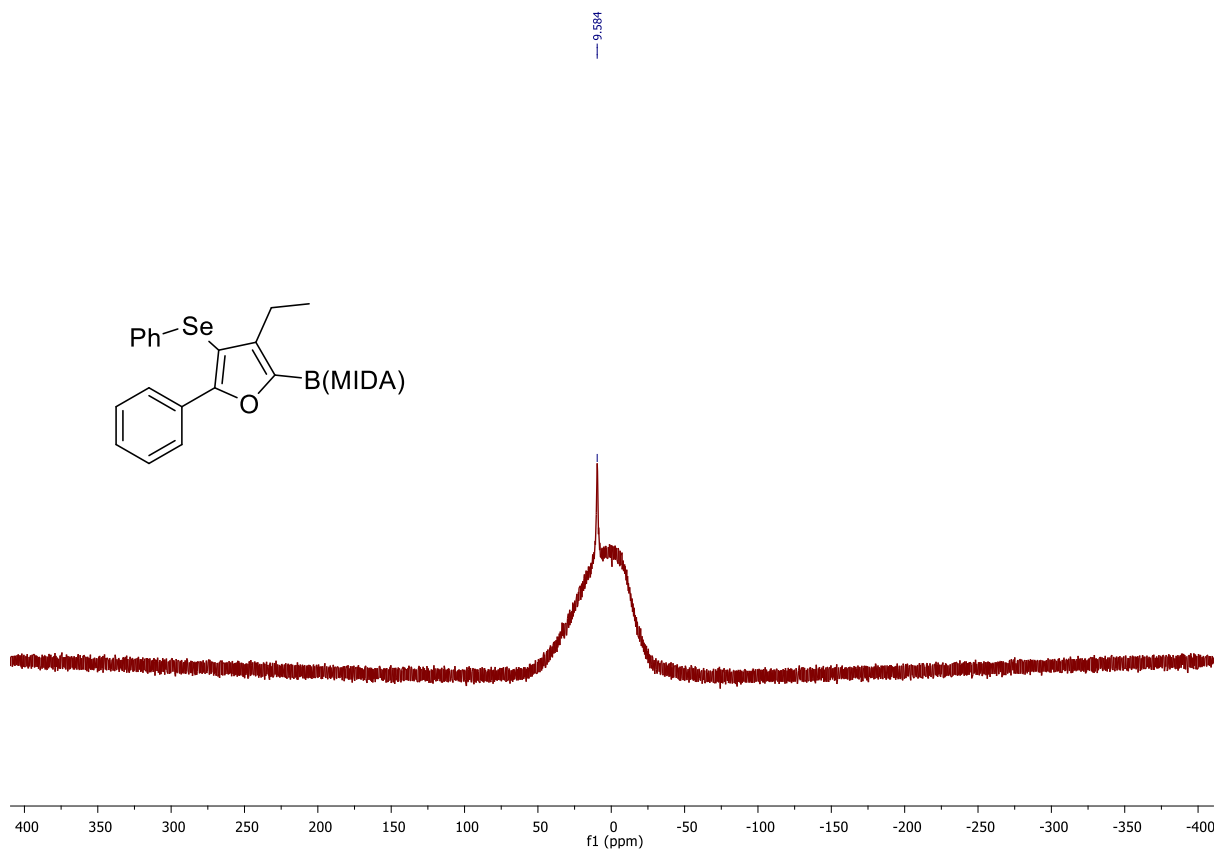


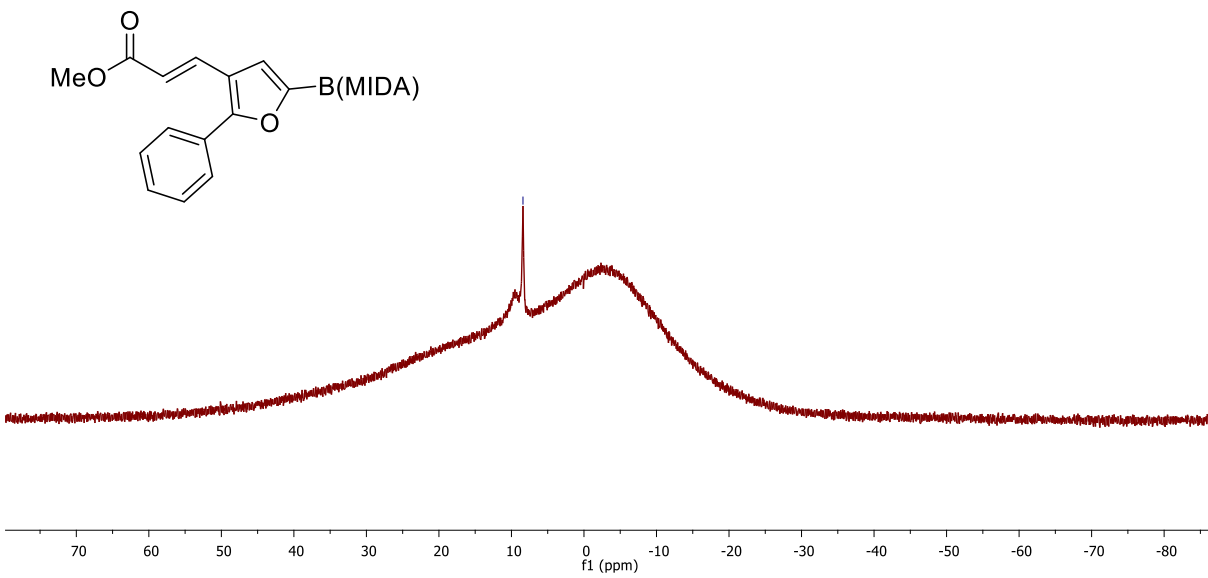
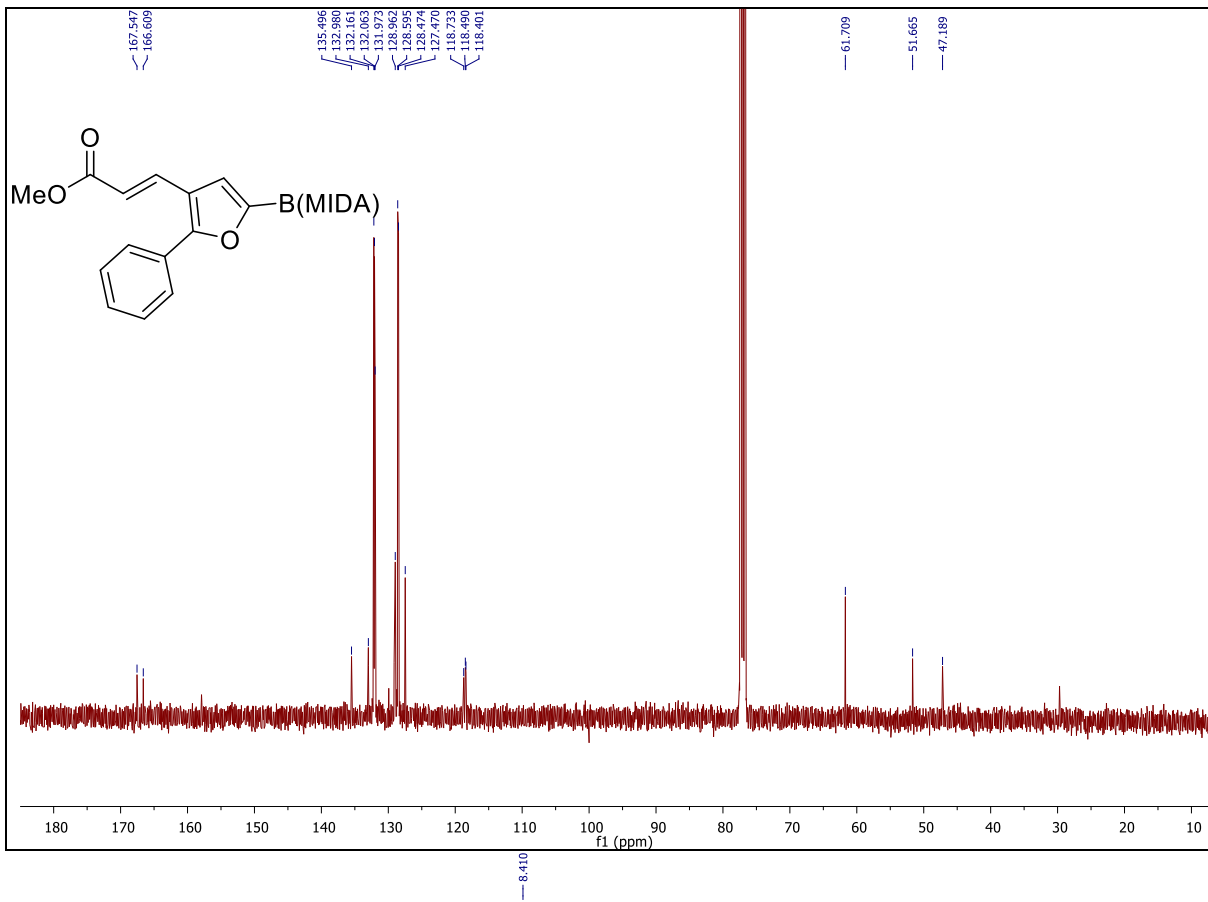


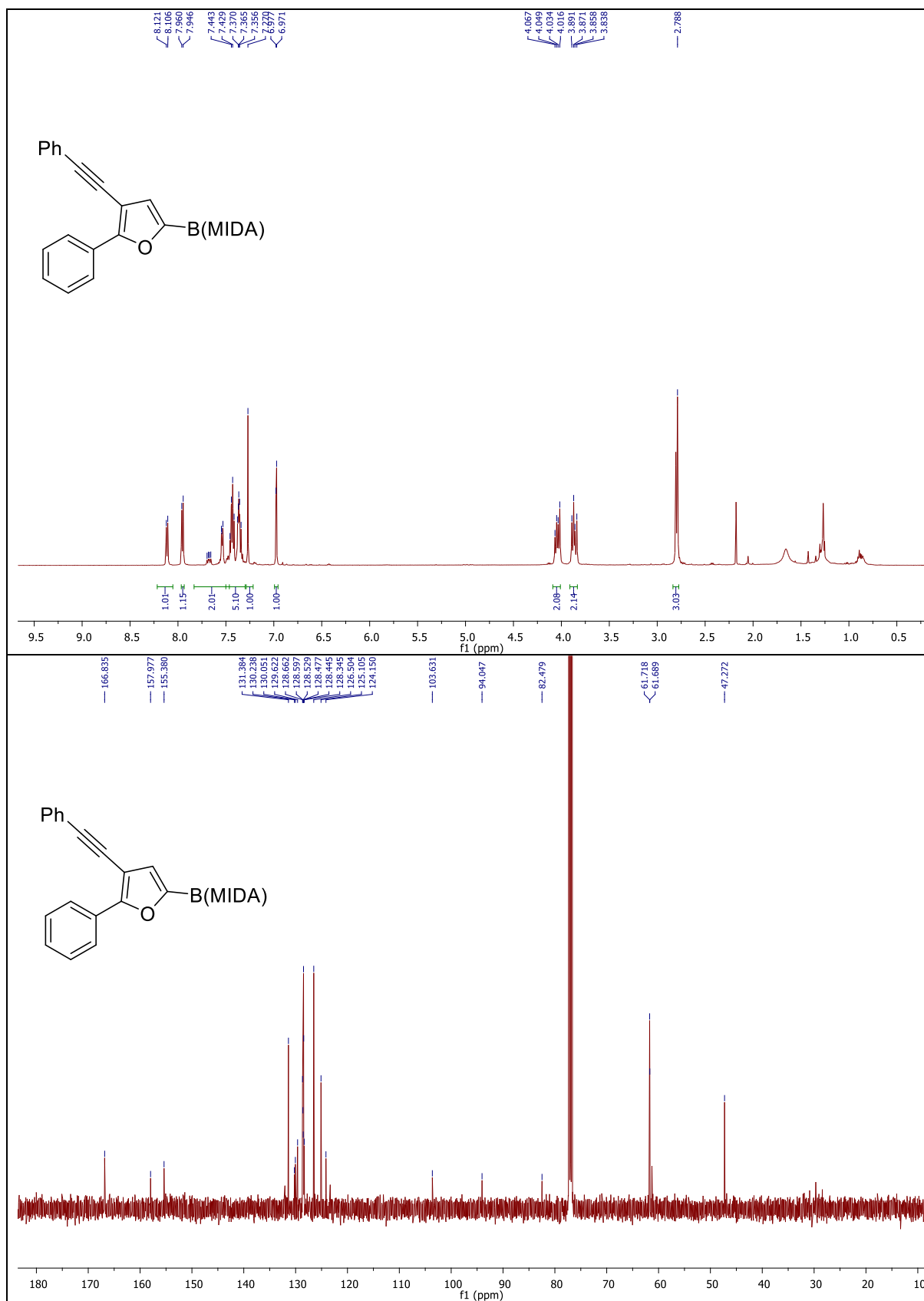


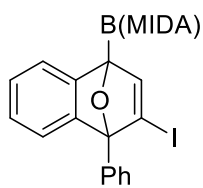
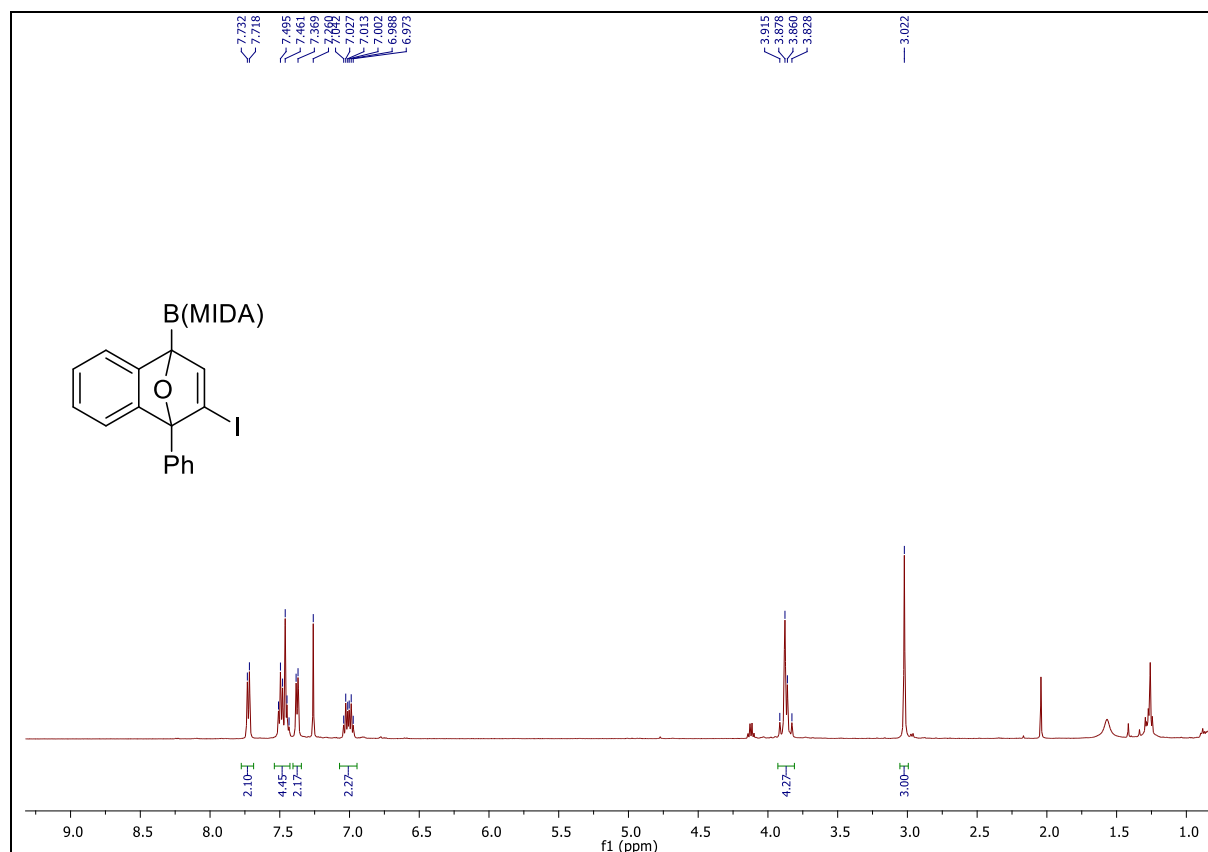
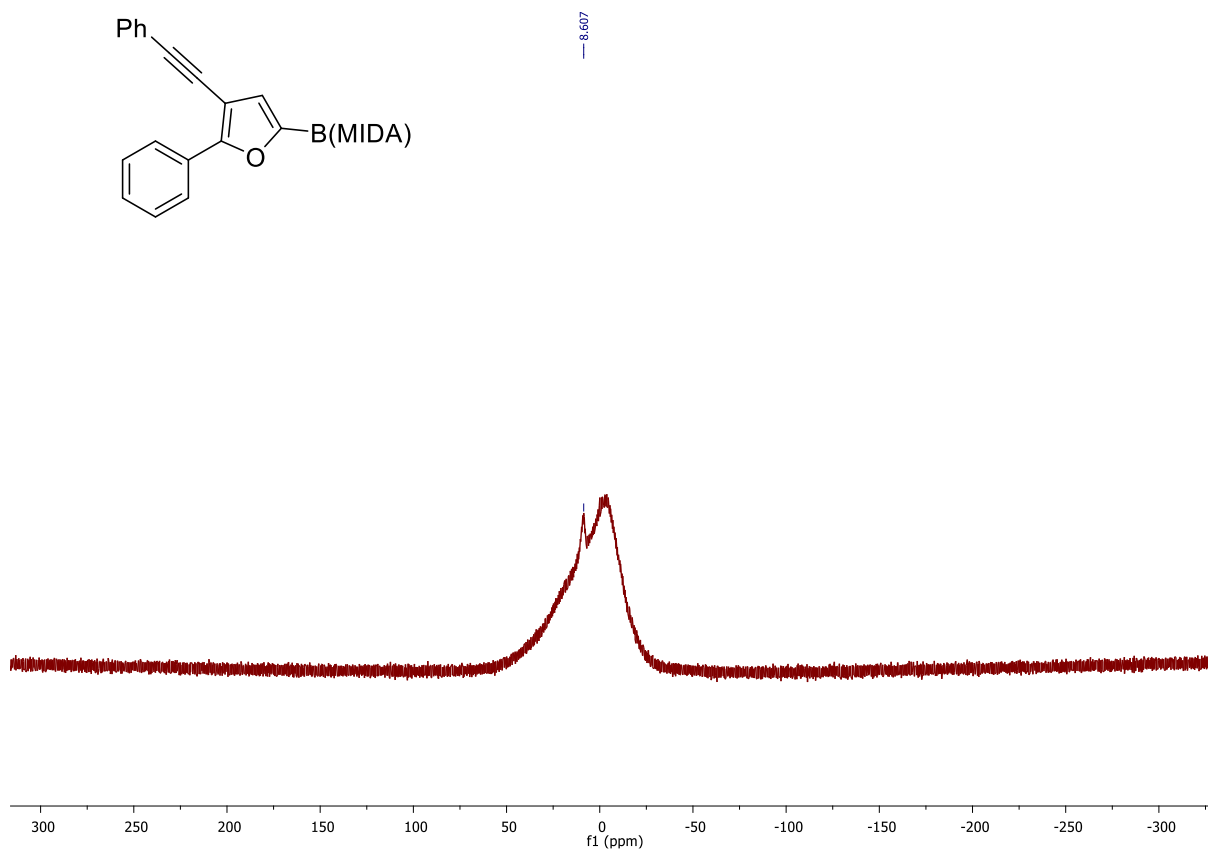
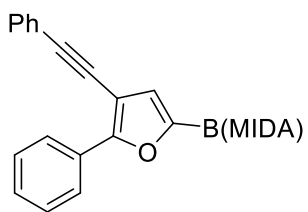


