# Supporting Information

# Cu-Catalyzed Decarboxylative Borylation

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**General Experimental**

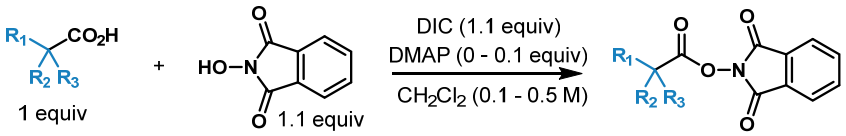
Tetrahydrofuran (THF), dichloromethane ($CH_2Cl_2$), *N*,*N*-dimethylformamide (DMF), and acetonitrile ($CH_3CN$) were obtained by passing the previously degassed solvents through an activated alumina column. *N*-hydroxyphthalimide (>98%) was purchase from Alfa Aesar (catalog # A13862). DIC (*N*,*N*'-diisopropylcarbodiimide) was purchased from Oakwood. $Cu(acac)_2$ was purchased from Aldrich (catalog # 51,436-5). $MgCl_2$ (<200 μm) was purchased from Sigma-Aldrich (lot # MKBX9508V). $B_2pin_2$ was purchased from Oakwood Chemical (catalog # 019250). $LiOH•H_2O$ was purchased from Sigma-Aldrich and grinded to floppy powder prior to use. All the other reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Yields refer to chromatographically and spectroscopically ($^1$H NMR) homogeneous material. TLC was performed on 0.25 mm E. Merck silica plates (60F-254), using short-wave UV light as the visualizing agent, and cerium ammonium molybdate (CAM) or $KMnO_4$ and heat as developing agents. NMR spectra were recorded on Bruker DRX-600, DRX-500, and AMX-400 instruments and are calibrated using residual undeuterated solvent ($CHCl_3$ at 7.26 ppm $^1$H NMR, 77.16 ppm $^{13}$C NMR). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Column chromatography was performed using E. Merck silica gel (60, particle size 0.043–0.063 mm). High-resolution mass spectra (HRMS) were recorded on Waters LC with G2-XS TOF mass spectrometer by electrospray ionization time of flight reflectron experiments. GCMS (EI) was recorded on Agilent 7820A GC systems and 5975 Series MSD. Melting points were recorded on a Fisher-Johns 12-144 melting point apparatus and are uncorrected.

**Handling of Cu Catalysts**

All Cu catalysts were handled open to air on the bench top, and the bottles were neither flame dried nor stored under inert atmosphere.

## Synthesis of Redox-Active Esters

### General Procedure A




Redox-active esters were prepared according to the previously reported procedure[1,2]. In short, a round-bottom flask or culture tube equipped with a stir bar was charged with carboxylic acid (1.0 equiv), *N*-hydroxy-phthalimide (1.1 equiv) and DMAP (0 – 0.1 equiv). Dichloromethane was added (0.1 – 0.5 M) followed by DIC (1.1 equiv), and the mixture was allowed to stir vigorously for 0.5 – 2 hours. The mixture was filtered (over Celite, $SiO_2$, or through a fritted funnel) and rinsed with additional $CH_2Cl_2$/$Et_2O$. The solvent was removed under reduced pressure, and purification by column chromatography (and recrystallization, if necessary) afforded the corresponding redox-active ester.

Redox-active esters shown below (**5**, **S1 – S25**) were reported in literature[1-8]. Please see these references for characterization as well as graphical supporting information[1,2] for the synthesis of redox-active esters.

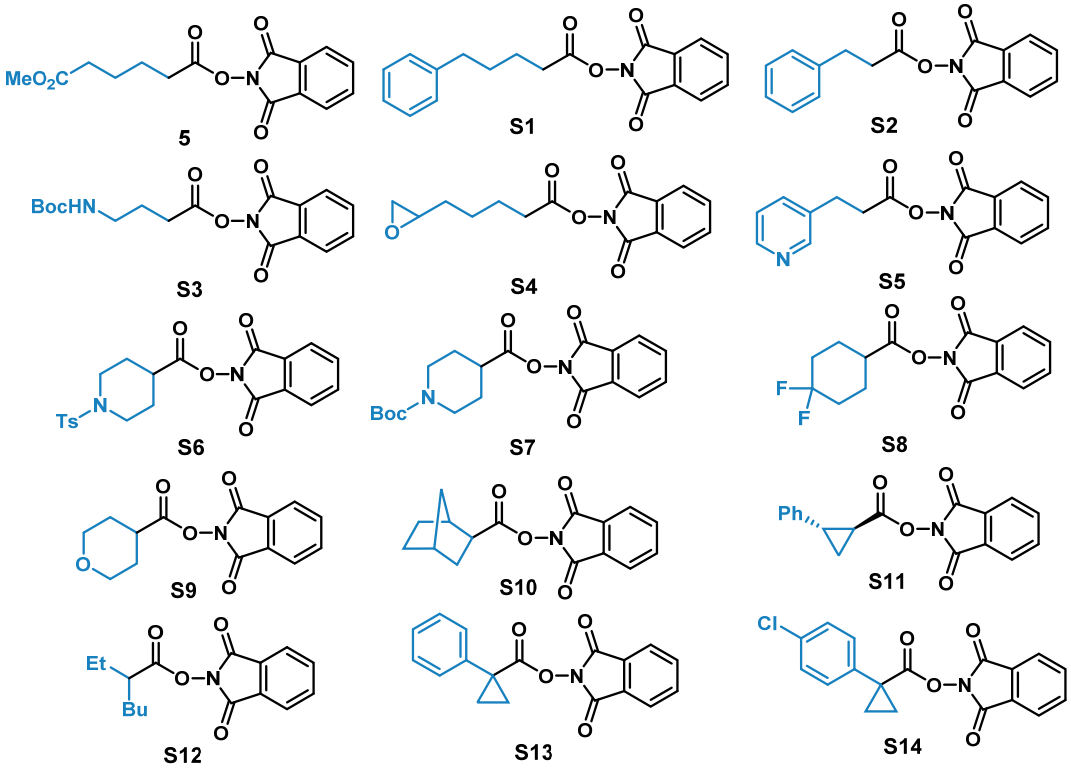



**Figure S1.** Known redox-active esters.

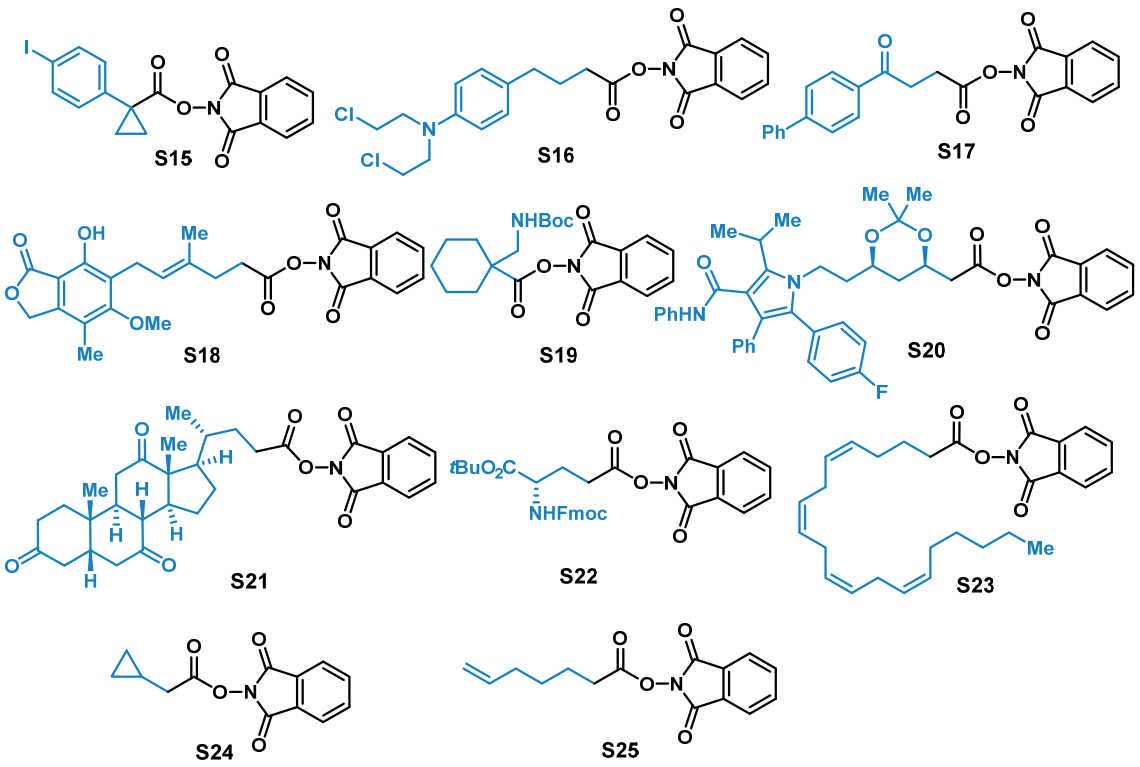



**Figure S1.** Known redox-active esters (continued).

New redox-active esters synthesized according to **General Procedure A** are listed below.

