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Organobase-Catalyzed 1,1-Diborylation of Terminal Alkynes under Metal-free Conditions

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1. General experimental

Anhydrous tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), Acetonitrile (MeCN), hexane, EtOAc, and dichloromehane (DCM) were purchased from J&K. All reagents were purchased at the highest commercial quality and used as received without further purification. All experiments were carried out under ambient air with no precautions taken to exclude moisture. Reactions were monitored by GC-MS or LC/MS. TLC was performed using 0.25 mm E. Merck silica plates (60F-254), using short-wave UV light as the visualizing agent, or $KMnO_4$ and heat as developing agents. Flash column chromatography was performed using 200-300 mesh silica gel obtained from Qingdao Haiyang Chemical Co., Ltd. NMR spectra were recorded on Bruker Ultrashield^{TM} 300 MHz and Advance III HD 600 MHz instruments and are calibrated using residual undeuterated solvent (TMS @ 0.00 ppm, $CDCl_3$ @ 7.26 ppm, ^{1}H NMR; $CDCl_3$ @ 77.16 ppm ^{13}C NMR). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. GC-MS results were recorded on an Agilent 8890-5977B GC/MSD instrument. High-resolution mass spectra (HRMS) were recorded on an Agilent 1200 HPLC/6520 Accurate-Mass Q-TOF LC/MS mass spectrometer by electrospray ionization time of flight reflectron experiments. HPLC analyses were conducted on a Agilent 1260 LC/MSC with a MZ PerfectChrom 100 C8 column (4.6 ID x 150 mm, 5 μm). Preparative HPLC were conducted on an Buchi Pure C850 instrument with a MZ PerfectChrom 100 C8 Prep column (30 ID x 150 mm, 5 μm).

2. General procedure

To a 5 mL vessel, base (10 mol% or 5 mol%), diboran reagent (0.1 mmol), solvent (2 mL), and alkyne (0.1 mmol) was charged in sequence, then the reaction was stirred for 24 h at room temperature. The reaction mixture was filtered through a short pad of celite^{TM} 545, washed with DCM (50 mL), and then extracted with saturated salt water (50 mL × 3 times). The organic layer was then dried over anhydrous Na_2SO_4, and concentrated. The crude product was purified by column chromatography with petroleum ether/EtOAc or MeCN/H_2O as eluents to afford the desired product.

Scale-up experiments: To a 100 mL vessel, bis(2,4-dimethylpentane-2,4-glycolato)diboron (12 mmol), MeCN (30 mL), methyl propiolate (12 mmol), and BTMG

(5 mol%), was charged in sequence, then the reaction was stirred for 24 h at room temperature. The reaction mixture was filtered through a short pad of celite™ 545, washed with DCM (75 mL), and then extracted with saturated salt water (80 mL × 3 times). The organic layer was then dried over anhydrous Na_2SO_4, and concentrated. The residue crude product was purified by column chromatography with petroleum ether/EtOAc as eluents to afford **3aa** in a yield of 90%.

3. Other unsuccessful alkynes

We have also tested other types of terminal alkynes in our transformations. Though propargyl amide and ethynylphosphoric acid derivatives could participate in the reaction, however, very low yields were determined by LC-MS and the products were very hard to be separated (Figure S1). No obvious yield improvement was observed by augmenting the catalyst loading or elevating the reaction temperature, and much more by-products were generated simultaneously. Unfortunately, no desired products were determined when employing propiolic acid, ethynylthioates, phenylacetylene, or internal alkynes as substrates (Figure S2).

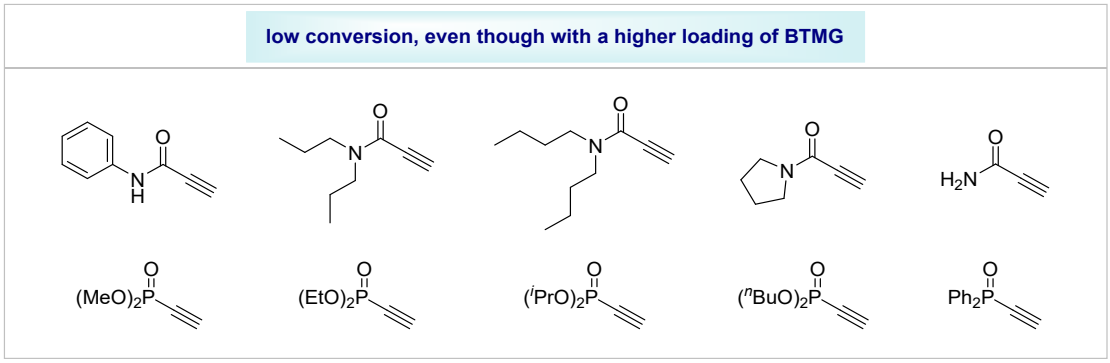


Figure S1. Low reactive terminal alkynes under current conditions

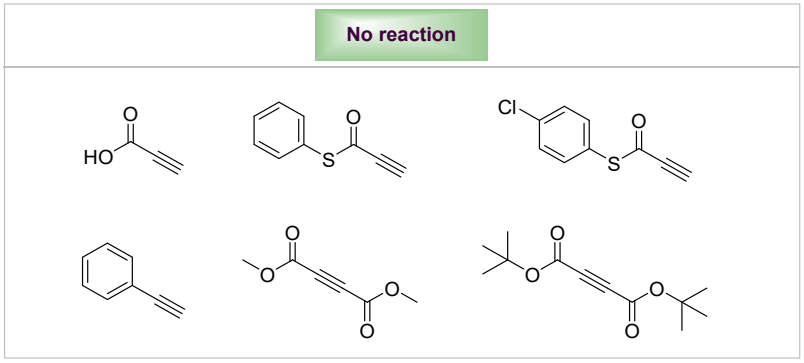
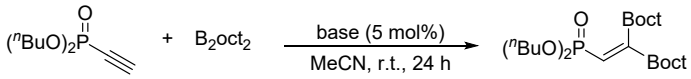


Figure S2. Inert terminal alkynes under current conditions

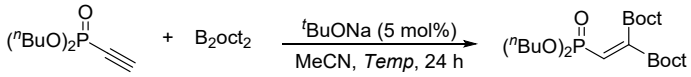
To meliorate our 1,1-diborylation condtions, we selected the less reactive dibutyl ethynylphosphonate as the substrate to explore the role of inorganic base similar to Sawamura's work (Figure S3).



Base	Cs_2CO_3	LiOH	NaOH	^{t}BuOLi	^{t}BuONa	^{t}BuOK
Yield (%)	~1	N.D.	N.D.	~1	~5	~3

Figure S3. Inorganic base optimization of dibutyl ethynylphosphonate with B_2oct_2

Then, we employed ^{t}BuONa as the catalyst and the temperature optimization experiments were carried out (Figure S4). Though slightly higher yield was obtained, much more by-products were generated at the same time. Therefore, a more compatible reaction system should be investigated to solve the problem of narrow substrate scope in our future work.



Temp (°C)	50	80	100
Yield (%)	~7, undesigned products	~10, much by-products	~5, much by-products

Figure S4. Temperature optimization of ^{t}BuONa catalyzed diborylation

4. Radical inhibition experiments

When the reaction was carried out under N_2 atmosphere or in the presence of TEMPO, the yield of the product was almost unchanged (figure S5, eq 1 and eq 3). Using BHT as radical capturing reagent, a lower yield was observed, which may attribute to the interaction of weakly acidic Ph-OH with organic base BTMG (eq 2). Therefore, we concluded that this reaction may not involved in a radical process.

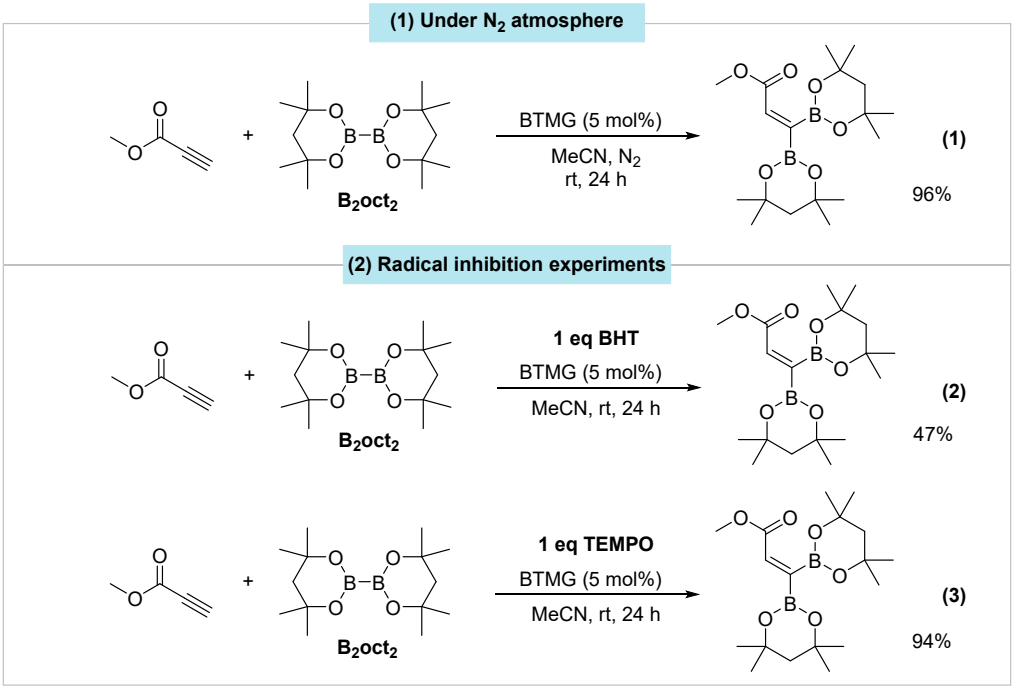


Figure S5. Radical inhibition experiments

5. Computational details

DFT calculations were performed using the Gaussian 09 package.[1] All of the structures are optimized at M06-2X/6-31G* lever of theory.[2-3] Vibrational analyses were performed to ensure intermediates to have no imaginary frequencies and the transition state structures to have only one imaginary frequency. Transition state structures were confirmed to connect appropriate reactants or products by intrinsic reaction coordinate (IRC) calculations.[4] A correction of −2.6 (2.6) kcal/mol was made in obtaining relative Gibbs free energies for two-to-one (one-to-two) transformations. Solvent effects were considered using Acetonitrile with the SMD[5] model at the M062X-D3/6-311++G**.[6-7]

To verify the the advantages of BTMG, we calculated the energy barriers of deprotonation and 1,2-boryl migration using the selected organic base DBU and inorganic base Na_2CO_3, which showed low yields for this reaction. As shown in table S1, DBU and Na_2CO_3 give higher barriers to catalyzing this reaction during the 1,2-boryl migration process. It is understandable that DBU with only one amino motif interacting with the C=N (in BTMG, two amino motifs can have the pi interaction with C=N) would be less reactive to deprotonate the Methyl propiolate **1a** when compared

with BTMG. The energy of TS2_DBU is also higher than TS2 may due to the non-covalent interactions between the protonated DBU and alkynyl diboron complex. When using the Na_2CO_3, the alkali metal cation could not be well stabilized in **TS2**(Na_2CO_3).

Table S1 Comparison of the energy barriers for deprotonation and 1,2-boryl migration with different bases.

base	Energy barriers (kcal/mol)	
	deprotonation	*1,2*-boryl migration
BTMG	23.1 (TS1)	23.8 (TS2)
DBU	25.9 (TS1_DBU)	28.4 (TS2_DBU)
Na_2CO_3	14.9 (TS1_Na_2CO_3)	26.2 (TS2_Na_2CO_3)

6. Cartesian coordinates

1a E = -305.070266

C	2.63025500	-0.40114300	-0.00000200
C	1.46527100	-0.10091800	0.00000300
H	3.66435400	-0.66768500	-0.00000700
C	0.06679700	0.30763400	0.00000100
O	-0.30694500	1.45249400	-0.00000100
O	-0.74249300	-0.75708900	0.00000100
C	-2.13457800	-0.43710700	-0.00000100
H	-2.39039900	0.14344900	-0.88884600
H	-2.65452000	-1.39324000	-0.00000900
H	-2.39040500	0.14343800	0.88884900

2a E = -900.767988

C	-2.96068100	-1.27469200	-0.06040700
C	-3.56311400	0.04052300	-0.58409700
C	-2.90463400	1.31863300	-0.04536300
C	2.96075000	1.27465000	-0.06040200

C	3.56317100	-0.04056200	-0.58403800
C	2.90458200	-1.31864500	-0.04536700
B	-0.85716700	0.02426600	-0.04664700
B	0.85719400	-0.02424100	-0.04670000
O	-1.54916400	-1.14288200	0.13366000
O	-1.48888100	1.22673900	-0.22159100
O	1.54923400	1.14285600	0.13371400
O	1.48884100	-1.22672400	-0.22175200
C	-3.57855900	-1.74352400	1.25691000
H	-4.64088600	-1.96791500	1.11577800
H	-3.07064900	-2.65411400	1.58723300
H	-3.48786500	-0.99753100	2.04758000
C	-3.14468300	-2.37210800	-1.10913300
H	-2.71793300	-3.31139600	-0.74619600
H	-4.20708400	-2.52615300	-1.32581300
H	-2.63285500	-2.09603600	-2.03555500
C	-3.16940000	1.58303400	1.43854600
H	-2.66432800	0.84402500	2.06465800
H	-2.77391100	2.56711800	1.70654600
H	-4.24130500	1.56259800	1.66170000
C	-3.36534500	2.51507600	-0.87139600
H	-4.44293000	2.67258600	-0.75813400
H	-2.84023700	3.41570200	-0.54101900
H	-3.14131100	2.35457600	-1.92985100
H	-4.64151800	0.06028300	-0.38608100
H	-3.43810100	0.06207900	-1.67457600
H	4.64154200	-0.06039300	-0.38583500
H	3.43836900	-0.06212900	-1.67454700

C	3.14468700	2.37206400	-1.10916000
H	2.71802000	3.31137800	-0.74619200
H	4.20707400	2.52604500	-1.32595300
H	2.63274100	2.09599200	-2.03551700
C	3.57871800	1.74356800	1.25684800
H	4.64093600	1.96831900	1.11544400
H	3.07057500	2.65397100	1.58731500
H	3.48855900	0.99751100	2.04752700
C	3.16910000	-1.58293400	1.43860900
H	2.77334600	-2.56690300	1.70663700
H	4.24097300	-1.56271900	1.66194200
H	2.66406500	-0.84372600	2.06451900
C	3.36536200	-2.51511400	-0.87129500
H	4.44295500	-2.67256100	-0.75799900
H	2.84030400	-3.41575500	-0.54087500
H	3.14135500	-2.35468900	-1.92976500

BTMG E = -519.572764

N	-0.54680700	-0.75621500	0.25726000
N	1.72033200	-0.94881100	-0.10849900
N	0.79246000	1.20261100	-0.13119900
C	0.56414500	-0.17096300	0.03123500
C	1.52886600	-2.38418500	-0.18531700
H	1.26495300	-2.81878900	0.78948100
H	2.45769500	-2.84072600	-0.54205400
H	0.71824600	-2.60573200	-0.87956600
C	2.89638100	-0.57024700	0.65729900
H	2.94234800	0.51346800	0.77186300

H	3.80222300	-0.90550900	0.14145600
H	2.88411700	-1.02315000	1.66118900
C	1.67425100	1.71017100	-1.15508800
H	1.93640600	0.90307100	-1.84027200
H	2.60390700	2.12972400	-0.73770500
H	1.17251900	2.50785300	-1.72002300
C	0.42402200	2.13484100	0.90551500
H	-0.27654400	2.90477800	0.55030500
H	1.31853000	2.65044200	1.28963000
H	-0.04067000	1.59555900	1.73190400
C	-1.88310600	-0.22110200	-0.00413300
C	-2.53607300	0.24758400	1.30292500
C	-1.96516100	0.88311000	-1.06999600
C	-2.67600800	-1.43377300	-0.52161300
H	-3.60534300	0.42932500	1.14845300
H	-2.42162000	-0.52109600	2.07304800
H	-2.09164600	1.17698900	1.66975000
H	-1.40987500	0.58920100	-1.96753200
H	-3.01339400	1.03280900	-1.35179300
H	-1.57388200	1.84146700	-0.72435500
H	-3.72488600	-1.17398300	-0.70251300
H	-2.23939900	-1.79557100	-1.45856100
H	-2.62949300	-2.24583200	0.20939000

TS1 E = -1725.415356

C	-1.70474700	3.17057600	-1.59980800
C	-2.16420100	2.04596500	-2.55465700
C	-1.20219500	0.85196000	-2.64004700

C	3.47723300	1.43365900	-0.17039200
C	3.67439400	0.82478600	1.22342800
C	2.66031100	1.25279800	2.30087500
B	-0.34850200	1.40258700	-0.47520200
B	1.10552500	1.16791700	0.40335500
O	-0.81486400	2.69168800	-0.58803200
O	-0.85186900	0.42487900	-1.32118300
O	2.10713300	1.32790700	-0.54369600
O	1.34131900	1.39479300	1.75402900
C	-0.96489200	4.28331500	-2.34448600
H	-1.63690100	4.77983700	-3.05236500
H	-0.60002400	5.02172900	-1.62520000
H	-0.10725600	3.89315500	-2.89726600
C	-2.91168600	3.76742900	-0.87804500
H	-2.58612000	4.55539800	-0.19267300
H	-3.62243000	4.19076600	-1.59570600
H	-3.42784600	2.99672600	-0.29491000
C	0.09974900	1.17233700	-3.38021800
H	0.68287300	1.92593900	-2.84339500
H	0.71561900	0.26932900	-3.42291100
H	-0.09779500	1.52603400	-4.39802800
C	-1.89901600	-0.32811800	-3.30585200
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H	-1.22263100	-1.18787800	-3.32807000
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H	-2.32837500	2.46143300	-3.55655700
H	-3.13384700	1.66296900	-2.21476500
H	4.69071400	1.03302800	1.58088200

H	3.58345600	-0.26036100	1.10100500
C	4.26918500	0.61502700	-1.18776100
H	4.10332900	1.01725000	-2.19252900
H	5.34227200	0.65399300	-0.96837500
H	3.93489600	-0.42678500	-1.16985300
C	3.86678700	2.91013800	-0.26851100
H	4.88007900	3.08221900	0.11091300
H	3.82780200	3.22719300	-1.31565700
H	3.16630900	3.53481800	0.28977800
C	3.01414400	2.57372600	2.98404200
H	2.24850600	2.80694100	3.73082700
H	3.98212300	2.49582200	3.49091500
H	3.05832000	3.40367800	2.27759300
C	2.61556000	0.14478000	3.35545100
H	3.62512100	-0.06604600	3.72557500
H	1.99616200	0.44092700	4.20840000
H	2.20713600	-0.76621200	2.90579800
C	1.12451800	-1.21015300	0.40132700
C	1.63868500	-2.10988900	-0.26971200
C	2.11433400	-3.21335500	-1.04255200
O	1.47353600	-4.21990600	-1.30667800
O	3.38411800	-3.05414600	-1.47250200
C	3.89072500	-4.13313800	-2.24798600
H	3.28897000	-4.27802300	-3.14892000
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H	3.88267900	-5.06098700	-1.67072600
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C	-0.78890000	-3.57314300	1.27068700
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H	-2.26028700	-2.63310200	-1.61611200
H	-2.42186100	-4.27907300	-0.93515300
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C	-4.43358700	-2.36186400	0.04030800
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H	-5.37262000	-2.03953900	0.50477500
C	-3.83616100	0.02103100	-0.07906900
H	-4.54064900	0.42991000	0.65618300
H	-4.33111300	0.01214400	-1.05746500
H	-2.94765400	0.64748900	-0.14152400
C	-1.98573900	-0.04731600	2.69562000
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H	-2.79557400	1.73598400	1.70444900
H	-3.27108500	-1.69135700	3.30648800
H	-3.54029200	-0.16649900	4.16807700
H	-4.16064700	-0.36293500	2.52803800

H	-1.15359100	0.22065900	4.68035900
H	-0.83429100	-1.38224500	3.97994900
H	0.04949600	0.04877800	3.38303400
H	-0.47601300	-0.82707100	1.31861000

II' E = -1725.444622

C	-2.78596800	1.67804500	-1.45014000
C	-2.76782100	0.83236800	-2.73531500
C	-1.37502400	0.39897100	-3.22015900
C	1.18908600	3.36885200	0.55358600
C	2.01805700	2.74469900	1.68998900
C	1.31476600	1.60681500	2.45767300
B	-0.68426200	0.57998900	-0.85227000
B	0.69318800	0.97722700	0.11374000
O	-1.91659300	1.10590100	-0.47127200
O	-0.53977400	0.04196800	-2.11890300
O	0.82779000	2.36903100	-0.37480900
O	0.44077400	0.89092600	1.58525200
C	-2.34674800	3.13169100	-1.65948500
H	-2.80479800	3.56573200	-2.55484400
H	-2.64345000	3.72852500	-0.79117400
H	-1.25785800	3.19867100	-1.72836100
C	-4.19259300	1.65658600	-0.85769400
H	-4.19042900	2.17150300	0.10786100
H	-4.90122000	2.16032300	-1.52388700
H	-4.53993400	0.62833400	-0.70216500
C	-0.64262200	1.49040900	-4.00506200
H	-0.41783700	2.35048400	-3.37279200

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C	-1.49982900	-0.84380500	-4.09828000
H	-2.11447100	-0.63756700	-4.98089200
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H	-1.96169300	-1.66579500	-3.53976900
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H	-3.35404000	-0.07327800	-2.53699800
H	2.33745500	3.52147200	2.39671700
H	2.92624000	2.34167400	1.22300700
C	2.06053500	4.37930700	-0.19308900
H	1.51474100	4.74720800	-1.06801600
H	2.32162300	5.23335200	0.44254200
H	2.97990800	3.89946800	-0.54173200
C	-0.09122100	4.06227500	1.04022200
H	0.09548600	4.73380600	1.88688300
H	-0.51255400	4.65395300	0.22019700
H	-0.83404800	3.30980800	1.32082500
C	0.48012600	2.15342100	3.62071600
H	0.00847000	1.33383200	4.17188700
H	1.11888900	2.70234000	4.32136300
H	-0.30809900	2.82234600	3.27395900
C	2.36809900	0.64953900	3.02507700
H	3.04842500	1.17514600	3.70497100
H	1.88193800	-0.15882700	3.58632200
H	2.95766800	0.21256800	2.21381500
C	2.04773400	0.16243800	-0.27711200
C	3.03843800	-0.47459200	-0.59688100

C	4.12893300	-1.35257600	-0.91760200
O	4.09517900	-2.56552900	-0.80478400
O	5.21504900	-0.70133400	-1.36171600
C	6.31781800	-1.53980800	-1.69258800
H	6.04346100	-2.23923900	-2.48602300
H	7.10691800	-0.86864400	-2.02882900
H	6.64253000	-2.11019900	-0.81914800
N	-1.08393500	-1.44451800	1.55715700
N	0.36085900	-2.69153500	0.27135100
N	-1.92526600	-2.86044500	-0.12058600
C	-0.89014200	-2.32482600	0.57700200
C	1.41510400	-2.61578700	1.28928000
H	1.62805200	-1.58350600	1.56997300
H	2.32360700	-3.04120700	0.86029800
H	1.10886500	-3.18660200	2.17108400
C	0.75189100	-2.99370000	-1.10653800
H	0.03909300	-2.53035900	-1.79087600
H	0.80630200	-4.07420200	-1.28072200
H	1.73425000	-2.55590500	-1.27871100
C	-1.88590100	-4.22184800	-0.61974800
H	-1.10951000	-4.78342800	-0.09865300
H	-1.69279600	-4.25919700	-1.69932700
H	-2.85515300	-4.69305600	-0.42196300
C	-3.03705200	-2.04704300	-0.58006400
H	-3.99274600	-2.40768100	-0.18289000
H	-3.08290900	-2.10200900	-1.67417700
H	-2.87029200	-1.00760400	-0.29095900
C	-2.10681500	-1.37420200	2.62293200

C	-2.87184000	-0.05641600	2.47597300
C	-3.03929300	-2.58330000	2.63698800
C	-1.30699400	-1.37133300	3.93428600
H	-3.50251700	0.11343400	3.35483200
H	-2.16258700	0.77093000	2.36659500
H	-3.50597400	-0.06542200	1.58524000
H	-2.47235100	-3.52075500	2.64063000
H	-3.63087200	-2.54438100	3.55667200
H	-3.73624500	-2.59475500	1.79885300
H	-1.96990700	-1.19231800	4.78648100
H	-0.80205200	-2.33274100	4.07675000
H	-0.54916600	-0.58364200	3.91283000
H	-0.35587500	-0.71283400	1.66279400