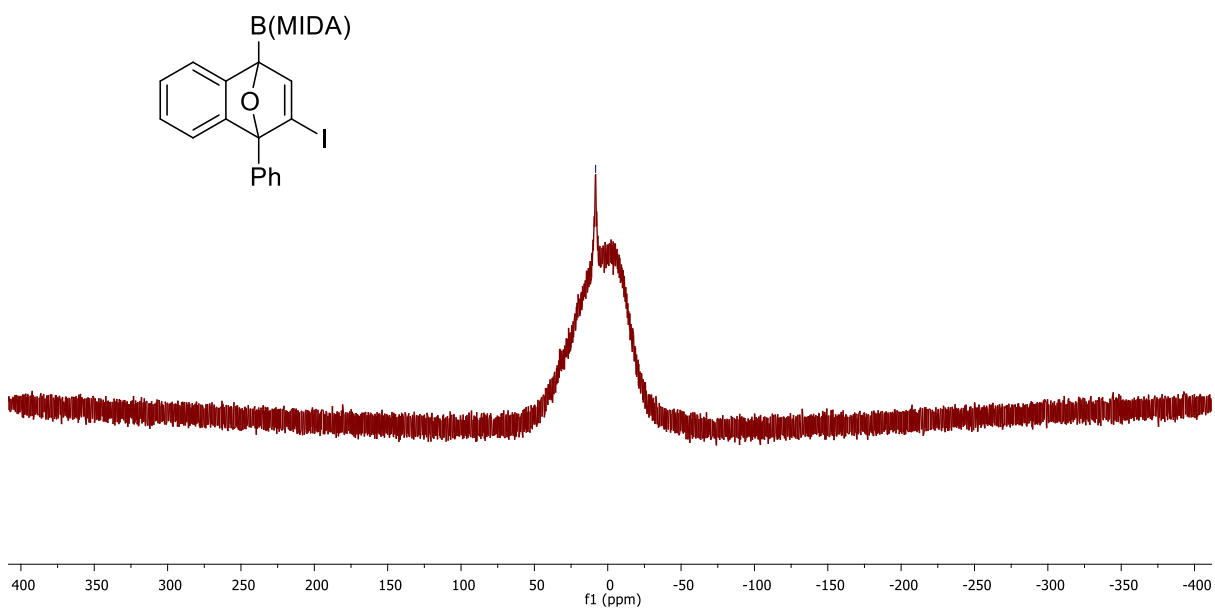
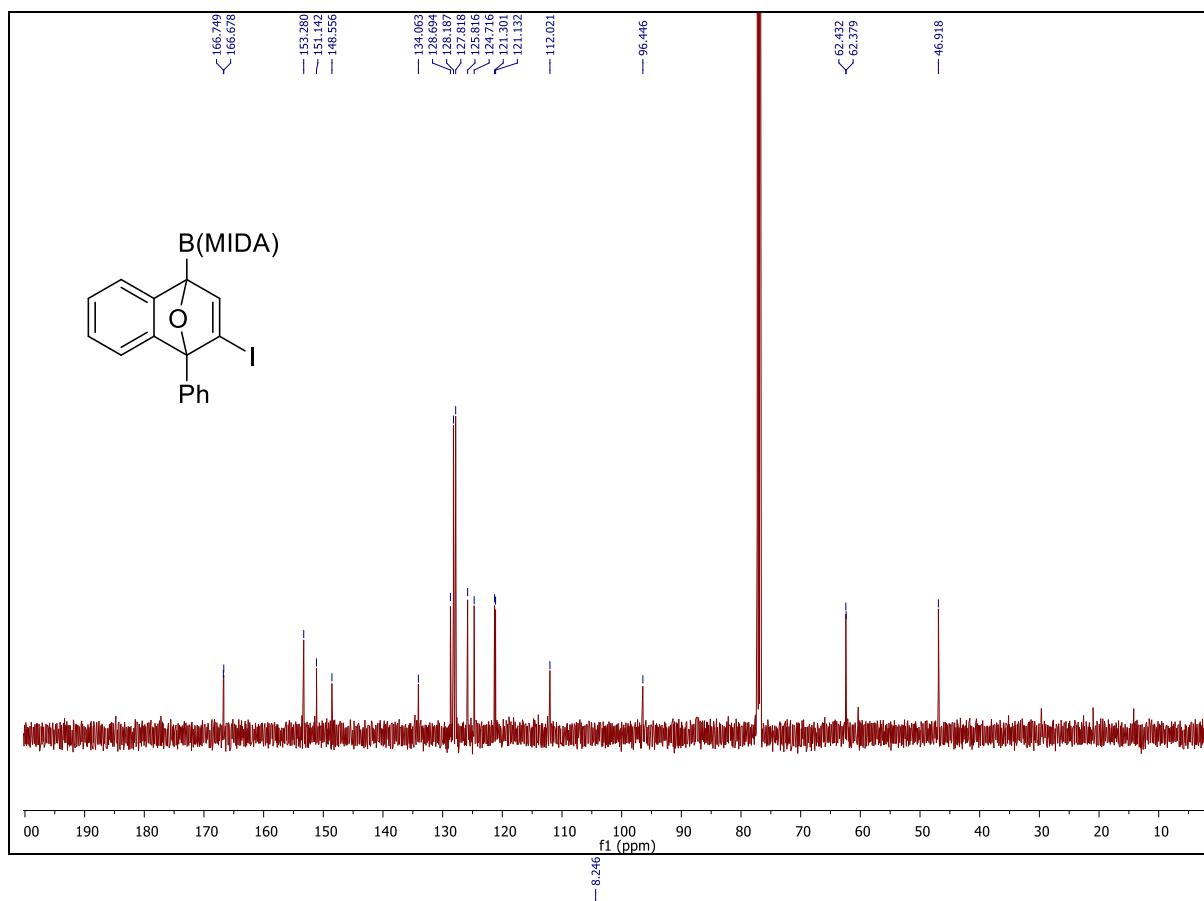


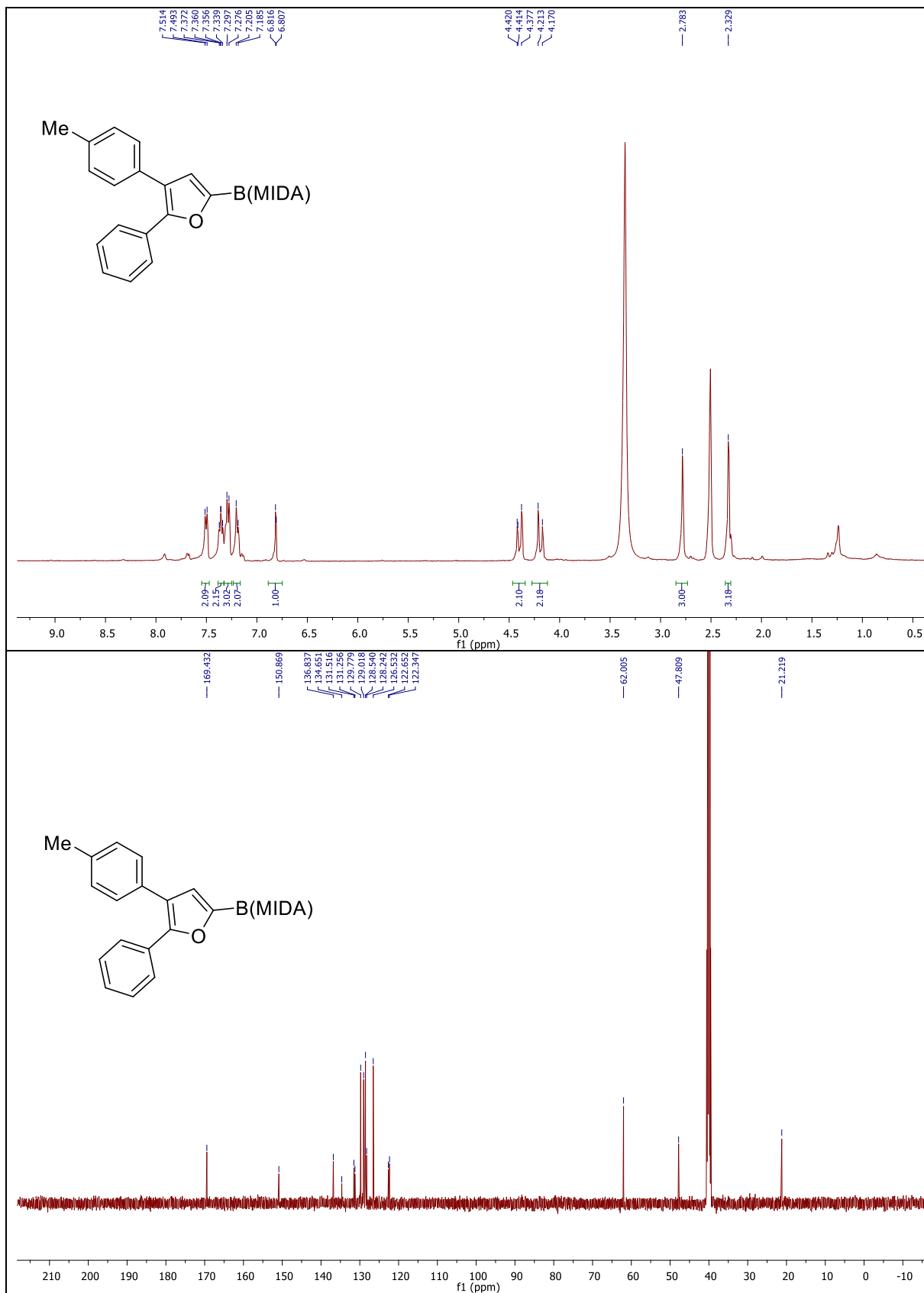


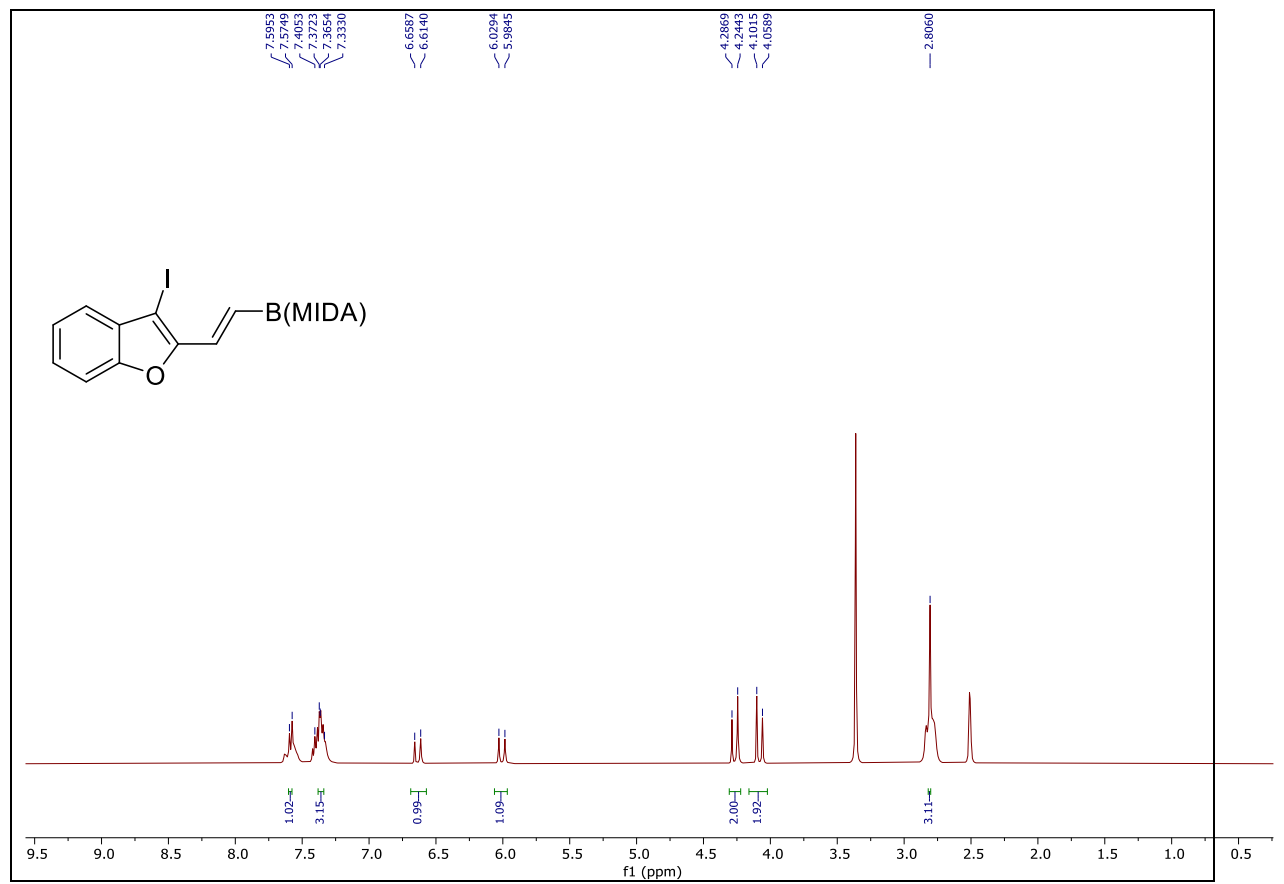
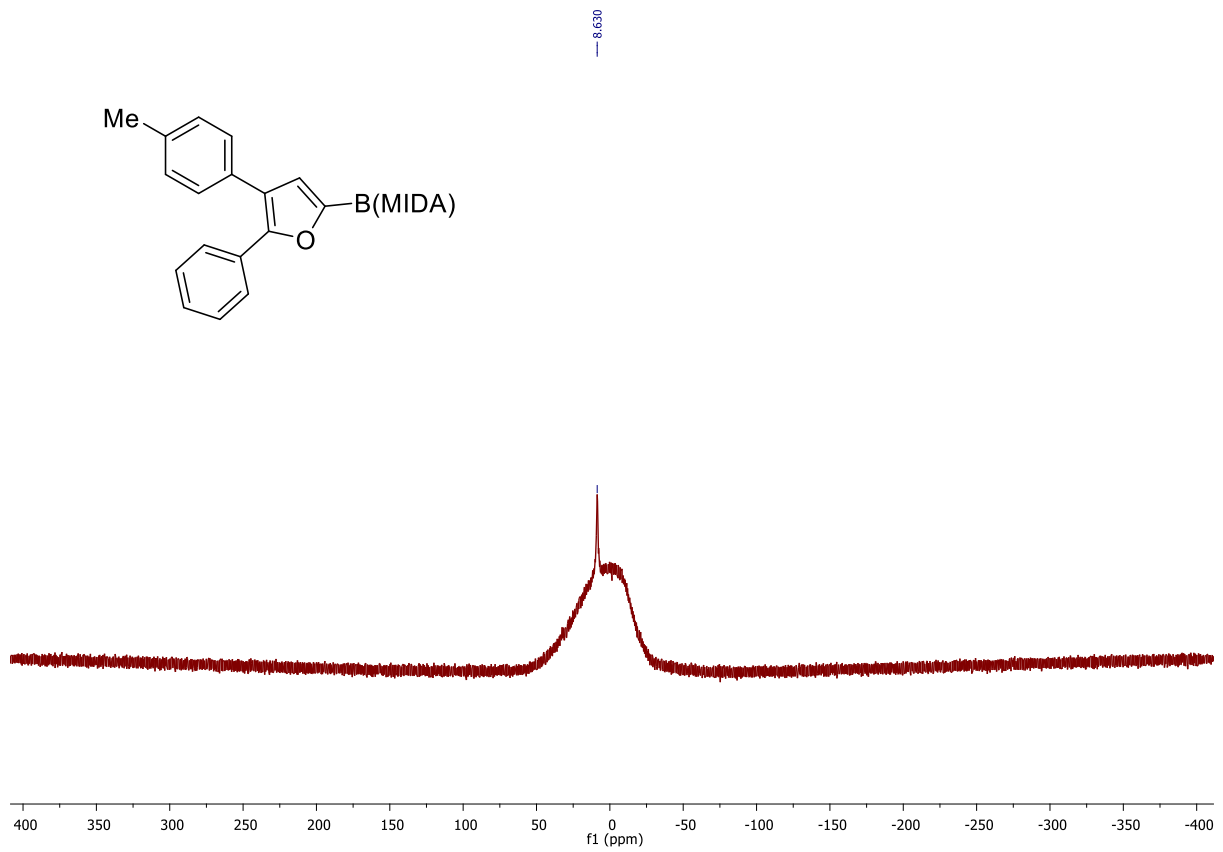


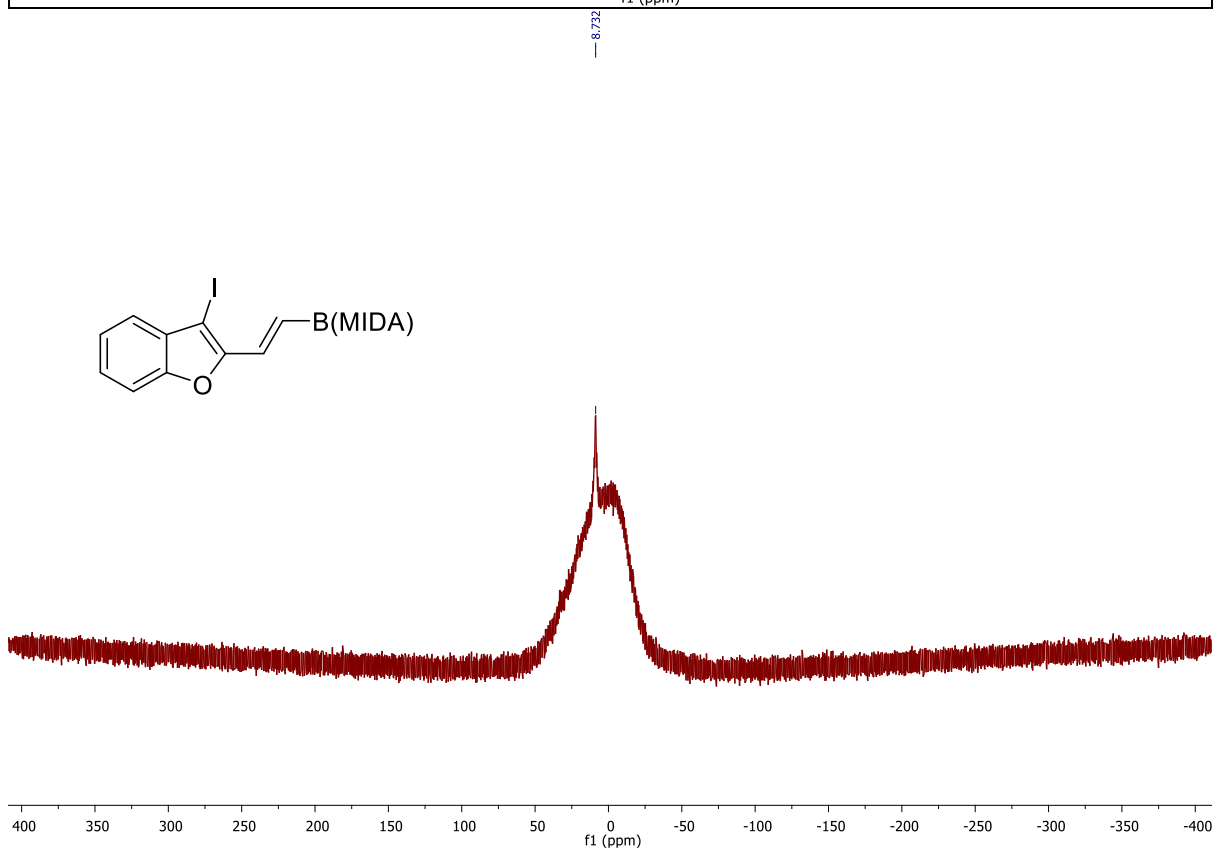
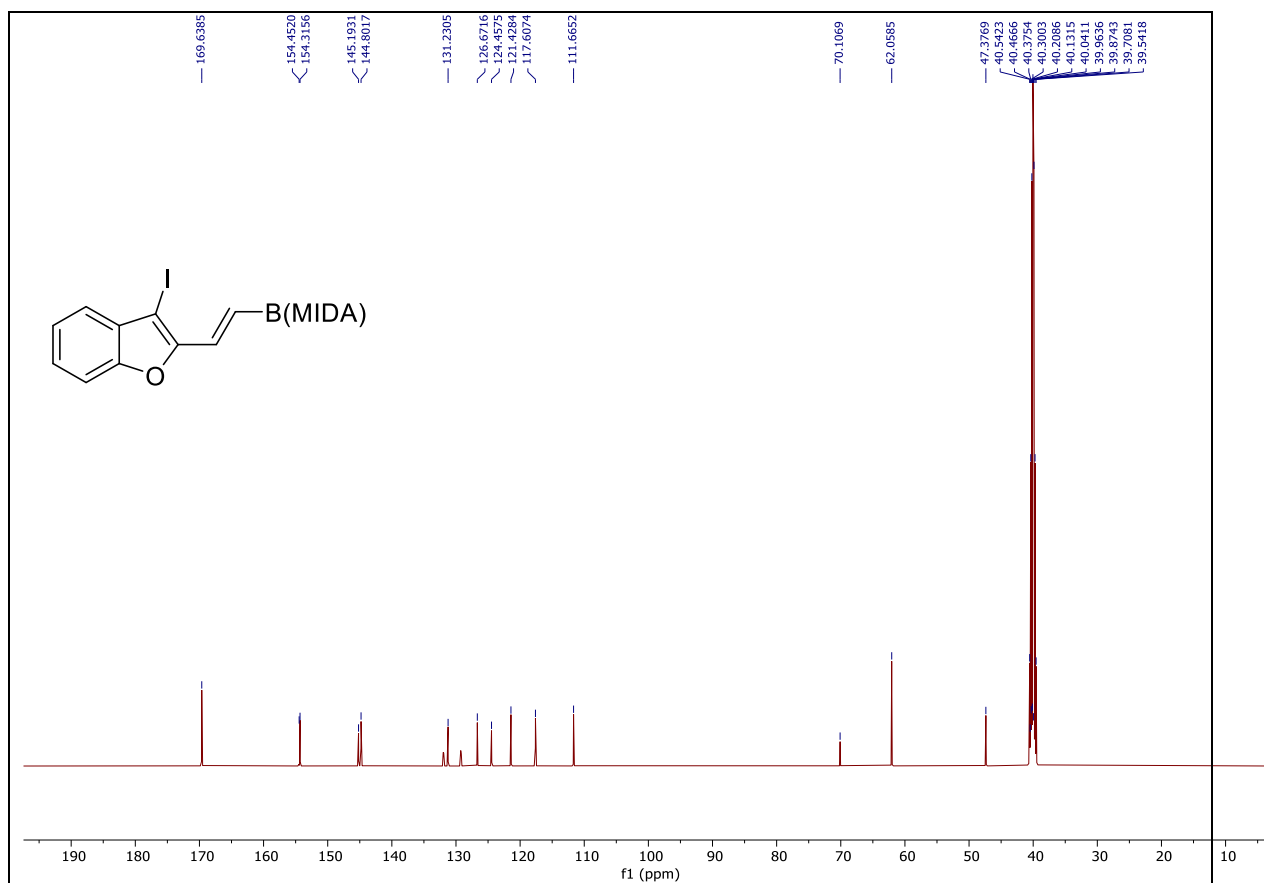