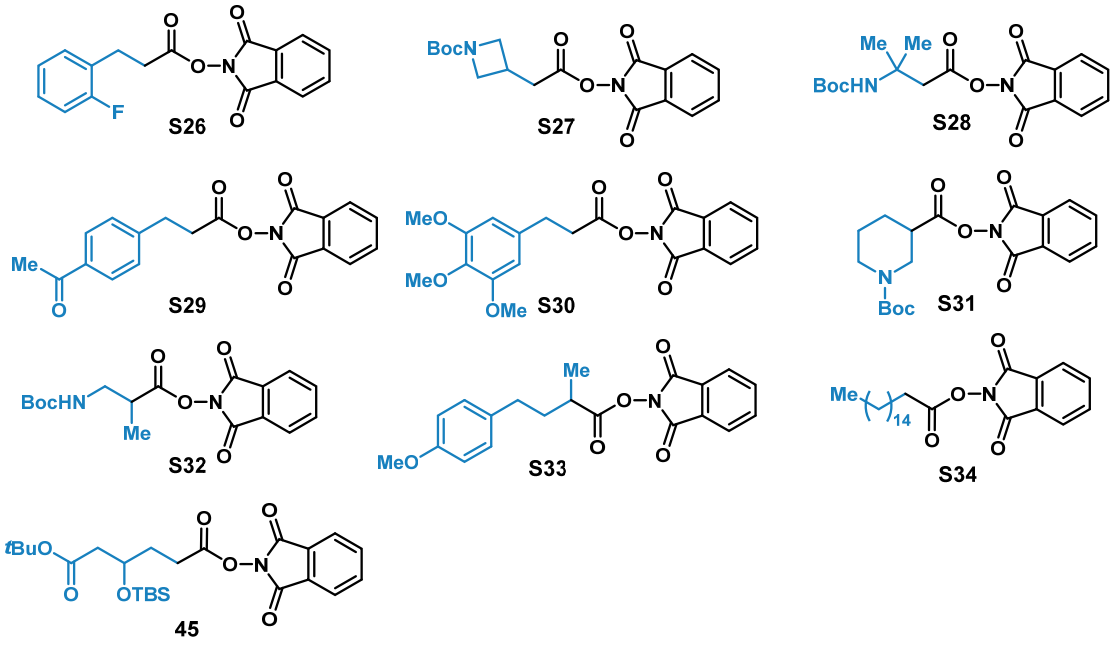



**Figure S2.** New redox-active esters.

## Optimization Details

All optimization reactions were carried out on 0.1 mmol scale. $LiOH•H_2O$ was grinded to floppy powder prior to use. The crude reaction mixture was analyzed by GC/FID with dodecane as internal standards.

*Evaluation of different metals*

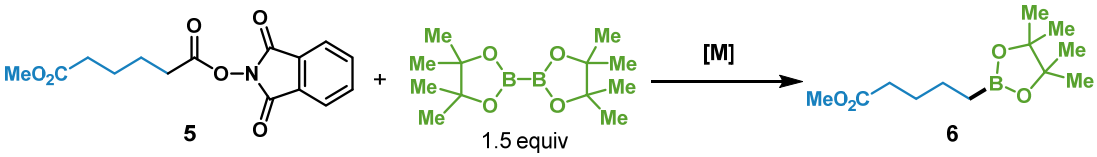



**Table S1.** Evaluation of different metals.

| Entry | Conditions | Yield |
|---|---|---|
| 1 | $NiCl_2•H_2O$, diOMe-bipy (13 mol%), MeLi (1.5 equiv), $MgBr_2•Et_2O$ (1.5 equiv) | 43% |
| 2 | $MnBr_2$ (5 mol%), TMEDA (20 mol%), EtMgBr (1.5 equiv), DME | 6% |
| 3 | $FeBr_2$ (10 mol%), $MgBr_2•Et_2O$ (1.5 equiv), *t*BuLi (1.5 equiv), THF | trace |
| 4 | CuTc/di*t*Bu-bipy/$Pcy_3$ (10/10/10 mol%), *t*BuOLi (1.5 equiv), THF/NMP | 0 |
| 5 | CuTc/di*t*Bu-bipy/$PPh_3$ (10/10/10 mol%), *t*BuOLi (1.5 equiv), THF/NMP | 0 |
| 6 | CuI/$PPh_3$ (10/10 mol%), *t*BuOLi (1.5 equiv), THF | 0 |
| 7 | CuI/*t*Bubipy (10/10 mol%), *t*BuOLi (1.5 equiv), $MgBr_2•Et_2O$ (0.2 equiv), THF | 11% |
| 8 | CuI/di*t*Bu-bipy (10/10 mol%), *t*BuOLi (1.5 equiv), THF | 13% |

*Evaluation of Cu sources and solvents*

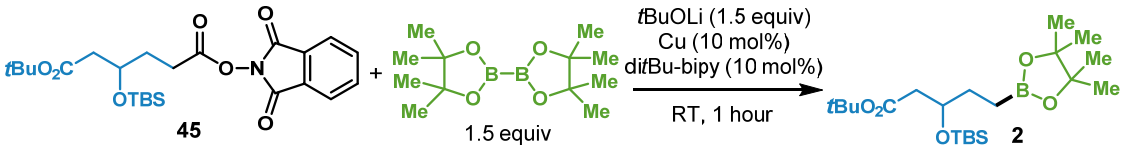



**Table S2.** Evaluation of Cu sources and solvents.

| Entry | Cu [w/ THF/DMF (4/1)] | Yield | Entry | Solvent [w/ $Cu(OAc)_2$] | Yield |
|---|---|---|---|---|---|
| 1 | CuCl | 12% | 1 | THF only | 11% |
| 2 | CuBr | 9% | 2 | THF/DMA 4/1 | 10% |
| 3 | CuCN | trace | 3 | THF/NMP 4/1 | 11% |
| 4 | $Cu(MeCN)_4PF_6$ | 8% | 4 | THF/NMP 9/1 | 18% |
| 5 | $CuCl_2$ | 11% | 5 | THF/MeCN 4/1 | 11% |
| 6 | $CuCl_2•H_2O$ | 19% | **6** | **dioxane/DMF 4/1** | **24%** |
| 7 | $CuBr_2$ | 9% | 7 | glyme/DMF 4/1 | 20% |
| 8 | $CuF_2$ | 0 | 8 | DMF only | 5% |
| 9 | $CuSO_4•5H_2O$ | Trace | | | |
| **10** | **$Cu(OAc)_2$** | **19%** | | | |

*Evaluation of bases*

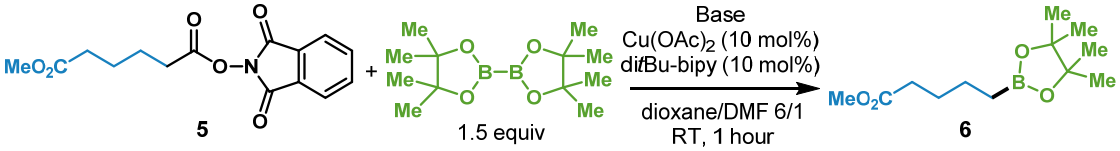



**Table S3.** Evaluation of bases.

| Entry | Base | Yield |
|---|---|---|
| 1 | *t*BuOLi (1.5 equiv) | 25% |
| 2 | MeOLi (in MeOH, 1.5 equiv) | <5% |
| 3 | MeONa | 0 |
| 4 | EtONa | 0 |
| 5 | *t*BuONa | 0 |
| 6 | *t*BuOK | 0 |
| 7 | $K_2CO_3$ | 0 |
| 8 | *t*BuOLi (old bottle, 4.0 equiv), $MgBr_2$•$Et_2O$ (0.2 equiv) | 40% |
| 9 | *t*BuOLi (new bottle, 4.0 equiv), $MgBr_2$•$Et_2O$ (0.2 equiv) | 29% |
| 10 | *t*BuOLi (in THF, 4.0 equiv), $MgBr_2$•$Et_2O$ (0.2 equiv) | 30% |
| 11 | LiOH (4.0 equiv), $MgBr_2$•$Et_2O$ (0.2 equiv) | 47% |
| **12** | **LiOH•$H_2O$ (4.0 equiv), $MgBr_2$•$Et_2O$ (0.2 equiv)** | **48%** |