TS2 E = -1725.422828

C	1.59978500	-2.43967700	-1.81077500
C	1.53280800	-3.50128200	-0.70820700
C	2.21614400	-3.05989300	0.60348100
C	3.02584400	2.53111400	1.40014600
C	3.16531100	3.25877800	0.03470500
C	2.33125100	2.57882100	-1.07558200
B	1.43096300	-0.83284700	-0.04491000
B	1.41773300	1.01172800	0.50193500
O	0.98905600	-1.24076400	-1.29739400
O	2.25504200	-1.62962000	0.69428400
O	2.65093500	1.17511400	1.20319100
O	1.16492600	1.99797200	-0.51006200
C	3.02426800	-2.11287000	-2.26606200

H	3.54150700	-3.01954500	-2.59818900
H	2.98796100	-1.40824000	-3.10296700
H	3.60029500	-1.65275900	-1.46078900
C	0.78365500	-2.87801800	-3.02134600
H	0.71373200	-2.05171400	-3.73724100
H	1.26568200	-3.72533400	-3.51935300
H	-0.22700400	-3.18322900	-2.73339800
C	3.65643000	-3.55633200	0.70293400
H	4.24841200	-3.27920100	-0.17243000
H	4.12519100	-3.11788800	1.58810700
H	3.67329900	-4.64709000	0.79939700
C	1.41295800	-3.55092400	1.80625000
H	1.29074700	-4.63945200	1.77128900
H	1.92457200	-3.27853000	2.73363800
H	0.42692900	-3.07348600	1.81294200
H	1.96401300	-4.44607700	-1.06159200
H	0.46747500	-3.68425000	-0.51255000
H	4.21668200	3.28469600	-0.27933200
H	2.84593000	4.30223200	0.15234300
C	1.97505500	3.23135600	2.26941400
H	1.82274600	2.66069700	3.19070400
H	2.29684400	4.24624900	2.52834600
H	1.01977900	3.29721600	1.73769500
C	4.36624900	2.49640100	2.12415700
H	4.76148600	3.50819900	2.26598800
H	4.25360600	2.01748600	3.10140000
H	5.08430600	1.91645300	1.53608100
C	3.15767300	1.50029800	-1.78622500

H	2.51410600	0.94179400	-2.47536100
H	3.97893100	1.95160100	-2.35400500
H	3.58184300	0.80203100	-1.05728700
C	1.84402500	3.60923900	-2.08782500
H	2.68414700	4.16817500	-2.51356100
H	1.30489100	3.11544500	-2.90443100
H	1.16493700	4.31499700	-1.59852200
C	0.25301600	0.26761700	1.08623900
C	-0.59816800	-0.59267500	1.47159300
C	-1.63573700	-0.82461400	2.38802700
O	-2.85530200	-0.60914800	2.22839500
O	-1.20899300	-1.41489100	3.53043400
C	-2.22285900	-1.70000600	4.48123100
H	-2.94961100	-2.41204500	4.07986700
H	-1.70729300	-2.13254300	5.33869000
H	-2.75385500	-0.79129600	4.77618300
N	-3.07247000	0.81651400	-0.08846400
N	-3.23983200	-1.36106800	-0.78723900
N	-2.18550100	0.15127200	-2.18664000
C	-2.81927900	-0.08950200	-1.02163300
C	-4.44276000	-1.65750700	-0.02216900
H	-4.20235400	-1.92589400	1.00930000
H	-4.96718400	-2.48319100	-0.51521200
H	-5.09049500	-0.77931000	-0.01400200
C	-2.29975200	-2.46095300	-0.95443600
H	-1.31411200	-2.06016500	-1.20325100
H	-2.63473100	-3.16680900	-1.72569900
H	-2.20844800	-2.98715900	0.00308200

C	-2.42248200	-0.68697500	-3.34974900
H	-3.38424500	-1.19236200	-3.25651300
H	-1.62980500	-1.43412100	-3.47522600
H	-2.43665100	-0.04559400	-4.23655300
C	-1.01391800	1.01303900	-2.28325600
H	-1.15951600	1.77452800	-3.05720100
H	-0.14211600	0.39750100	-2.52676900
H	-0.80440700	1.47937500	-1.32606900
C	-3.27027200	2.27979600	-0.08801600
C	-3.57398700	2.82489300	-1.48098300
C	-4.49890600	2.49446500	0.80978400
C	-2.06042900	2.96925300	0.55647300
H	-3.92948400	3.85464300	-1.37836100
H	-2.69616800	2.84299000	-2.12663100
H	-4.36301500	2.24047500	-1.96627000
H	-4.33837700	2.03982100	1.79328500
H	-4.68173800	3.56388300	0.95007900
H	-5.38966600	2.04358800	0.35945700
H	-2.27956500	4.03395300	0.69139800
H	-1.86121000	2.52907600	1.53954300
H	-1.14517400	2.87683400	-0.03469300
H	-3.10352400	0.37957000	0.85611900

III' E = -1725.484634

C	3.54518600	1.12463700	-1.07066400
C	4.53272700	0.42047900	-0.13176900
C	4.17922800	0.52356000	1.36203600
C	-2.87122800	2.63793000	0.40753500

C	-2.91335600	2.57016300	-1.13354400
C	-1.52626200	2.60729000	-1.78872300
B	1.82828500	0.57186000	0.55016300
B	-0.71611400	1.44504000	0.15983300
O	2.22417500	0.67834100	-0.77493600
O	2.76701800	0.54777100	1.55529500
O	-1.63853200	2.12989900	0.91153300
O	-0.72329500	1.56998600	-1.21986300
C	3.55820200	2.65175400	-0.96228300
H	4.57028500	3.05515000	-1.07262500
H	2.92403600	3.07296000	-1.74818400
H	3.15047000	2.97738700	-0.00215800
C	3.83277500	0.71460100	-2.51146400
H	3.07237900	1.13894200	-3.17467800
H	4.81734200	1.07058700	-2.83173600
H	3.80966400	-0.37630500	-2.61022000
C	4.76230900	1.77201700	2.02866600
H	4.43169100	2.69236600	1.54565300
H	4.43825700	1.80237000	3.07265900
H	5.85661600	1.74184600	2.00106500
C	4.71041800	-0.70550300	2.10135300
H	5.80294100	-0.75147800	2.03887100
H	4.41687700	-0.65983900	3.15398700
H	4.30384900	-1.62421200	1.66809000
H	5.55031900	0.79360200	-0.30047800
H	4.53179500	-0.64123700	-0.41683500
H	-3.53834200	3.38192000	-1.52599100
H	-3.38394500	1.62845400	-1.44159900

C	-3.96759400	1.76238600	1.01611700
H	-3.97410000	1.89045500	2.10301700
H	-4.95317300	2.02783400	0.61768500
H	-3.76222500	0.70576700	0.81063700
C	-3.02578100	4.06804600	0.92516700
H	-4.03288300	4.43998600	0.70851800
H	-2.87331500	4.07462100	2.00788900
H	-2.30381900	4.75091900	0.47174100
C	-0.79117300	3.93538700	-1.59165400
H	0.15030500	3.91217800	-2.14921300
H	-1.39042500	4.77887500	-1.95094100
H	-0.55478500	4.09548700	-0.53676900
C	-1.63991500	2.29961900	-3.27756100
H	-2.18532600	3.09294000	-3.79868700
H	-0.63871000	2.21653600	-3.71224200
H	-2.16671600	1.35355900	-3.43668100
C	0.31419000	0.53917900	0.90326300
C	-0.16185900	-0.23176700	1.91476300
C	-1.47767300	-0.43349500	2.35810100
O	-2.27050900	-1.31784400	1.91409300
O	-1.83936600	0.25266000	3.47393900
C	-3.01009400	-0.21433700	4.11867500
H	-2.89222700	-1.24979300	4.45470300
H	-3.15562000	0.44124600	4.97889600
H	-3.87977400	-0.16592000	3.45719500
N	-1.34887300	-2.30137300	-0.37891900
N	0.61012000	-3.01862800	0.59979700
N	0.63263000	-2.38859200	-1.63898400

C	-0.05306800	-2.55829700	-0.47906800
C	-0.09533800	-3.56986400	1.75162100
H	-0.24571700	-2.78380900	2.49847900
H	0.51956000	-4.37341900	2.16942300
H	-1.06007900	-3.97031300	1.44036300
C	1.95397900	-2.54800200	0.91403300
H	2.33667600	-1.93961100	0.09324300
H	2.62467700	-3.39798900	1.08821100
H	1.88605700	-1.91430700	1.80688300
C	1.72868300	-3.25729100	-2.01832700
H	1.75386800	-4.13078000	-1.36519700
H	2.69499900	-2.73895900	-1.96209900
H	1.57705200	-3.59008700	-3.05224900
C	0.42160800	-1.22034900	-2.48274900
H	-0.07273600	-1.48418600	-3.42687800
H	1.39656800	-0.77565000	-2.70187700
H	-0.15408400	-0.46762000	-1.94251100
C	-2.44612200	-2.53868000	-1.33723900
C	-2.04836400	-3.50644000	-2.45104200
C	-3.56375700	-3.17860700	-0.49815500
C	-2.95200800	-1.20560000	-1.89366200
H	-2.94609200	-3.77349600	-3.01712100
H	-1.32703500	-3.08033000	-3.15065500
H	-1.62711900	-4.42658000	-2.03074600
H	-3.81188000	-2.54041400	0.35569200
H	-4.45988900	-3.32132200	-1.11031600
H	-3.24350700	-4.15468800	-0.11811800
H	-3.85535400	-1.36265300	-2.49302500

H	-3.19556500	-0.53838200	-1.06072600
H	-2.20036000	-0.71433200	-2.51470600
H	-1.67967100	-1.95203000	0.56808900

TS3 E = -1725.481699

C	3.67757200	1.05418500	-1.08862900
C	4.58662700	0.24272200	-0.15572400
C	4.23412800	0.33087300	1.33861700
C	-2.71294100	2.82444100	0.62058400
C	-2.90028100	2.73814500	-0.90904900
C	-1.58135800	2.76571900	-1.69444400
B	1.91118800	0.56454200	0.50807100
B	-0.62288800	1.59879500	0.17470300
O	2.31425000	0.74881600	-0.79840800
O	2.82000100	0.40792100	1.52265700
O	-1.43029500	2.32979700	1.00586300
O	-0.73439500	1.72437300	-1.19378800
C	3.84943900	2.57079400	-0.97215800
H	4.90058900	2.86304200	-1.06692500
H	3.27584700	3.06085500	-1.76461900
H	3.46655700	2.93706100	-0.01708400
C	3.92191900	0.62573700	-2.53217000
H	3.21255000	1.13347700	-3.19284400
H	4.93973400	0.87912700	-2.84621200
H	3.78281700	-0.45525000	-2.63976800
C	4.86375800	1.53485300	2.04237600
H	4.54781500	2.48289200	1.60602700
H	4.56183100	1.53128000	3.09349500

H	5.95601800	1.47690200	1.99146700
C	4.70313000	-0.93971800	2.04805200
H	5.79282200	-1.03269500	1.99067900
H	4.40543400	-0.90804000	3.10002000
H	4.25724800	-1.82649200	1.58813000
H	5.63450300	0.52802200	-0.30792800
H	4.49552200	-0.80782900	-0.46515800
H	-3.55950300	3.54500300	-1.25196200
H	-3.39575000	1.79113400	-1.15791700
C	-3.73405200	1.94099000	1.33980100
H	-3.60965900	2.04301700	2.42228500
H	-4.75793100	2.21647800	1.06402400
H	-3.56503600	0.88789100	1.08726700
C	-2.82803100	4.25717200	1.13876000
H	-3.85280800	4.62183800	1.01299600
H	-2.57646900	4.27559000	2.20281700
H	-2.15540400	4.93937900	0.61357000
C	-0.82325300	4.08951200	-1.57448400
H	0.06919900	4.05378600	-2.20707400
H	-1.44552800	4.93207100	-1.89424300
H	-0.50103100	4.26102100	-0.54449800
C	-1.83520400	2.44801800	-3.16329000
H	-2.42084500	3.24308200	-3.63589600
H	-0.87985500	2.35456800	-3.68901200
H	-2.38160200	1.50557100	-3.26633000
C	0.38573200	0.59557700	0.83227100
C	-0.19965500	-0.22371900	1.71677100
C	-1.40413600	-0.54366300	2.26692300

O	-2.22021900	-1.47007200	1.83765200
O	-1.72581700	0.03465000	3.45208200
C	-2.75561500	-0.59824200	4.19131000
H	-2.50140300	-1.63766800	4.42297500
H	-2.84611200	-0.02459500	5.11492100
H	-3.70390400	-0.58516500	3.64667500
N	-1.51048700	-2.36668300	-0.35877600
N	0.51859300	-3.10275400	0.43457700
N	0.40120900	-2.36332300	-1.76587200
C	-0.24208100	-2.59248600	-0.57515400
C	-0.09869100	-3.71310000	1.60059300
H	-0.23296300	-2.97249300	2.39715600
H	0.55672600	-4.51517100	1.95672900
H	-1.07022700	-4.12519400	1.32690200
C	1.86742700	-2.61364300	0.67290900
H	2.16324900	-1.93114100	-0.12674400
H	2.57998700	-3.44742200	0.72153900
H	1.87886900	-2.05528000	1.61660300
C	1.44583900	-3.23732300	-2.25289300
H	1.45967100	-4.15843300	-1.66811000
H	2.43797500	-2.76609800	-2.19657000
H	1.24759800	-3.48679400	-3.30291700
C	0.24546800	-1.10253500	-2.47044300
H	-0.21296300	-1.23797900	-3.45929100
H	1.23032500	-0.63936200	-2.59740300
H	-0.35030500	-0.41295700	-1.87332400
C	-2.62967000	-2.43529400	-1.31055300
C	-2.31513200	-3.20826000	-2.59405400

C	-3.73513800	-3.19143500	-0.55247500
C	-3.13566200	-1.02109800	-1.61415400
H	-3.25269500	-3.40001200	-3.12610800
H	-1.65321700	-2.66584800	-3.27050300
H	-1.85555500	-4.17422200	-2.35714100
H	-3.94826500	-2.69598400	0.39965300
H	-4.65440200	-3.22396800	-1.14667900
H	-3.41774600	-4.21904700	-0.34476400
H	-4.04972400	-1.05881200	-2.21726000
H	-3.36120800	-0.51062100	-0.67166200
H	-2.38761100	-0.43193100	-2.14945100
H	-1.84889400	-1.93714800	0.79187300

3aa+BTMG E = -1725.489042

C	3.56976500	-0.31128800	-1.19055000
C	4.06506800	-1.61360800	-0.54666300
C	3.78739100	-1.73672400	0.96118200
C	-1.35228300	3.58558100	0.83600800
C	-0.61337500	4.15781100	-0.38036300
C	0.86626400	3.73886400	-0.47736300
B	1.77418900	-0.40316200	0.42420900
B	0.06054900	1.66572500	0.59626600
O	2.19032300	-0.13096800	-0.86013300
O	2.54645900	-1.11009100	1.30148100
O	-1.19457300	2.16342200	0.82110900
O	1.07723300	2.45711200	0.12317700
C	4.32304400	0.94109700	-0.73486200
H	5.40654400	0.80931800	-0.82399200

H	4.02121200	1.79129400	-1.35316000
H	4.07700500	1.19016600	0.30008900
C	3.63900400	-0.43174100	-2.70839200
H	3.17589300	0.44690300	-3.16848400
H	4.67824000	-0.49948800	-3.04582900
H	3.10392100	-1.32467800	-3.04723000
C	4.87807000	-1.11068400	1.83126200
H	5.02790800	-0.05260300	1.61342300
H	4.59350400	-1.20331800	2.88316200
H	5.82859000	-1.63225000	1.67915600
C	3.64859400	-3.21114900	1.33911600
H	4.57846900	-3.75079700	1.13098200
H	3.41807100	-3.30191100	2.40438400
H	2.84055100	-3.67904900	0.76920900
H	5.13664100	-1.74593800	-0.73820400
H	3.54510300	-2.43412300	-1.05950900
H	-0.69103300	5.25152800	-0.39504400
H	-1.14398800	3.78561400	-1.26724200
C	-2.84578500	3.86373900	0.71834000
H	-3.37894600	3.34693700	1.52156100
H	-3.04371400	4.93771400	0.79616500
H	-3.23376800	3.50336500	-0.23861700
C	-0.83416900	4.10249900	2.18014900
H	-0.86206800	5.19655900	2.22054700
H	-1.46061400	3.70480800	2.98365000
H	0.19058200	3.76833000	2.36183300
C	1.80961700	4.73016100	0.20267600
H	2.82973700	4.33535100	0.17273500

H	1.79130700	5.68950200	-0.32457400
H	1.54040800	4.90711900	1.24545300
C	1.26304400	3.59881800	-1.94710900
H	1.10207600	4.54040400	-2.48281700
H	2.31860500	3.32367600	-2.02915000
H	0.66417400	2.81692300	-2.42455900
C	0.38760800	0.16073100	0.89547700
C	-0.47697600	-0.55033000	1.60200500
C	-1.45861200	-1.00428200	2.36668100
O	-2.55848600	-1.67559100	1.98680400
O	-1.35563600	-0.84663800	3.71698600
C	-1.50860500	-2.05845600	4.43917100
H	-0.76526700	-2.79635900	4.10959100
H	-1.33662700	-1.81242700	5.48800000
H	-2.51155700	-2.47323900	4.31122800
N	-2.70253600	-1.55063100	-0.64311900
N	-0.97677800	-3.05294100	-0.87057500
N	-1.03411900	-1.22996000	-2.32629500
C	-1.62502100	-1.89347400	-1.26535800
C	-1.68239000	-3.99759300	-0.02274100
H	-1.62335100	-3.72181300	1.03835900
H	-1.23356500	-4.98689100	-0.16120700
H	-2.73361900	-4.02762600	-0.31104100
C	0.45911100	-3.04255300	-0.65152900
H	0.91911800	-2.21561900	-1.19362400
H	0.90296500	-3.98651000	-0.99319700
H	0.67644600	-2.91275700	0.41991600
C	-0.33774400	-1.92490400	-3.38541800

H	-0.53461100	-2.99534900	-3.31479800
H	0.74835400	-1.75634900	-3.33853400
H	-0.69372800	-1.55958900	-4.35764900
C	-0.81424500	0.20095200	-2.28110800
H	-1.23938700	0.70132500	-3.16285000
H	0.26508100	0.40722500	-2.23663400
H	-1.27593600	0.60636000	-1.38127700
C	-3.83640800	-0.76242300	-1.13869900
C	-3.96765600	-0.72367500	-2.66582400
C	-5.06836700	-1.48692200	-0.56787800
C	-3.81140800	0.65655100	-0.55314000
H	-4.94066600	-0.29571500	-2.93060800
H	-3.19566500	-0.11673800	-3.14249200
H	-3.91573400	-1.73621100	-3.08132900
H	-5.00025600	-1.53461900	0.52365700
H	-5.99113000	-0.96395100	-0.84104600
H	-5.11784300	-2.51035100	-0.95466900
H	-4.79410400	1.12862800	-0.66813600
H	-3.55602600	0.62512600	0.51112900
H	-3.07674400	1.29272200	-1.05173500
H	-2.63399500	-1.67868800	0.96674600

TS1_DBU E = -1667.717728

C	2.20088200	-3.47049400	-0.68104700
C	2.95733800	-2.33697700	-1.38668600
C	2.10168100	-1.41937200	-2.27277300
C	-3.55846300	-1.83596500	0.16706600
C	-3.51664800	-0.91506300	1.39936200

C	-2.28255500	-1.06564400	2.31003700
B	0.33869100	-1.82689100	-0.62090800
B	-1.15177700	-1.44450800	0.14941900
O	0.94180800	-2.99712800	-0.20812300
O	0.93028800	-1.01790200	-1.56696500
O	-2.30393900	-1.84000500	-0.50695800
O	-1.11411700	-1.38163200	1.55176400
C	1.95580900	-4.69560900	-1.56284000
H	2.90506100	-5.11230000	-1.91589500
H	1.43568900	-5.45894400	-0.97719800
H	1.33621500	-4.46191100	-2.42884600
C	2.98510000	-3.90712800	0.55677700
H	2.44247100	-4.69823800	1.08163800
H	3.97669900	-4.28108800	0.28019400
H	3.10738900	-3.06298200	1.24387000
C	1.65936400	-2.04988500	-3.59558300
H	0.90058200	-2.81655000	-3.43217700
H	1.20968600	-1.27993000	-4.22925000
H	2.50675300	-2.49421500	-4.12866700
C	2.89220300	-0.14569400	-2.56743200
H	3.77227100	-0.36812000	-3.18034800
H	2.25730600	0.56556600	-3.10432700
H	3.22982700	0.31993100	-1.63365300
H	3.79679800	-2.74340100	-1.96398100
H	3.38899900	-1.69730200	-0.60351700
H	-4.42756500	-1.06264300	1.99335500
H	-3.53435300	0.11384000	1.02555000
C	-4.57970700	-1.27757700	-0.82256900

H	-4.59305600	-1.89580900	-1.72547500
H	-5.58462600	-1.27156800	-0.38492700
H	-4.30441200	-0.25569600	-1.10106700
C	-3.89514000	-3.29133900	0.50184900
H	-4.81336800	-3.36457400	1.09520500
H	-4.03357700	-3.85308800	-0.42739400
H	-3.07639600	-3.76219700	1.05068800
C	-2.44930200	-2.15661200	3.36879900
H	-1.53155400	-2.22712800	3.96195100
H	-3.28043000	-1.91578400	4.04041000
H	-2.63653800	-3.13380600	2.92109400
C	-2.02027200	0.27030600	3.01091900
H	-2.90382500	0.59526400	3.57170200
H	-1.18646900	0.17104400	3.71579700
H	-1.77645800	1.03338500	2.26498200
C	-1.32784200	0.78044500	-0.31261200
C	-1.99350100	1.71618000	-0.75802700
C	-2.74964400	2.80441600	-1.30962800
O	-2.29846300	3.86223600	-1.70446300
O	-4.07336500	2.53297700	-1.34727400
C	-4.87493900	3.57191700	-1.89510600
H	-4.58483000	3.77975900	-2.92813500
H	-5.90085800	3.20761600	-1.85252700
H	-4.76902800	4.49038100	-1.31207400
N	1.19809800	0.64554200	0.93894100
H	0.23892900	0.51773600	0.48348800
N	3.09461600	1.98297200	1.02681400
C	1.92356700	1.62889500	0.47206900

C	1.38596200	2.41697200	-0.68631800
H	0.64067800	1.79943000	-1.18929000
H	2.19598000	2.61843900	-1.39590900
C	0.75416000	3.73359400	-0.20009800
H	0.01665400	4.05239500	-0.94333900
H	0.18182900	3.53293900	0.71462100
C	1.78974400	4.83390400	0.03367100
H	2.27172800	5.07240800	-0.92513000
H	1.28199600	5.74810700	0.35893500
C	2.88557500	4.49005800	1.04969000
H	3.56316200	5.34670700	1.14135300
H	2.44788500	4.32650200	2.04362600
C	3.72948500	3.26229000	0.68415300
H	3.98546400	3.27338900	-0.38122500
H	4.67289400	3.28035900	1.23508700
C	3.56651800	1.29885300	2.23272600
H	3.19587200	1.82157300	3.12572800
H	4.65861600	1.35442700	2.24037900
C	3.10046500	-0.14988400	2.22214500
H	3.58574900	-0.67136600	1.38926100
H	3.40087200	-0.64639200	3.14838900
C	1.59074100	-0.20845200	2.05564200
H	1.23340500	-1.21901100	1.84359800
H	1.07513400	0.12907400	2.96165000