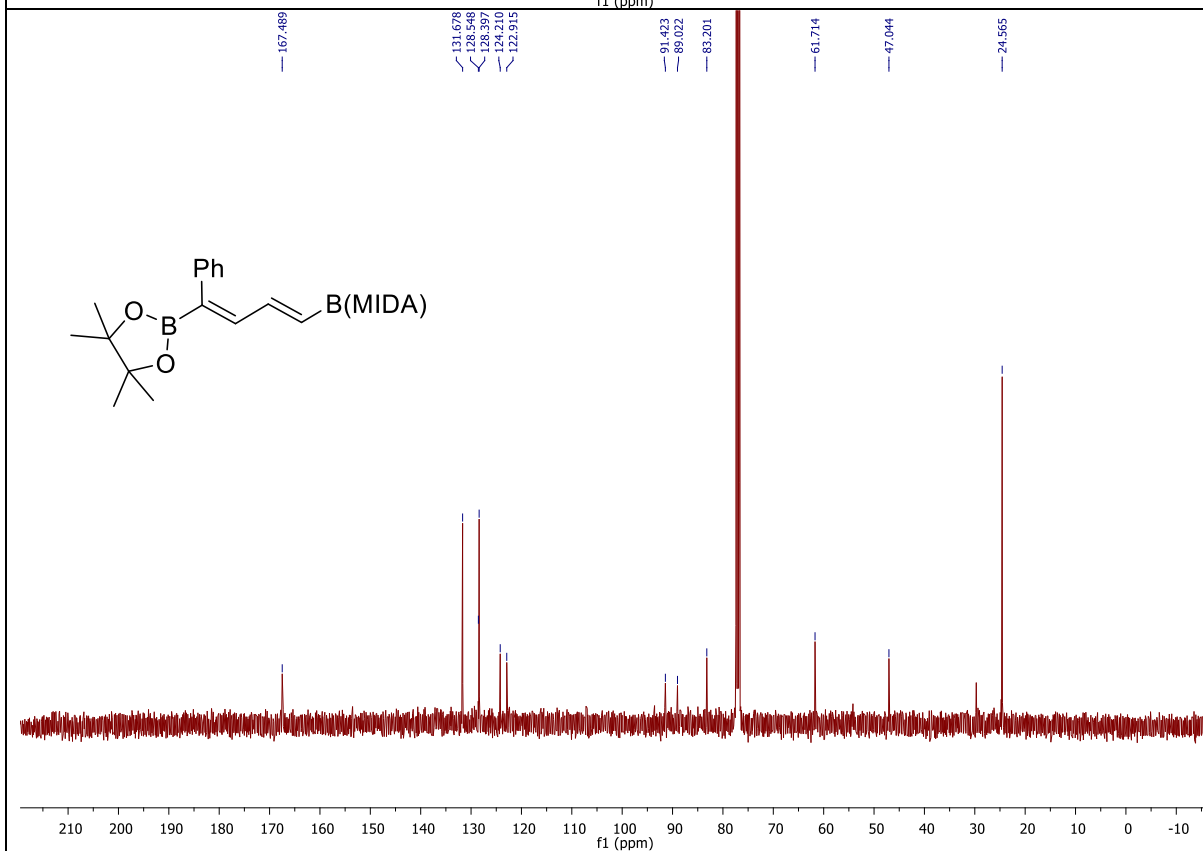
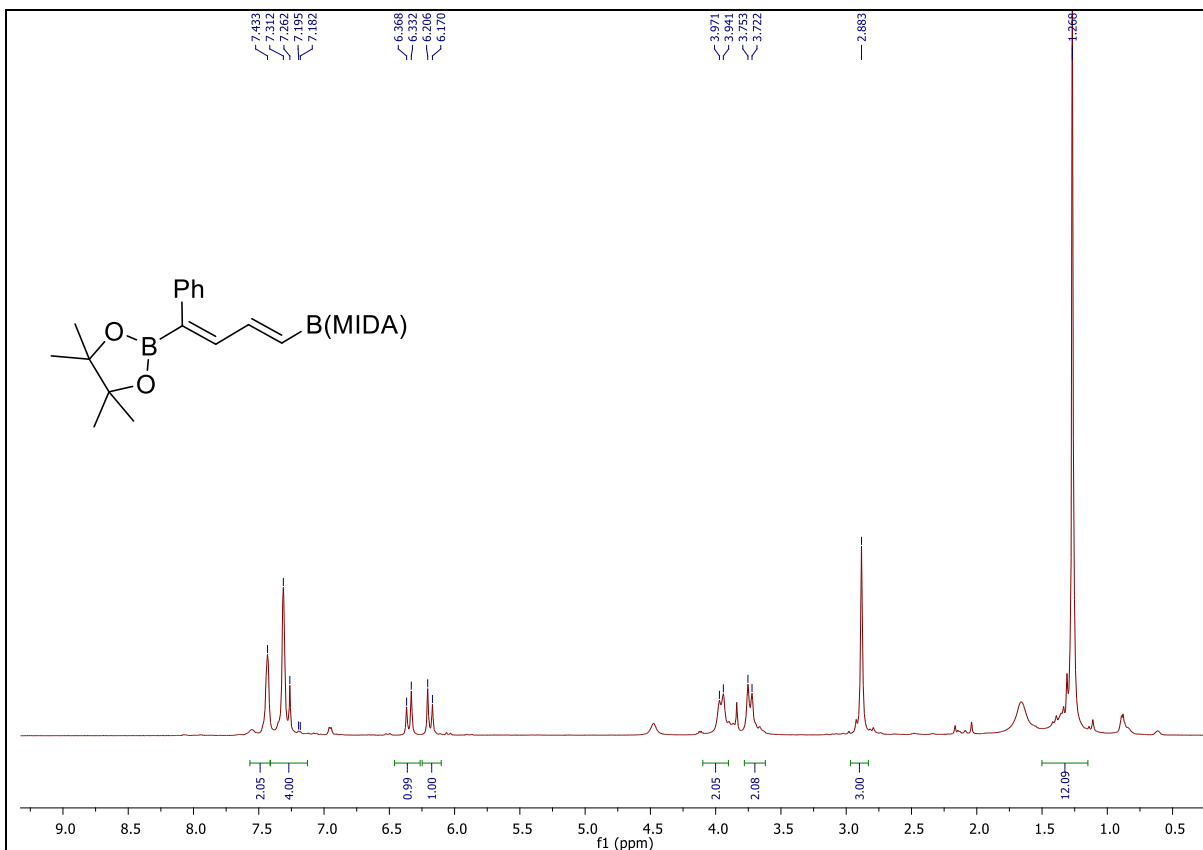


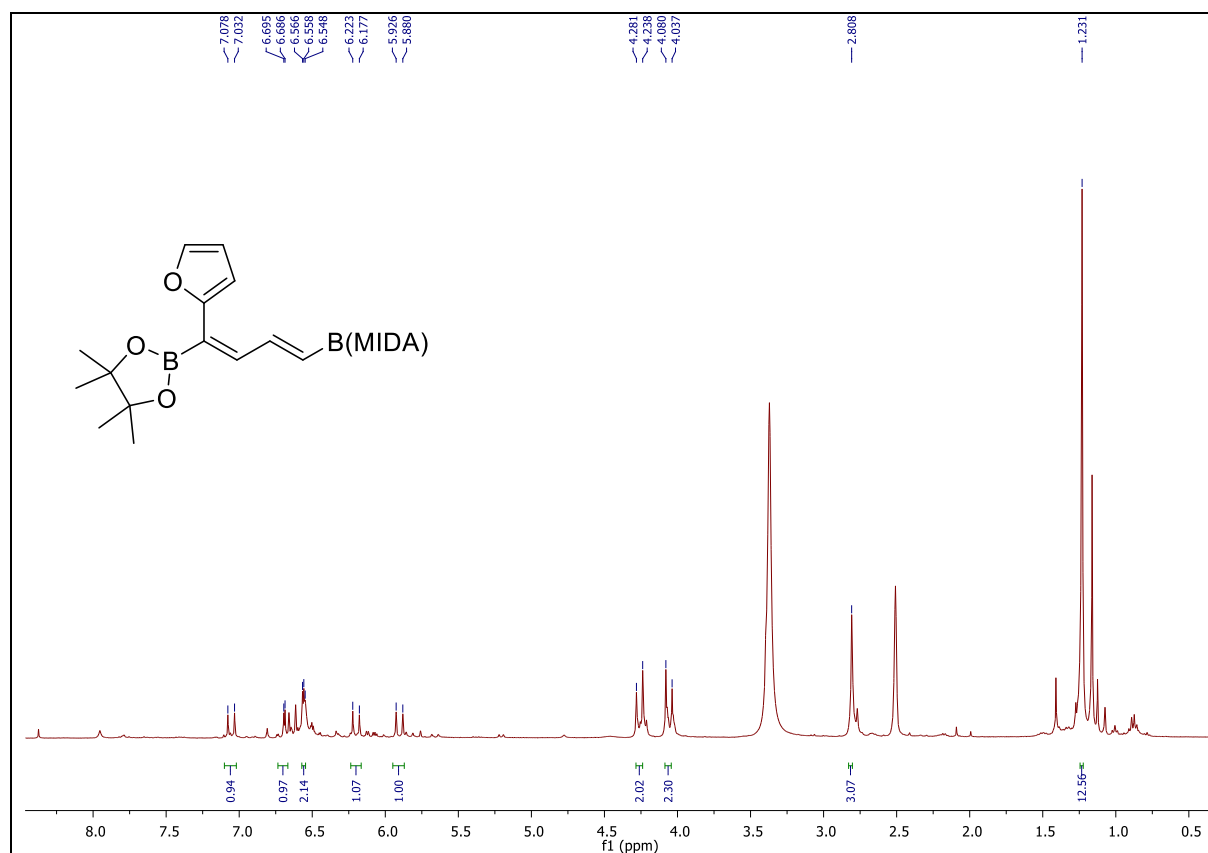
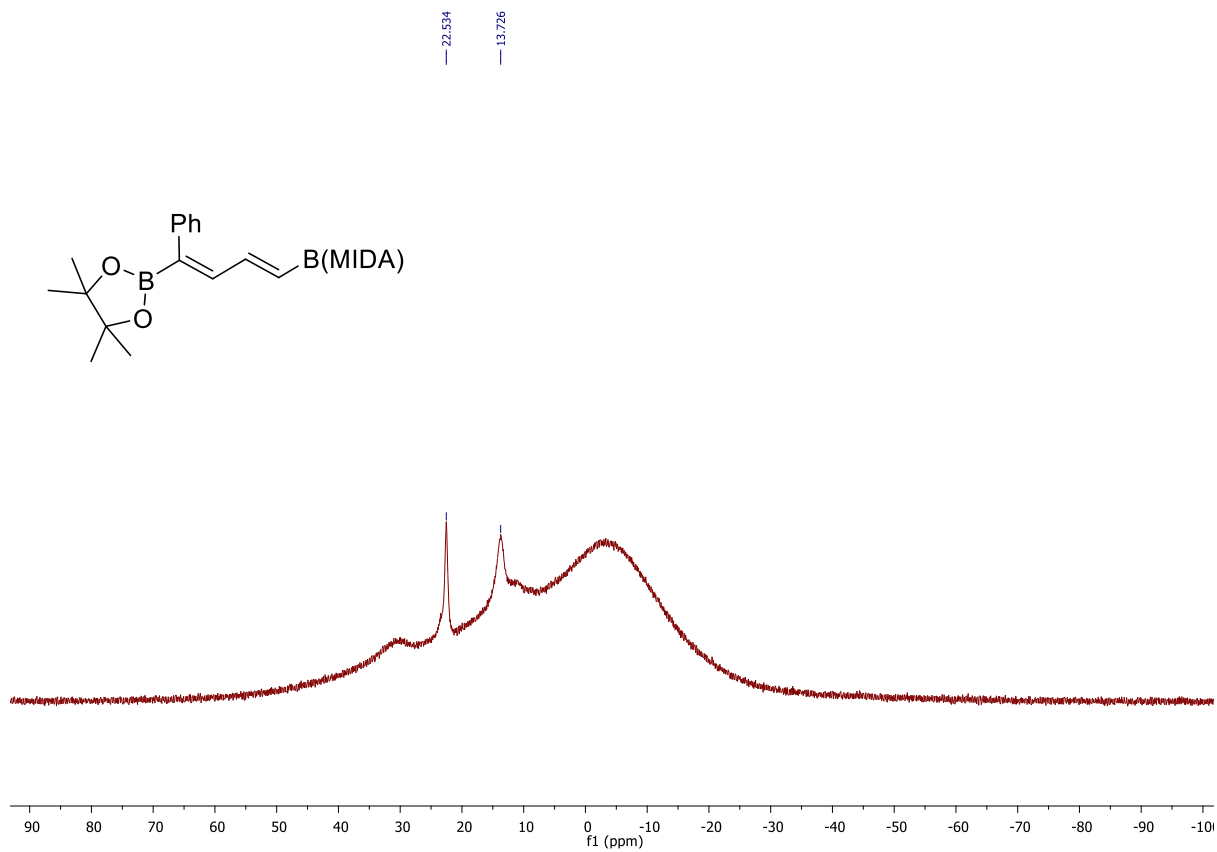