*Evaluation of Cu/ligand*

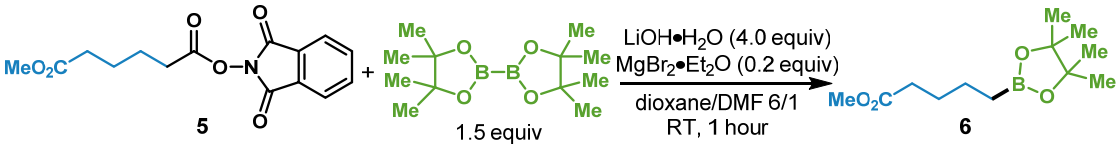
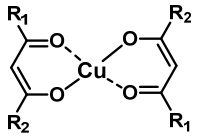


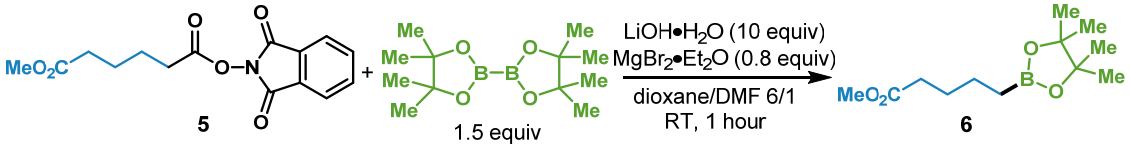

**Table S4.** Evaluation of Cu/ligand.

| Entry | Cu/ligand | Yield |
|---|---|---|
| 1 | $Cu(OAc)_2$/di*t*Bu-bipy/$PPh_3$ (10/10/10 mol%) | 35% |
| 2 | $Cu(OAc)_2$/di*t*Bu-bipy/$PCy_3$ (10/10/10 mol%) | 35% |
| 3 | $Cu(OAc)_2$/di*t*Bu-bipy/$PCy_3$•$HBF_4$ (10/10/10 mol%) | 34% |
| 4 | $Cu(OAc)_2$/di*t*Bu-bipy/dppe (10/10/10 mol%) | 19% |
| 5 | $Cu(OAc)_2$/dppe (10/10 mol%) | 34% |
| 6 | $Cu(OAc)_2$/dppe (10/15 mol%) | 16% |
| 7 | $Cu(OAc)_2$/dppe (10/20 mol%) | trace |
| **8** | **$Cu(acac)_2$ (10 mol%)** | **47%** |
| 9 | **L1**, $R_1 = R_2 =$ *t*Bu (10 mol%) | 45% |
| 10 | **L1**, $R_1 = R_2 =$ *i*Pr (10 mol%) | 35% |
| 11 | **L1**, $R_1 = R_2 =$ Ph (10 mol%) | 45% |
| 12 | **L1**, $R_1$, $R_2 =$ *t*Bu, Me (10 mol%) | 48% |
| 13 | **L1**, $R_1 = R_2 = CF_3$ (10 mol%) | 31% |
| 14 | **L1**, $R_1$, $R_2 =$ *t*Bu, $CF_3$ (10 mol%) | 30% |




**L1**

*Evaluation of equivalents and additives*




*Cu/ligands and additives*

**Table S5.** Cu/ligands and additives.

| Entry | Conditions | Yield |
|---|---|---|
| 1 | $Cu(OAc)_2$/di*t*Bu-bipy (10/10 mol%) | 62% |
| 2 | $Cu(acac)_2$ (10 mol%) | 51% |
| **3** | **$Cu(acac)_2$ (20 mol%)** | **62%** |
| 4 | $Cu(acac)_2$ (30 mol%) | 63% |
| 5 | $Cu(acac)_2$ (20 mol%), additive $H_2O$ (50 µL, 28 equiv) | 59% |
| 6 | $Cu(acac)_2$ (20 mol%), additive *t*BuOLi (2 equiv) | 60% |
| 7 | $Cu(acac)_2$ (10 mol%), CuCl (10 mol%) | 59% |
| 8 | $Cu(acac)_2$ (10 mol%), $Cu(OAc)_2$ (10 mol%) | 50% |
| 9 | $Cu(acac)_2$ (10 mol%), $Cu(ClO_4)_2$•$6H_2O$ (10 mol%) | 48% |
| 10 | $Cu(acac)_2$/CuCl/di*t*Bu-bipy (10/10/10 mol%) | 59% |
| 11 | $Cu(acac)_2$/$Cu(OAc)_2$/di*t*Bu-bipy (10/10/10 mol%) | 59% |

*Magnesium sources*

**Table S6.** Magnesium sources.

| Entry | Instead of $MgBr_2$•$Et_2O$ (w/ 20 mol% $Cu(acac)_2$) | Yield |
|---|---|---|
| 1 | $MgCl_2$ | 61% |
| 2 | $Mg(OTf)_2$ | 19% |
| 3 | $Mg(ClO_4)_2$ | 12% |
| 4 | MgO | trace |
| 5 | $Mg(OAc)_2$•$4H_2O$ | 24% |

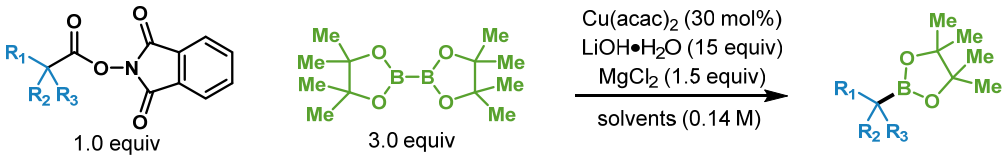
*Final conditions and deviations*

**Table S7.** Final conditions and deviations.

| Entry | With $Cu(acac)_2$ (20 mol%) | Yield |
|---|---|---|
| 1 | LiOH•$H_2O$ (15 equiv), $MgBr_2$•$Et_2O$ (0.8 equiv) | 69% |
| 2 | LiOH•$H_2O$ (20 equiv), $MgBr_2$•$Et_2O$ (0.8 equiv) | 69% |
| 3 | LiOH•$H_2O$ (30 equiv), $MgBr_2$•$Et_2O$ (0.8 equiv) | 67% |
| **4** | **LiOH•$H_2O$ (15 equiv), $MgCl_2$ (1.5 equiv), dioxane/DMF 4/1** | **69%** |
| **5** | **Same as entry 4 with $Cu(acac)_2$ (30 mol%), $B_2pin_2$ (3.0 equiv)** | **86%** |
| 6 | Same as entry 5, LiOH•$H_2O$ not grinded | 66% |

**Cu-Catalyzed Decarboxylative Borylation of Redox-Active Ester**

**General Procedure B**



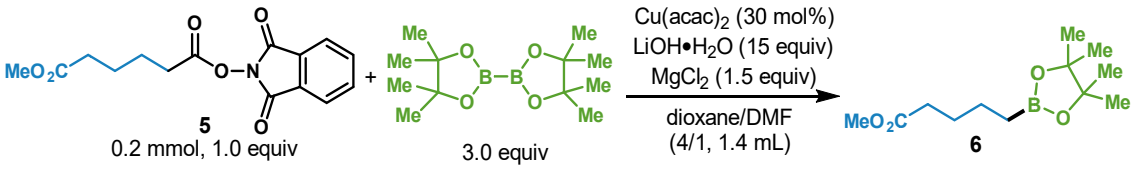

To a 15 mL culture tube equipped with a stir bar were added redox-active ester (1.0 equiv), $B_2pin_2$ (3.0 equiv), LiOH•$H_2O$ (15 equiv), $Cu(acac)_2$ (30 mol%) and $MgCl_2$ (1.5 equiv). The tube was evacuated and backfilled with argon for 3 times. Degassed dioxane/DMF (6:1 – 1:2 ratio, 0.14 M) was added and the resulting mixture was stirred under 1000 rpm at RT until dark brown color was observed (typical reaction time < 10 min). The reaction mixture was diluted with $Et_2O$ or EtOAc (7 mL for 0.2 mmol scale) and saturated $NH_4Cl$ (7 mL for 0.2 mmol scale), and the resulting mixture was shaken vigorously until getting a clear biphasic solution. The organic phase was collected and dried over anhydrous $Na_2SO_4$, evaporated and purified by silica gel chromatography to afford the desired product.