TS2_DBU E = -1667.730020

C	-2.96604800	0.27946500	1.89953800
C	-3.91436200	-0.37373500	0.88496800

C	-3.91864600	0.30252500	-0.49904200
C	1.00879100	2.98405800	-1.96236300
C	1.66882200	3.57693700	-0.68076400
C	1.18873300	2.88268800	0.60724900
B	-1.54366900	0.57786800	-0.00993200
B	0.16321600	1.13340200	-0.67602000
O	-1.64509100	0.27911300	1.33544600
O	-2.63542400	0.88750200	-0.76615000
O	-0.09521400	2.15575300	-1.63382700
O	1.09860300	1.48265300	0.36106400
C	-3.32797200	1.72074300	2.26140400
H	-4.36807900	1.79448500	2.59677700
H	-2.67752900	2.06779100	3.07101700
H	-3.18123500	2.38389600	1.40562700
C	-2.90141700	-0.56770800	3.16591100
H	-2.12002800	-0.18045500	3.82853400
H	-3.85622600	-0.53604100	3.70051400
H	-2.67449500	-1.61104700	2.92540700
C	-4.96484400	1.40836100	-0.61982000
H	-4.87000400	2.16004800	0.16576900
H	-4.84714200	1.90592500	-1.58650300
H	-5.97121400	0.97959900	-0.56731400
C	-4.15566300	-0.74332000	-1.58750300
H	-5.09289000	-1.28156300	-1.40649900
H	-4.21022500	-0.25681300	-2.56565300
H	-3.32728300	-1.45842200	-1.60729700
H	-4.93360800	-0.41510800	1.28780600
H	-3.56825900	-1.40909200	0.76308700

H	1.46626900	4.65278000	-0.60222500
H	2.75905400	3.46593100	-0.75361800
C	2.02579300	2.15144800	-2.74994700
H	1.54567600	1.72396100	-3.63535600
H	2.88304700	2.75822900	-3.06270500
H	2.39353000	1.32567800	-2.12963000
C	0.45069000	4.09917800	-2.83901300
H	1.24169600	4.79682400	-3.13505500
H	-0.00707100	3.67551100	-3.73763600
H	-0.31779400	4.65096200	-2.28842500
C	-0.16564000	3.42948400	1.07447900
H	-0.53094900	2.81470900	1.90438500
H	-0.06580700	4.46546500	1.41674000
H	-0.90048200	3.39755500	0.26442700
C	2.21863000	3.06605800	1.71888400
H	2.42564500	4.12860200	1.88407600
H	1.85106500	2.63755600	2.65791300
H	3.15778400	2.56888400	1.45054600
C	-0.11563000	-0.31556800	-0.94201300
C	-0.62168700	-1.47041700	-1.05691100
C	-0.71667500	-2.80962200	-1.42352200
O	-0.30128700	-3.80074400	-0.77793100
O	-1.38760200	-3.00787100	-2.58685400
C	-1.54015500	-4.36653300	-2.96890800
H	-2.09258600	-4.92789900	-2.21100900
H	-2.09630100	-4.34559100	-3.90615800
H	-0.56820600	-4.84508900	-3.11575100
N	1.06286400	-2.69999700	1.23889200

H	0.58030800	-3.27805700	0.51051900
N	2.75691600	-1.16568400	1.59412100
C	2.20915100	-2.15579800	0.89518700
C	2.88606600	-2.71956300	-0.32737500
H	2.27130100	-3.55798700	-0.66459200
H	3.86432100	-3.12444500	-0.03440000
C	3.05140700	-1.70732600	-1.47569000
H	3.20164000	-2.28388000	-2.39431100
H	2.11449800	-1.15148600	-1.59832900
C	4.22131600	-0.74194200	-1.29843000
H	5.15725400	-1.31593000	-1.22628900
H	4.30537900	-0.12171300	-2.19771300
C	4.09561700	0.16584900	-0.07672400
H	4.95178800	0.85101000	-0.04896300
H	3.18210600	0.77085000	-0.13260800
C	4.06711000	-0.60161900	1.24561100
H	4.81276200	-1.40783700	1.24226400
H	4.32726100	0.06640400	2.06940600
C	1.96971400	-0.50133900	2.64907200
H	1.37442900	0.28911500	2.17700500
H	2.67701900	-0.04963300	3.34918400
C	1.07935400	-1.51214200	3.35784300
H	1.69305600	-2.23759700	3.90332900
H	0.44237900	-0.99360600	4.07920500
C	0.21916900	-2.21515000	2.32251200
H	-0.30128700	-3.07679700	2.75016200
H	-0.51837000	-1.52360300	1.90122900

TS1_Na_2CO_3 E = -1794.252176

C	-3.10154100	1.82352000	-0.28742000
C	-2.23490900	2.99953400	0.18635300
C	-1.40641900	2.72059700	1.44392100
C	-0.06887900	-3.15206000	1.91866200
C	0.56002600	-3.62929500	0.59825900
C	-0.16955700	-3.20746700	-0.68949400
B	-1.20220700	0.44224900	0.60685400
B	-0.54271600	-1.14702000	0.64790000
O	-2.44818600	0.56778000	0.00144500
O	-0.61379700	1.54219700	1.20897100
O	-0.33901300	-1.74782000	1.85885100
O	-0.76135900	-1.90275400	-0.50892900
C	-4.48258400	1.78436100	0.36273600
H	-5.05455900	2.67341000	0.07908200
H	-5.02460600	0.89966900	0.01496900
H	-4.42941400	1.74216700	1.45124300
C	-3.26009300	1.90492400	-1.80686700
H	-3.90726200	1.09439900	-2.16895800
H	-3.73767100	2.84796900	-2.09096800
H	-2.28014600	1.85551700	-2.29586400
C	-2.22375100	2.47945400	2.71276600
H	-2.77000100	1.53532000	2.65378000
H	-1.54953300	2.41631600	3.57162000
H	-2.93719200	3.29200000	2.88373600
C	-0.42732300	3.86696600	1.67861900
H	-0.96161900	4.77323000	1.97916000
H	0.27722700	3.59872800	2.47185900

H	0.13602500	4.10951900	0.76877300
H	-2.86518200	3.88378600	0.33862500
H	-1.52423500	3.23924600	-0.61553400
H	0.66342100	-4.72102500	0.61786900
H	1.56611200	-3.20116600	0.55879800
C	0.94510900	-3.34259300	3.04263100
H	0.53323800	-2.96307400	3.98239900
H	1.19317300	-4.40193100	3.16841100
H	1.85774100	-2.78547300	2.81284200
C	-1.38317100	-3.85139900	2.26949100
H	-1.27401300	-4.94087100	2.24432200
H	-1.69640400	-3.55482100	3.27527800
H	-2.17655700	-3.55870000	1.57719500
C	-1.29167600	-4.16119500	-1.09577800
H	-1.76086800	-3.80332900	-2.02045300
H	-0.88428300	-5.15724000	-1.29523300
H	-2.06303600	-4.25120700	-0.32909500
C	0.83233900	-3.08775200	-1.83496900
H	1.28951500	-4.06204400	-2.04000300
H	0.34052400	-2.72734600	-2.74545700
H	1.61580100	-2.37512000	-1.56902200
C	1.92068400	-0.58195000	0.26627100
C	2.95919800	0.10180600	0.24382800
C	3.88915700	1.19112900	0.21758100
O	3.52414300	2.36213300	0.08952800
O	5.17181100	0.85849900	0.33155400
C	6.09556100	1.94597700	0.28694900
H	5.89815600	2.64825500	1.09966200

H	7.08034500	1.49579300	0.39833400
H	6.01745400	2.47162500	-0.66718800
Na	-1.84767700	-0.58185000	-1.94271900
Na	1.25052500	1.88369500	-0.10181000
O	-0.40339200	-0.17931700	-3.54990700
O	1.68571900	0.02557100	-2.82748500
O	-0.00152000	1.02064200	-1.70699000
C	0.36662300	0.30497900	-2.70141600
H	2.09310800	0.09729500	-1.94317000

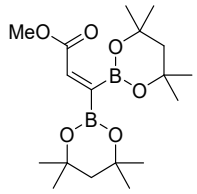
TS2_Na_2CO_3 E = -1794.236668

C	-0.12676300	-2.21747900	1.57908900
C	0.82590500	-2.98850800	0.65899200
C	0.54313400	-2.88029200	-0.84646900
C	-3.70486200	0.34068300	-1.18927900
C	-4.14939800	1.52652500	-0.32180400
C	-3.19374000	1.86063000	0.84476600
B	-0.23006300	-0.61654200	-0.33128600
B	-1.44425700	0.99943300	-0.74824900
O	-0.44000600	-0.93271700	0.98216800
O	0.35946600	-1.49136800	-1.21735700
O	-2.40752400	0.63500600	-1.69439800
O	-1.86122000	1.42530900	0.56607700
C	-1.45134300	-2.92743400	1.85335800
H	-1.26430600	-3.86729200	2.38282100
H	-2.07754900	-2.29299800	2.48889500
H	-2.01227000	-3.15106500	0.94490700
C	0.56813900	-1.92586300	2.90418000

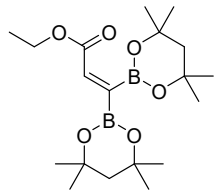
H	-0.11370500	-1.38854700	3.57409400
H	0.85479400	-2.86303100	3.39263700
H	1.45640800	-1.31112800	2.74073500
C	-0.69313800	-3.63400100	-1.33264900
H	-1.60724100	-3.14958600	-0.98569400
H	-0.71820200	-3.63432900	-2.42667000
H	-0.68462000	-4.67020800	-0.97981600
C	1.77022300	-3.37449800	-1.61013600
H	1.88576700	-4.45554600	-1.48550000
H	1.65468100	-3.17172600	-2.68174900
H	2.68543800	-2.90675800	-1.22750700
H	0.83270700	-4.04660800	0.94746400
H	1.82830300	-2.57955600	0.82109900
H	-5.15896300	1.35677200	0.07176300
H	-4.20554400	2.39166400	-0.99358300
C	-4.61699600	0.22555900	-2.40544500
H	-4.25870600	-0.57449900	-3.05997100
H	-5.64553800	0.00135300	-2.10456500
H	-4.60838000	1.16067300	-2.97224200
C	-3.67424100	-0.98796800	-0.42988500
H	-4.64735000	-1.21311100	0.02020200
H	-3.42278000	-1.79300700	-1.12919900
H	-2.91701900	-0.96574600	0.35929600
C	-3.62462900	1.18300100	2.14665300
H	-2.88844100	1.38975700	2.93193600
H	-4.59377500	1.56969500	2.47835500
H	-3.70497100	0.09958500	2.03108800
C	-3.14857300	3.37533900	1.05061200

H	-4.15187100	3.77589800	1.23123000
H	-2.51736300	3.62611500	1.91042800
H	-2.73350900	3.85958400	0.16148300
C	-0.01190600	1.27079500	-1.05519100
C	1.20052100	1.63470400	-1.10278400
C	2.53436700	1.95511500	-1.28157100
O	3.24713900	1.50985800	-2.21065900
O	3.04648300	2.75866100	-0.31843700
C	4.43630300	3.03470400	-0.43195200
H	4.62759900	3.69817800	-1.28014100
H	4.71581000	3.51617300	0.50412400
H	5.00663500	2.11405100	-0.56306400
Na	0.24668000	1.30361900	1.56333900
Na	2.40384200	-0.52489500	-1.80785900
O	2.27253800	0.67199700	1.94790400
O	4.42548600	0.51670000	1.48393000
O	2.97191900	-0.68783000	0.28886100
C	3.13602800	0.15087700	1.21990100
H	4.97136900	0.01856400	0.85750700

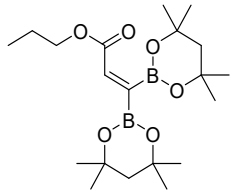
7. Characterization data



Methyl 3,3-bis(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)propanoate (**3aa**). 94% yield. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.63 (s, 1H), 3.70 (s, 3H), 1.91 (s, 2H), 1.79 (s, 2H), 1.39 (s, 12H), 1.29 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.86, 136.61, 70.89, 70.81, 51.47, 49.04, 48.62, 31.75, 31.58. A signal for the sp^2-carbon directly attached to the boron atom was not observed. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 367.2463; Found 367.2468.

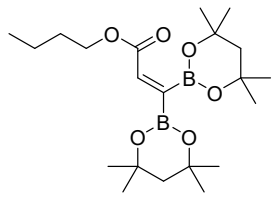


Ethyl 3,3-bis(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)acrylate (**3ba**). 93% yield. Colorless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.65 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.92 (s, 2H), 1.80 (s, 2H), 1.40 (s, 12H), 1.31 (s, 12H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.49, 137.23, 70.91, 70.82, 60.26, 49.08, 48.74, 31.80, 31.62, 14.52. A signal for the sp^2-carbon directly attached to the boron atom was not observed. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 381.2620; Found 381.2620.

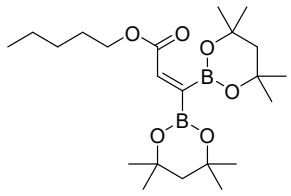


Propyl 3,3-bis(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)acrylate (**3ca**). 93% yield. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.66 (s, 1H), 4.07 (t, *J* = 6.8 Hz, 2H), 1.92

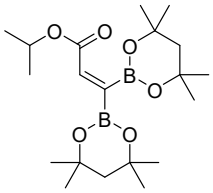
(s, 2H), 1.80 (s, 2H), 1.70 – 1.63 (m, 2H), 1.40 (s, 12H), 1.31 (s, 12H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.65, 137.22, 70.90, 70.81, 65.99, 49.08, 48.75, 31.80, 31.61, 22.22, 10.57. A signal for the sp^2-carbon directly attached to the boron atom was not observed. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 395.2776; Found 395.2783.



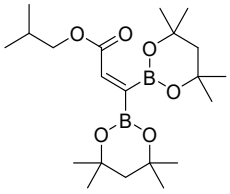
Butyl 3,3-bis(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)acrylate (**3-da**). 87% yield. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.65 (s, 1H), 4.11 (t, *J* = 6.7 Hz, 2H), 1.92 (s, 2H), 1.80 (s, 2H), 1.65 – 1.57 (m, 13H), 1.40 (s, 12H), 1.40 – 1.34 (m, 2H), 1.31 (s, 12H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.66, 137.25, 70.90, 70.81, 64.22, 49.08, 48.75, 31.81, 31.62, 30.96, 19.27, 13.86. A signal for the sp^2-carbon directly attached to the boron atom was not observed. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 409.2933; Found 409.2940.



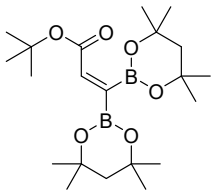
Pentyl 3,3-bis(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)acrylate (**3-ea**). 88% yield. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.65 (s, 1H), 4.10 (t, *J* = 6.8 Hz, 2H), 1.92 (s, 2H), 1.80 (s, 2H), 1.66 – 1.60 (m, 2H), 1.40 (s, 12H), 1.35 – 1.27 (m, 16H), 0.92 – 0.84 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.63, 137.25, 70.88, 70.79, 64.50, 49.08, 48.74, 31.80, 31.61, 28.61, 28.19, 22.48, 14.08. A signal for the sp^2-carbon directly attached to the boron atom was not observed. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 423.3089; Found 423.3088.



Isopropyl 3,3-bis(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)acrylate (**3-fa**). 91% yield. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.04 (hept, *J* = 6.3 Hz, 1H), 1.92 (s, 2H), 1.79 (s, 2H), 1.40 (s, 12H), 1.30 (s, 12H), 1.23 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.00, 137.83, 70.85, 70.77, 67.43, 49.01, 48.73, 31.80, 31.60, 22.09. A signal for the sp^2-carbon directly attached to the boron atom was not observed. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 395.2776; Found 395.2786.

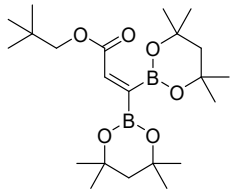


Isobutyl 3,3-bis(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)acrylate (**3-ga**). 87% yield. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.66 (s, 1H), 3.89 (d, *J* = 6.8 Hz, 2H), 1.97 – 1.90 (m, 1H), 1.92 (s, 2H), 1.80 (s, 2H), 1.40 (s, 12H), 1.31 (s, 12H), 0.92 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.71, 137.19, 70.90, 70.80, 70.60, 49.07, 48.76, 31.81, 31.61, 27.89, 19.31. A signal for the sp^2-carbon directly attached to the boron atom was not observed. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 409.2933; Found 409.2941.

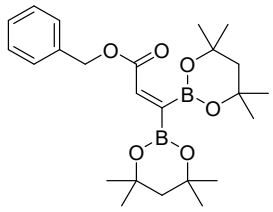


tert-Butyl 3,3-bis(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)acrylate (**3-ha**). 86% yield. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.58 (s, 1H), 1.91 (s, 2H), 1.78 (s, 2H), 1.44 (s, 9H), 1.39 (s, 12H), 1.29 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.87, 139.61,

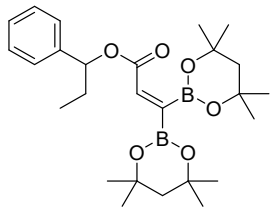
79.87, 70.75, 70.65, 48.94, 48.76, 31.80, 31.55, 28.25. A signal for the sp^2-carbon directly attached to the boron atom was not observed. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+Na]^+$ 431.2752; Found 431.2756.



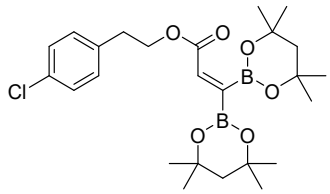
Neopentyl 3,3-bis(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)acrylate (**3-ia**). 90% yield. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.67 (s, 1H), 3.80 (s, 2H), 1.92 (s, 2H), 1.80 (s, 2H), 1.39 (s, 12H), 1.32 (s, 12H), 0.93 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.93, 137.15, 73.86, 70.91, 70.78, 49.04, 48.78, 31.81, 31.59, 31.46, 26.65. A signal for the sp^2-carbon directly attached to the boron atom was not observed. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 423.3089; Found 423.3098.



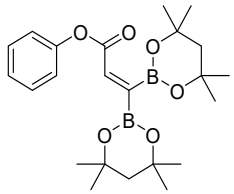
Benzyl 3,3-bis(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)acrylate (**3-ja**). 92% yield. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 4H), 7.30 – 7.27 (m, 1H), 6.71 (s, 1H), 5.17 (s, 2H), 1.86 (s, 2H), 1.80 (s, 2H), 1.37 (s, 12H), 1.30 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.26, 136.72, 136.30, 128.53, 128.28, 128.09, 70.92, 70.84, 66.16, 48.95, 48.69, 31.75, 31.54. A signal for the sp^2-carbon directly attached to the boron atom was not observed. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 443.2776; Found 443.2779.



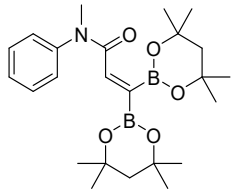
1-Phenylpropyl 3,3-bis(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)acrylate (**3-ka**). 78% yield. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.31 (m, 2H), 7.31 – 7.27 (m, 2H), 7.23 (td, *J* = 7.2 Hz, *J* = 1.4 Hz, 1H), 6.72 (s, 1H), 5.76 (t, *J* = 6.6 Hz, 1H), 1.97 – 1.90 (m, 1H), 1.90 (s, 2H), 1.88 – 1.81 (m, 1H), 1.80 (s, 2H), 1.38 (s, 6H), 1.34 (s, 6H), 1.31 (s, 12H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.81, 140.84, 137.46, 128.28, 127.58, 126.75, 70.92, 70.81, 49.00, 48.75, 31.81, 31.59, 31.50, 29.46, 10.12. A signal for the sp^2-carbon directly attached to the boron atom was not observed. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 471.3089; Found 471.3092.



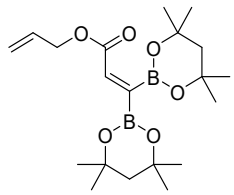
4-Chlorophenethyl 3,3-bis(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)acrylate (**3-la**). 93% yield. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (dt, *J* = 9.0 Hz, *J* = 2.5 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.63 (s, 1H), 4.30 (t, *J* = 7.1 Hz, 2H), 2.91 (t, *J* = 7.1 Hz, 2H), 1.92 (s, 2H), 1.81 (s, 2H), 1.40 (s, 12H), 1.31 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.39, 136.64, 132.38, 130.37, 128.68, 70.95, 70.83, 64.54, 49.10, 48.73, 34.60, 31.79, 31.58. A signal for the sp^2-carbon directly attached to the boron atom was not observed. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 491.2543; Found 491.2548.



Phenyl 3,3-bis(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)acrylate (**3-ma**). 73% yield. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.11 – 7.06 (m, 2H), 6.84 (s, 1H), 1.84 (s, 4H), 1.35 (s, 12H), 1.34 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.48, 150.99, 136.21, 129.47, 125.68, 121.89, 71.12, 71.02, 48.96, 48.77, 31.82, 31.62. A signal for the sp^2-carbon directly attached to the boron atom was not observed. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+Na]^+$ 451.2439; Found 451.2435.

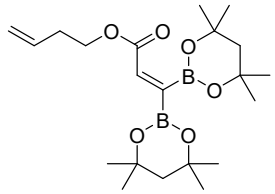


N-Methyl-N-phenyl-3,3-bis(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)acrylamide (**3-na**). 53% yield. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.31 – 7.26 (m, 1H), 7.22 – 7.18 (m, 2H), 6.57 (s, 1H), 3.33 (s, 3H), 1.95 (s, 2H), 1.72 (s, 2H), 1.42 (s, 12H), 1.22 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.25, 143.93, 137.12, 129.25, 127.29, 70.51, 70.28, 49.16, 48.73, 37.84, 31.72, 31.70. A signal for the sp^2-carbon directly attached to the boron atom was not observed. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 442.2936; Found 442.2944.

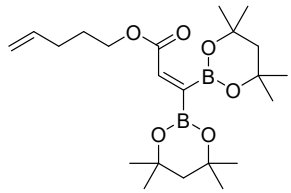


Allyl 3,3-bis(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)acrylate (**3-oa**). 89% yield. Colorless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.67 (s, 1H), 5.92 (ddt, *J* = 17.2 Hz, *J*

= 10.4 Hz, *J* = 5.7 Hz, 1H), 5.31 (dq, *J* = 17.2 Hz, *J* = 1.5 Hz, 1H), 5.20 (dq, *J* = 10.4 Hz, *J* = 1.2 Hz, 1H), 4.63 (dt, *J* = 5.7 Hz, *J* = 1.4 Hz, 2H), 1.92 (s, 2H), 1.80 (s, 2H), 1.40 (s, 12H), 1.31 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.24, 136.81, 132.48, 118.17, 71.22, 71.02, 65.18, 49.01, 48.71, 31.75, 31.51. A signal for the sp^2-carbon directly attached to the boron atom was not observed. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 393.2620; Found 393.2625.

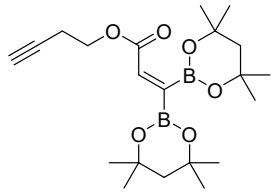


But-3-en-1-yl 3,3-bis(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)acrylate (**3-pa**). 95% yield. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.65 (s, 1H), 5.79 (ddt, *J* = 17.0 Hz, *J* = 10.3 Hz, *J* = 6.7 Hz, 1H), 5.10 (dq, *J* = 17.2 Hz, *J* = 1.6 Hz, 1H), 5.04 (dq, *J* = 10.3 Hz, *J* = 1.2 Hz, 1H), 4.16 (t, *J* = 6.9 Hz, 2H), 2.39 (qt, *J* = 6.8 Hz, *J* = 1.3 Hz, 2H), 1.92 (s, 2H), 1.80 (s, 2H), 1.40 (s,12H), 1.31 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.47, 136.99, 134.29, 117.15, 70.91, 70.81, 63.52, 49.09, 48.74, 33.25, 31.80, 31.61. A signal for the sp^2-carbon directly attached to the boron atom was not observed. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 407.2776; Found 407.2783.

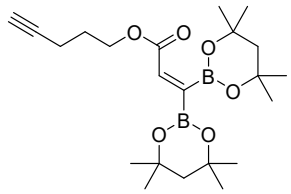


Pent-4-en-1-yl 3,3-bis(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)acrylate (**3-qa**). 93% yield. Colorless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.65 (s, 1H), 5.79 (ddt, *J* = 16.9 Hz, *J* = 10.2 Hz, *J* = 6.6 Hz, 1H), 5.02 (dq, *J* = 17.1 Hz, *J* = 1.6 Hz, 1H), 4.97 (dd, *J* = 10.2 Hz, *J* = 1.5 Hz, 1H), 4.12 (t, *J* = 6.7 Hz, 2H), 2.12 (q, *J* = 6.9 Hz, 2H), 1.92 (s, 2H), 1.80 (s, 2H), 1.73 (d, *J* = 6.7 Hz, 2H), 1.40 (s, 12H), 1.31 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.58, 137.75, 137.09, 115.27, 70.91, 70.82, 63.78, 49.09, 48.75, 31.81, 31.62,

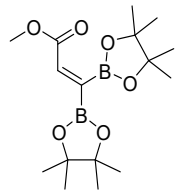
30.16, 28.10. A signal for the sp^2-carbon directly attached to the boron atom was not observed. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 421.2933; Found 421.2940.