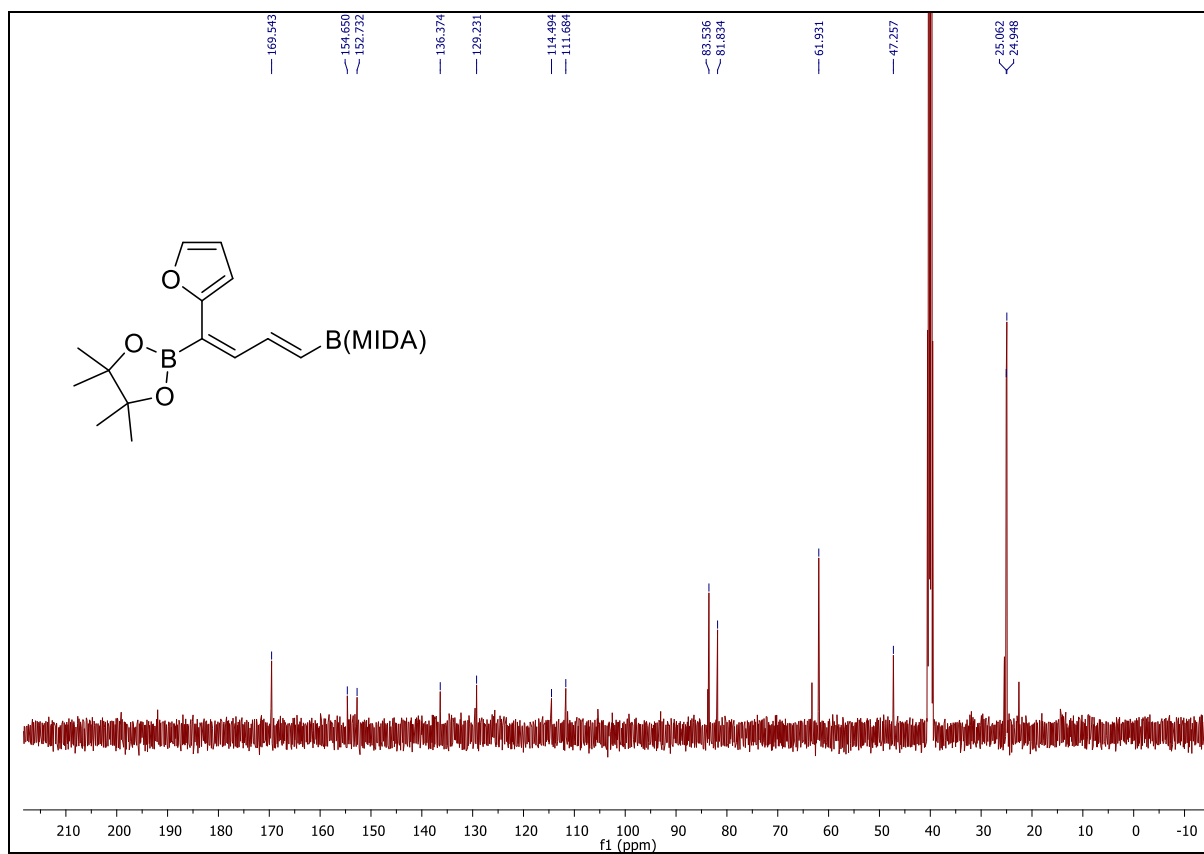


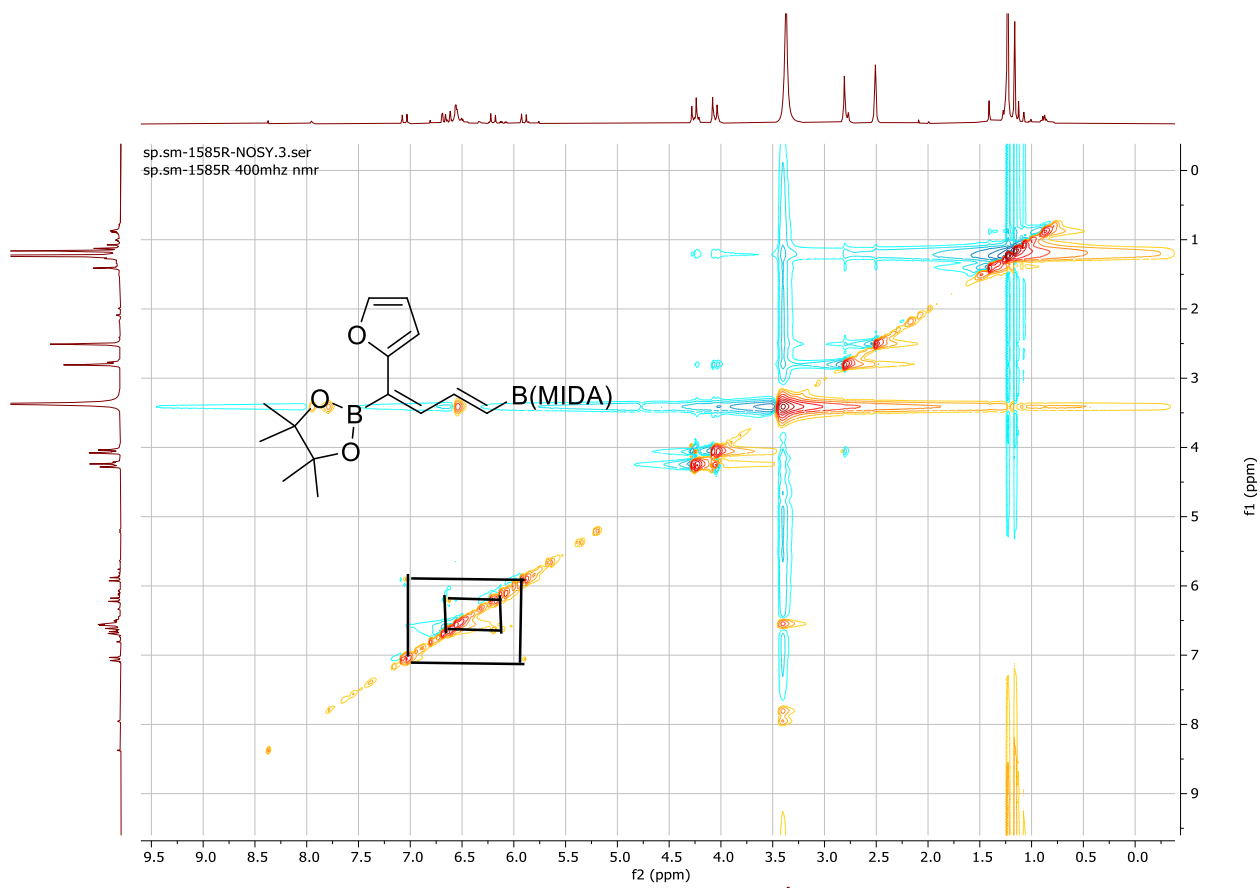




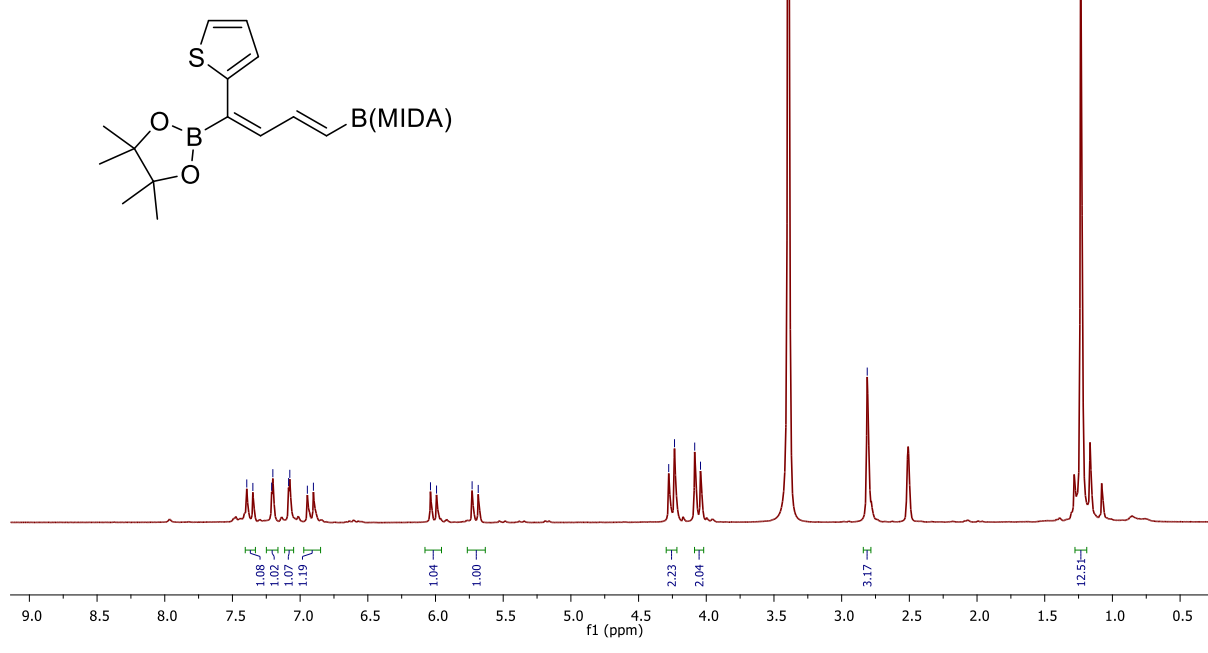


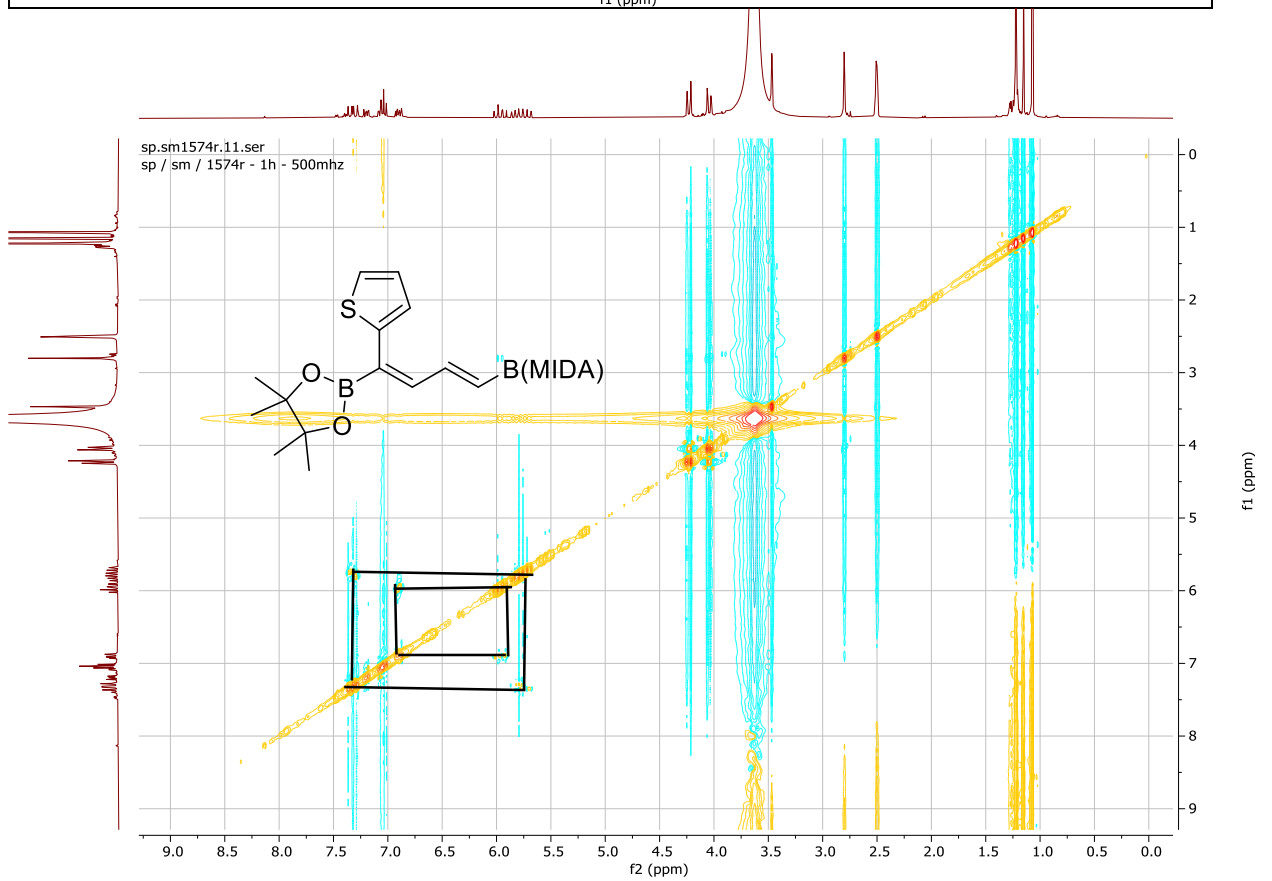
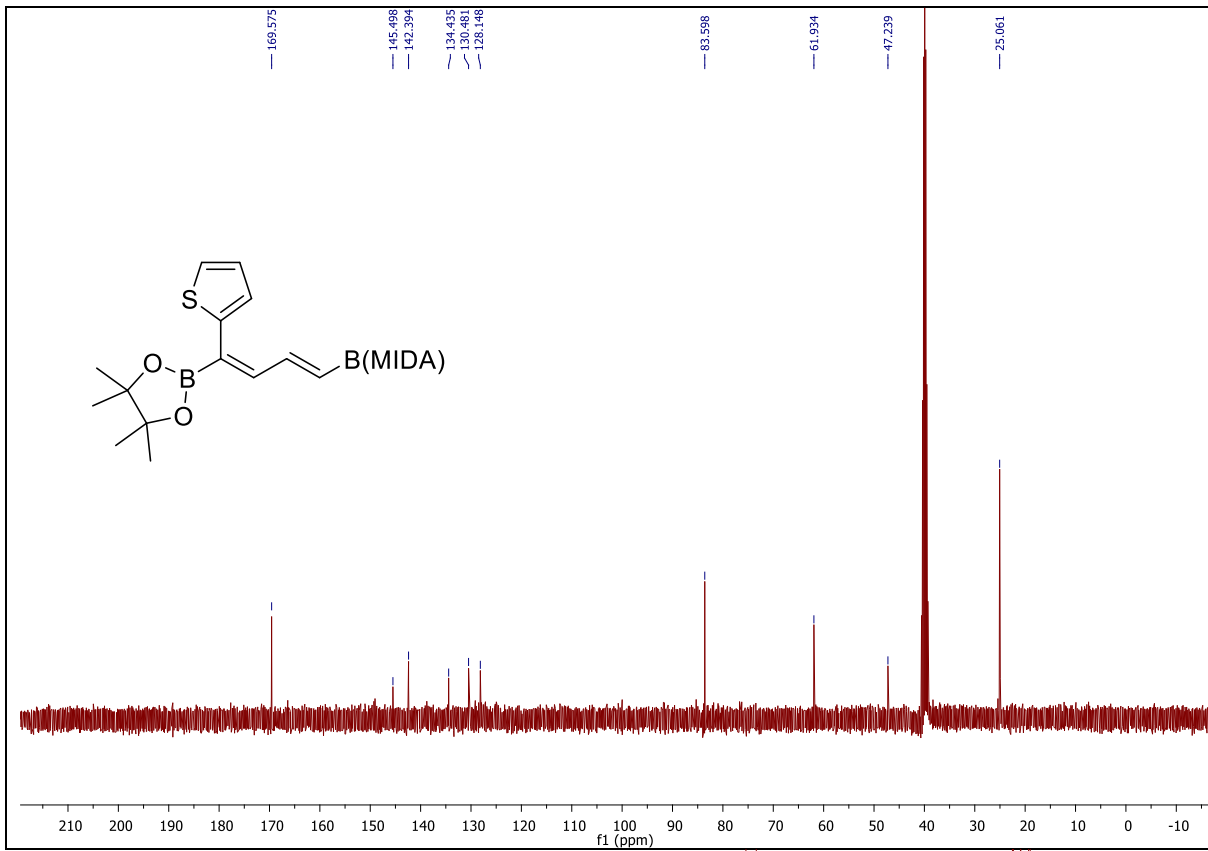


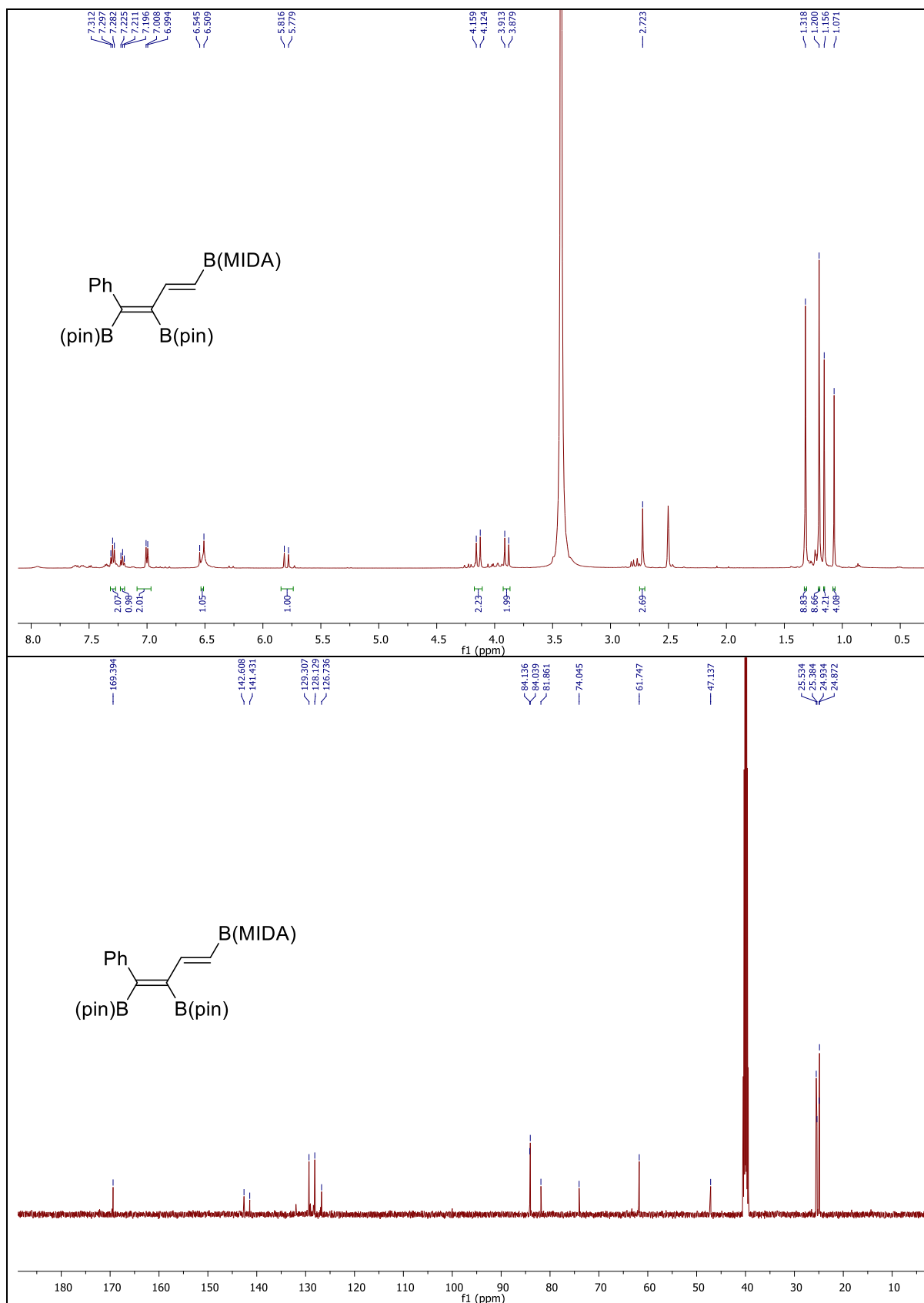


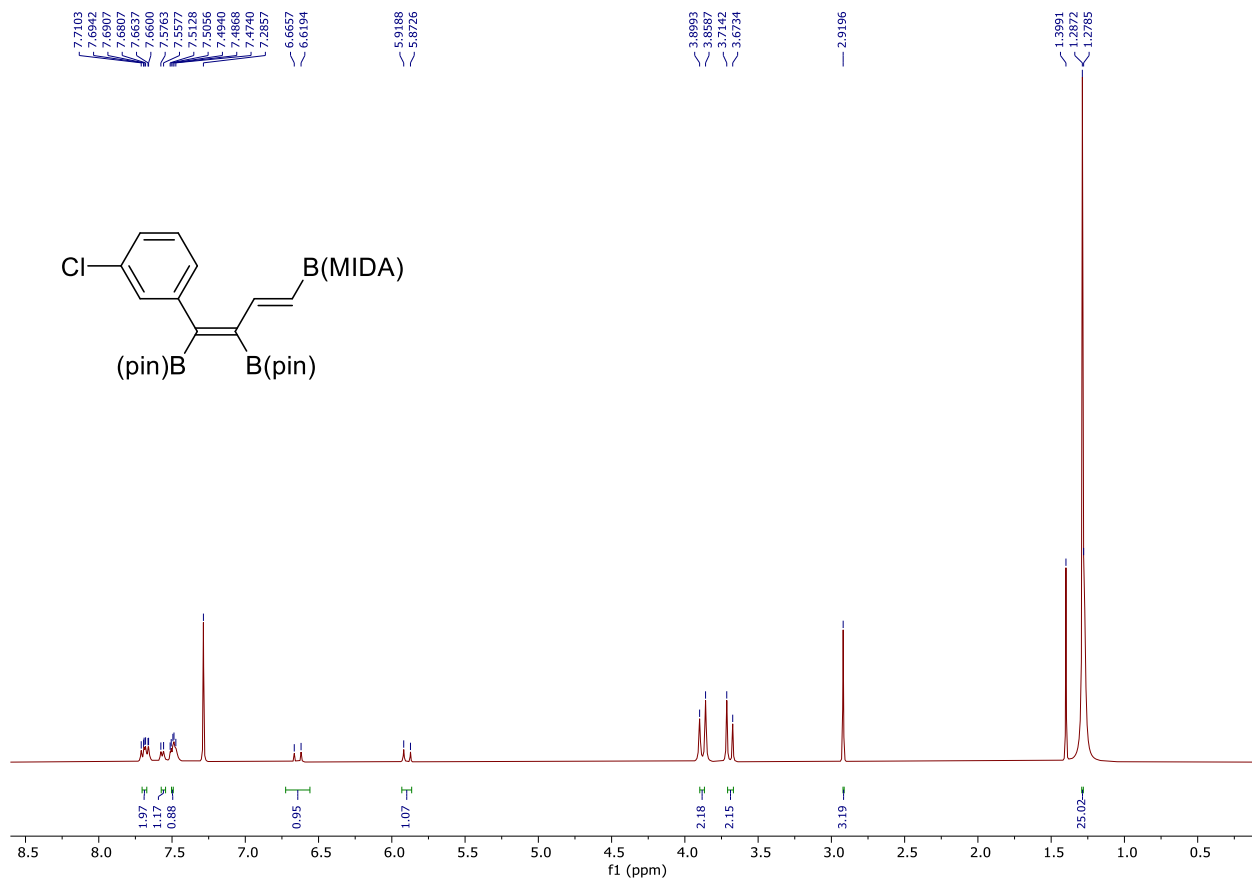
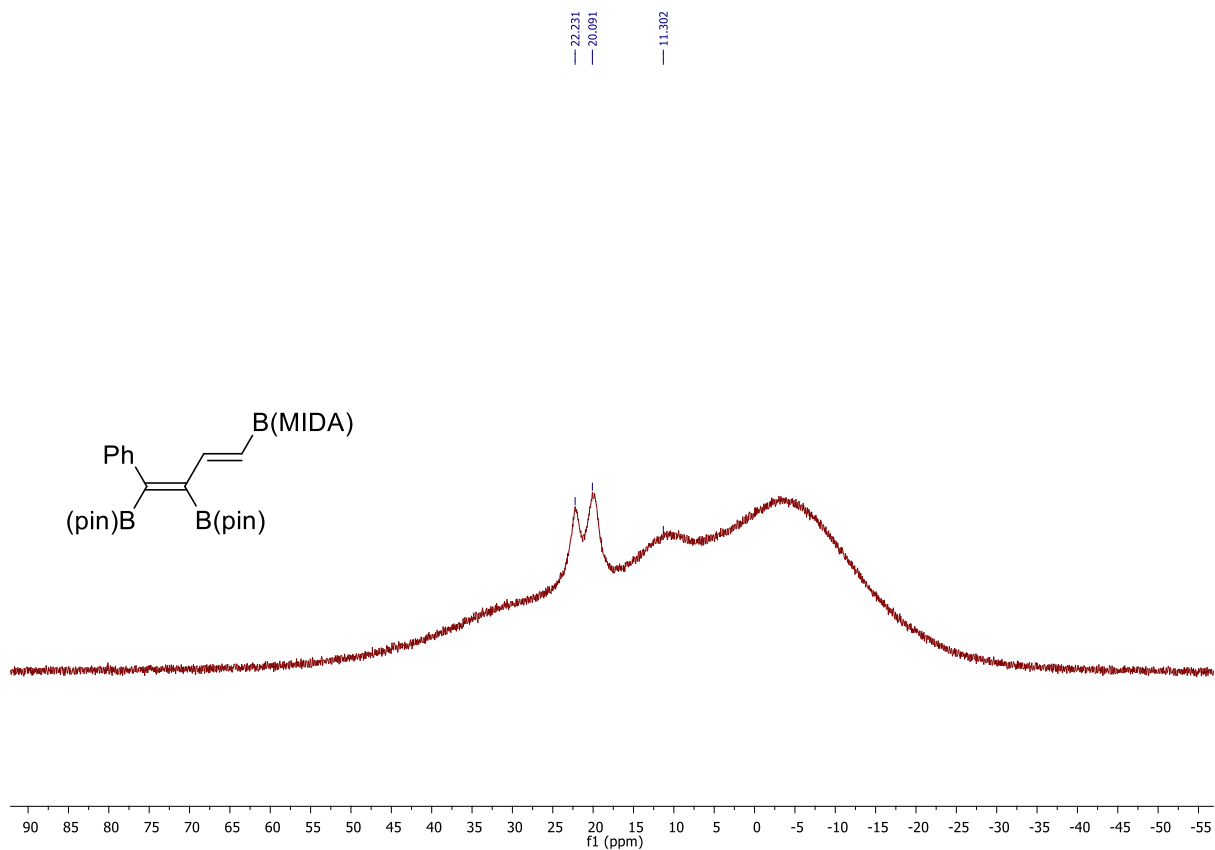