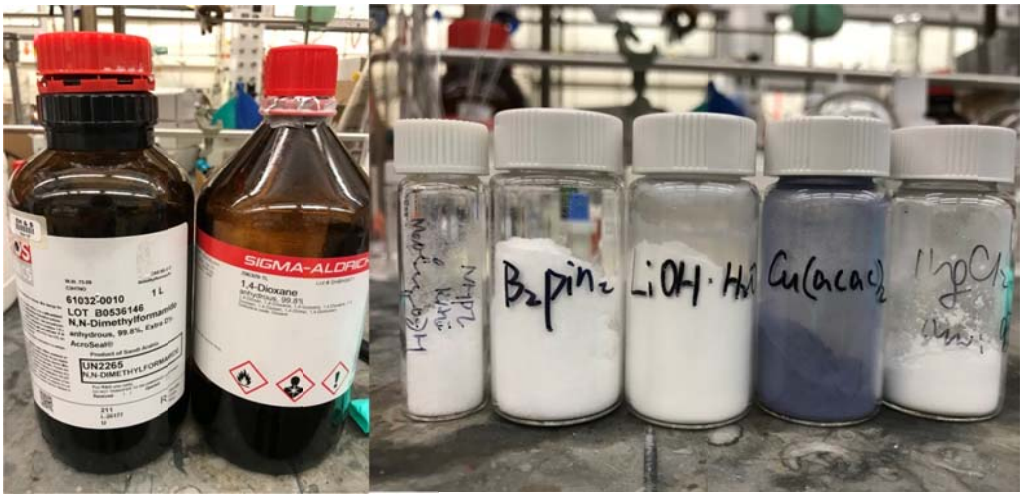
***Notes:***

1. LiOH•$H_2O$ was grinded to floppy powder prior to use, otherwise lower yield was observed (see entry 6 vs entry 5 in the last optimization table).
2. Substrates **29** and **33** were obtained using MTBE/DMF = 6/1 as solvent.
3. All the primary substrates use dioxane/DMF = 4/1 as solvent.
4. Dioxane/DMF ratio used for secondary substrates varied from 6/1 to 1/2.
5. For cases that the borylation product is close to $B_2pin_2$ on TLC and difficult to separate: upon completion, the reaction mixture was diluted with EtOAc and bubbled with air until green color was observed (typically < 3 min). Excess $B_2pin_2$ could be consumed this way.
6. For cases that the borylation product is close to phthalimide (PhthH) on TLC and difficult to separate: upon completion, the reaction mixture was diluted with EtOAc and washed with $NH_4Cl$ followed by $K_2CO_3$ (10% aq). PhthH could be washed away by $K_2CO_3$.

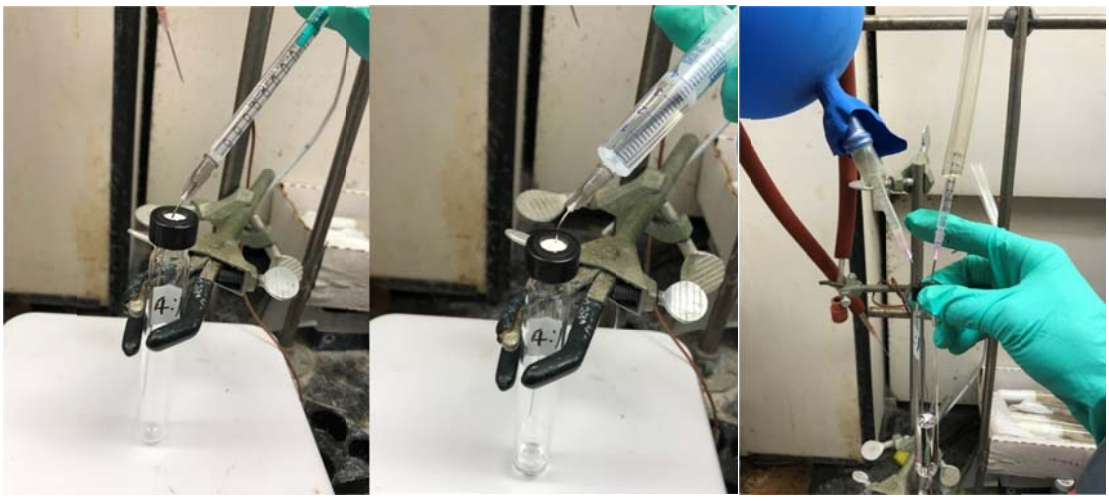
**Graphical Supporting Information for General Procedure B**

**Cu-Catalyzed Borylation Reaction:**

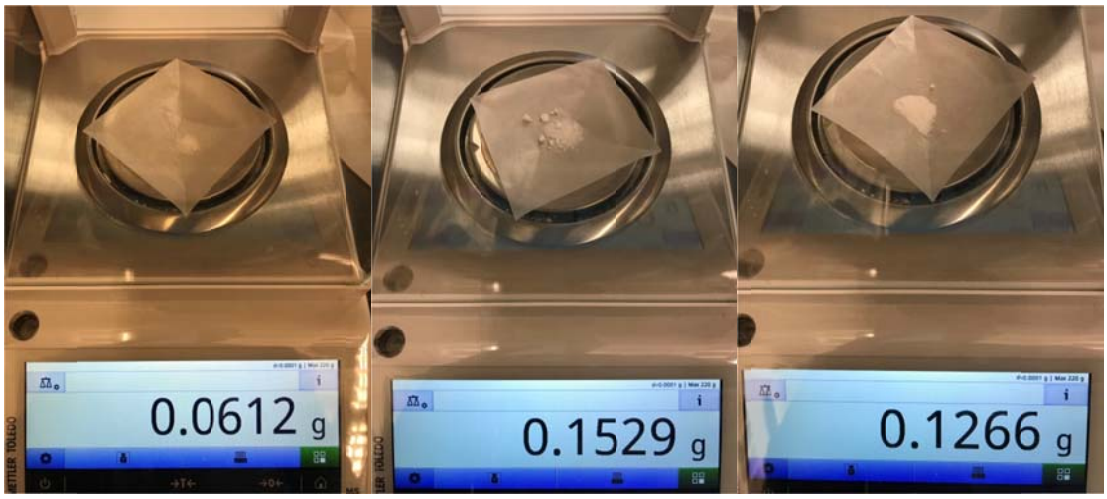



**(Left)** DMF and dioxane. **(Right)** Reagents used in this reaction.



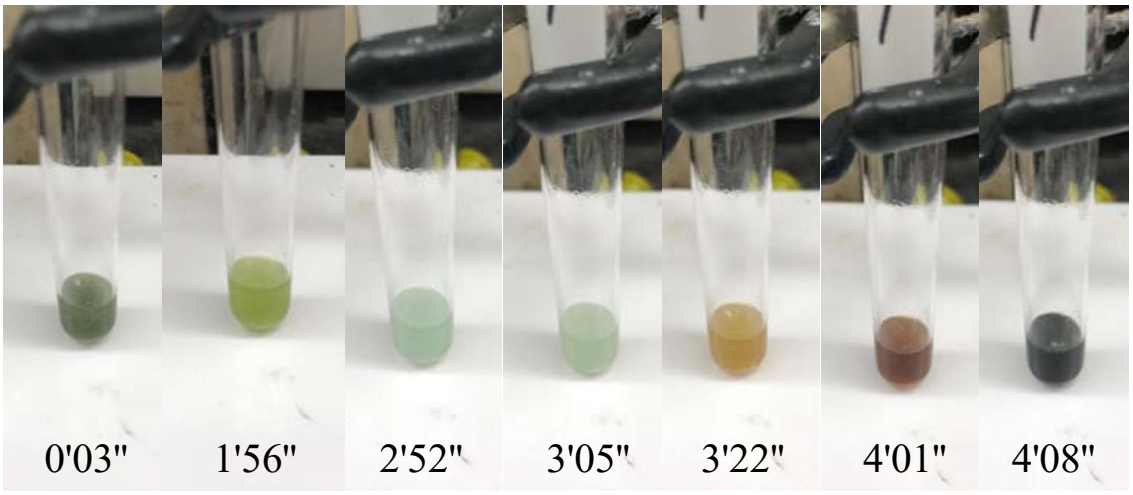
**(Left)** DMF (1 mL). **(Center)** Dioxane (4 mL). **(Right)** The mixed solvents were evacuated and backfilled with argon for twice.