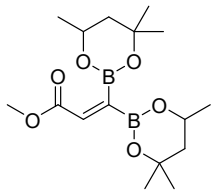
But-3-yn-1-yl 3,3-bis(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)acrylate (**3-ra**). 82% yield. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.66 (s, 1H), 4.22 (t, *J* = 7.0 Hz, 2H), 2.53 (td, *J* = 7.0 Hz, *J* = 2.7 Hz, 2H), 1.98 (t, *J* = 2.7 Hz, 1H), 1.92 (s, 2H), 1.80 (s, 2H), 1.40 (s, 12H), 1.31 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.18, 136.48, 80.32, 70.97, 70.87, 69.99, 62.14, 49.09, 48.73, 31.79, 31.59, 19.14. A signal for the sp^2-carbon directly attached to the boron atom was not observed. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 405.2620; Found 405.2620.



Pent-4-yn-1-yl 3,3-bis(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)acrylate (**3-sa**). 88% yield. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.57 (s, 1H), 4.16 (t, *J* = 6.3 Hz, 2H), 2.23 (td, *J* = 7.1 Hz, *J* = 2.6 Hz, 2H), 1.90 (t, *J* = 2.6 Hz, 1H), 1.87 (s, 2H), 1.81 (p, *J* = 6.7 Hz, 2H), 1.76 (s, 2H), 1.34 (s, 12H), 1.26 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.19, 136.41, 116.47, 83.13, 70.80, 70.67, 68.88, 62.62, 48.82, 48.48, 31.56, 31.38, 27.66, 15.10. A signal for the sp^2-carbon directly attached to the boron atom was not observed. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 419.2776; Found 419.2781.

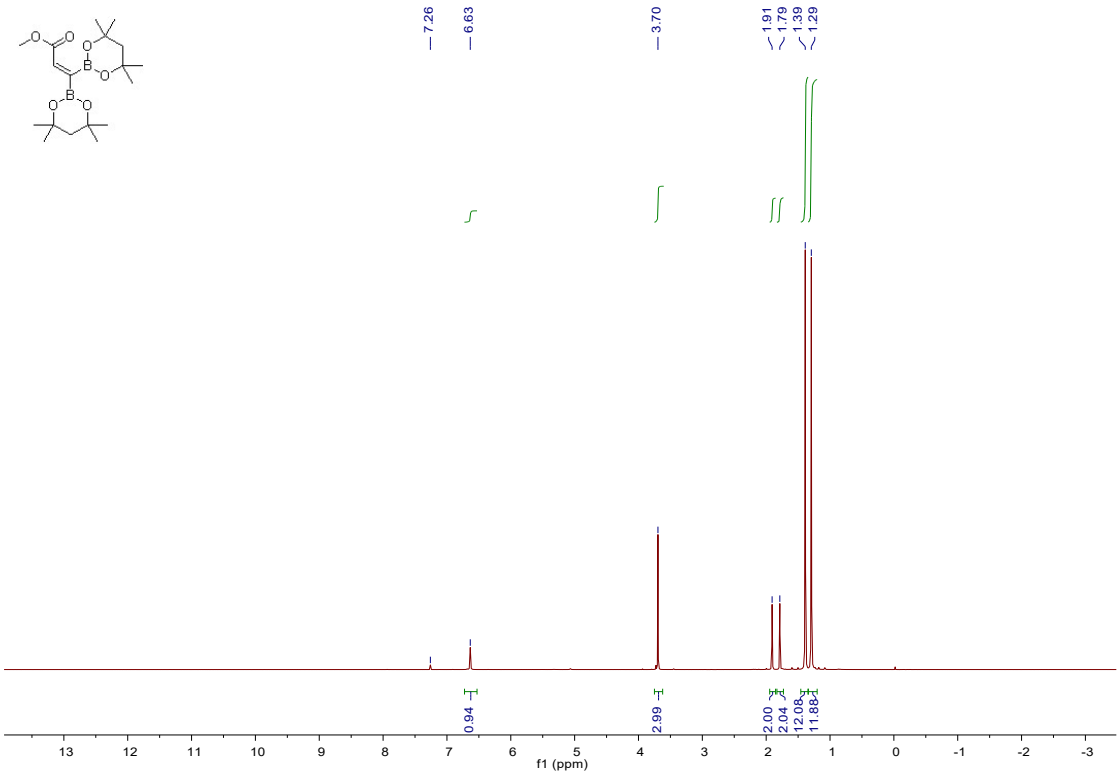


Methyl 3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (**3-ab**)[8]. 80% yield. Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.71 (s, 1H), 3.69 (s, 3H), 1.30 (s, 12H), 1.19 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.21, 140.98, 83.89, 83.85, 51.93, 25.02, 24.78, 24.64. A signal for the sp^2-carbon directly attached to the boron atom was not observed. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 339.2150; Found 339.2155.

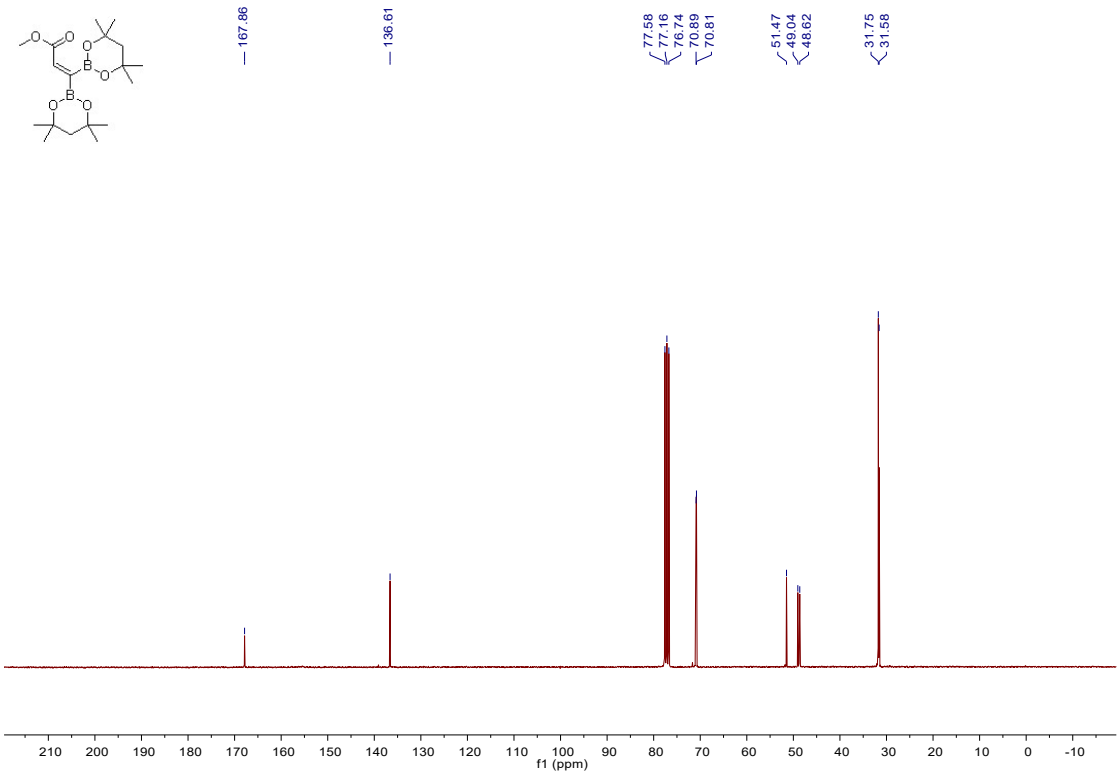


Methyl 3,3-bis(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)acrylate (**3af**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.62 (s, 1H), 4.45 – 4.07 (m, 2H), 3.71 (s, 3H), 1.83 – 1.60 (m, 3H), 1.53 – 1.41 (m, 1H), 1.37 (s, 3H), 1.30 (s, 3H), 1.28 – 1.19 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.96, 136.97 (d, J_{B-C} = 0.9 Hz), 71.13 (d, J_{B-C} = 2.1 Hz), 71.04 (d, J_{B-C} = 2.8 Hz), 65.18 (d, J_{B-C} = 3.4 Hz), 65.03 (d, J_{B-C} = 3.5 Hz), 51.57, 45.99 (d, J = 4.4 Hz), 45.75, 31.35 (d, J = 2.2 Hz), 31.21, 28.18 (d, J = 2.9 Hz), 27.63 (d, J = 3.9 Hz), 23.30 (d, J = 1.7 Hz), 23.07. A signal for the sp^2-carbon directly attached to the boron atom was not observed. HRMS (ESI-TOF, m/z): HRMS (ESI) Calcd for $[M+H]^+$ 339.2150; Found 339.2156.