- 7.394
- 7.349
- 7.210
- 7.202
- 7.085
- 7.076
- 6.947
- 6.902
- 6.037
- 5.992
- 5.730
- 5.685
- 4.277
- 4.235
- 4.188
- 4.093
- 2.811
- 1.235

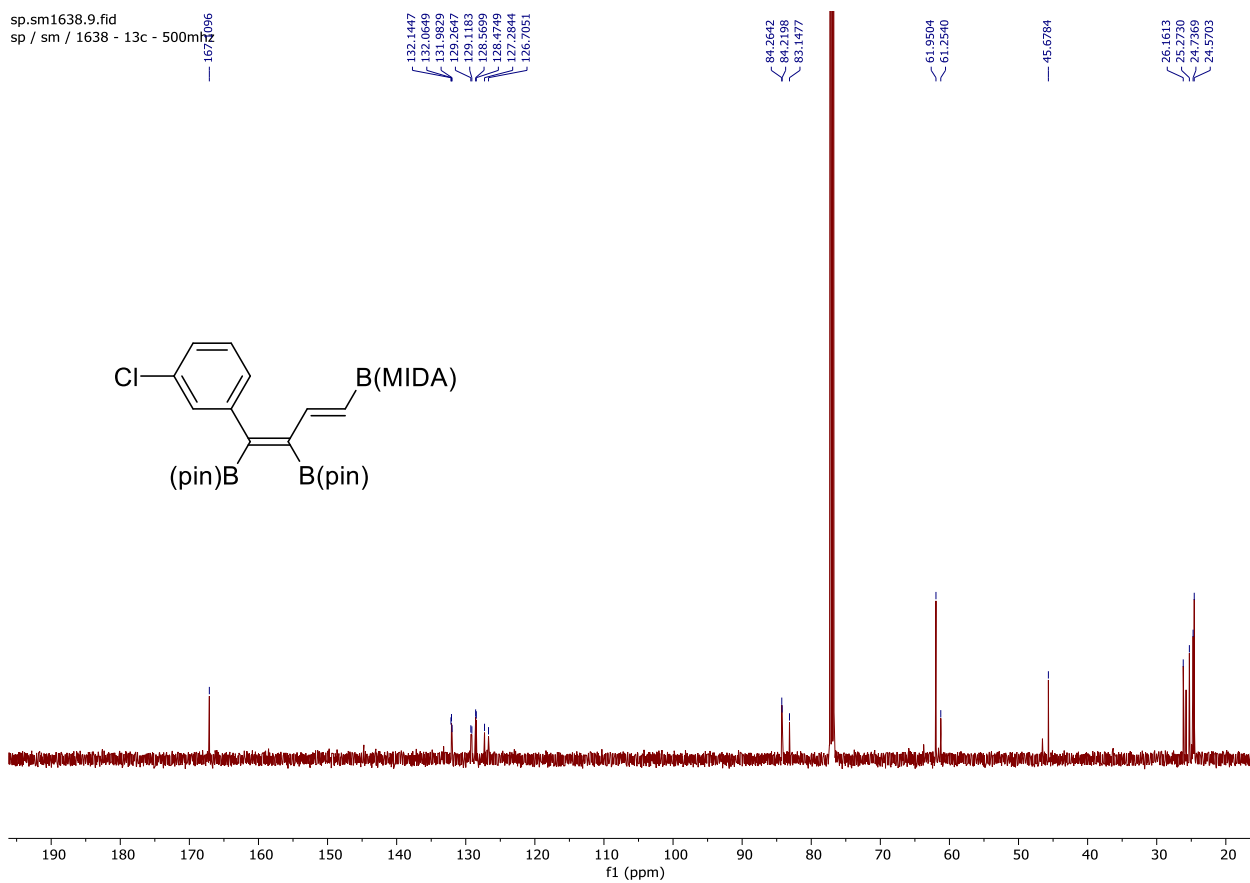


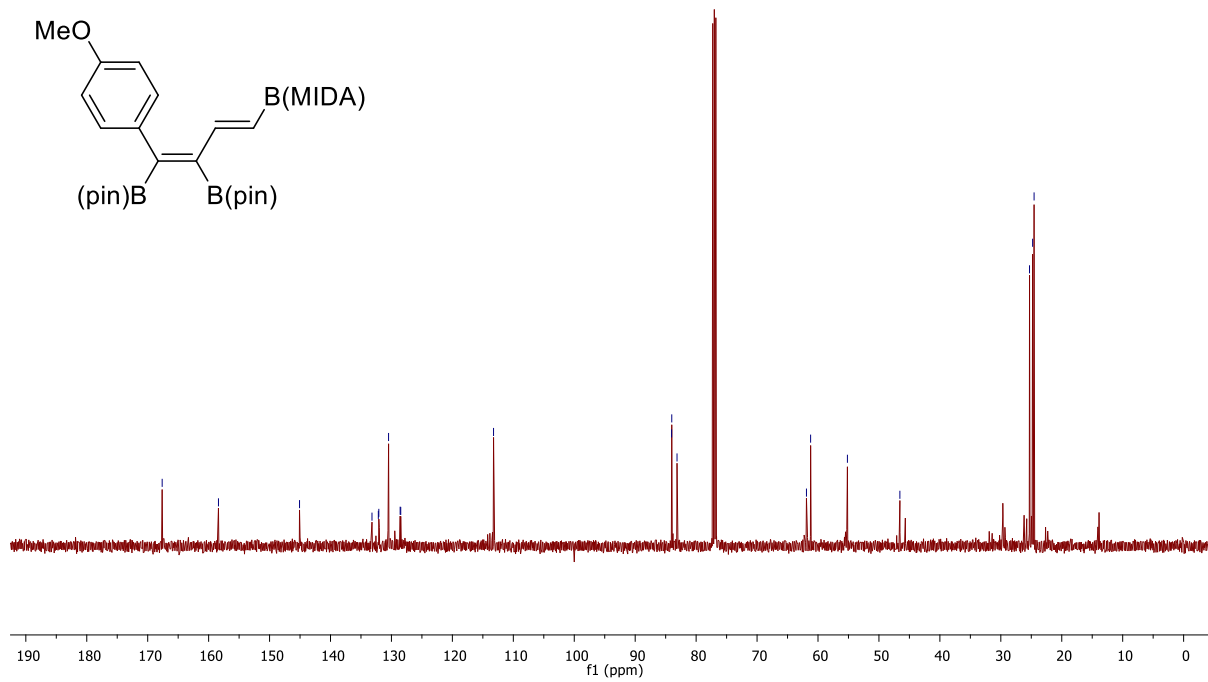
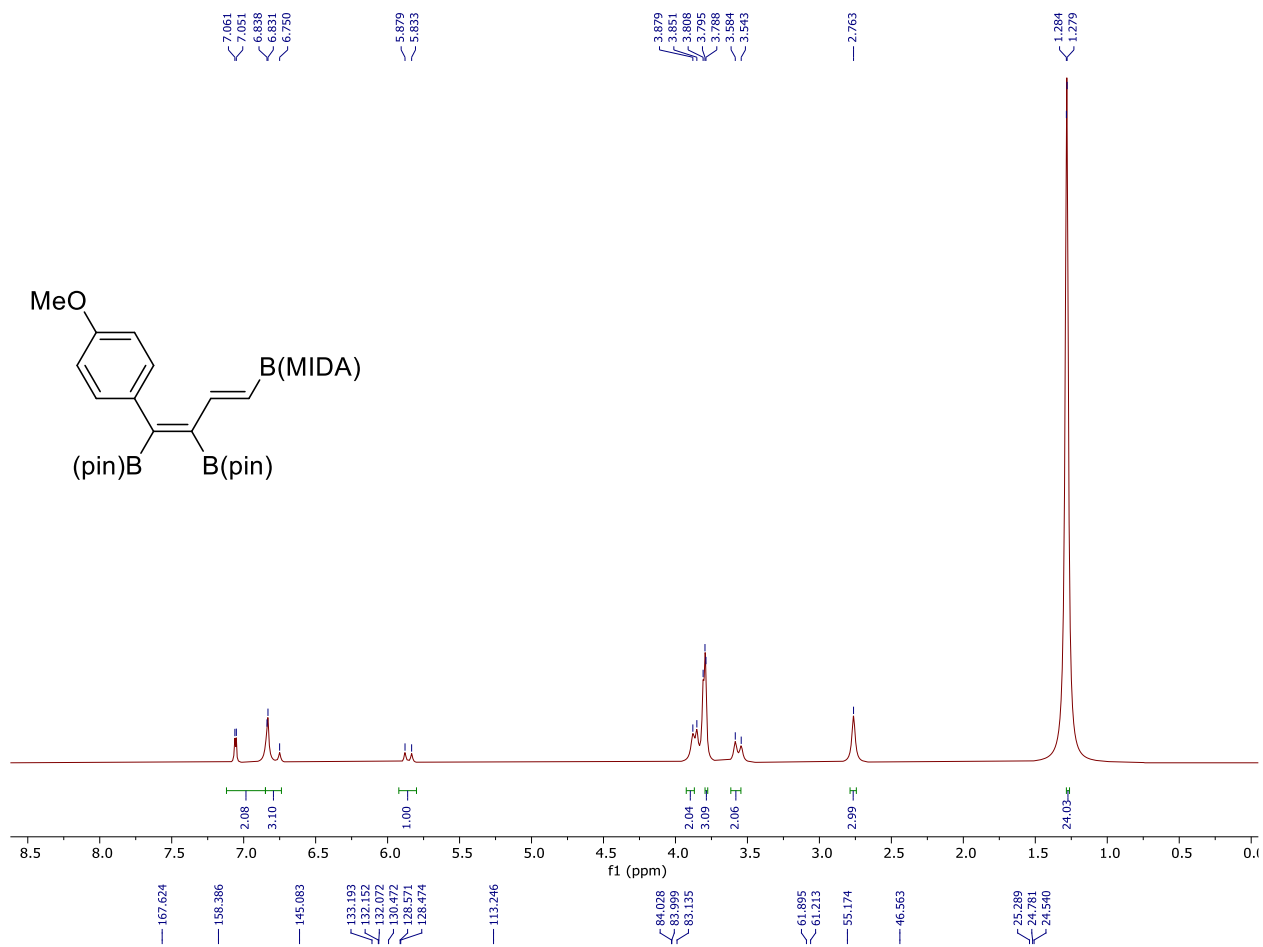


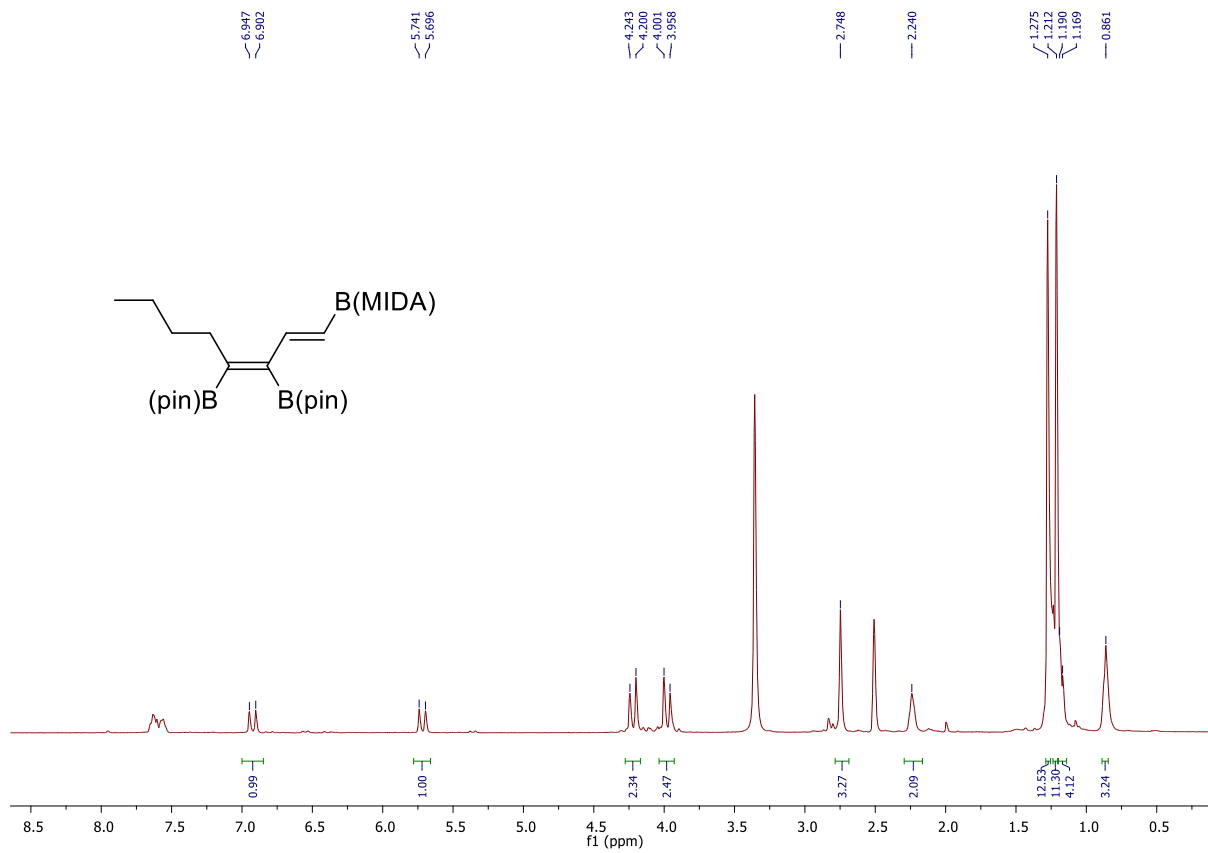
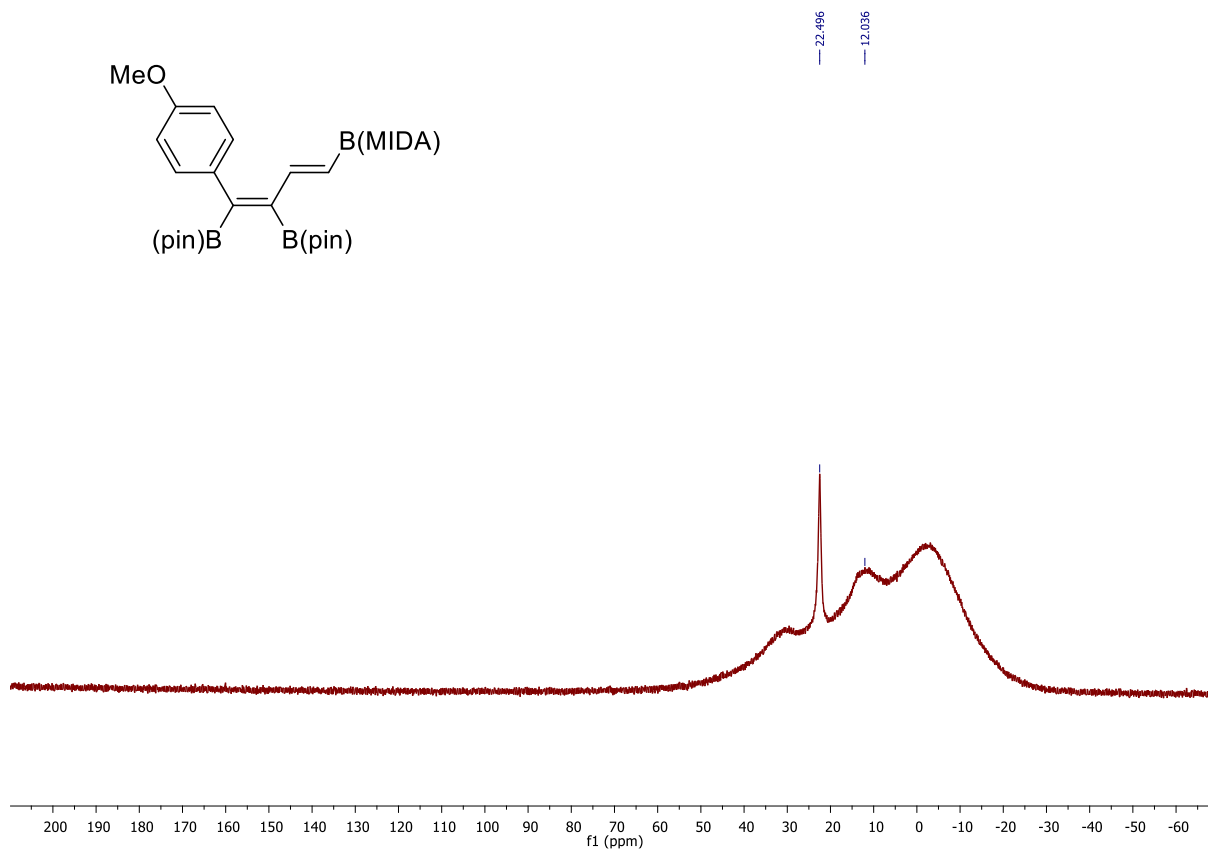