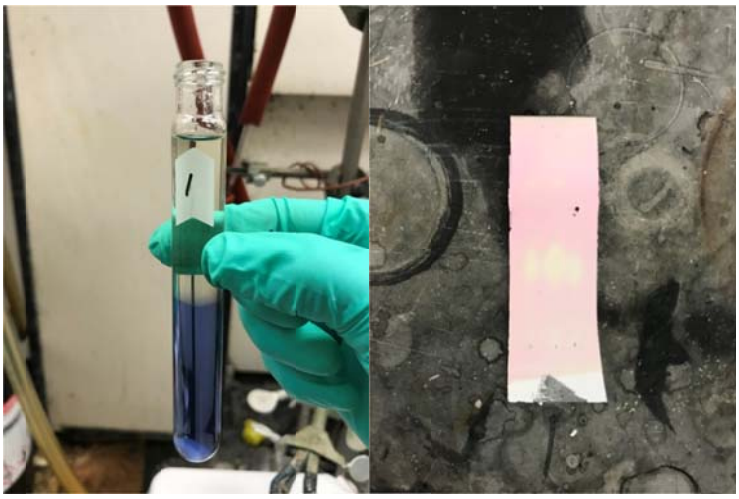

**(Left)** RAE **5** (0.2 mmol, 1.0 equiv). **(Center)** $B_2pin_2$ (3.0 equiv). **(Right)** $LiOH•H_2O$ (15 equiv).


**(Left)** $Cu(acac)_2$ (30 mol%). **(Center)** $MgCl_2$ (1.5 equiv). **(Right)** Put all the five materials into a 15 mL culture tube equipped with a stir bar.

**(Left)** The tube was evacuated and backfilled with argon for three times. **(Right)** Dioxane/DMF (4:1, 1.4 mL) was added.




**(Above)** After addition of solvent, the color change was recorded. The reaction was done (4'08") when dark brown color was observed.



**(Left)** The crude reaction was diluted with EtOAc (7 mL) and saturated $NH_4Cl$ (7 mL), and the resulting mixture was shaken vigorously until getting a clear biphasic solution. **(Right)** TLC after stained with $KMnO_4$ (line 1: crude reaction mixture; line 2: co-spot; line 3: authentic product).

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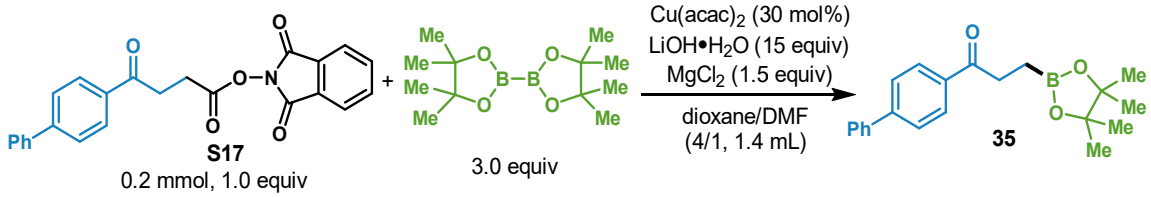
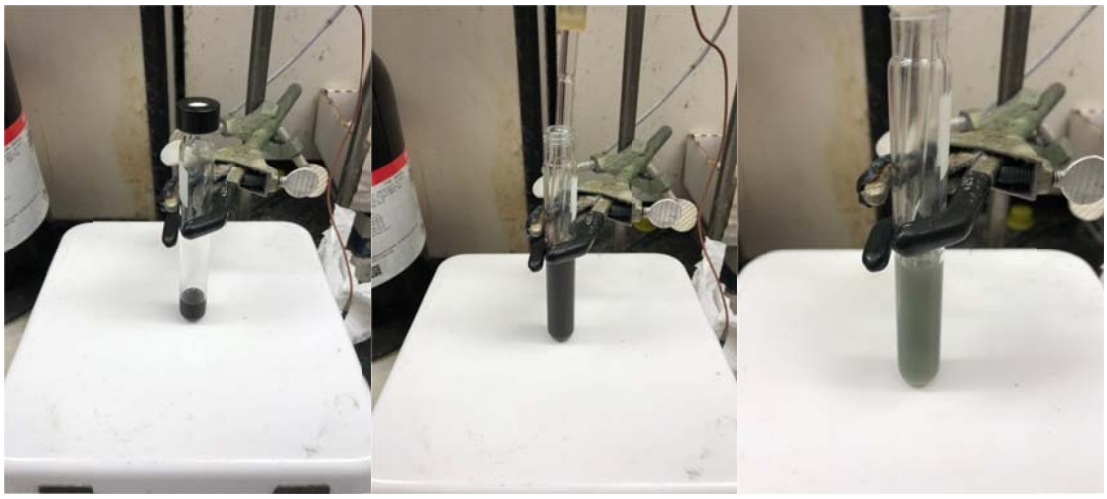
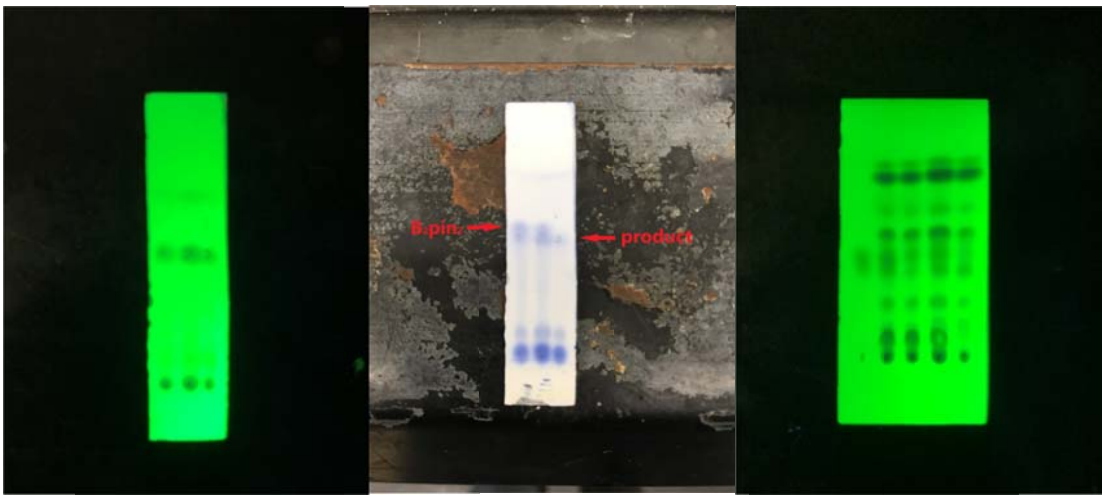
**Removal of $B_2pin_2$ and Phthalimide:**



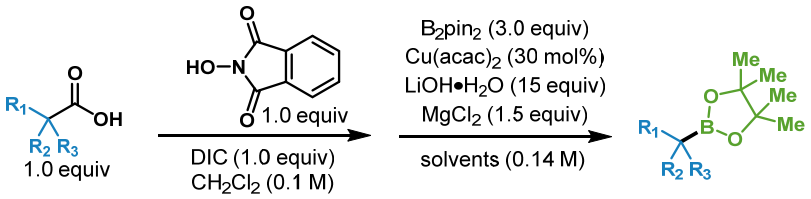
**(Left)** After completion of borylation. **(Center)** Reaction mixture was diluted with EtOAc and bubbled with air. **(Right)** After ~3 min, the mixture color changed to green.




**(Left)** TLC (hexane:$CH_2Cl_2$:EtOAc 6:1:1) under UV (line 1: crude reaction mixture immediately after completion; line 2: co-spot of line 1 and 3; line 3: crude reaction mixture after bubbling with air). **(Center)** The same TLC after CAM stein. **(Right)** TLC (hexane:EtOAc 2:1) after washing with $K_2CO_3$ (10% aq). Line 1: PhthH authentic sample; line 2: co-spot of line 1 and 3; line 3: crude reaction mixture before washing with $K_2CO_3$ (10% aq); line 4: co-spot of line 3 and 5; line 5: crude reaction mixture after washing with $K_2CO_3$ (10% aq).