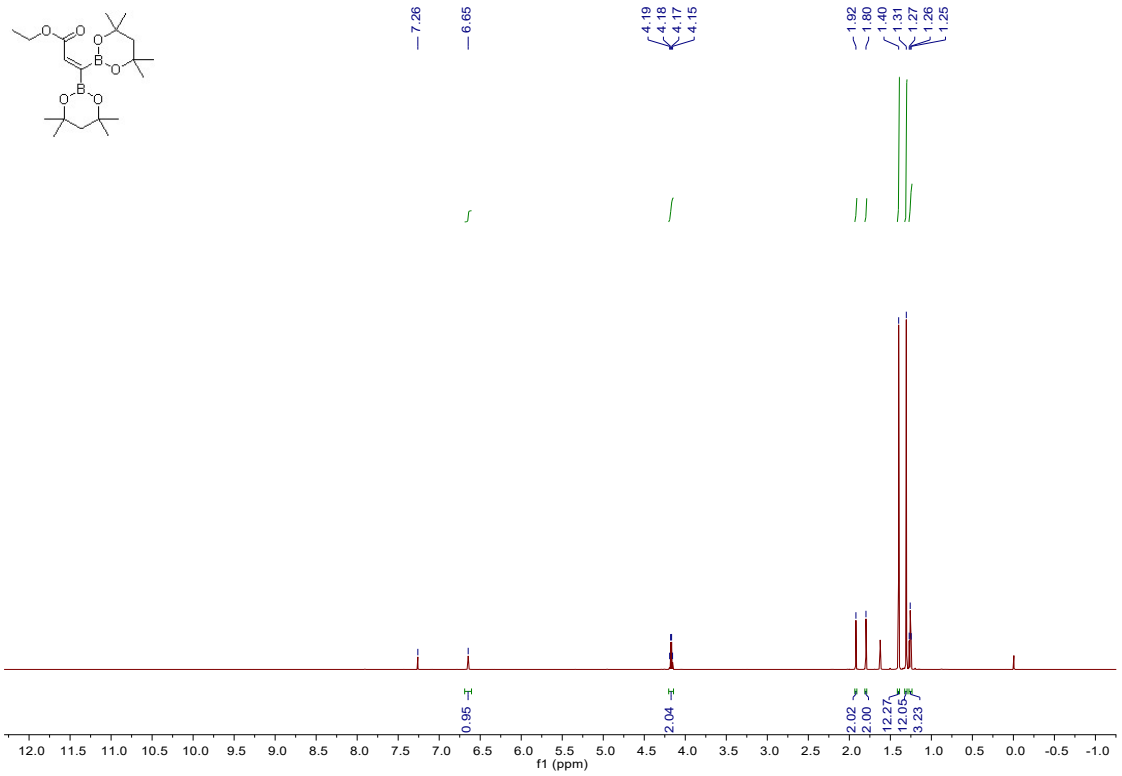
8. NMR spectra



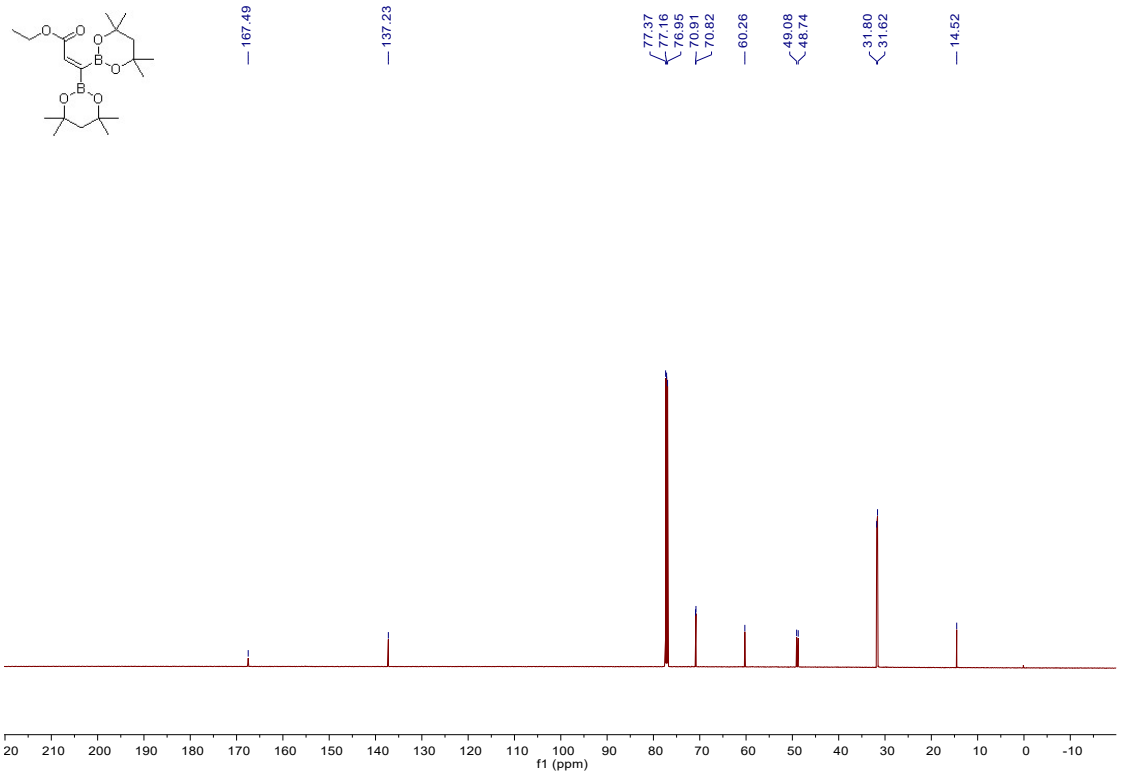
^{1}H NMR spectrum of compound **3aa**



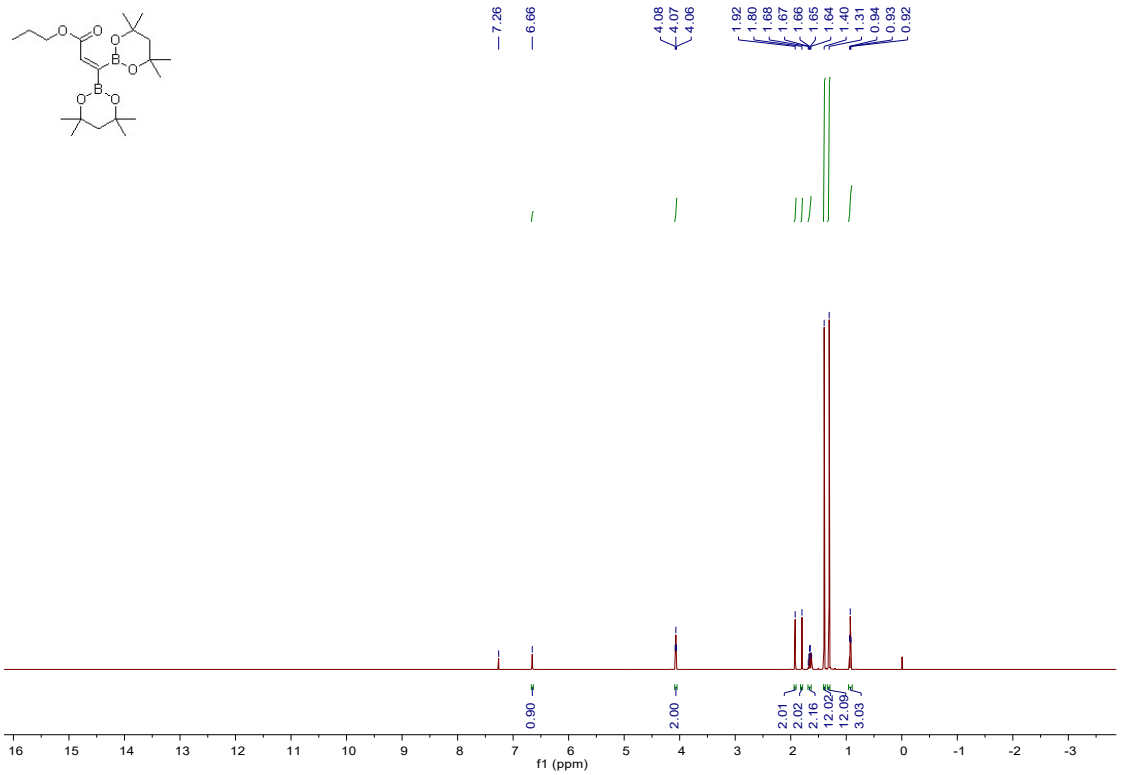
^{13}C NMR spectrum of compound **3aa**



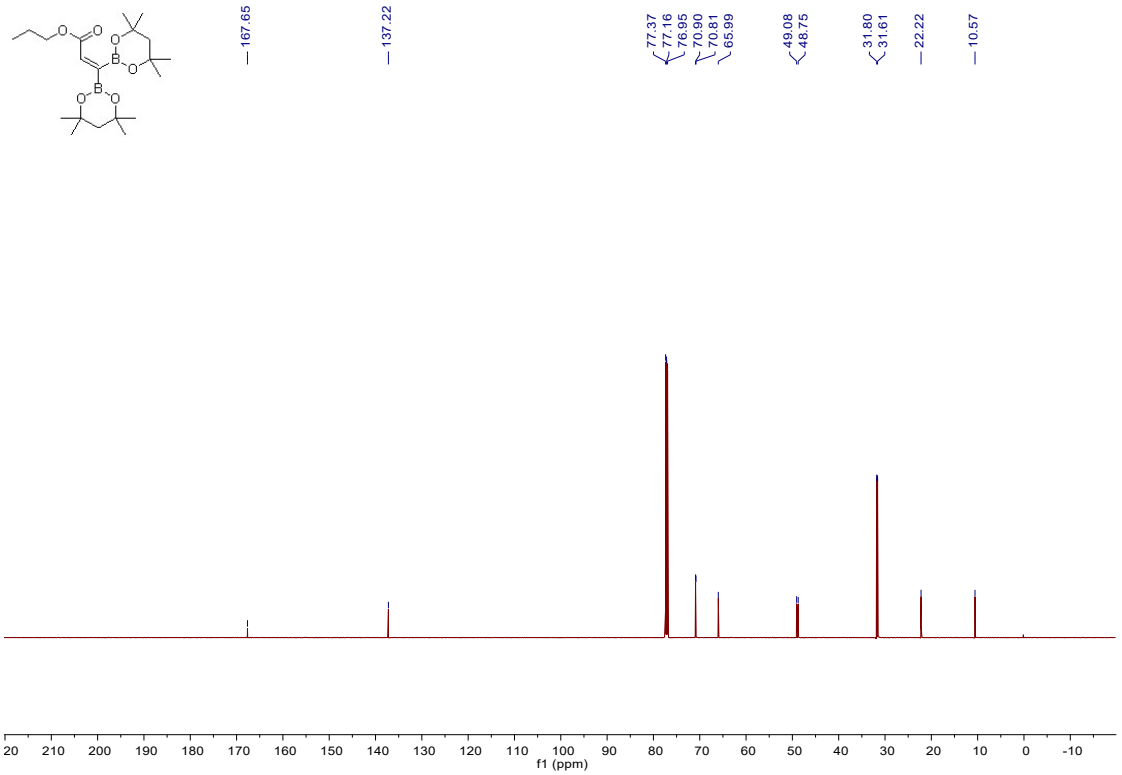
^{1}H NMR spectrum of compound **3ba**



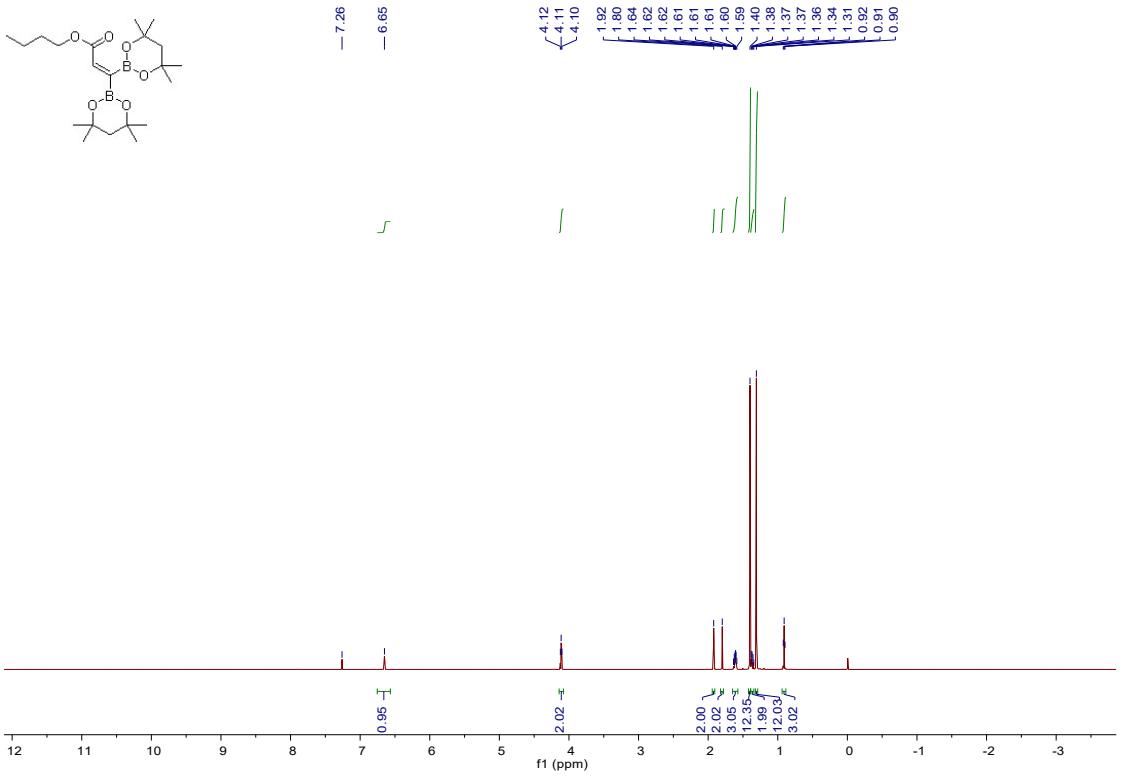
^{13}C NMR spectrum of compound **3ba**



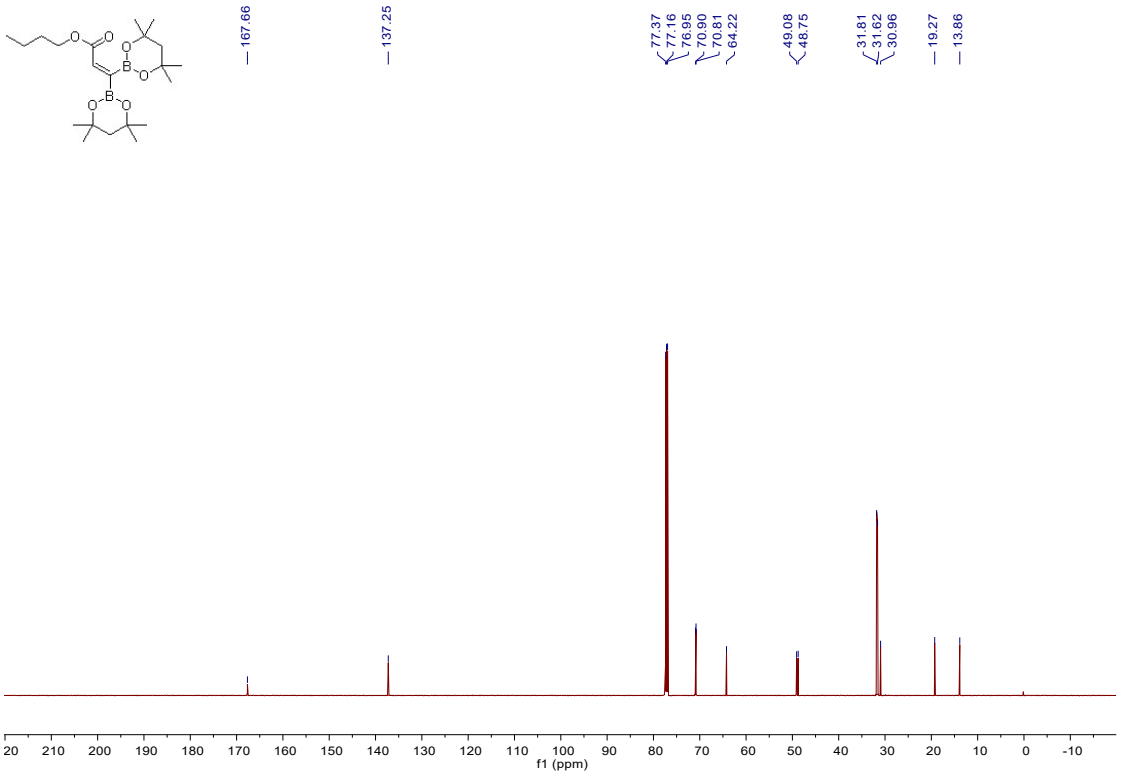
^{1}H NMR spectrum of compound **3ca**



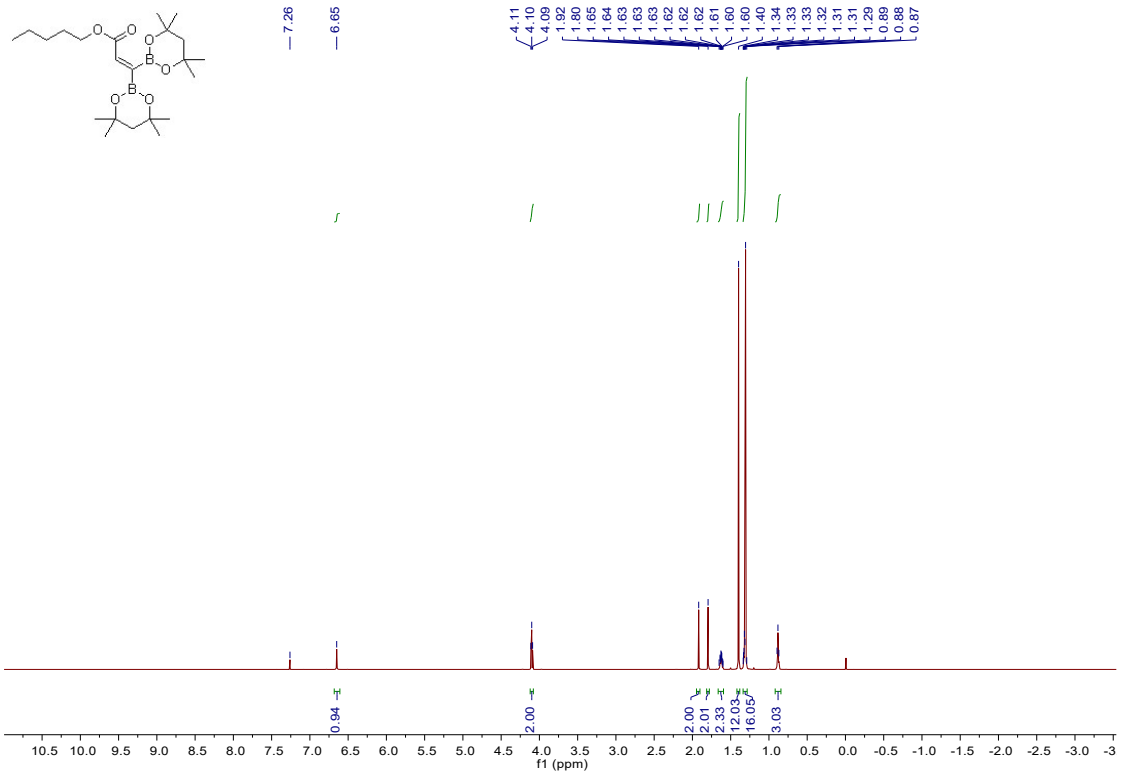
^{13}C NMR spectrum of compound **3ca**



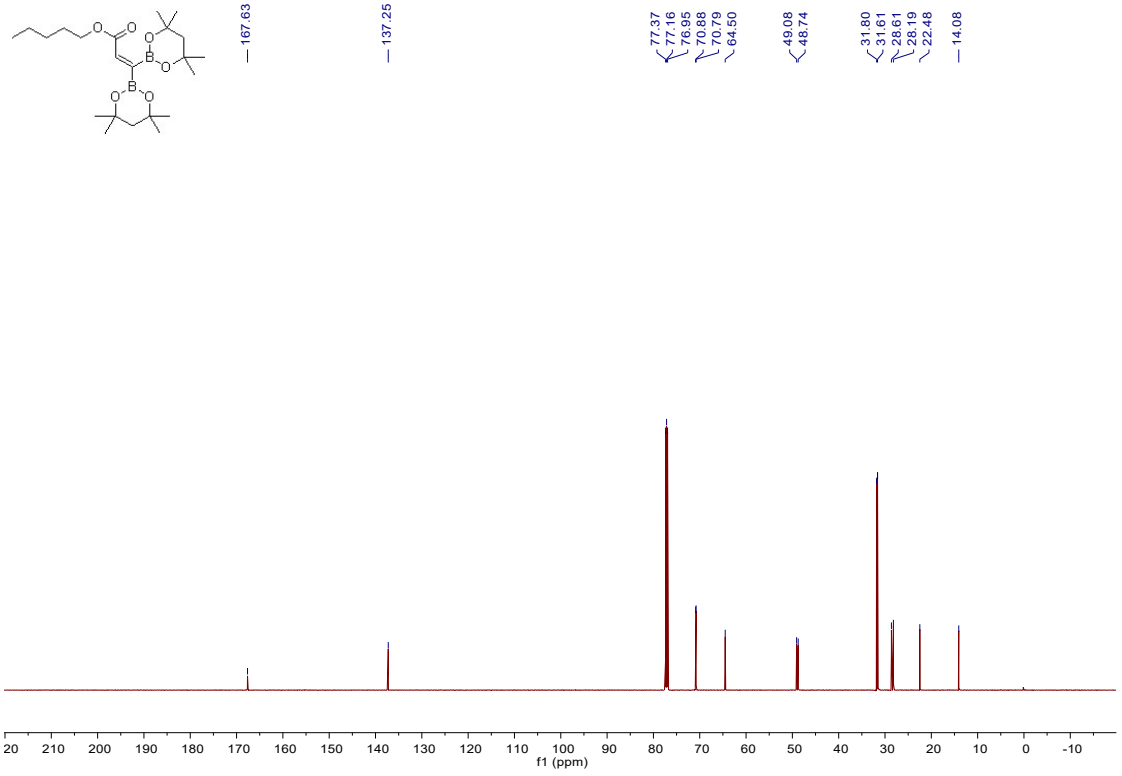
^{1}H NMR spectrum of compound **3da**



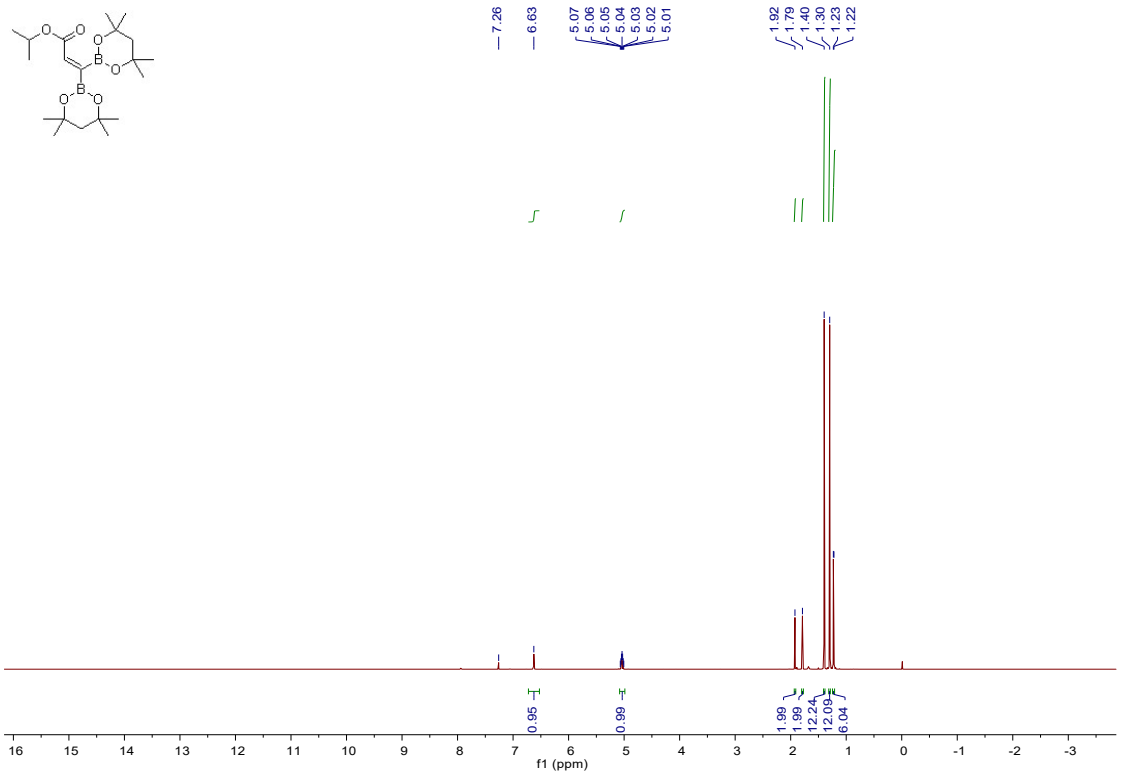
^{13}C NMR spectrum of compound **3da**



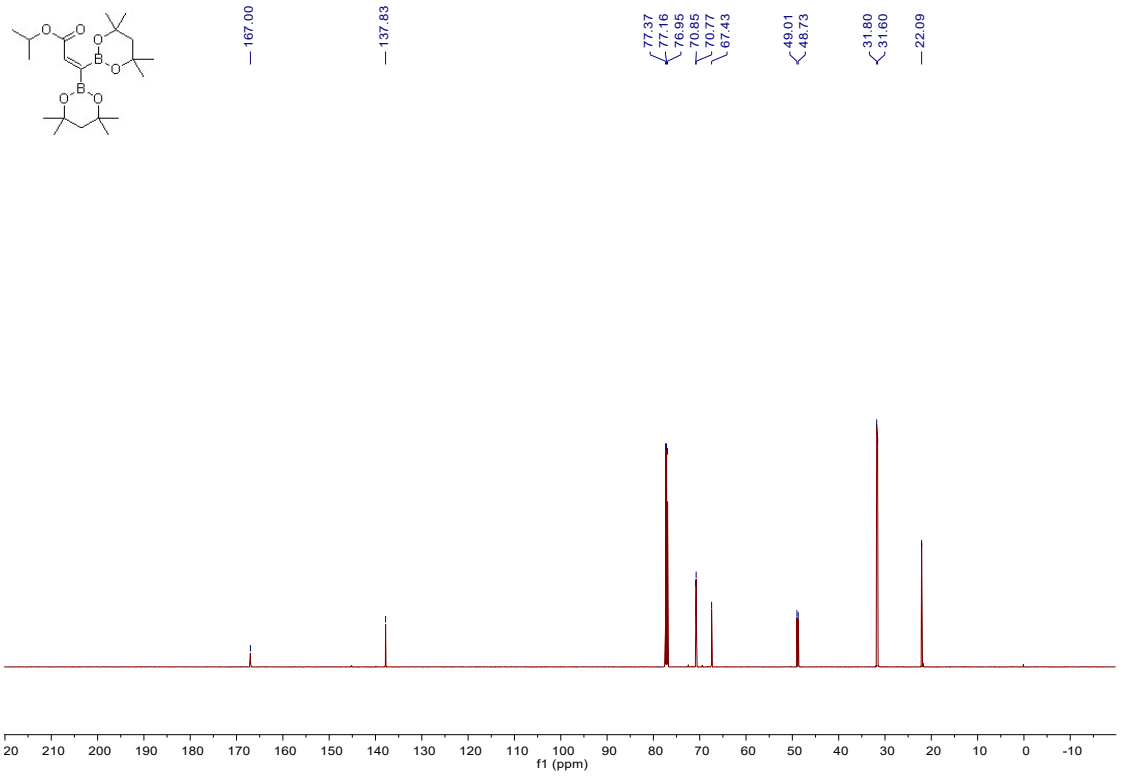
^{1}H NMR spectrum of compound **3ea**



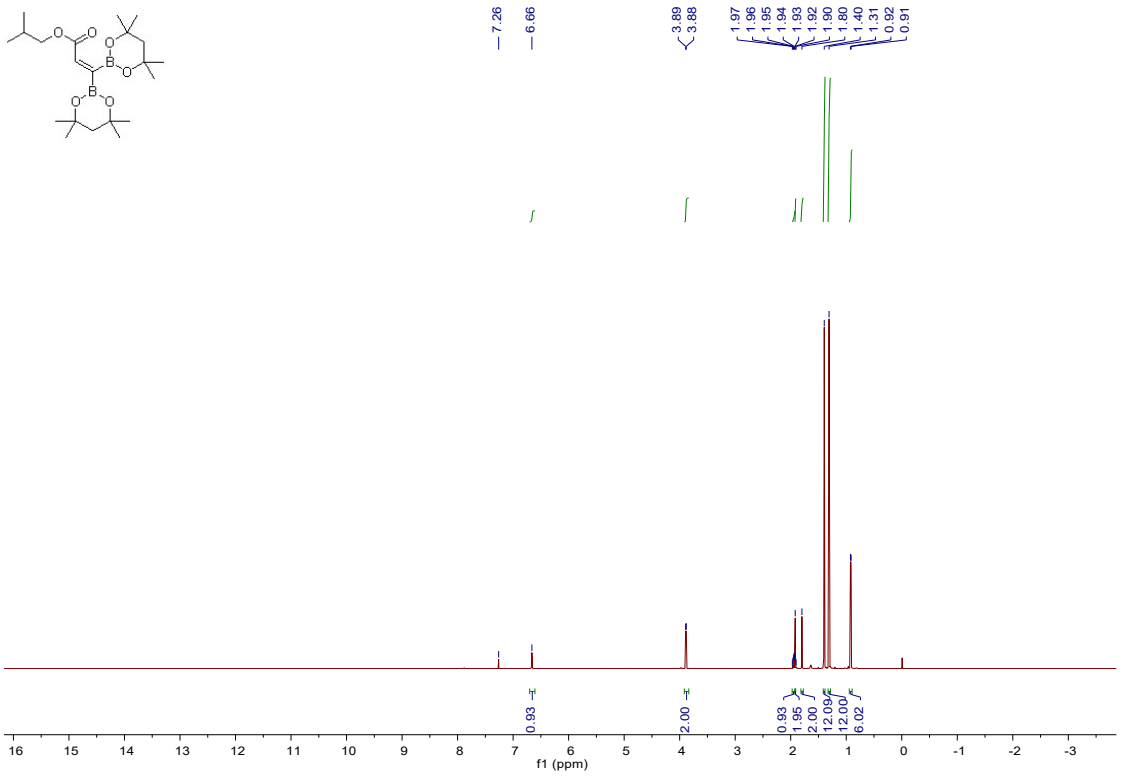
^{13}C NMR spectrum of compound **3ea**