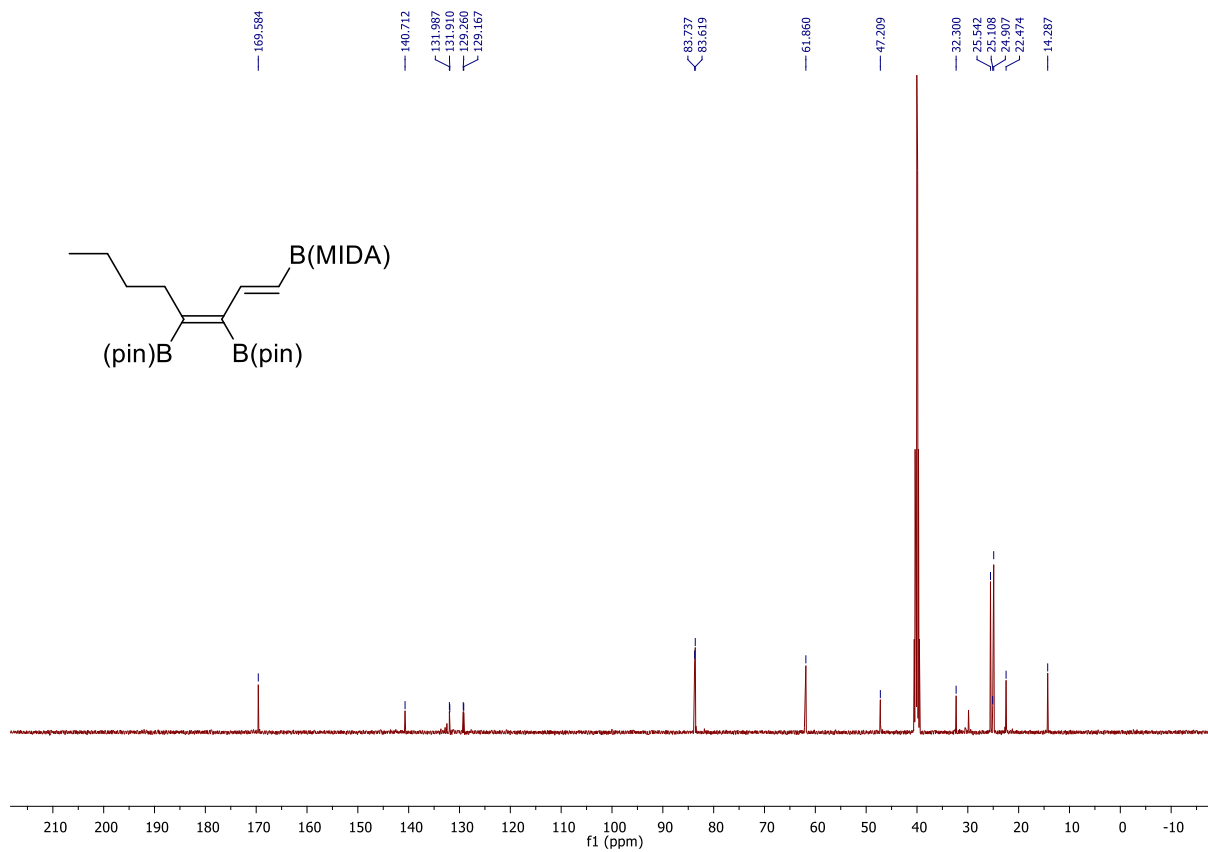


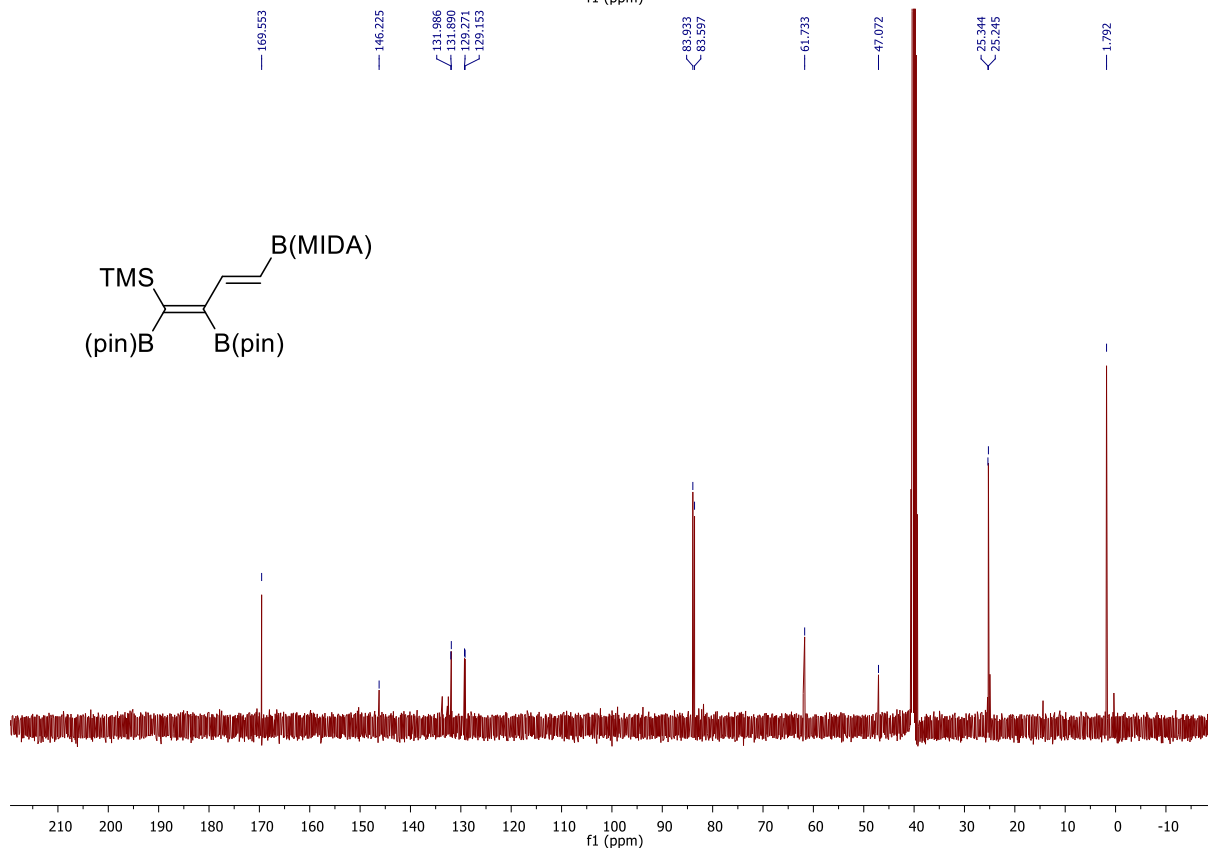
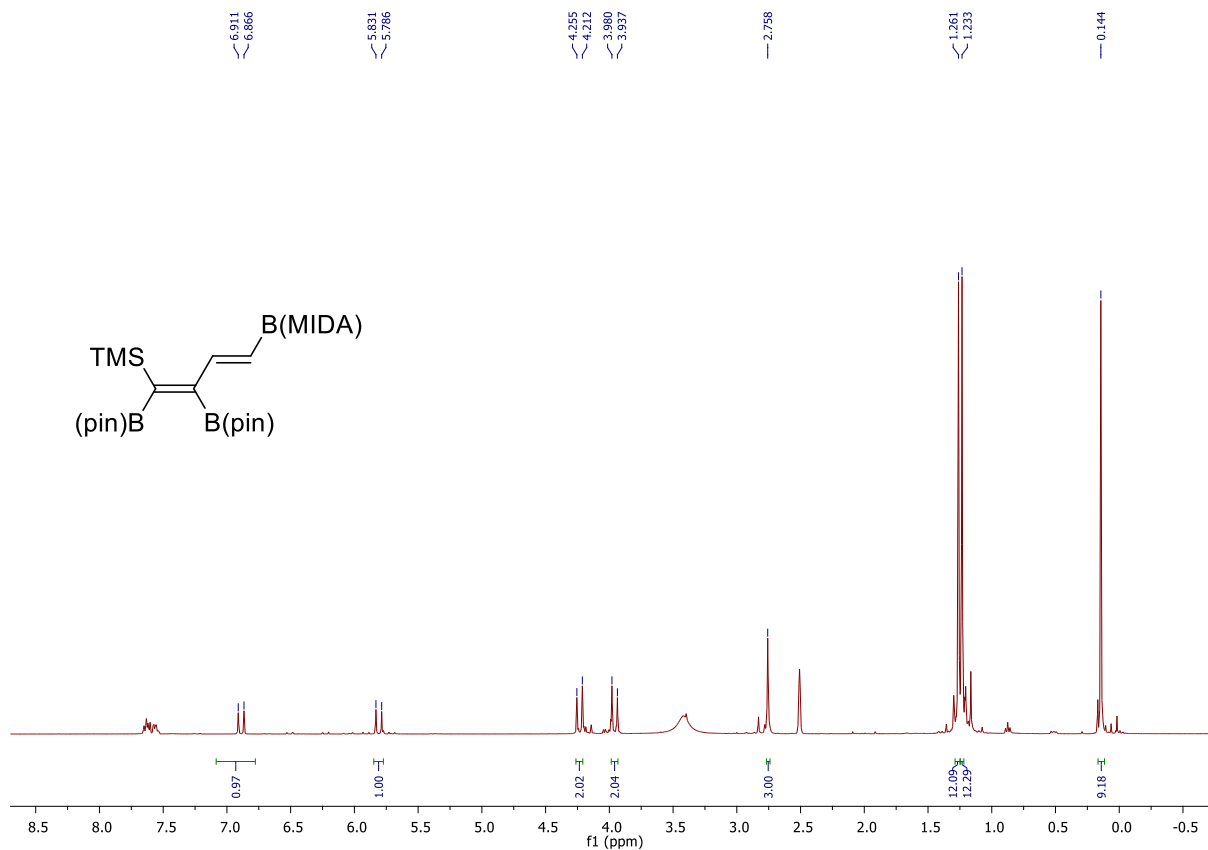
sp.sm1638.9.fid
sp / sm / 1638 - 13c - 500mhz

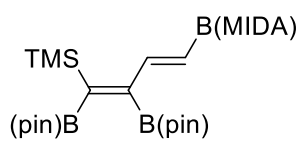




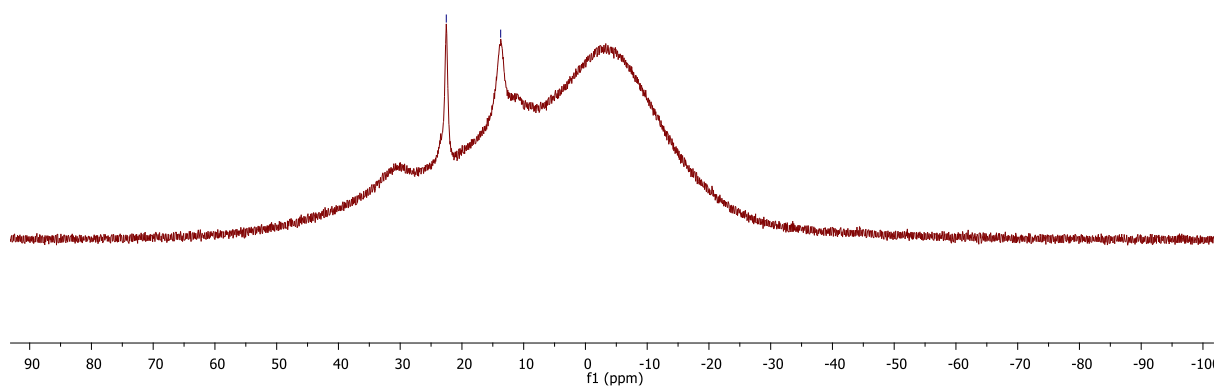


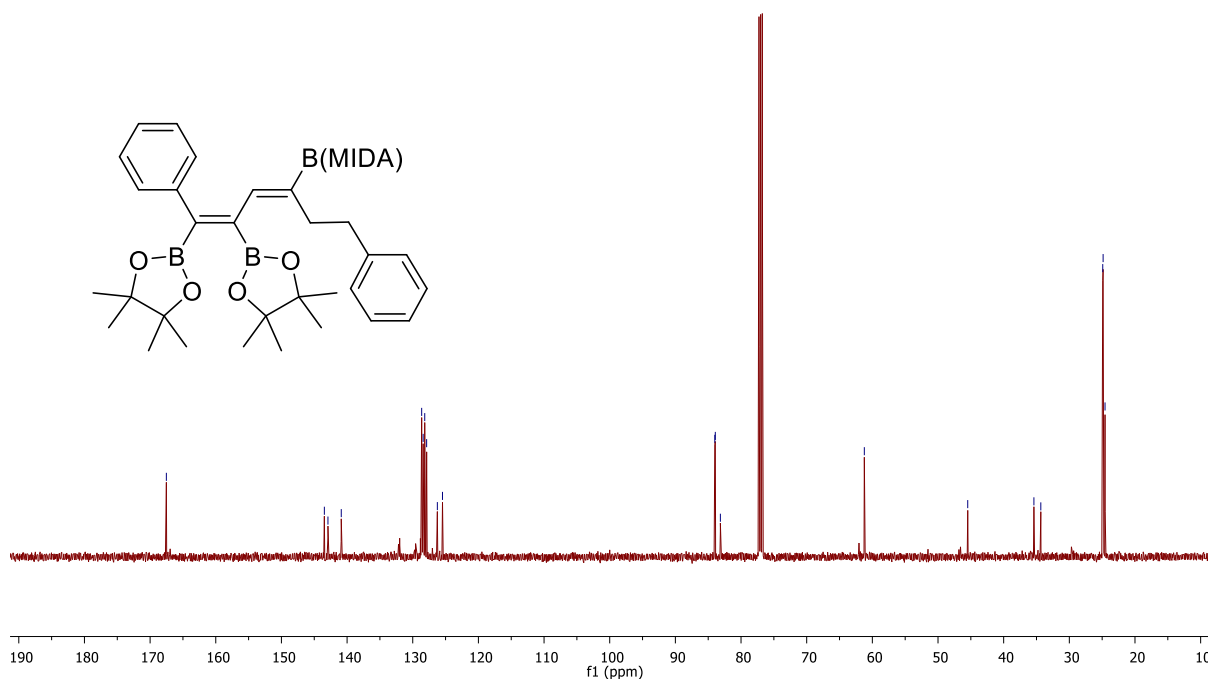
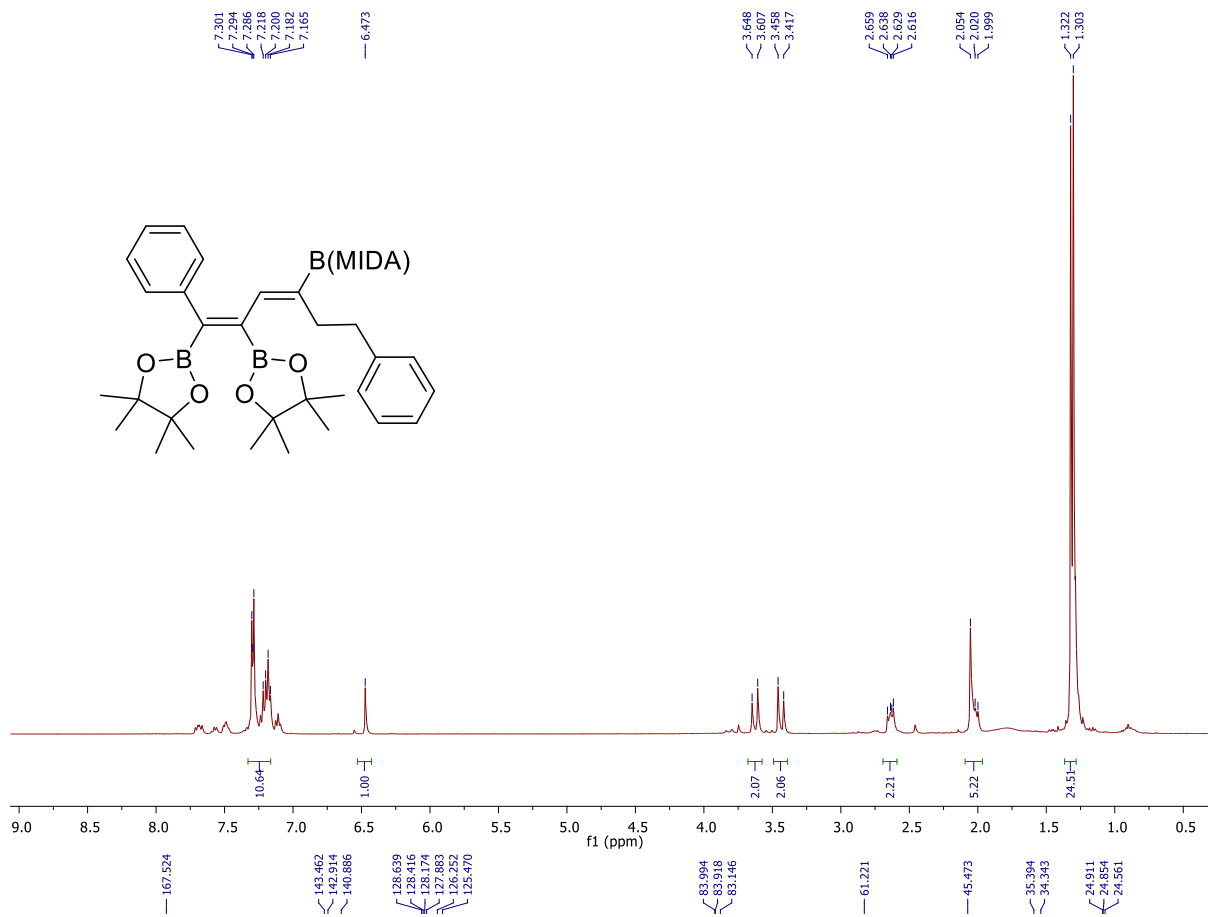


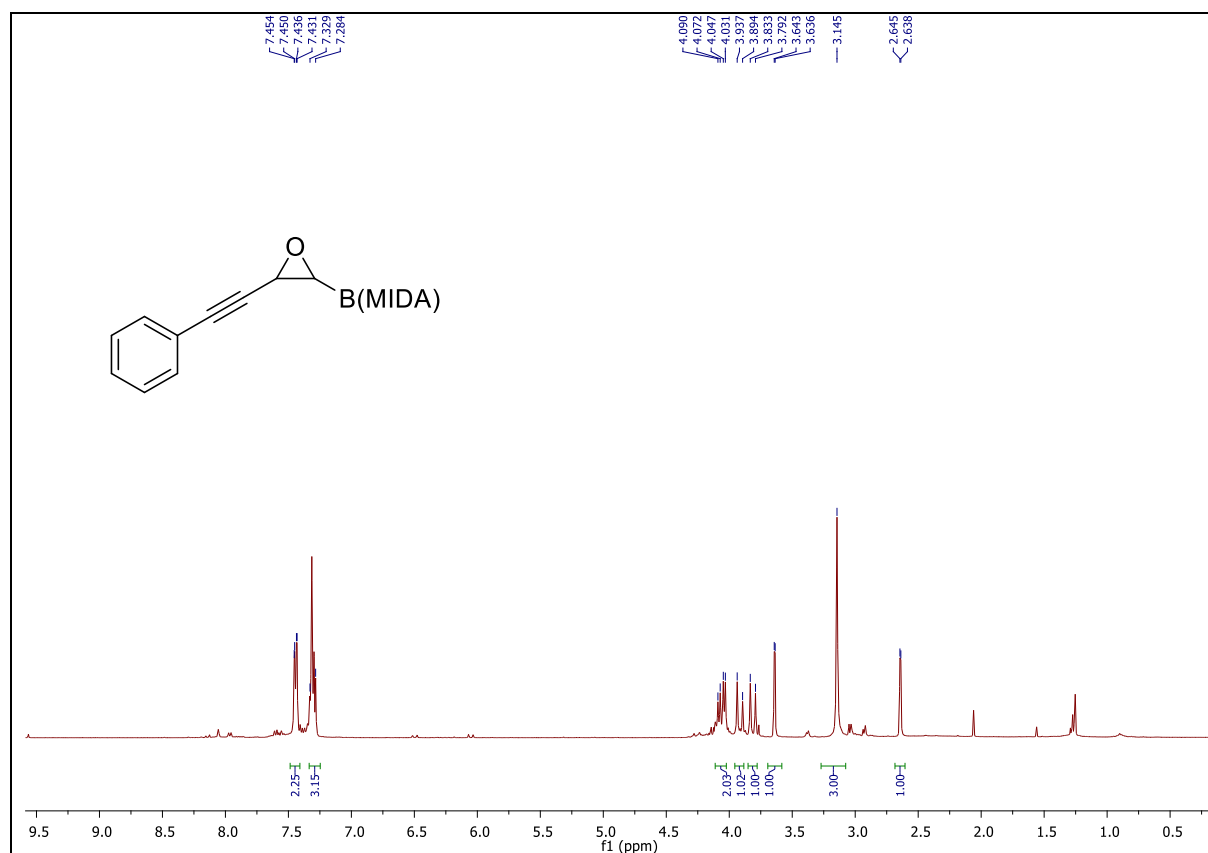
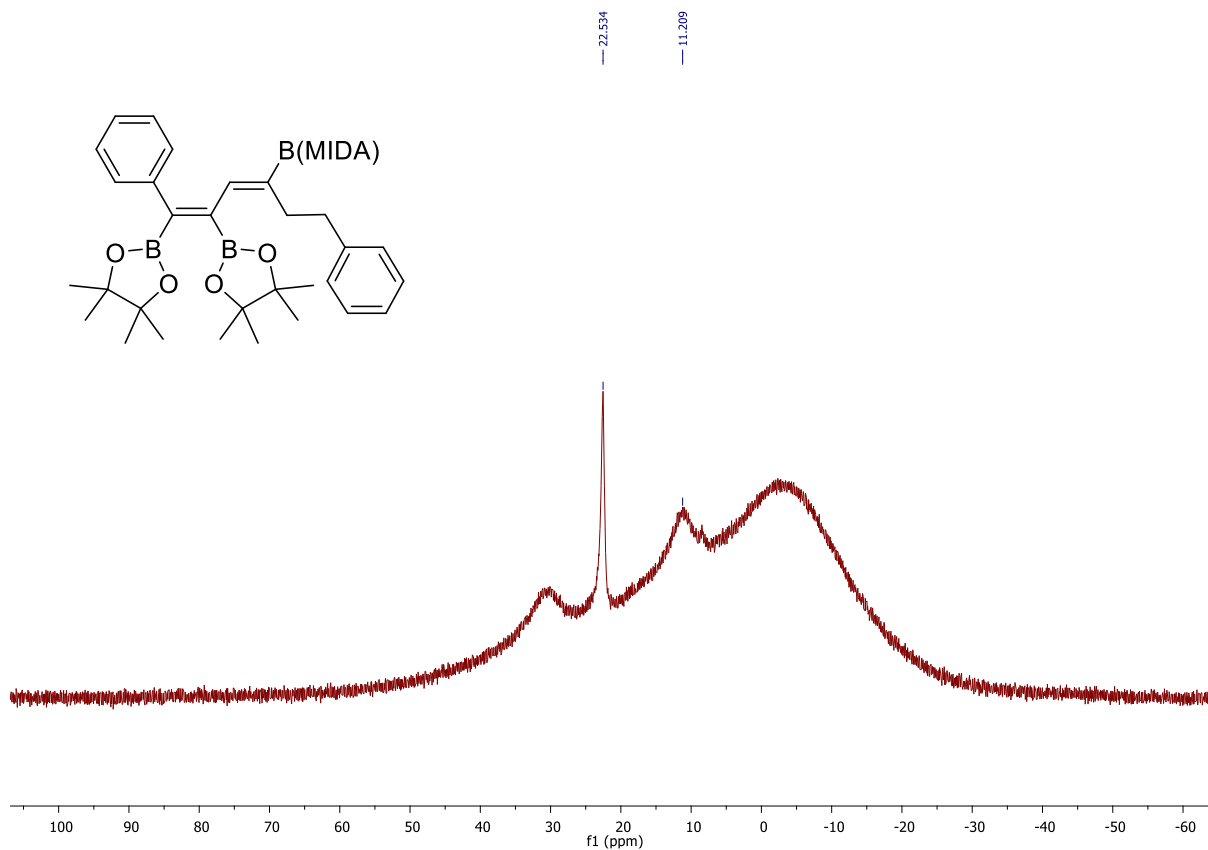