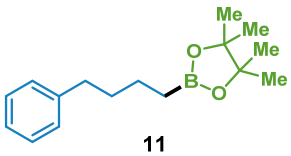
**One-pot Cu-Catalyzed Decarboxylative Borylation from Carboxylic Acid**

**General Procedure C**



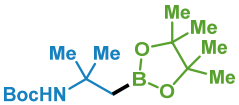

To a 15 mL culture tube equipped with a stir bar were added carboxylic acid (0.2 mmol, 1.0 equiv) and NHPI (1.0 equiv). The tube was evacuated and backfilled with argon for three times followed by addition of $CH_2Cl_2$ (2 mL, 0.1 M) and DIC (1.0 equiv). The resulting mixture was stirred under 1000 rpm at RT for 2 h before removal of the solvent by rotavapor. Then $B_2pin_2$ (3.0 equiv), LiOH•$H_2O$ (15 equiv), $Cu(acac)_2$ (30 mol%) and $MgCl_2$ (1.5 equiv) were added and the tube was evacuated and backfilled with argon for three times. Degassed dioxane/DMF (4:1, 1.4 mL, 0.14 M) was added and the resulting mixture was stirred at RT until dark brown color was observed (typical reaction time < 15 min). The reaction mixture was diluted with EtOAc and saturated $NH_4Cl$, and the resulting mixture was shaken vigorously until getting a clear biphasic solution. The organic phase was collected and dried over anhydrous $Na_2SO_4$, evaporated and purified by silica gel chromatography to afford the desired product.

This one-pot procedure was demonstrated with 4 examples:



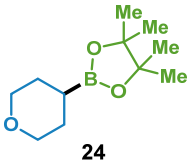

**11**

57%
vs 70%



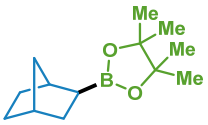

**18**

54%
vs 70%




**24**

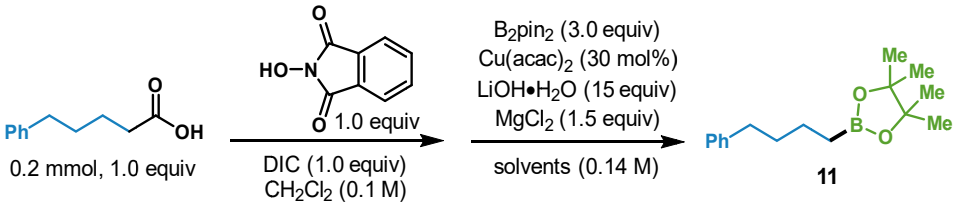
48%
vs 66%




**27**

54%, *dr* 10:1
vs 59%, *dr* 10:1

**Graphical Supporting Information for General Procedure C**



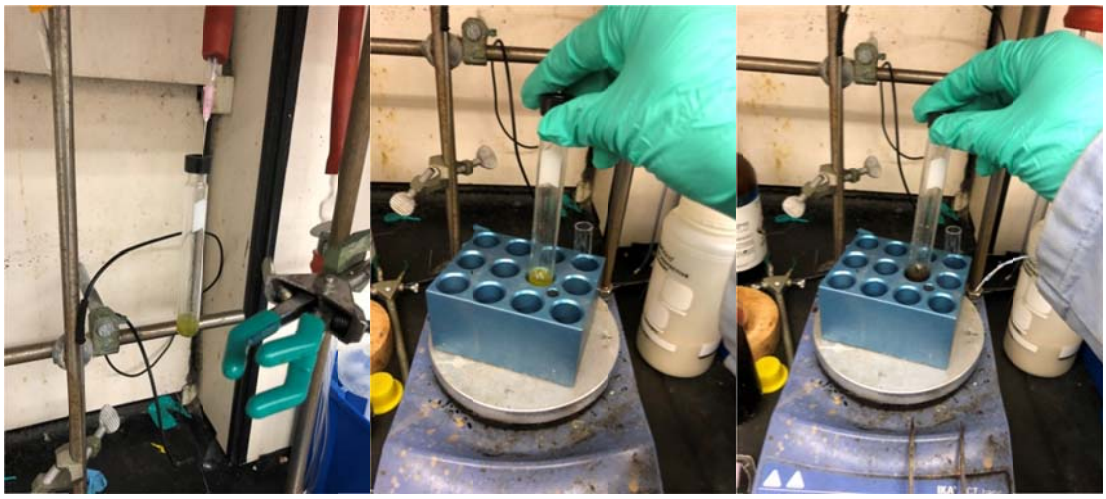

**(Left)** *N*-Hydroxyphthalimide and 5-Phenylvaleric acid (Sigma-Aldrich). **(Center)** 5-Phenylvaleric acid (0.2 mmol). **(Right)** *N*-Hydroxyphthalimide (1.0 equiv).

**(Left)** Add the acid and NHPI to a 15 mL culture tube. **(Center)** $CH_2Cl_2$ (2 mL). **(Right)** The tube was evacuated and backfilled with argon for three times and $CH_2Cl_2$ was added.

**(Left)** Add DIC (1.0 equiv). **(Center)** After stirring at RT for 2h. **(Right)** $CH_2Cl_2$ was removed by rotavapor.


**(Left)** After removal of $CH_2Cl_2$. **(Center)** Reagents used for decarboxylative borylation. **(Right)** $B_2pin_2$ (3.0 equiv).


**(Left)** $Cu(acac)_2$ (30 mol%). **(Center)** $MgCl_2$ (1.5 equiv). **(Right)** $LiOH•H_2O$ (15 equiv).



**(Left)** Add the four materials to the tube and the tube was evacuated and backfilled with argon for three times. **(Center)** Add solvent (dioxane/DMF = 4/1, 1.4 mL) to the tube. **(Right)** 10 mins after addition of solvent, the color changed to dark brown, which indicated the completion of the borylation reaction.

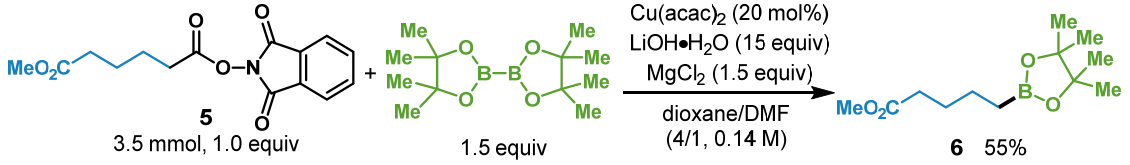
**(Left)** Quench the reaction with saturated $NH_4Cl$ (aq) and EtOAc. **(Center)** Transfer the crude reaction mixture to a separation funnel. **(Right)** Organic phase was collected and dried over anhydrous $Na_2SO_4$.

**(Left)** Crude TLC (right top spot is the product). **(Center)** Purification by flash column chromatography (silica gel). **(Right)** TLC after column.


**(Left)** Weight of empty vial. **(Center)** Weight of vial with product (29.5 mg, 57% yield).

**Gram-Scale Cu-Catalyzed Decarboxylative Borylation of Redox-Active Ester**

**General Procedure D**

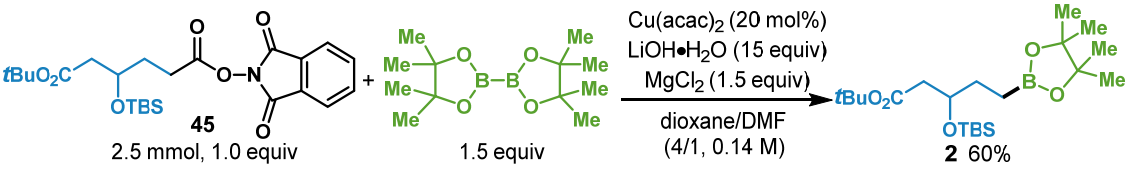



To a 50 mL flask equipped with a stir bar were added redox-active ester **5** (1.07 g, 3.5 mmol), $B_2pin_2$ (1.33 g, 1.5 equiv), LiOH•$H_2O$ (2.21 g, 15 equiv), $Cu(acac)_2$ (183 mg, 20 mol%) and $MgCl_2$ (499 mg, 1.5 equiv). The flask was evacuated and backfilled with argon for three times. Degassed dioxane/DMF (4/1, 17.5 mL) was added at once and the resulting mixture was stirred under 1000 rpm at RT until the reaction color turned dark brown (typically < 10 min). The reaction mixture was diluted with $Et_2O$ (50 mL) and washed with saturated $NH_4Cl$ (30 mL), $K_2CO_3$ (10% aq, 30 mL) and brine (30 mL) successively. The organic phase was dried over anhydrous $Na_2SO_4$, evaporated and purified by flash column chromatography (silica gel, hexanes to 100:1 $CH_2Cl_2$:$Et_2O$) to afford 466 mg (55%) of the borylation product **6**.