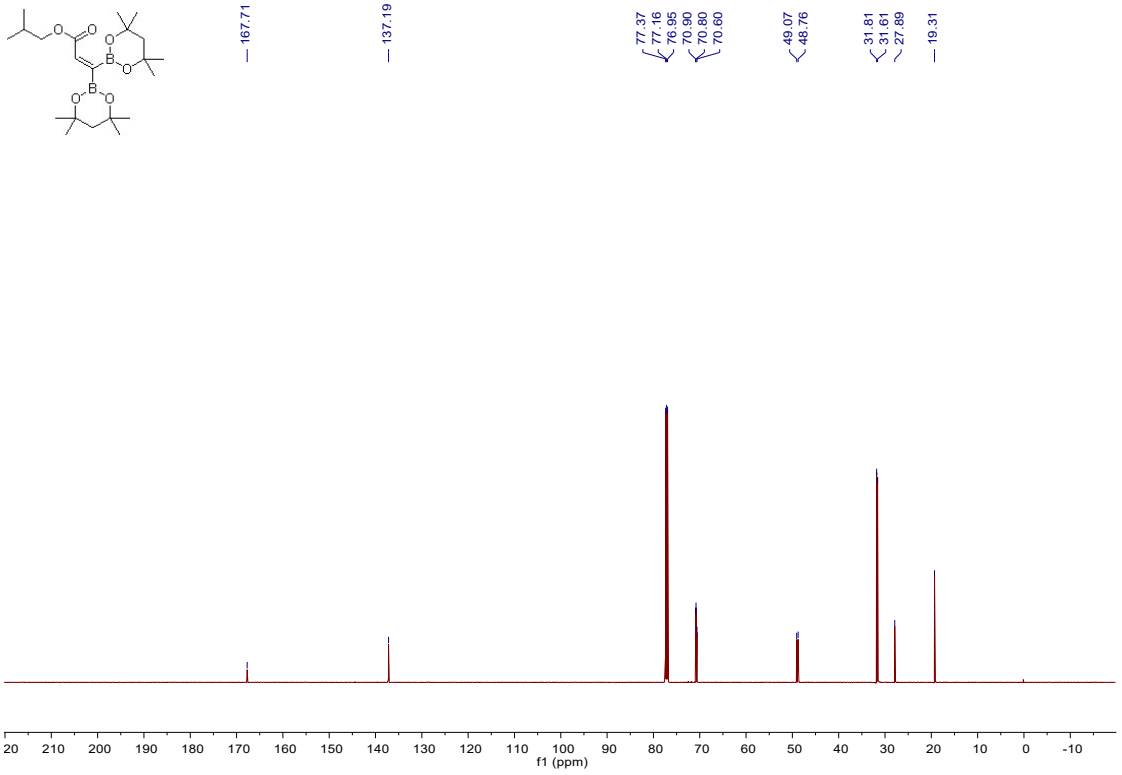
^{1}H NMR spectrum of compound **3fa**



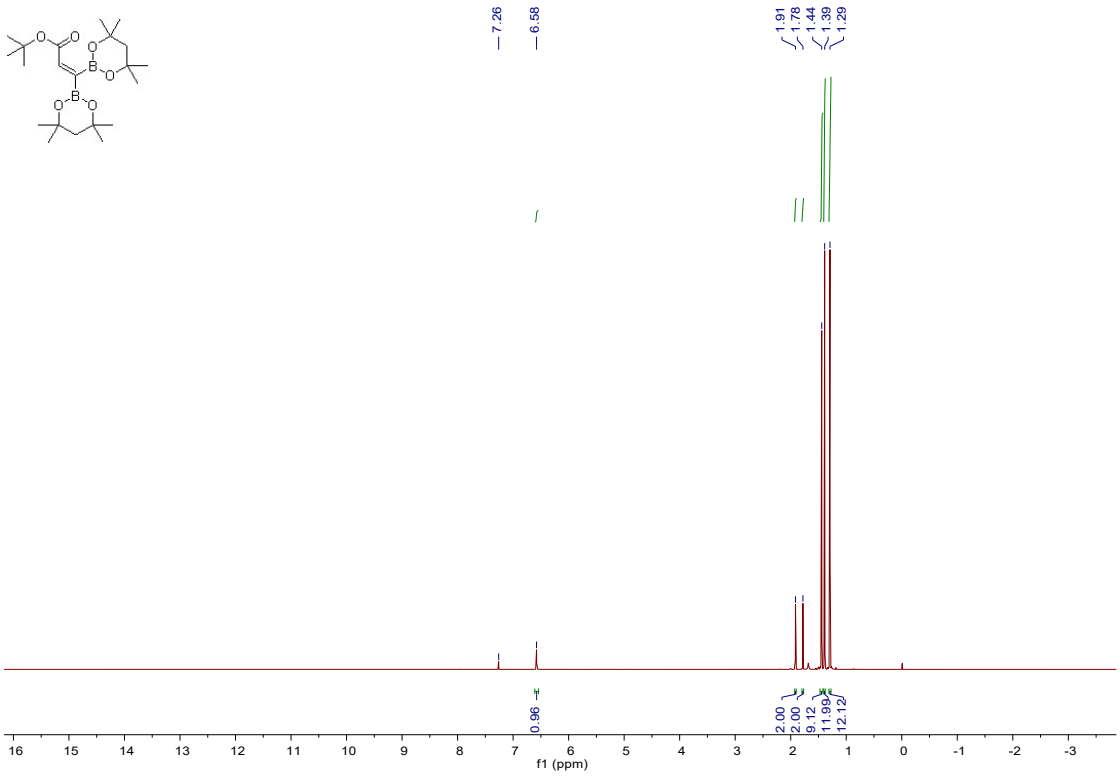
^{13}C NMR spectrum of compound **3fa**



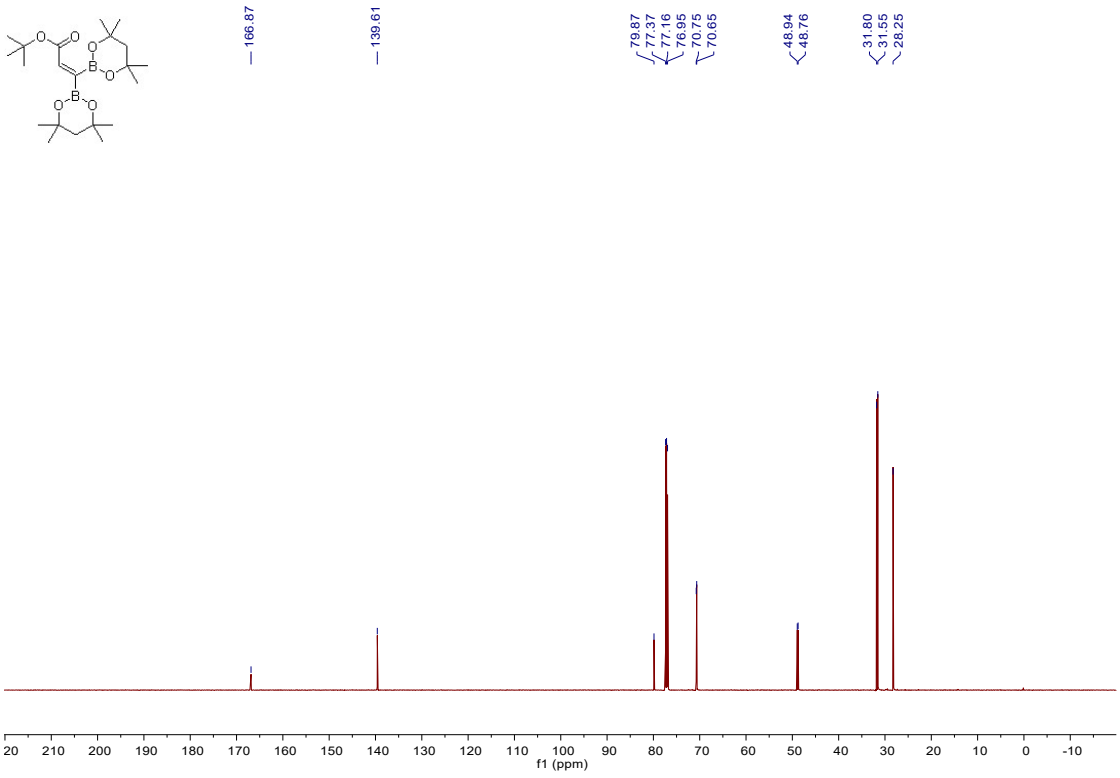
^{1}H NMR spectrum of compound **3ga**



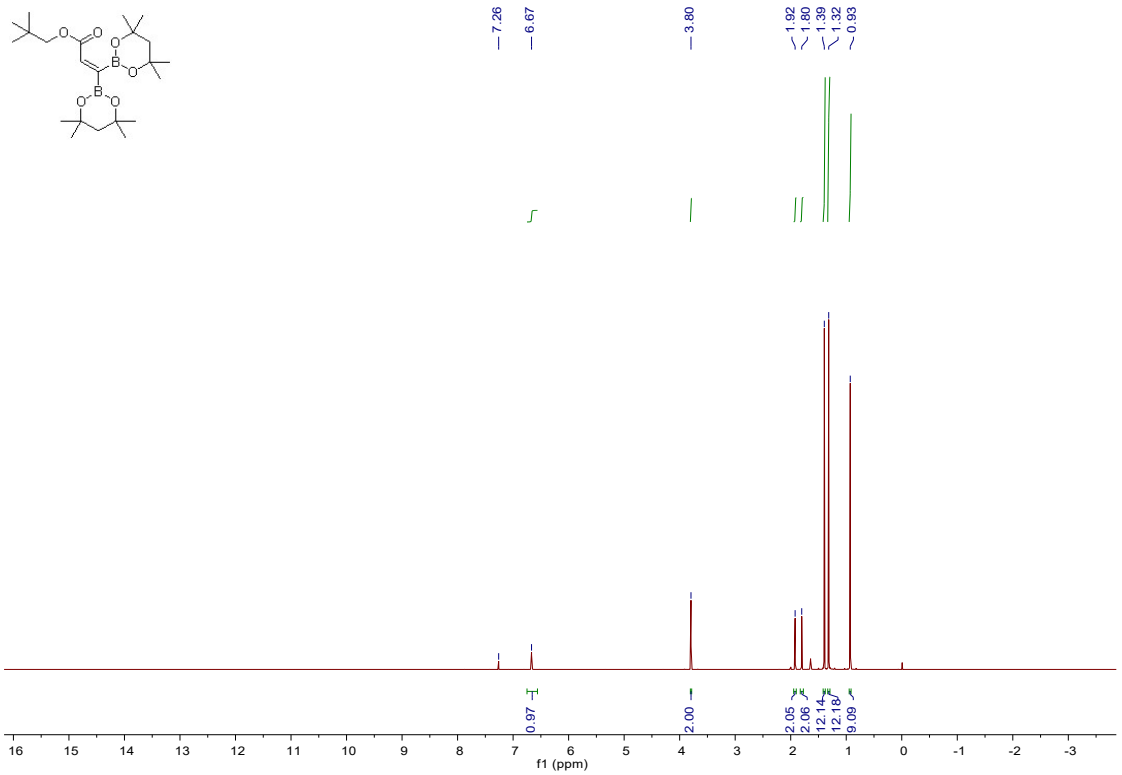
^{13}C NMR spectrum of compound **3ga**



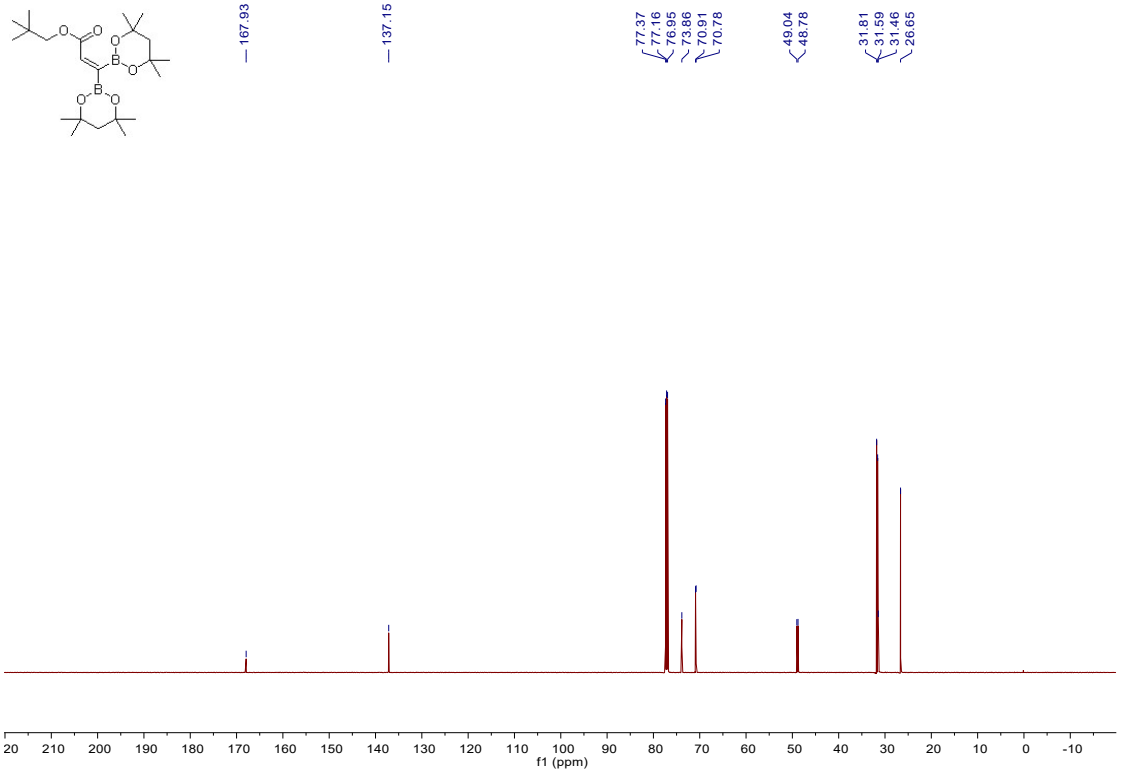
^{1}H NMR spectrum of compound **3ha**



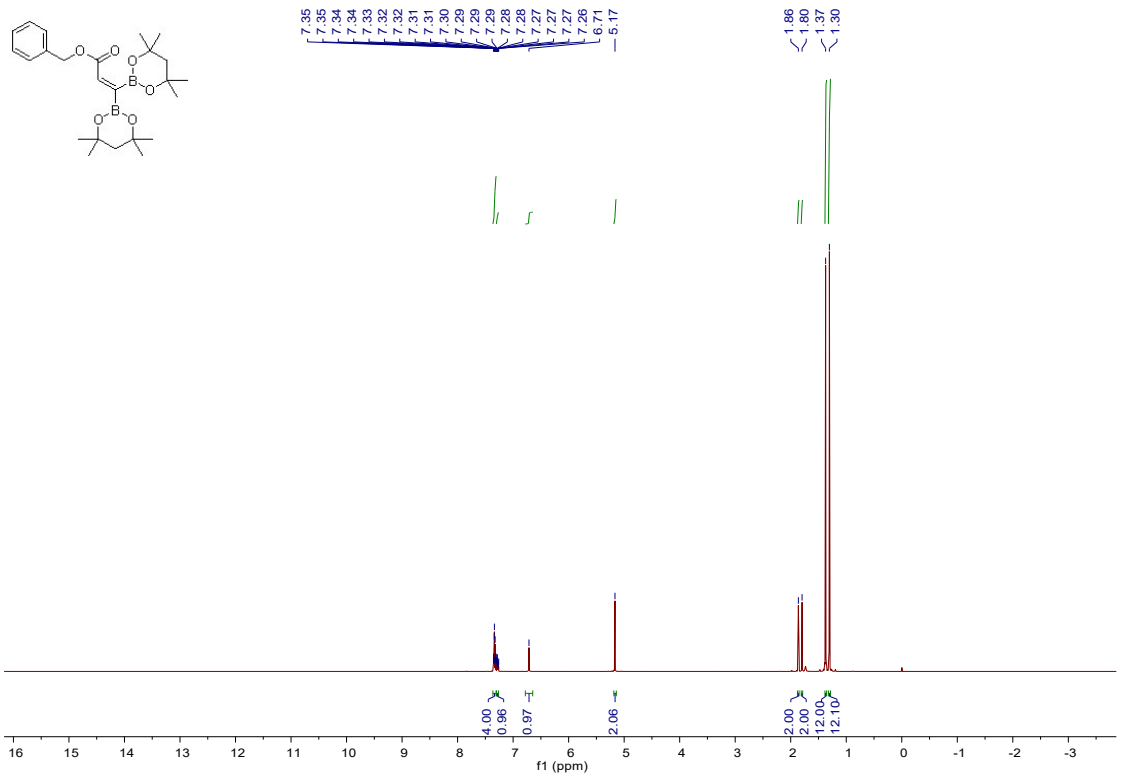
^{13}C NMR spectrum of compound **3ha**



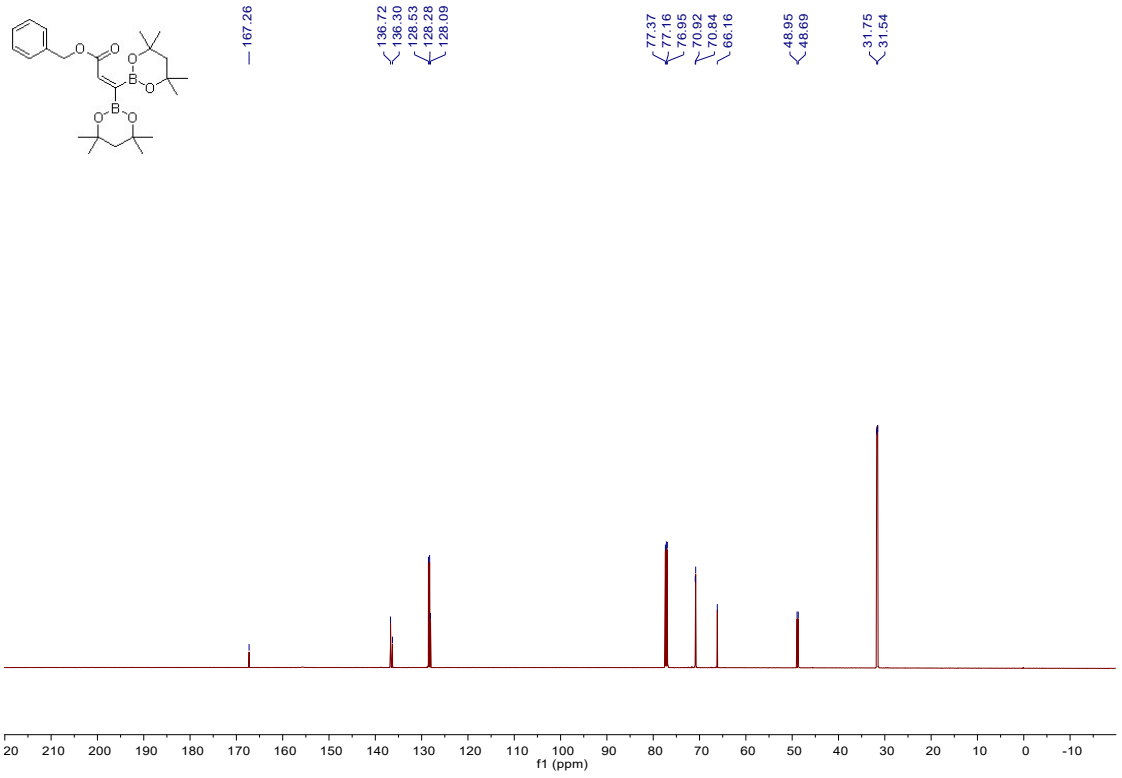
^{1}H NMR spectrum of compound **3ia**



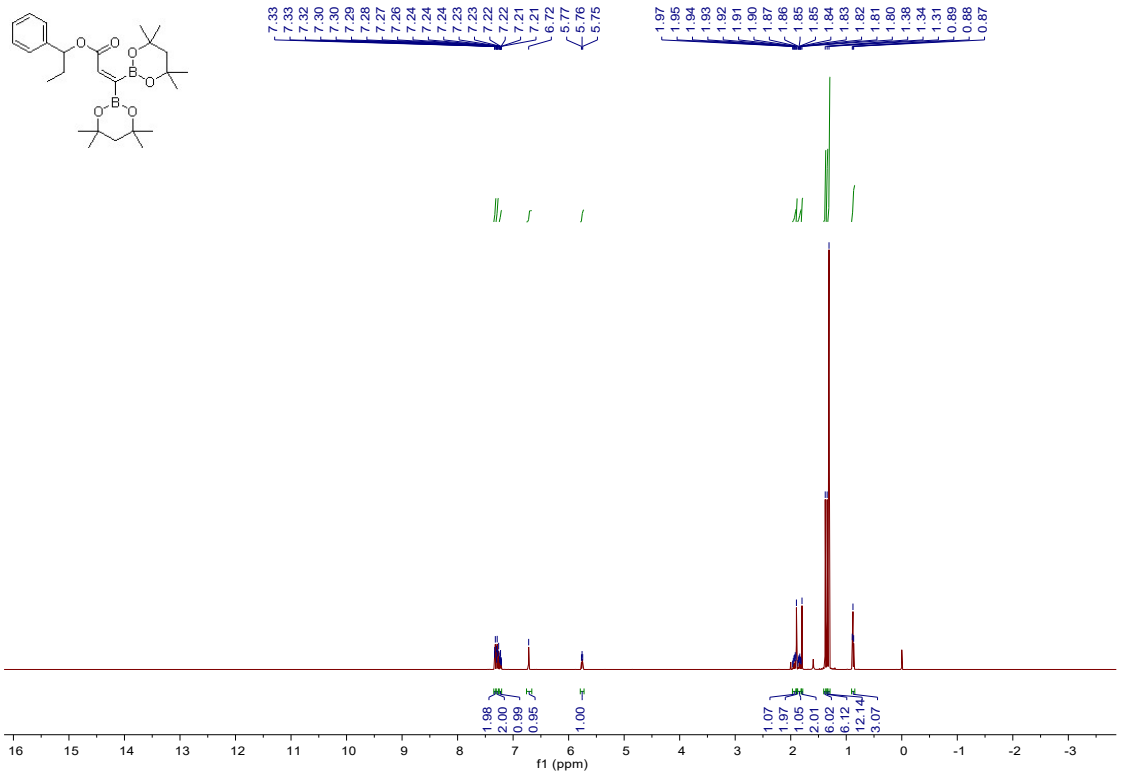
^{13}C NMR spectrum of compound **3ia**



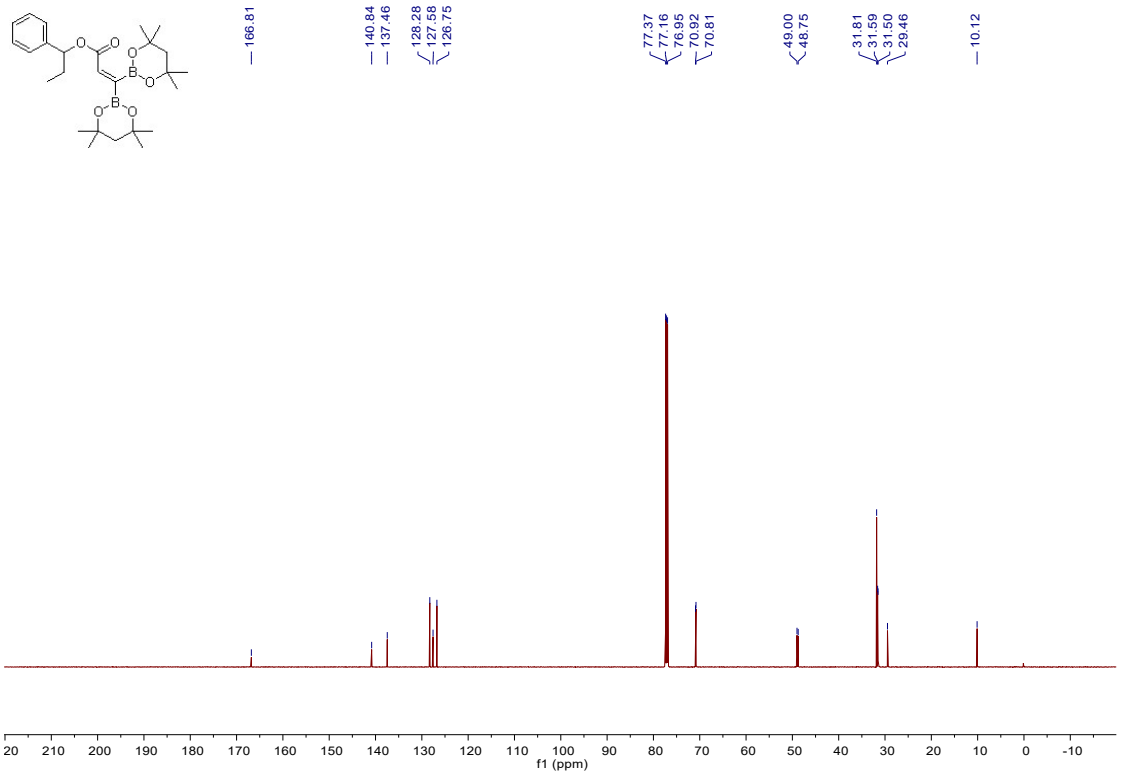
^{1}H NMR spectrum of compound **3ja**



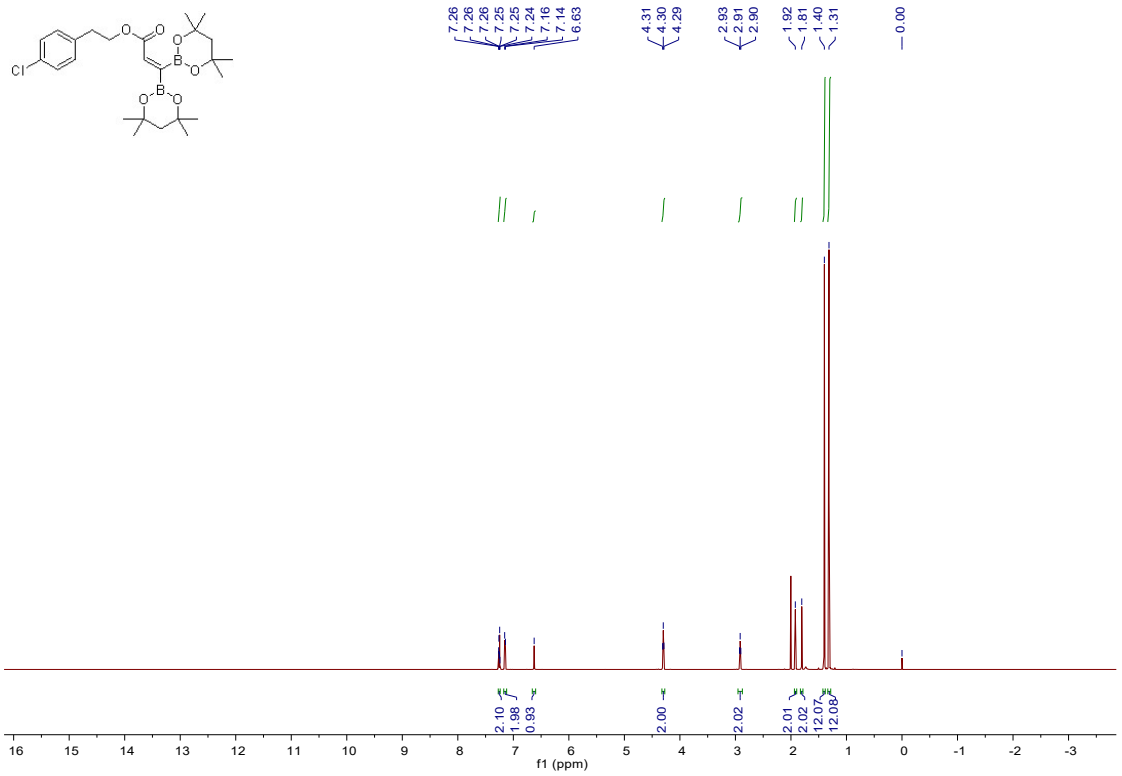
^{13}C NMR spectrum of compound **3ja**



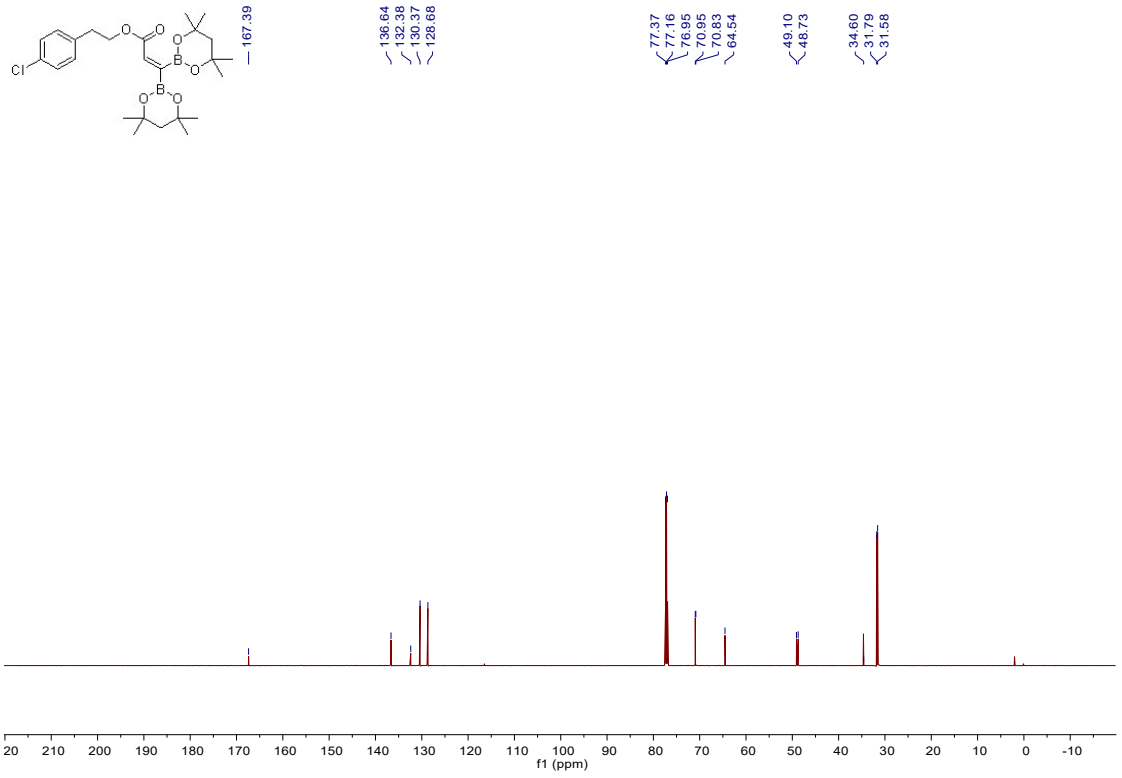