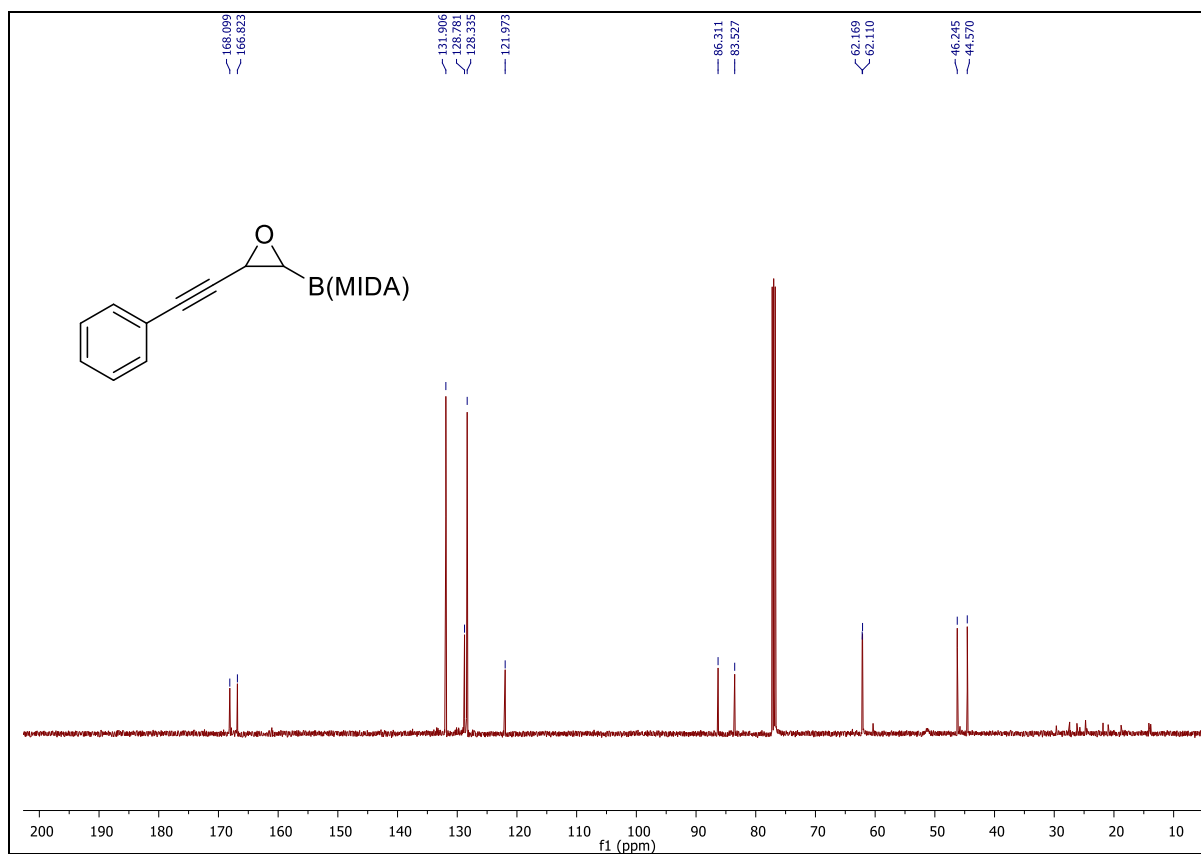


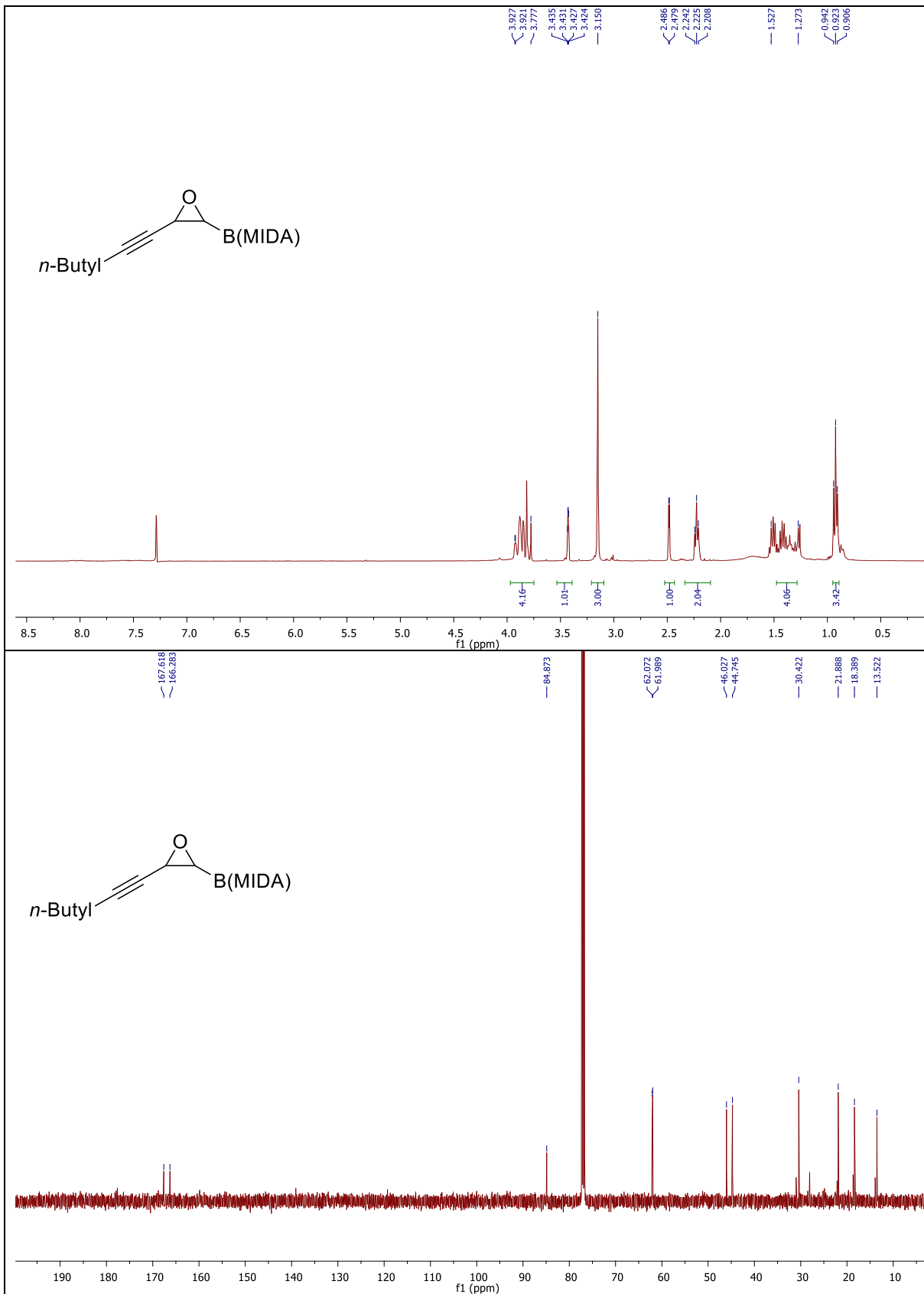
— 22.534
— 13.726

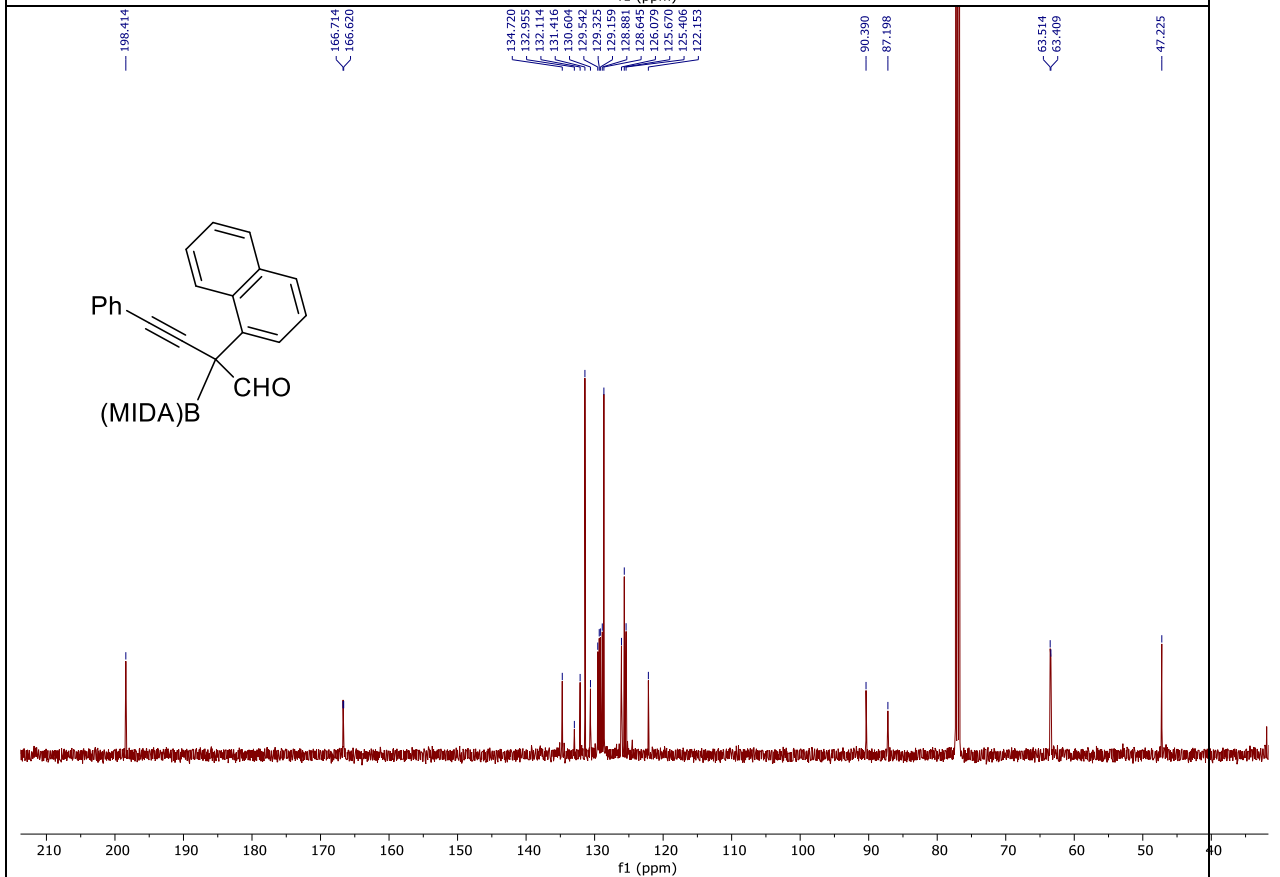
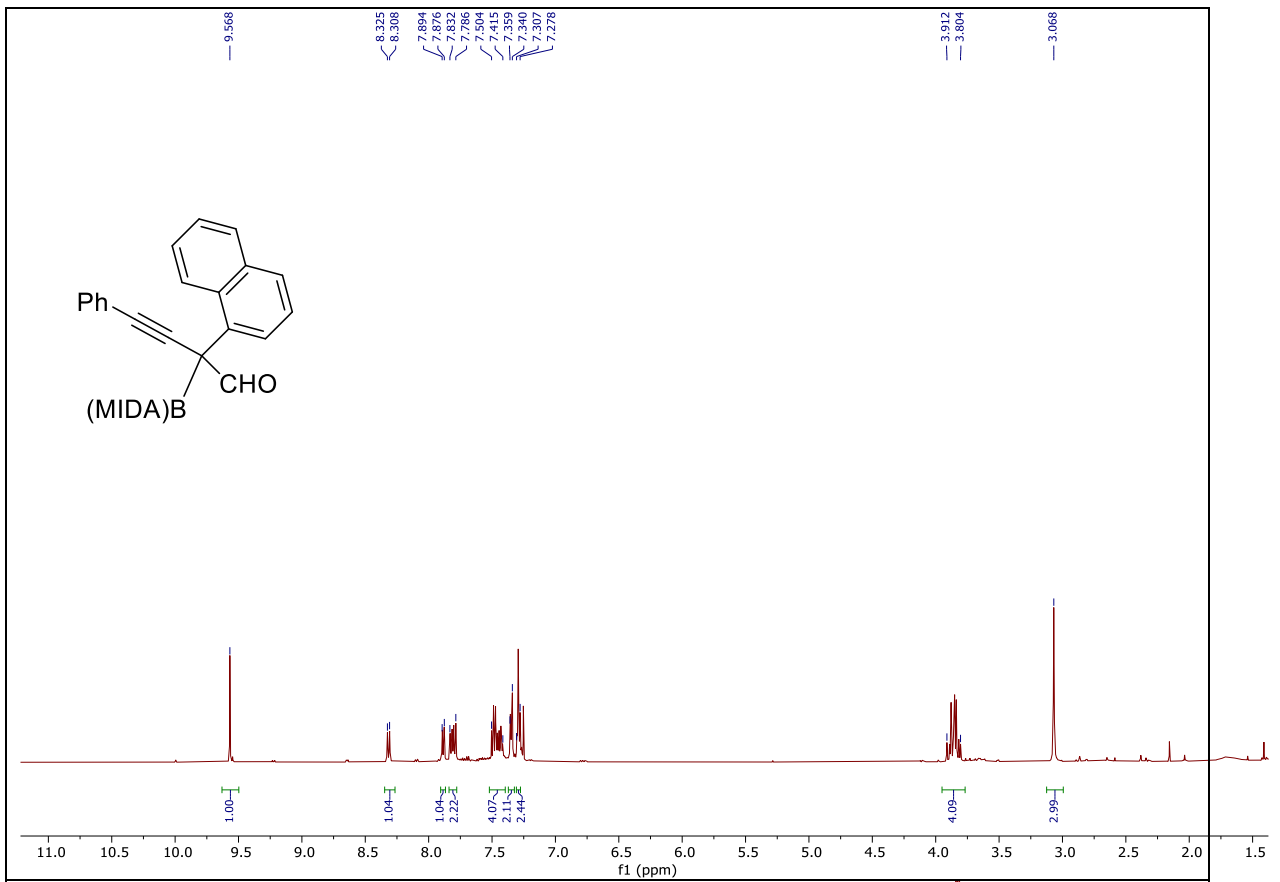


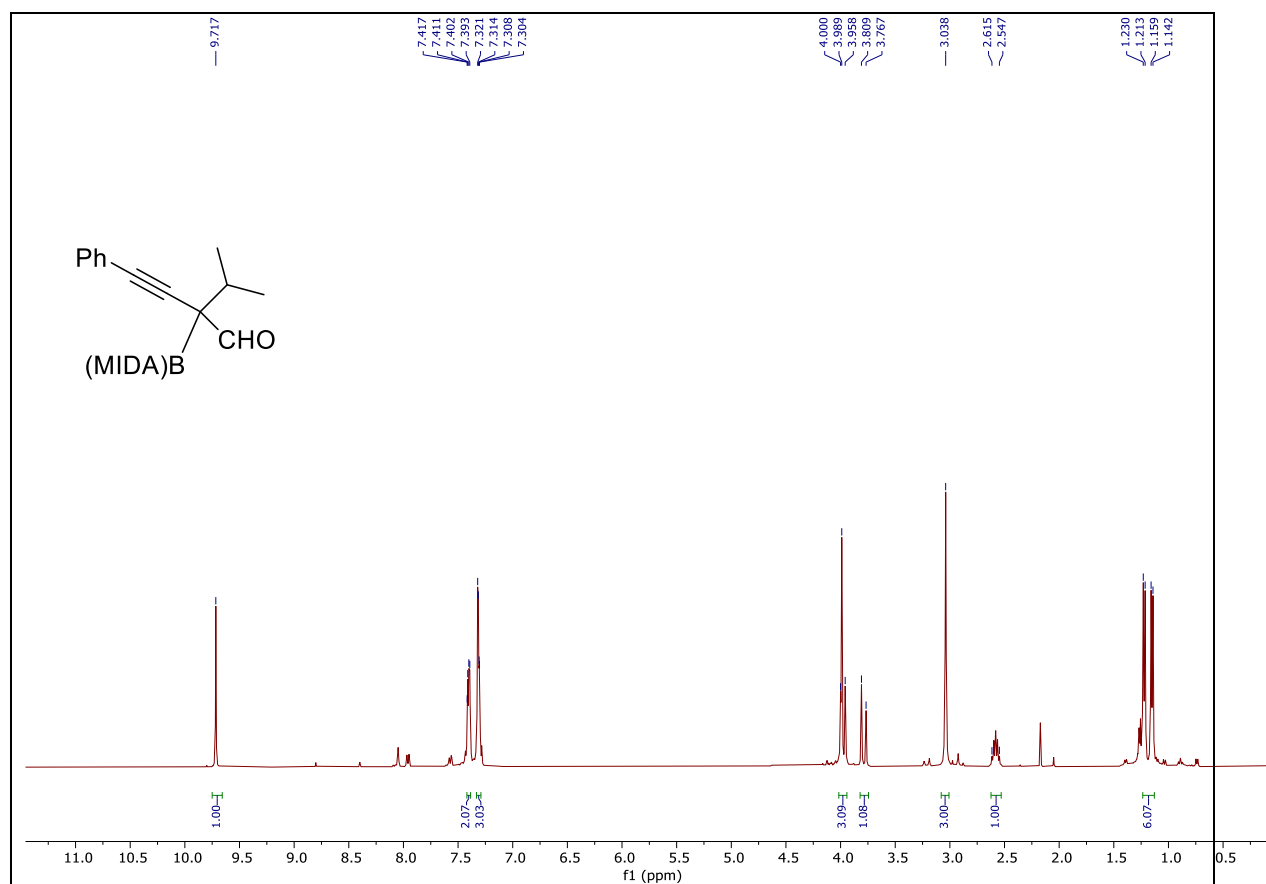
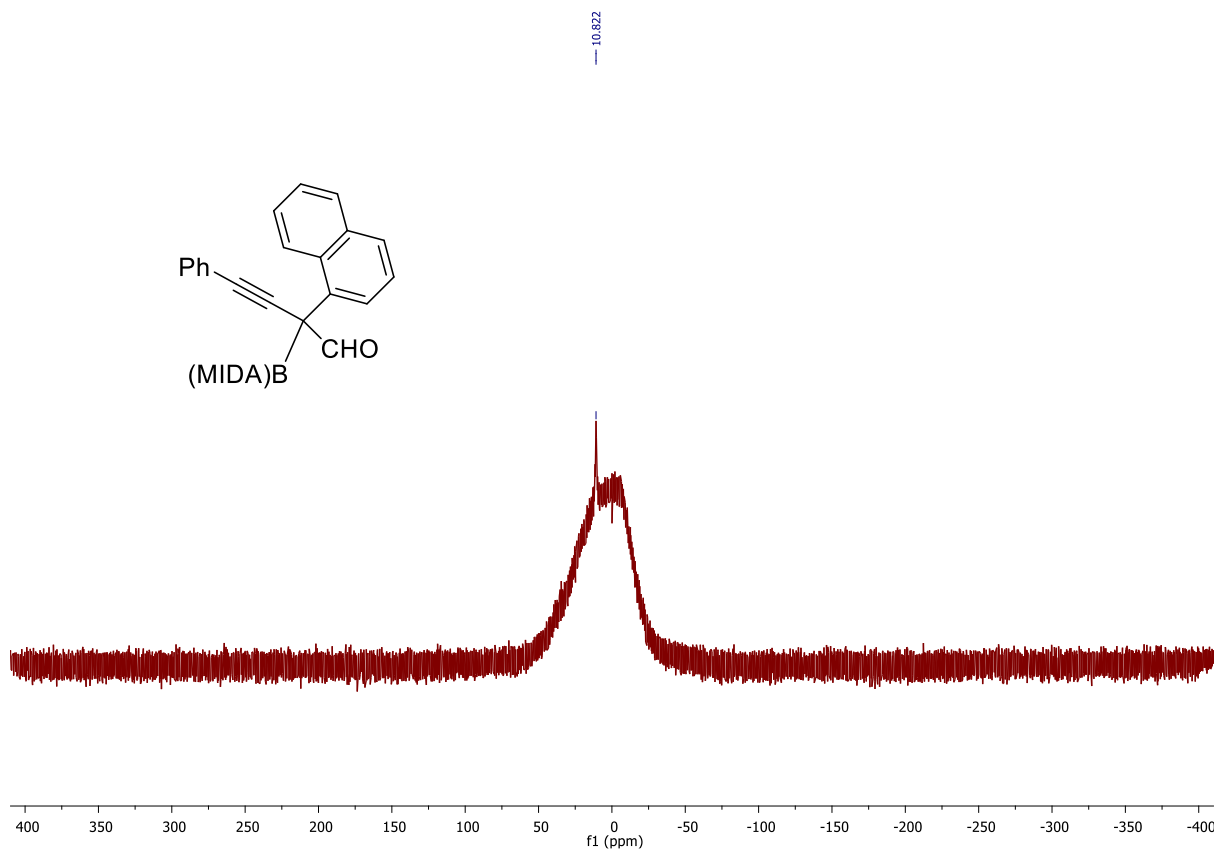