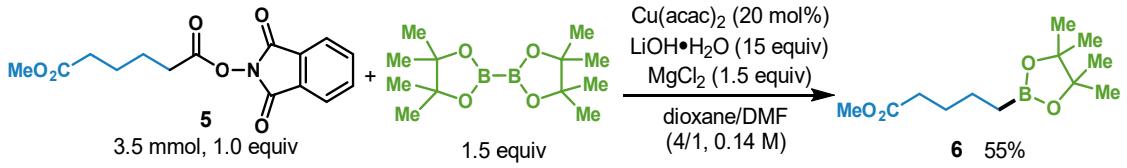
***Notes:***

LiOH•$H_2O$ was grinded to floppy powder prior to use.

This procedure was also demonstrated on 2.5 mmol scale (1.19 g) with redox-active ester **45**, $Cu(acac)_2$ (20 mol%) and $B_2pin_2$ (1.5 equiv). Purification by flash column chromatography (silica, 20:1 hexanes:$Et_2O$) afforded 622 mg (60%) of the borylation prodcut **2**.

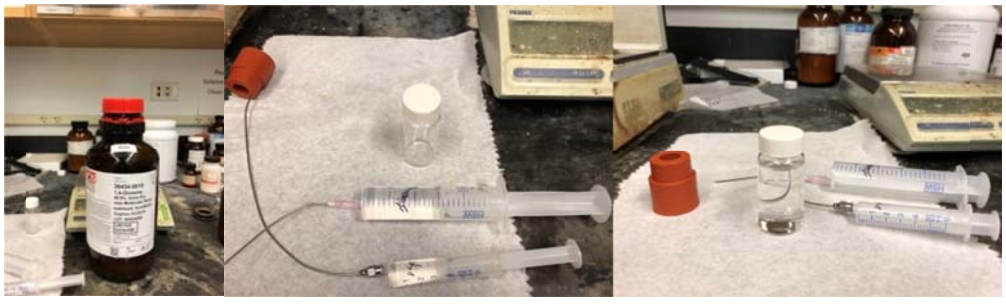


**Graphical Supporting Information for General Procedure D**




**(Left)** Reagents for this reaction. **(Center)** RAE **5** (1.07 g, 3.5 mmol). **(Right)** $B_2pin_2$ (1.33 g, 1.5 equiv).

**(Left)** $Cu(acac)_2$ (183 mg, 20 mol%). **(Center)** $MgCl_2$ (499 mg, 1.5 equiv). **(Right)** $LiOH•H_2O$ (2.21 g, 15 equiv).



**(Left)** Dioxane (1 L sealed bottle, Acros). **(Center)** Prepare the solvent, DMF (4 mL), dioxane (16 mL). **(Right)** Premix the solvent in a 25 mL scintillation vial.

**(Left)** Evacuate the flask and backfill with argon for three times. **(Center left)** After addition of solvent (17.5 mL). **(Center Right)** 5 min after addition. **(Right)** 6 min.

**(Left)** 6.5 min. **(Center left)** 7 min. **(Center right)** 7.5 min. **(Right)** 8 min.

**(Left)** Quench the reaction by adding 10 mL $NH_4Cl$ (aq) and 10 mL $Et_2O$. **(Center)** Transfer to a separation funnel. **(Right)** The organic phase was dried over anhydrous $Na_2SO_4$.

**Troubleshooting: Frequently Asked Questions**

**Question 1:**

Do I need to run the reaction in glovebox?

**Answer:**

We do not set up or run the reaction in glovebox. A glovebox is not necessary for this reaction. We do evacuate the air from the tube via vacuum manifold though.

**Question 2:**

How sensitive is this reaction to water and air?

**Answer:**

Addition of ~30 equivalents of $H_2O$ resulted in <5% drop in yield. Running the reaction under air without inert atmosphere resulted in ~20% drop in yield.

**Question 3:**

Why do you need 15 equivalents of $LiOH•H_2O$?

**Answer:**

The solubility of $LiOH•H_2O$ in organic solvent is limited. So 15 equivalents is necessary to increase the actually effective amounts of $LiOH•H_2O$.

**Question 4:**

Can I use LiOH instead of $LiOH•H_2O$?

**Answer:**

LiOH resulted in similar yield (within 5% difference) as long as LiOH was also grinded to floppy powder prior to use.

**Question 5:**

Is $MgCl_2$ essential for this reaction?

**Answer:**

Without $MgCl_2$, the yield dropped to <20%. However, instead of $MgCl_2$, many other metal salts also proved to be effective, such as $MgBr•Et_2O$, LiCl, $FeCl_3•6H_2O$, $CoCl_2$, $NiCl_2•6H_2O$, $CrCl_3$, $MnCl_2•4H_2O$, $ZrCl_4$ (control studies showed no product formation in the absence of Cu). We chose $MgCl_2$ because it's cheap, environment friendly and easy to handle.

**Question 6:**

How do I purify my products?

**Answer:**

The pinacol alkylboronate esters are not stable on preparative TLC due to possible oxidation of C–B bond or hydrolytic cleavage of pinacol esters. In all cases shown in this paper, we purify the products by flash column chromatography with gradient elution. For products that were very unstable on silica gel, deactivated silica gel (35 wt% $H_2O$) could be used as suggested in reference 5.

Two major impurities, namely $B_2pin_2$ and phthalimide (PhthH), could be removed by methods shown below:

a. Upon completion, the reaction mixture was diluted with EtOAc and bubbled with air. Observing of green color (typically < 2 min) indicated complete consumption of excess $B_2pin_2$.

b. Upon completion, the reaction mixture was diluted with EtOAc and washed with $NH_4Cl$ followed by $K_2CO_3$ (10% aq) for three times. PhthH could be washed away by $K_2CO_3$.

**Question 7:**

Are the Bpin products volatile?

**Answer:**

Most of products reported in this study are not volatile except the radical clock products **43** and **44**. You can use pentane and $Et_2O$ for workup and column chromatography and keep the temperature of rotavapor water bath below 30 °C.

**Question 8:**

Sometimes emulsion formed during the workup. What should I do?

**Answer:**

After addition of $NH_4Cl$ solution, shake the reaction tube vigorously until getting a clear biphasic solution. Intermittent introduce of air (oxygen) could help break the metal aggregates. If lighter color was observed but emulsion still existed, add more $H_2O$ or brine and shake again.

**Question 9:**

I'm working on small scales, and the general procedure requires relatively high concentration (0.14 M). Can I dilute the reaction?

**Answer:**

The reaction can be diluted to 0.07 M by the addition of more solvent, thus diluting all reaction components, obtaining essentially the same yield, although the reaction will take a little longer to completion. Further dilution will cause decrease in yield.

**Question 10:**

Is this reaction exothermic? Does that affect the yield?

**Answer:**

The reaction became exothermic when brown color was observed. We didn't observe any appreciable ill effect to the yield though.

**Question 11:**

Dose longer reaction time cause decrease in yield?

**Answer:**

We left the reaction running overnight sometimes and no significant decrease of yield was observed.

**Question 12:**

Does the base-sensitive group survive under current base conditions?

**Answer:**

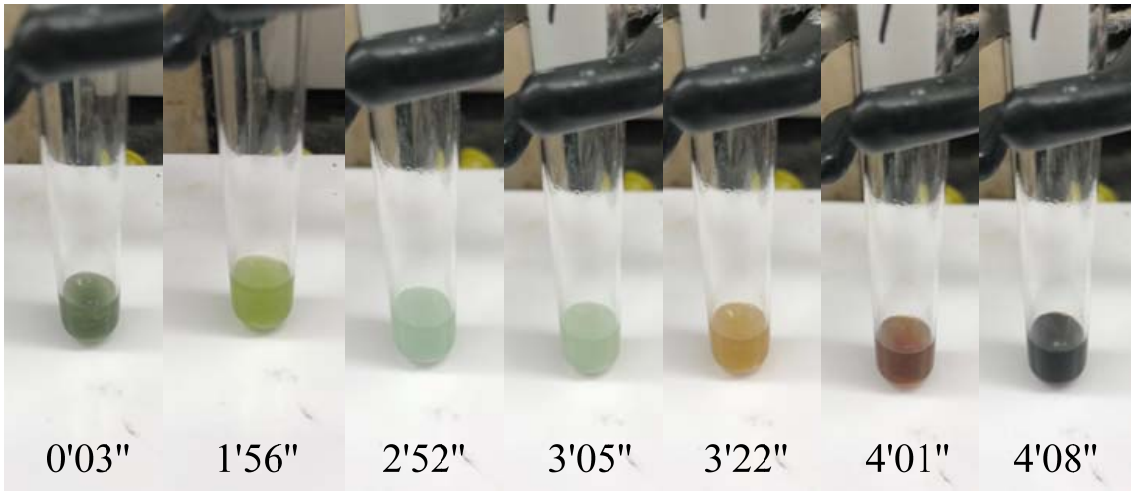
Base-sensitive functional groups such as ketone, ester, lactone, amide, free phenol, epoxide and carbamates such as Boc and Fmoc are all tolerated in this method.