^{1}H NMR spectrum of compound **3ka**



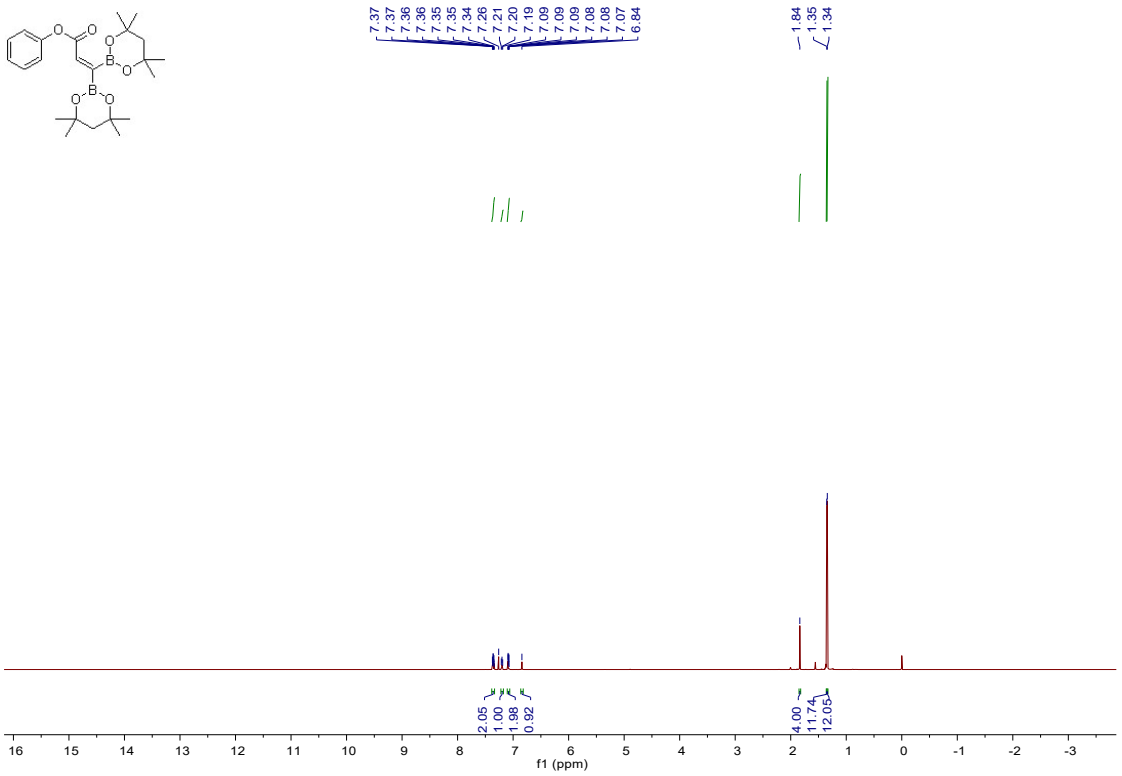
^{13}C NMR spectrum of compound **3ka**



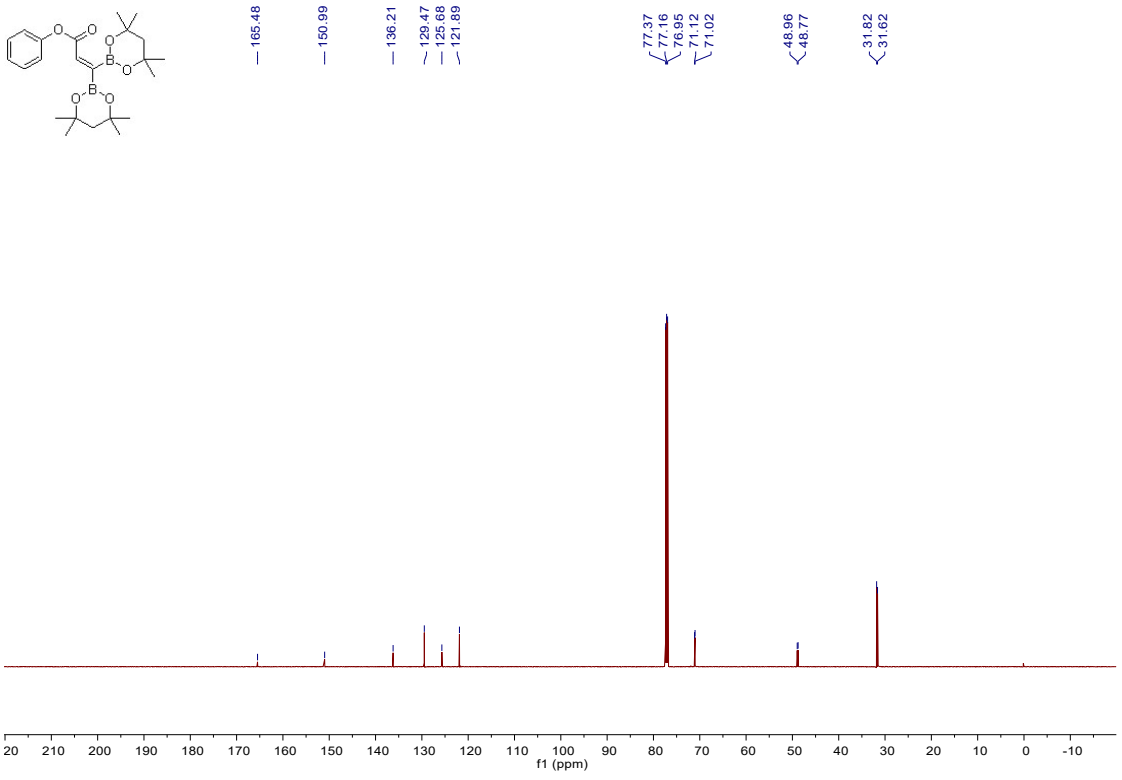
^{1}H NMR spectrum of compound **3la**



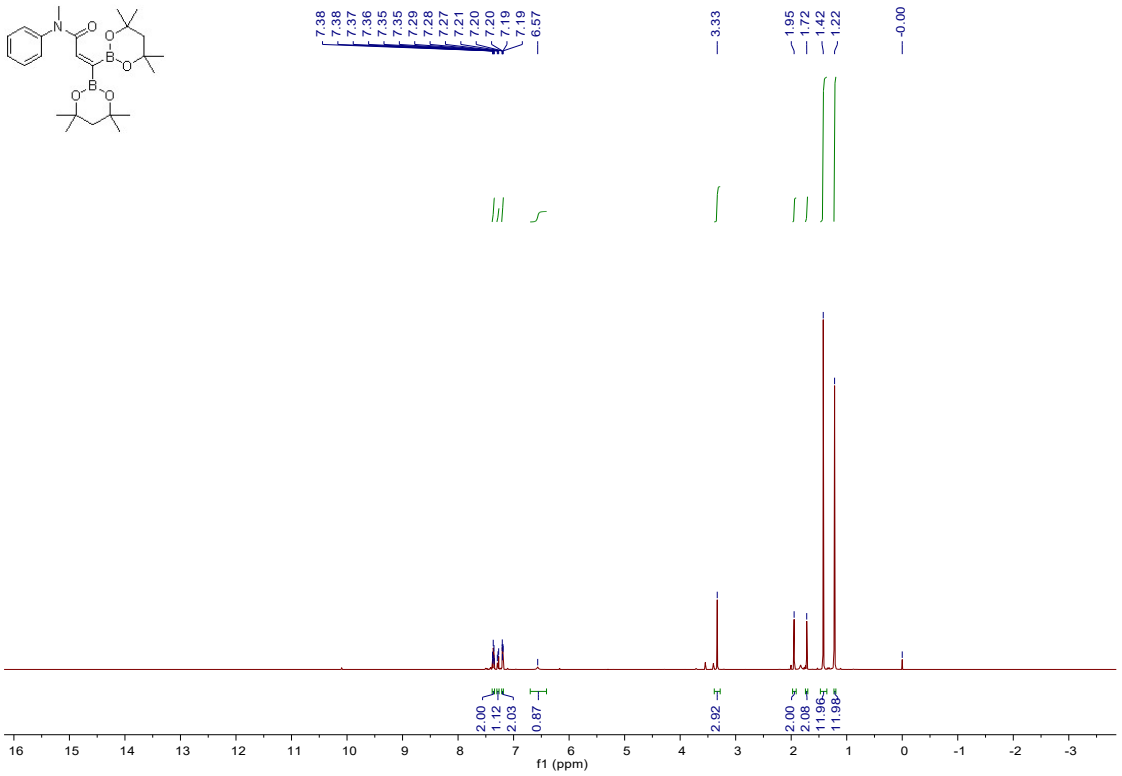
^{13}C NMR spectrum of compound **3la**



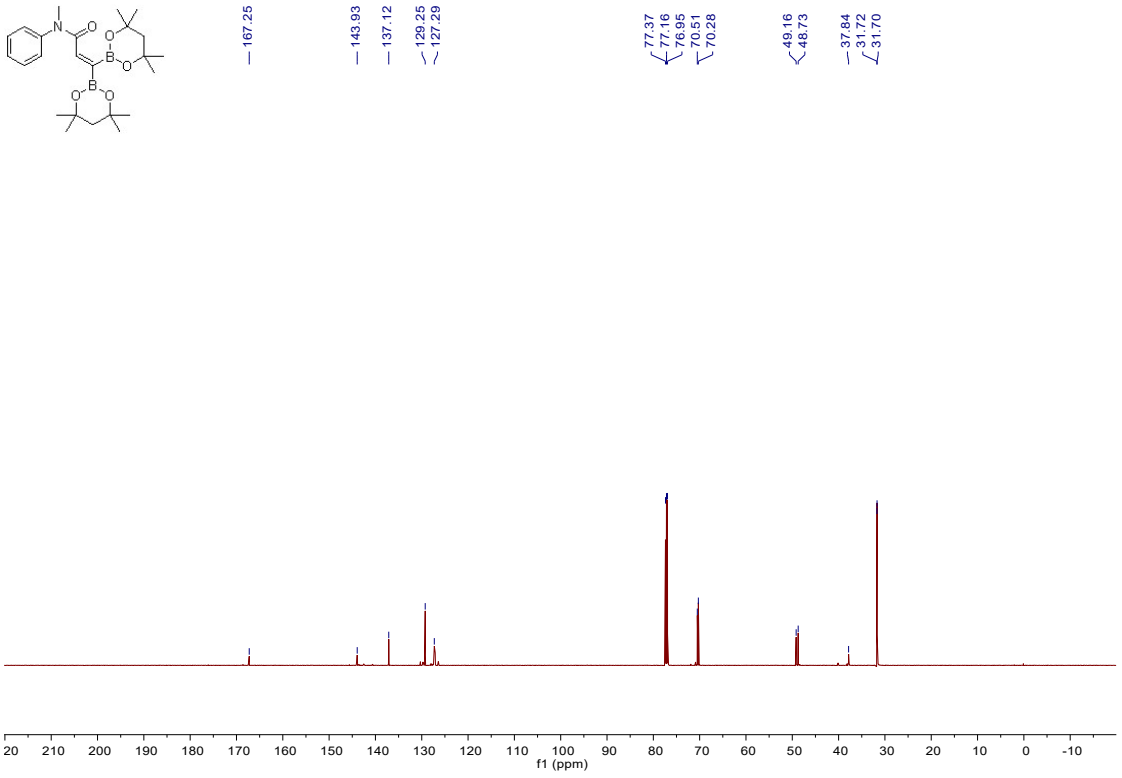
^{1}H NMR spectrum of compound **3ma**



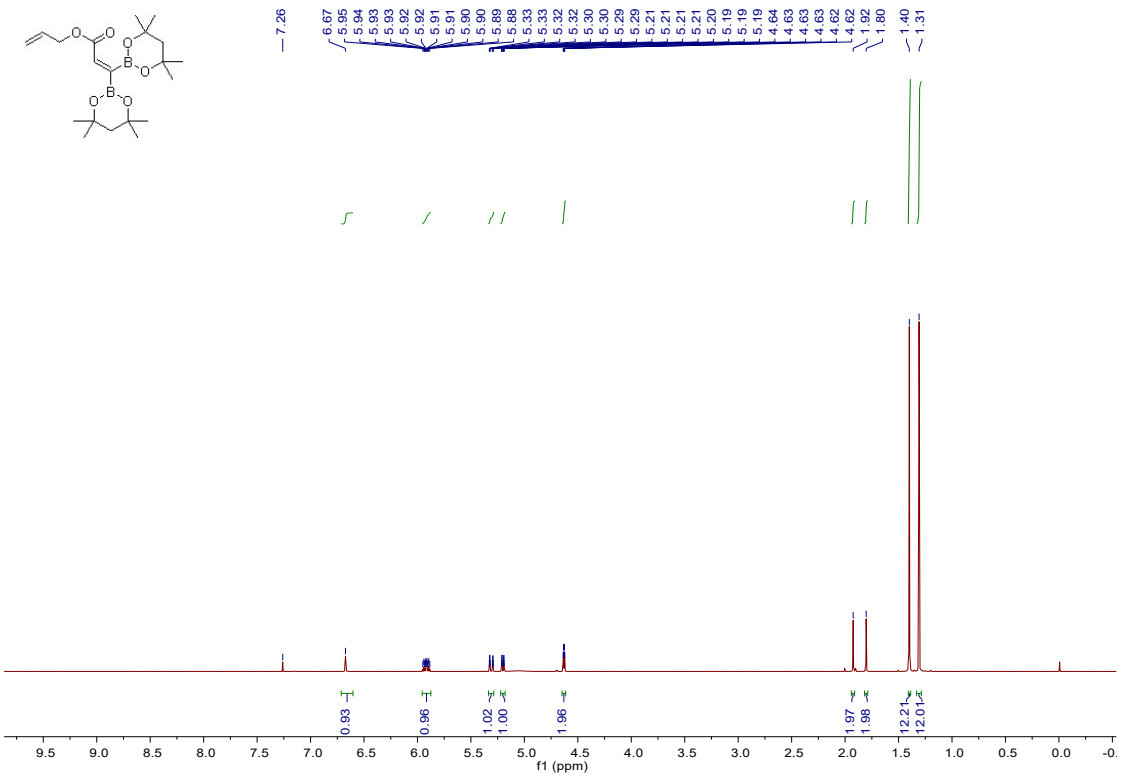
^{13}C NMR spectrum of compound **3ma**



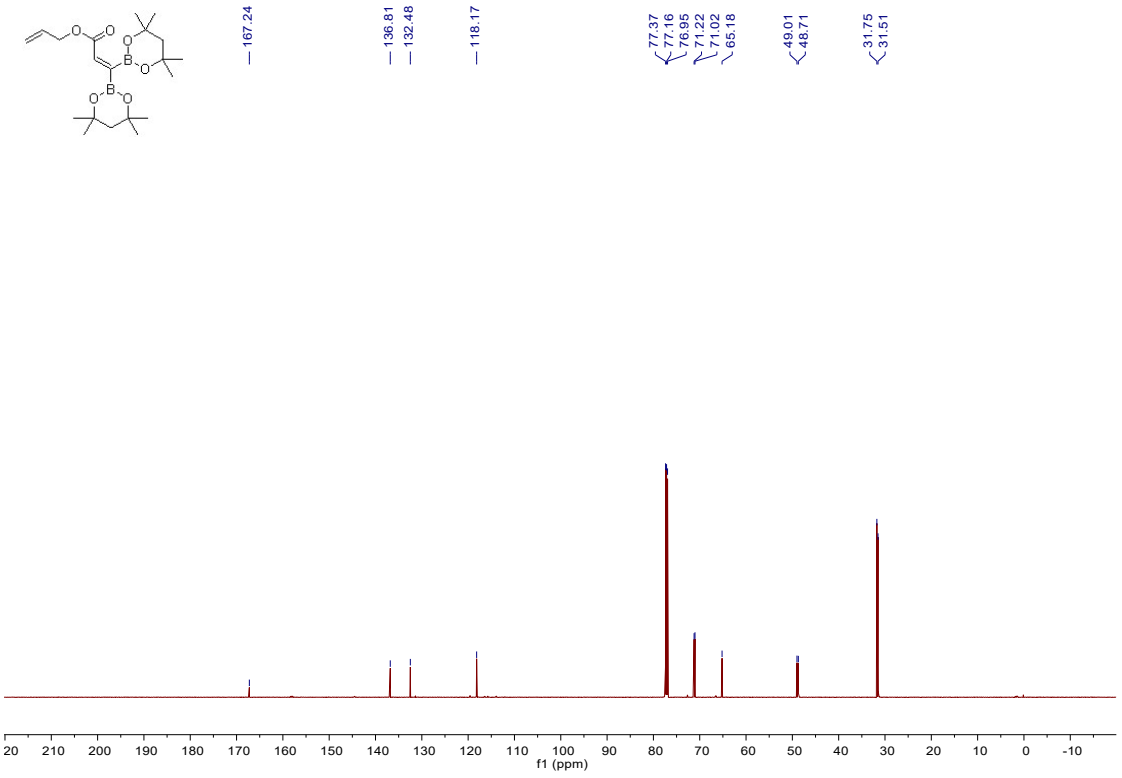
^{1}H NMR spectrum of compound **3na**



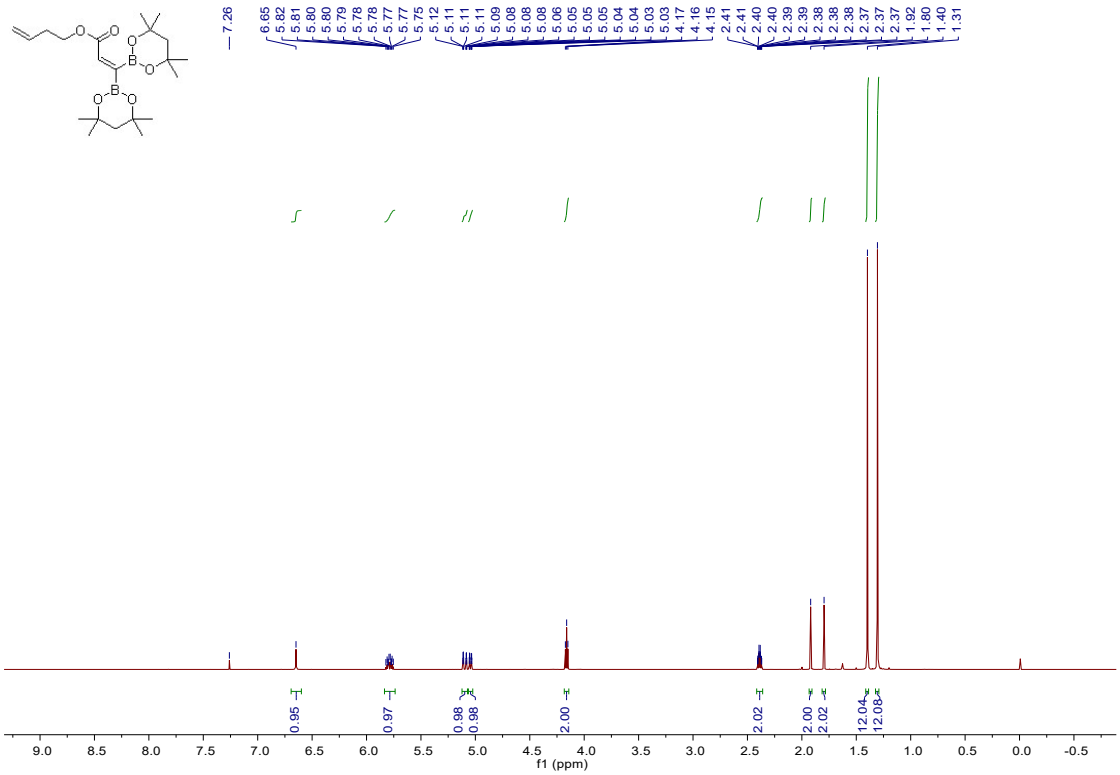
^{13}C NMR spectrum of compound **3na**



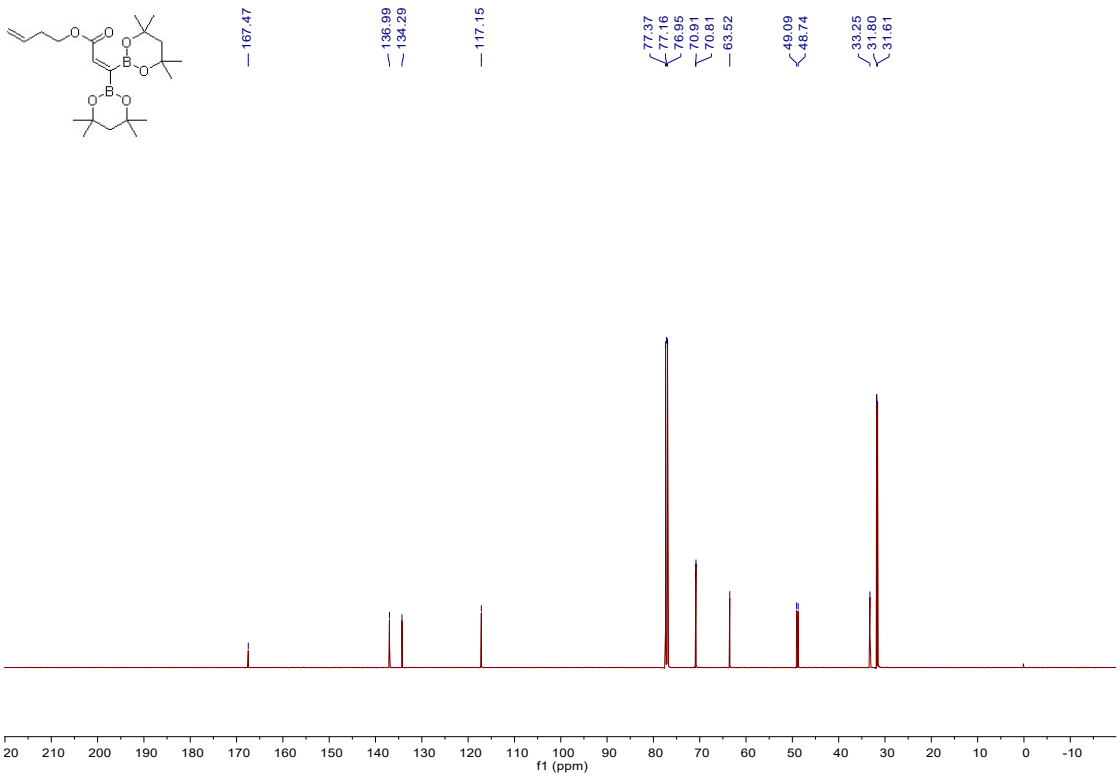
^{1}H NMR spectrum of compound **3oa**



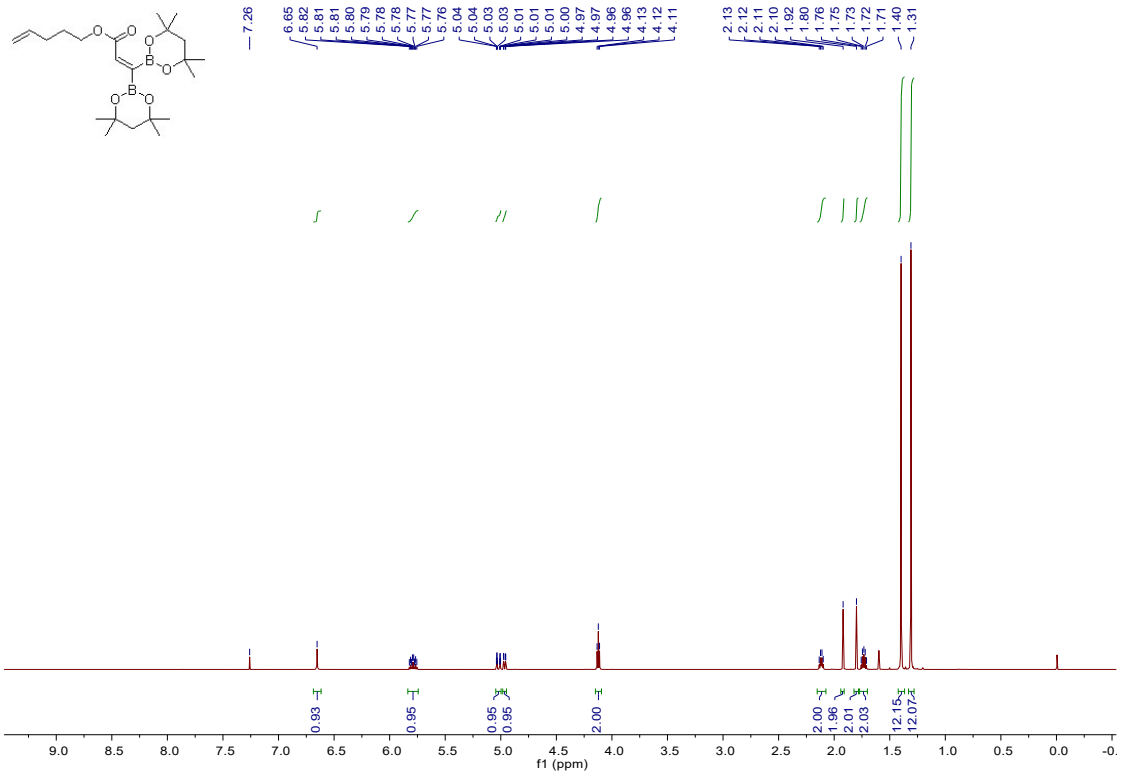
^{13}C NMR spectrum of compound **3oa**



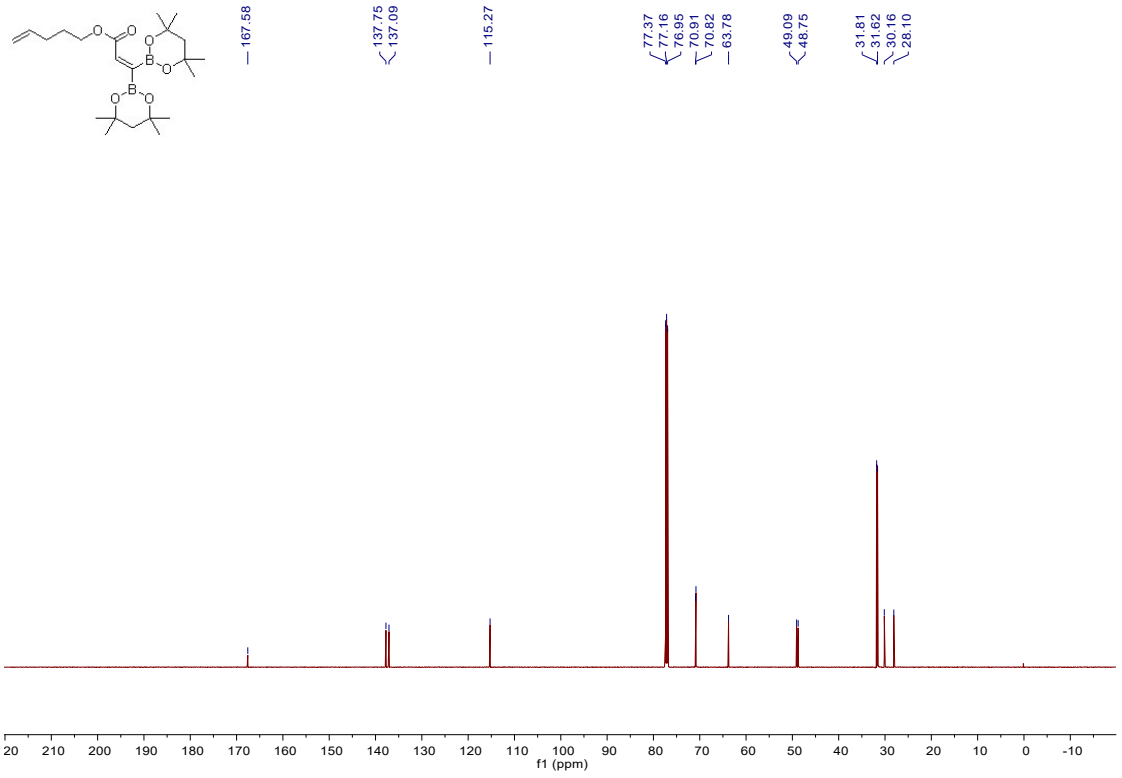
^{1}H NMR spectrum of compound **3pa**