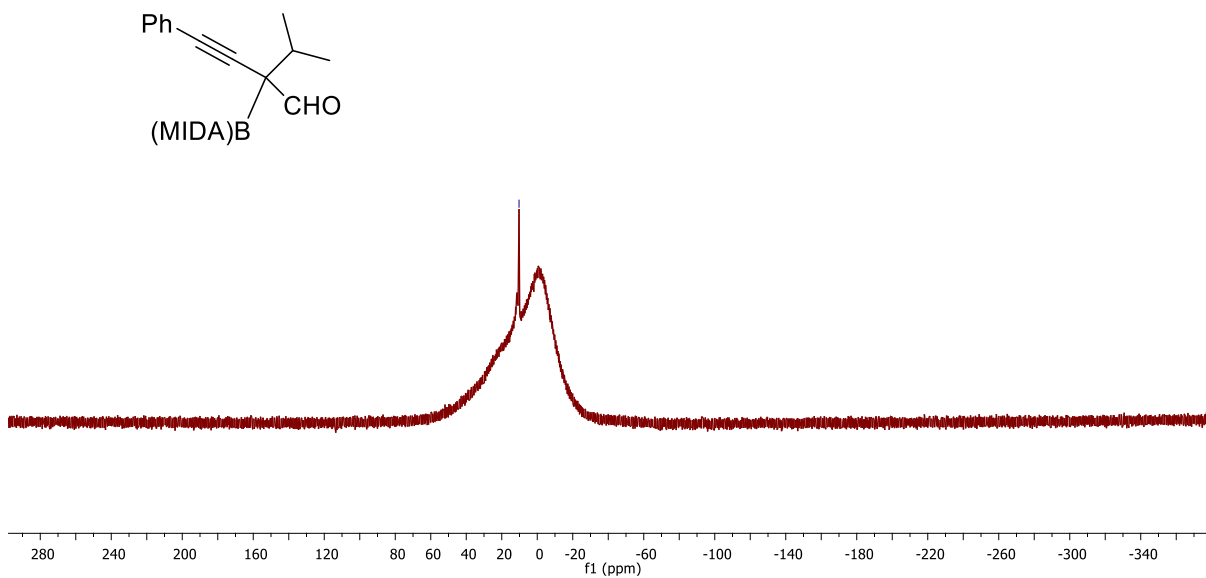
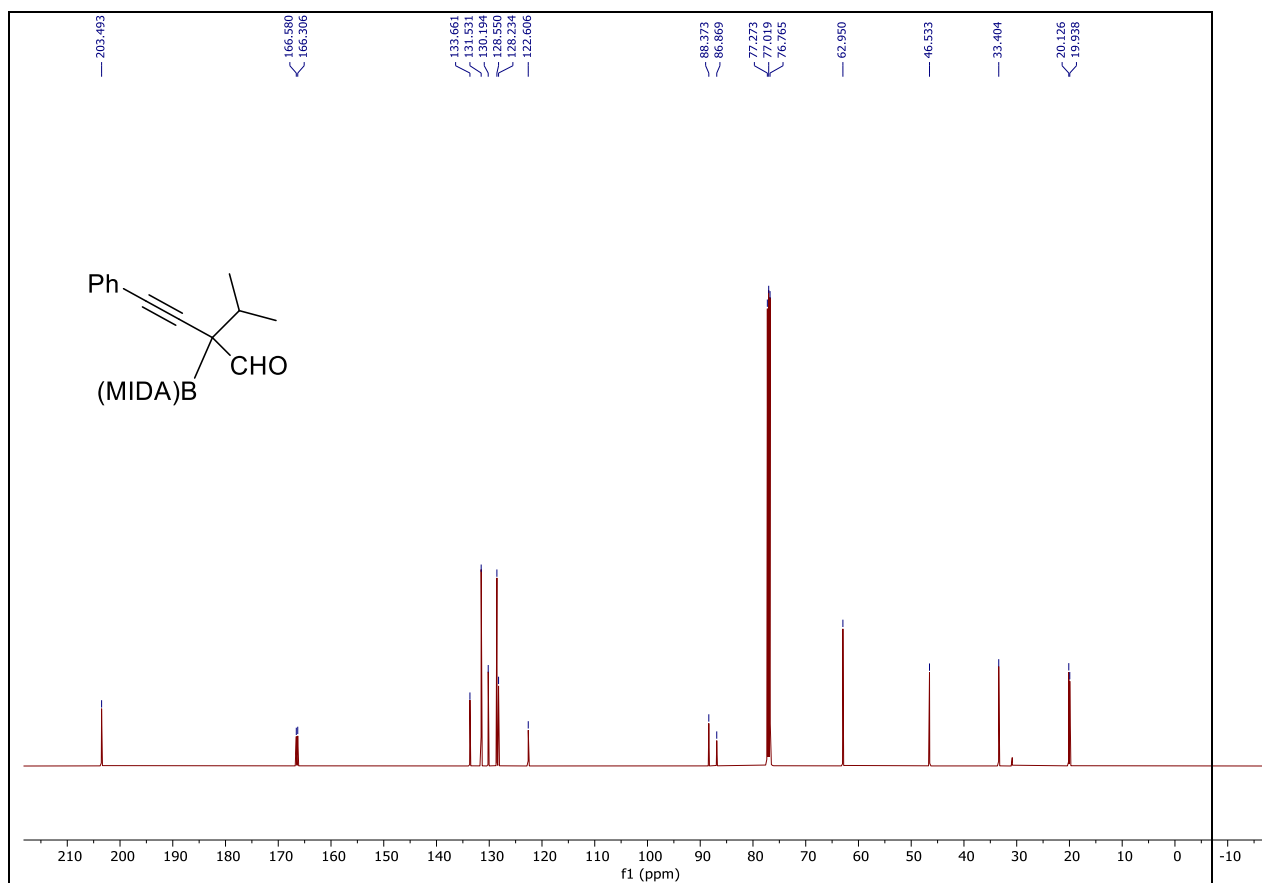


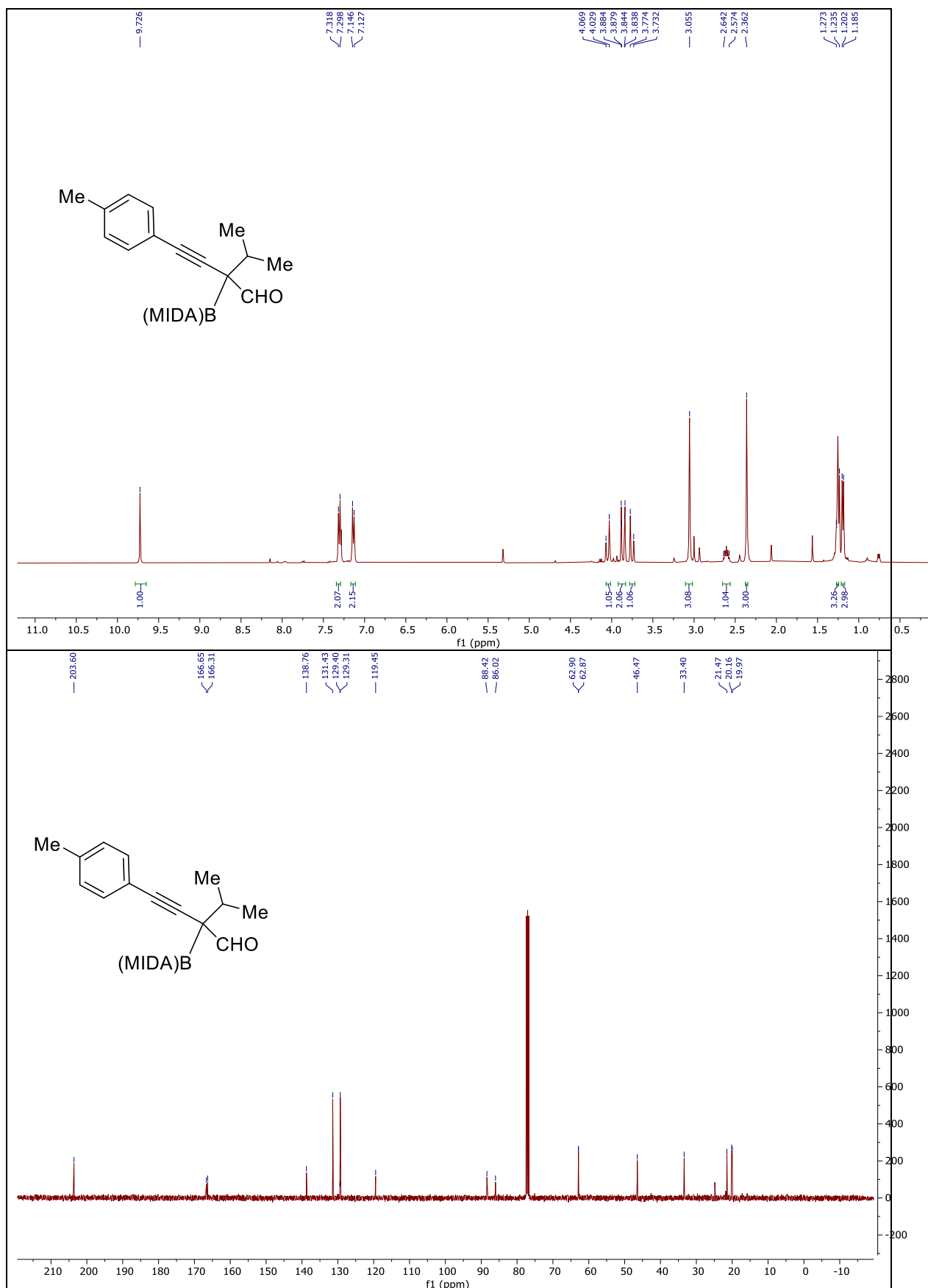


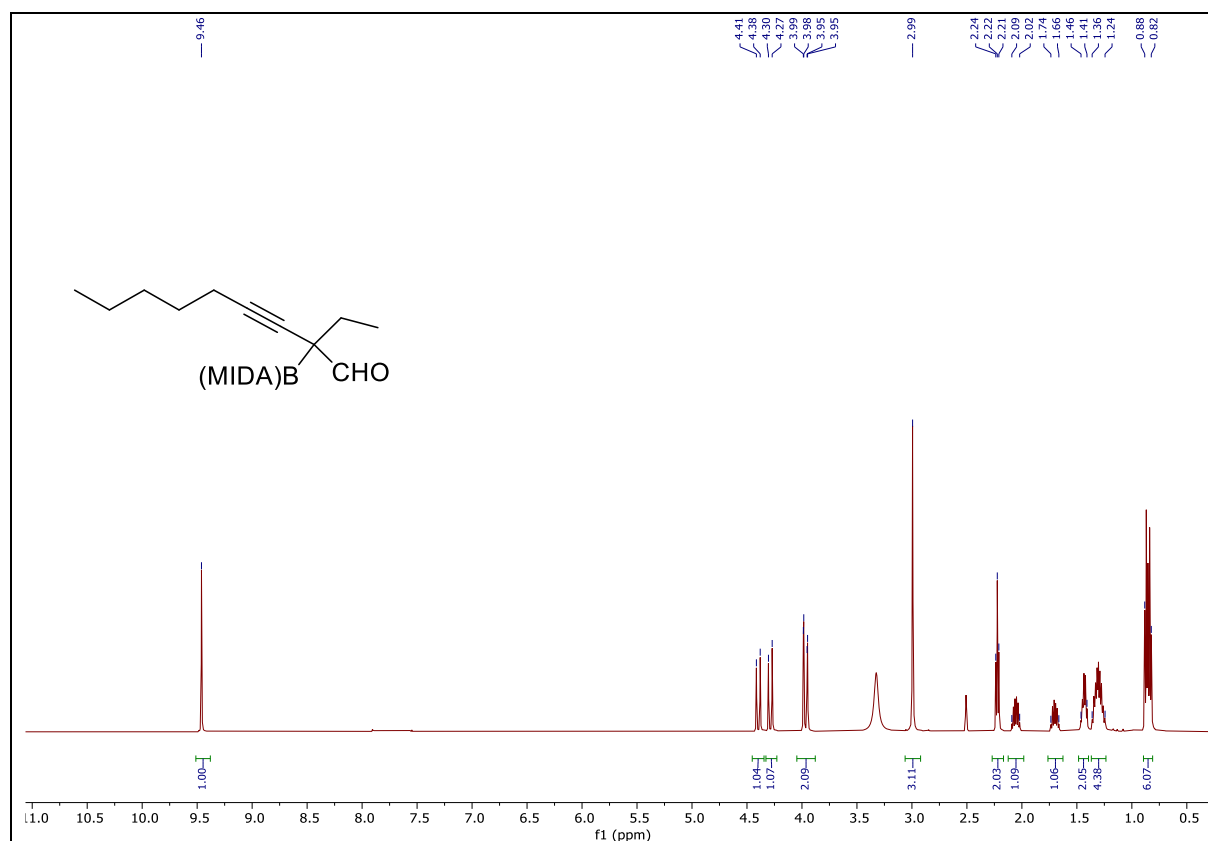
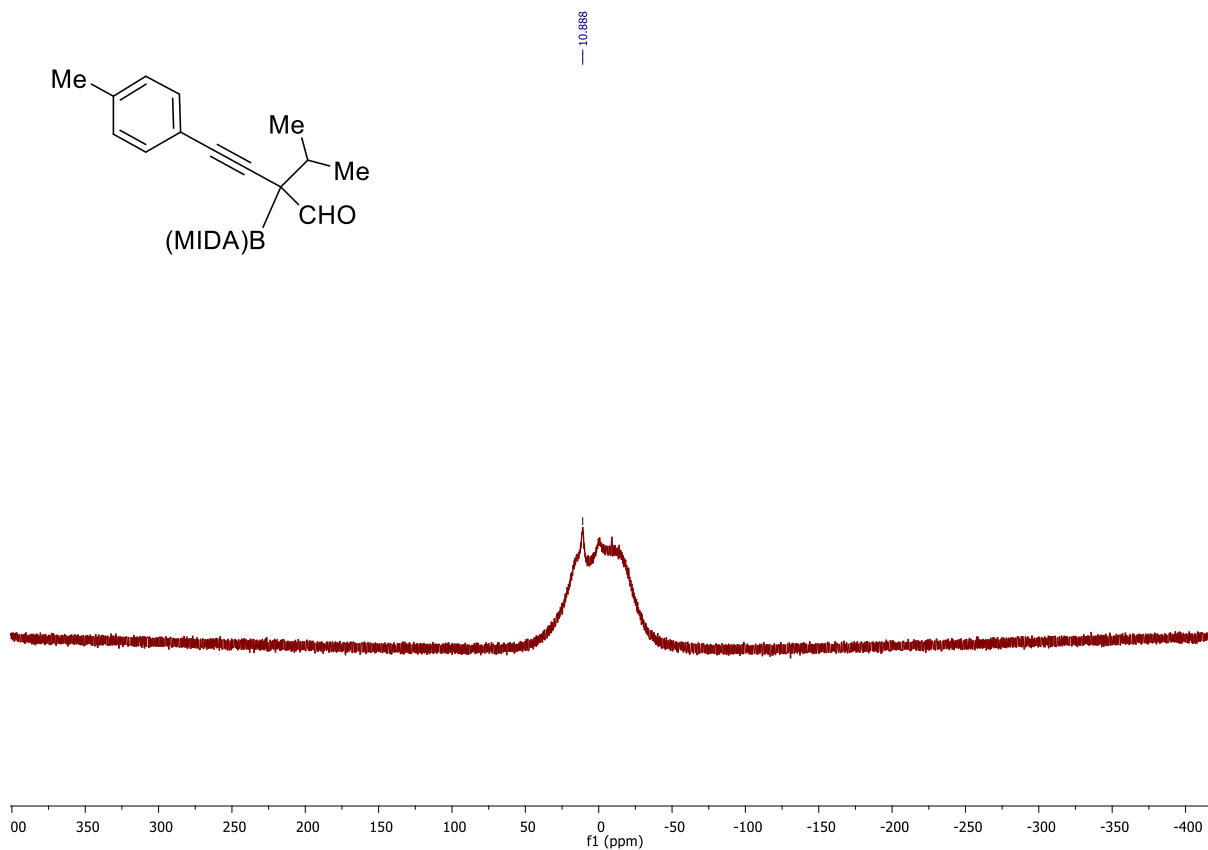


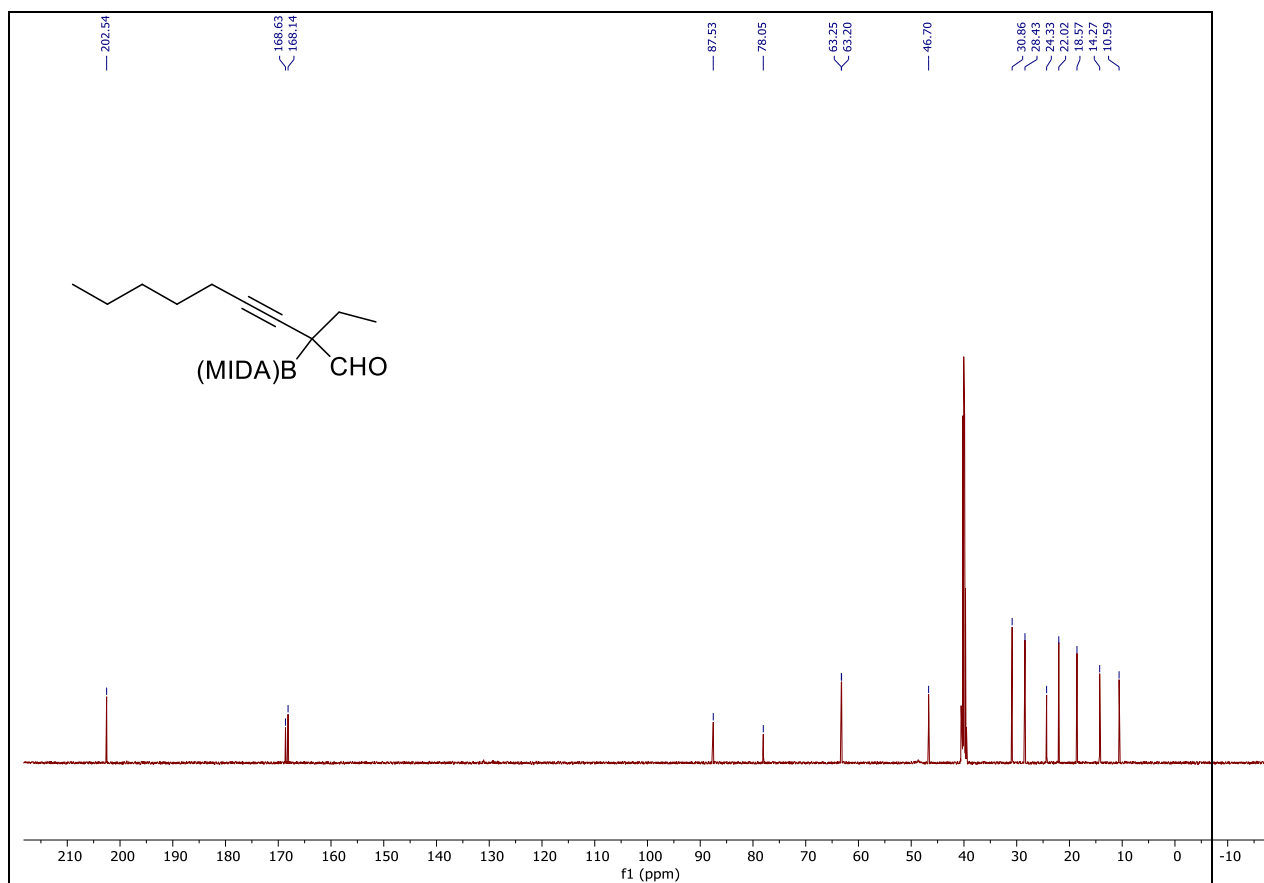












10.872