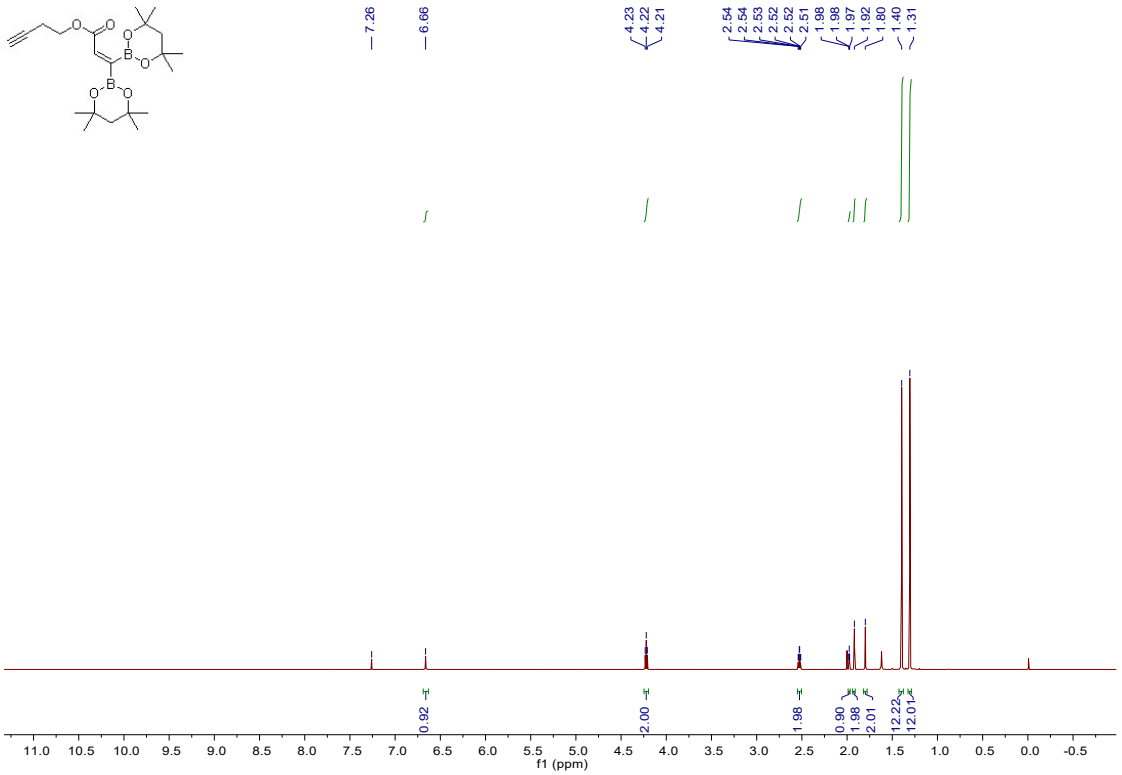
^{13}C NMR spectrum of compound **3pa**



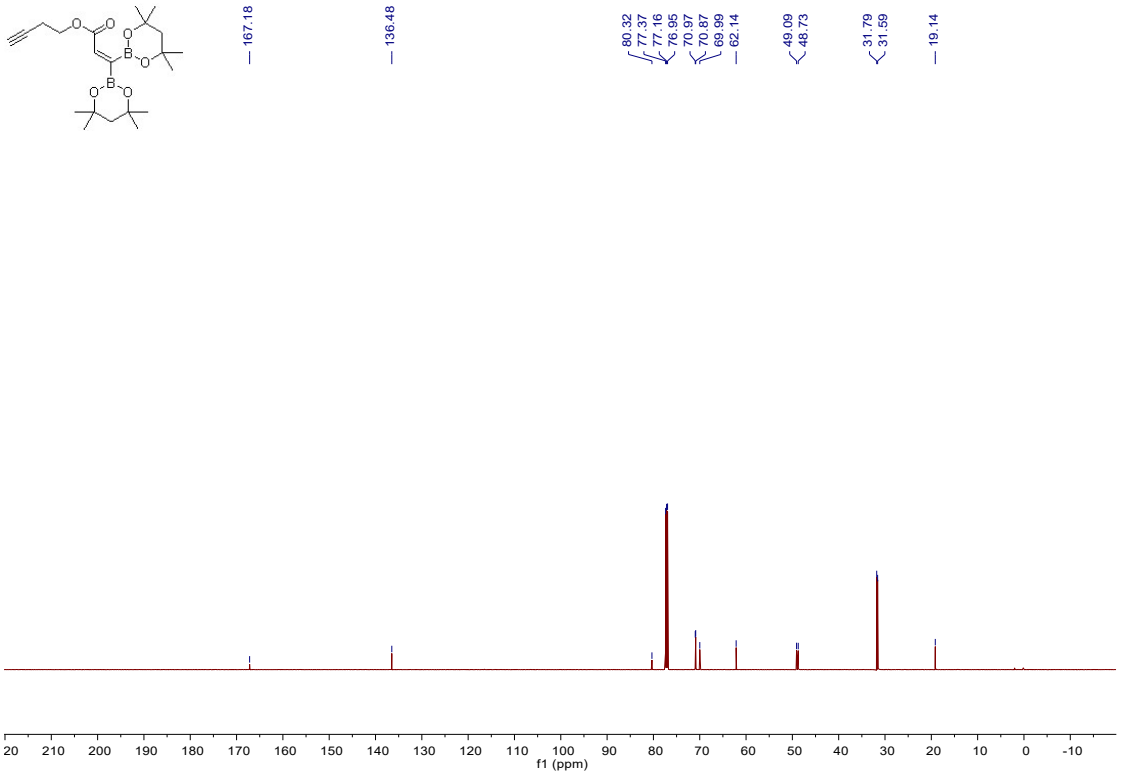
^{1}H NMR spectrum of compound **3qa**



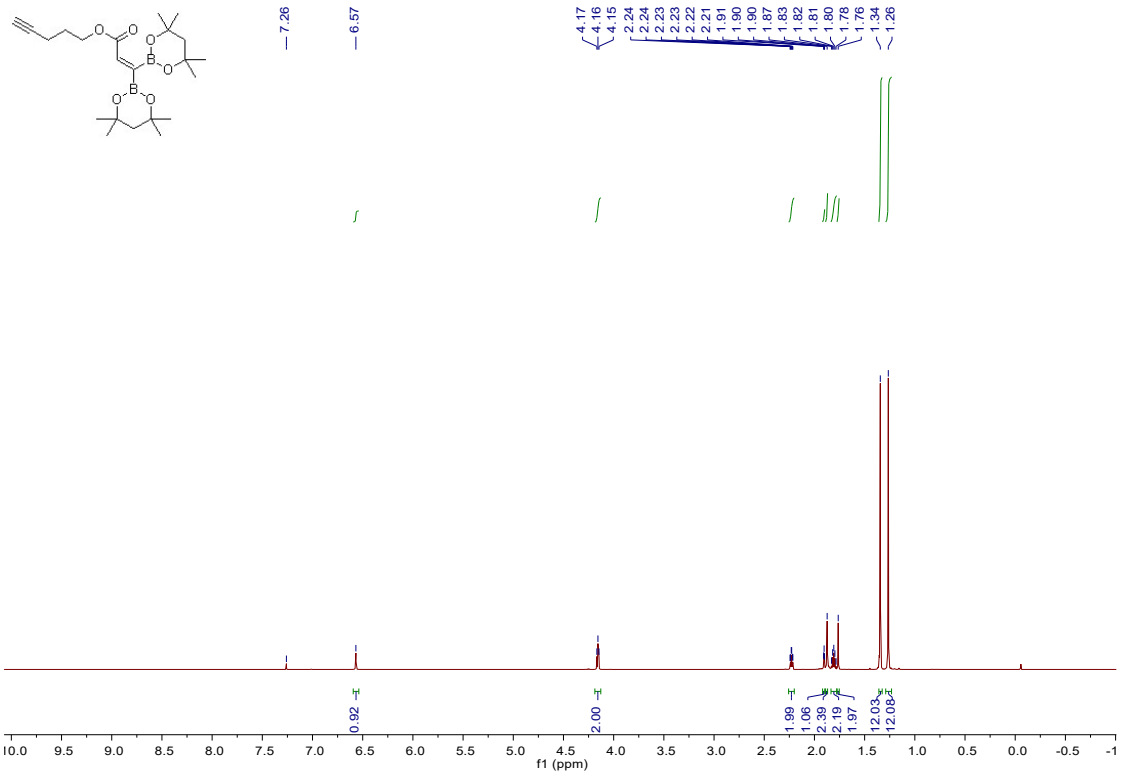
^{13}C NMR spectrum of compound **3qa**



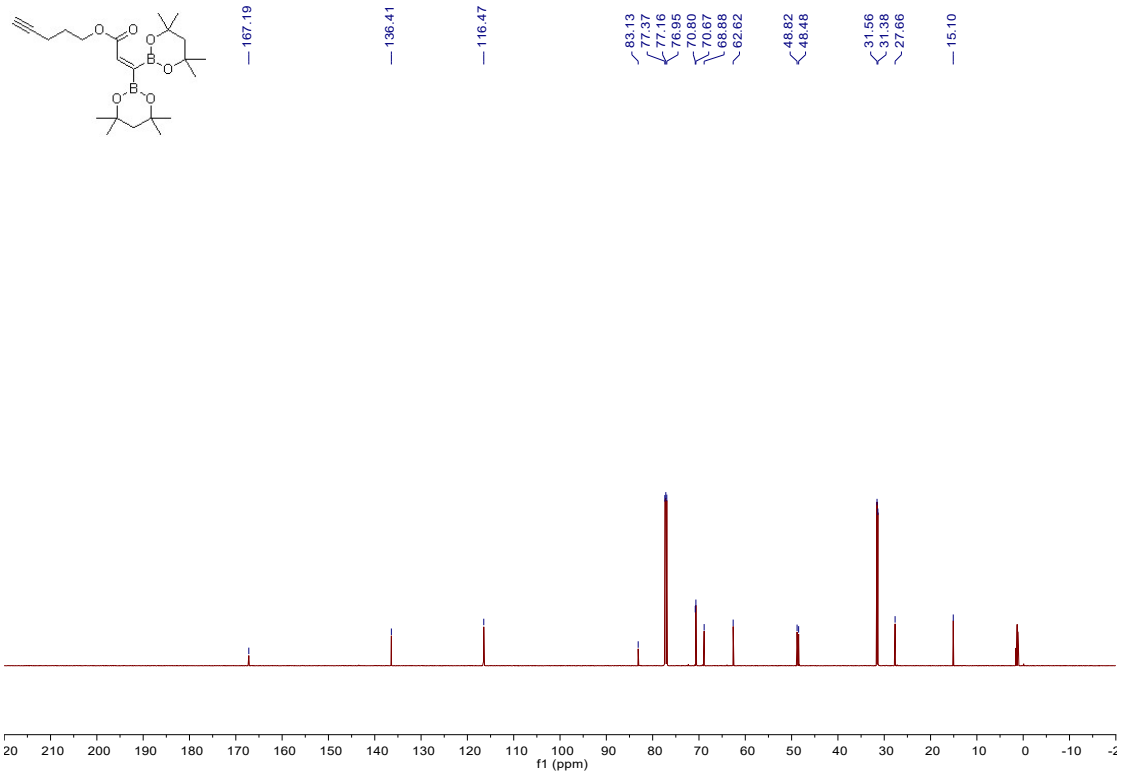
^{1}H NMR spectrum of compound **3ra**



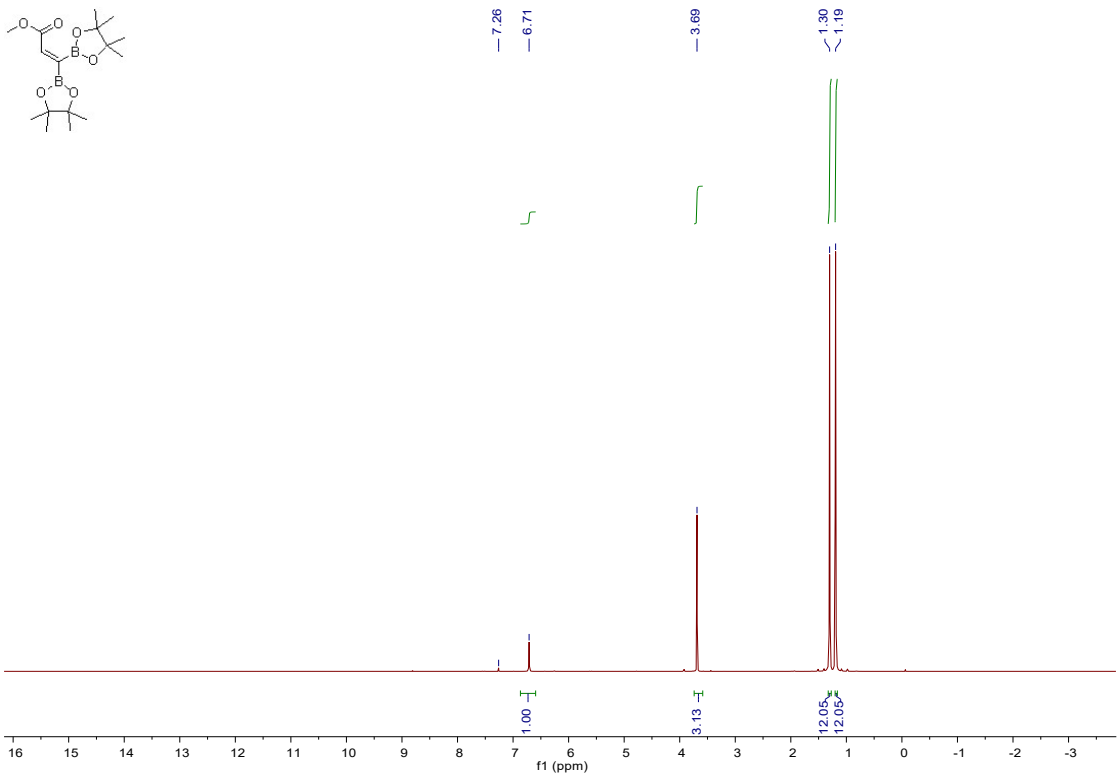
^{13}C NMR spectrum of compound **3ra**



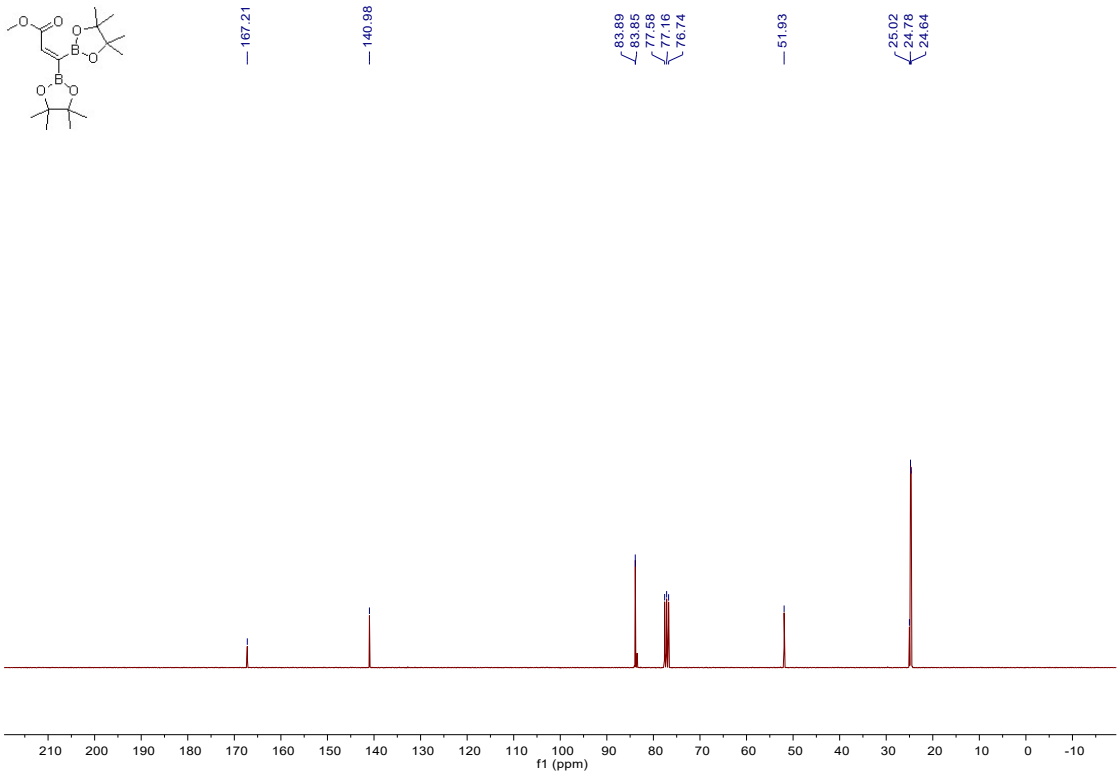
^{1}H NMR spectrum of compound **3sa**



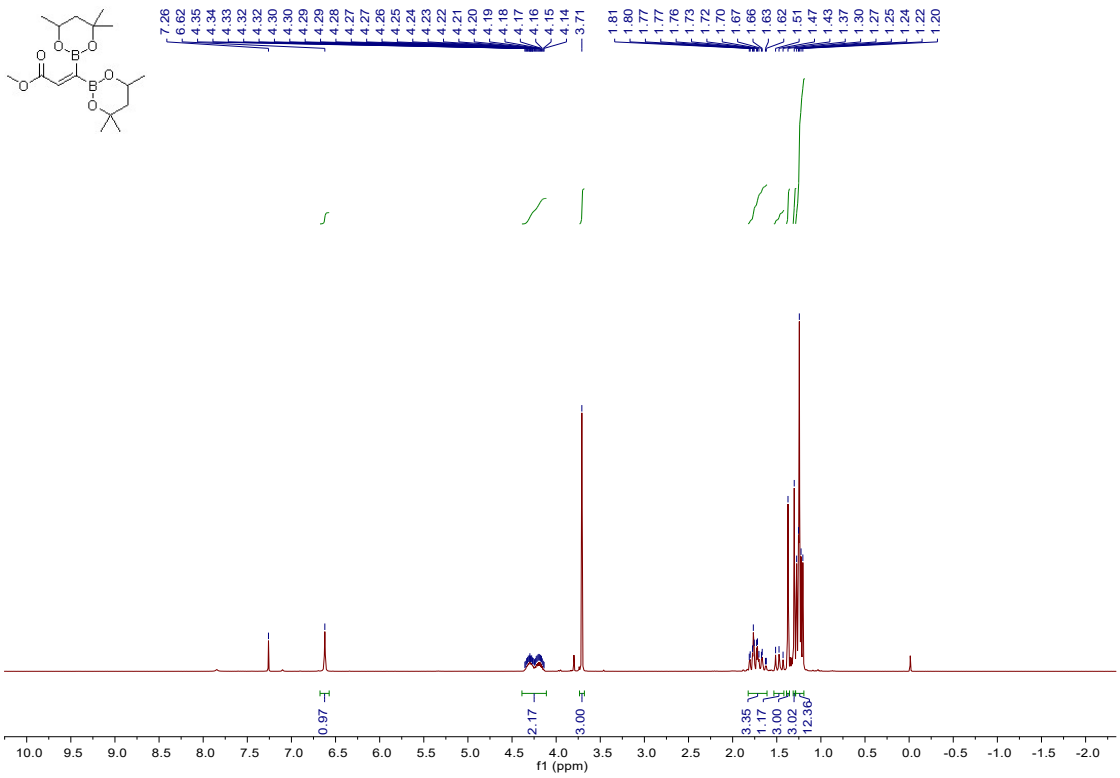
^{13}C NMR spectrum of compound **3sa**



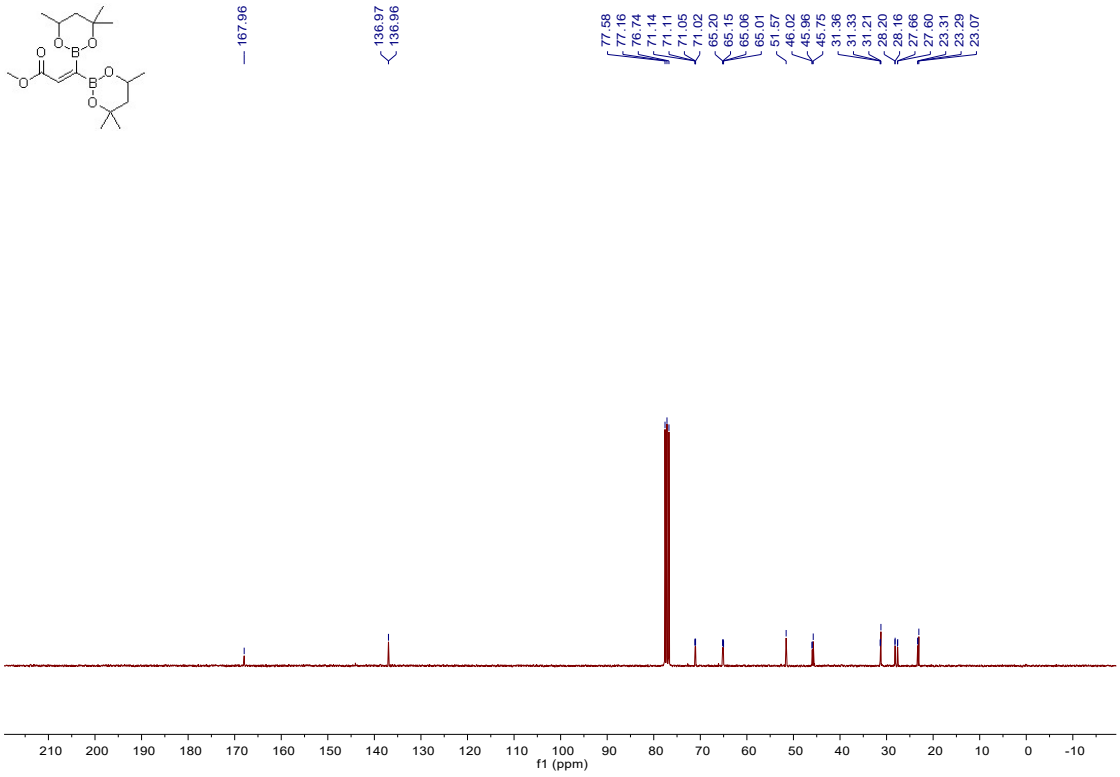
^{1}H NMR spectrum of compound **3ab**



^{13}C NMR spectrum of compound **3ab**



^{1}H NMR spectrum of compound **3af**



^{13}C NMR spectrum of compound **3af**

9. Reference

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