**Question 13:**

How's the color changing during the transformation and which color indicates the completion of this reaction?

**Answer:**

Color change of this reaction was recorded graphically. The observation of dark brown color (4'08") indicated the completion of the reaction.




**Question 14:**

What's the limitation of current copper-catalyzed decarboxylative borylation?

**Answer:**

Substrates containing alkyl or aryl halogens (Br or I) gave lower yields due to competing

protodehalogenation and borylation of halogens. Tertiary and amino acid substrates are in general not working well in this method. Please see '**Unsuccessful or Challenging Substrates**' section for the problematic examples we've tried.

**Question 15:**

Could external ligand on copper improve the yield?

**Answer:**

We've screened common nitrogen, phosphine and acac-type ligands and no appreciable improvement was observed.

**Question 16:**

Is a rigorous stirring rate required to maintain high yields? Does it have any effect on the yield?

**Answer:**

Rigorous stirring rate is not necessary. Stirring control experiments have been done under stir rates of 200, 400, 600, 800, 1000 and 1200 rpm on substrate **11**. All entries gave essentially the same yield of product (<5% difference).

**Question 17:**

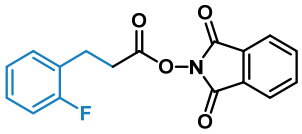
This is a heterogeneous reaction. Does the yield drop in a larger scale?

**Answer:**

We obtained similar yield when scaling up the reaction to 1 gram scale. Larger scale was not tested. We believe that it is very important to use well-grinded powder of $LiOH•H_2O$, $MgCl_2$ and $Cu(acac)_2$ for scale up.

**Experimental Procedures and Characterization Data for Redox-Active Esters**

**Compound S26**



***1,3-dioxoisoindolin-2-yl 3-(2-fluorophenyl)propanoate***

Following General Procedure A on 1.0 mmol scale with 3-(2-fluorophenyl)propionic acid. Purification by flash column chromatography (silica, 8:1 hexanes:EtOAc) afforded 246 mg (79%) of the title compound **S26**.

**Physical State**: white solid.

**m.p.:** 102 – 104 ºC.

$R_f$ = 0.45 (4:1 hexanes:EtOAc).

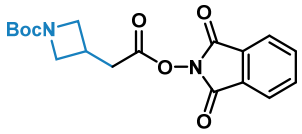
**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.28 (t, *J* = 7.6, 1H), 7.26 – 7.21 (m, 1H), 7.11 (td, *J* = 7.5, 1.3 Hz, 1H), 7.08 – 7.03 (m, 1H), 3.13 (t, *J* = 7.7 Hz, 2H), 3.05 – 2.97 (m, 2H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 168.9, 162.0, 161.3 (d, *J* = 245.6 Hz), 134.9, 130.9 (d, *J* = 4.4 Hz), 129.1, 128.8 (d, *J* = 8.2 Hz), 126.1 (d, *J* = 15.4 Hz), 124.4 (d, *J* = 3.6 Hz), 124.1, 115.6 (d, *J* = 21.9 Hz), 31.3 (d, *J* = 1.7 Hz), 24.5 (d, *J* = 2.8 Hz) ppm.

**$^{19}$F NMR (376 MHz, $CDCl_3$):** δ -118.6 ppm.

**HRMS (ESI-TOF):** calc'd for $C_{17}H_{13}FNO_4$ $[M+H]^+$ 314.0823; found 314.0829.

**Compound S27**



***tert-butyl 3-(2-((1,3-dioxoisoindolin-2-yl)oxy)-2-oxoethyl)azetidine-1-carboxylate***

Following General Procedure A on 2.0 mmol scale with 2-(1-(*tert*-butoxycarbonyl)azetidin-3-yl)acetic acid. Purification by flash column chromatography (silica, 3:1 hexanes:EtOAc) afforded 540 mg (75%) of the title compound **S27**.

**Physical State**: white amorphous solid.

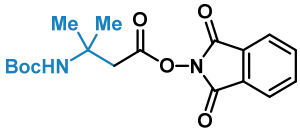
$R_f$ = 0.25 (3:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.86 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.14 (t, *J* = 8.2 Hz, 2H), 3.71 (dd, *J* = 8.9, 4.7 Hz, 2H), 3.04 – 2.95 (m, 3H), 1.42 (s, 9H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 167.9, 161.8, 156.3, 135.0, 128.9, 124.1, 79.7, 54.0, 35.4, 28.5, 25.1 ppm.

**HRMS (ESI-TOF):** calc'd for $C_{18}H_{21}N_2O_6$ $[M+H]^+$ 361.1394; found 361.1393.

**Compound S28**




***1,3-dioxoisoindolin-2-yl 3-((tert-butoxycarbonyl)amino)-3-methylbutanoate***

Following General Procedure A on 1.0 mmol scale with 3-((*tert*-butoxycarbonyl)amino)-3-methylbutanoic acid. Purification by flash column chromatography (silica, 4:1 hexanes:EtOAc) afforded 297 mg (82%) of the title compound **S28**.

**Physical State**: white solid.

**m.p.:** 103 – 105 ºC.

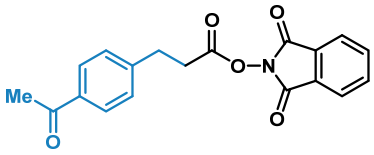
$R_f$ = 0.30 (4:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.87 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.77 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.79 (s, 1H), 3.13 (s, 2H), 1.46 (s, 6H), 1.40 (s, 9H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 167.1, 162.0, 154.7, 134.9, 129.0, 124.0, 79.4, 51.3, 40.4, 28.5, 27.8 ppm.

**HRMS (ESI-TOF):** calc'd for $C_{18}H_{22}N_2O_6Na$ $[M+Na]^+$ 385.1370; found 385.1375.

**Compound S29**




***1,3-dioxoisoindolin-2-yl 3-(4-acetylphenyl)propanoate***

Following General Procedure A on 1.0 mmol scale with 3-(4-acetylphenyl)propanoic acid. Purification by flash column chromatography (silica, 3:1 hexanes:EtOAc) afforded 239 mg (71%) of the title compound **S29**.

**Physical State**: white solid.

**m.p.:** 159 – 160 ºC.

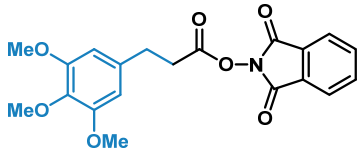
$R_f$ = 0.20 (4:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 3.16 (t, *J* = 7.7 Hz, 2H), 3.01 (t, *J* = 7.7 Hz, 2H), 2.59 (s, 3H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 197.9, 168.7, 162.0, 144.8, 135.9, 135.0, 129.0, 129.0, 128.7, 124.2, 32.3, 30.6, 26.8 ppm.

**HRMS (ESI-TOF):** calc'd for$C_{19}H_{16}NO_5$ $[M+H]^+$ 338.1023; found 338.1028.

**Compound S30**




***1,3-dioxoisoindolin-2-yl 3-(3,4,5-trimethoxyphenyl)propanoate***

Following General Procedure A on 1.0 mmol scale with 3-(3,4,5-trimethoxyphenyl)propanoic acid. Purification by flash column chromatography (silica, 6:1 hexanes:EtOAc) afforded 327 mg (85%) of the title compound **S30**.

**Physical State**: light yellow solid.

**m.p.:** 124 – 126 ºC.

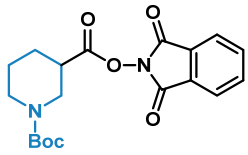
$R_f$ = 0.4 (4:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.91 – 7.86 (m, 2H), 7.82 – 7.77 (m, 2H), 6.47 (d, *J* = 1.8 Hz, 2H), 3.87 (d, *J* = 2.8 Hz, 6H), 3.83 (d, *J* = 2.8 Hz, 3H), 3.07 – 3.02 (ddd, *J* = 9.9, 5.5, 2.3 Hz, 2H), 3.00 – 2.96 (m, 2H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 169.0, 162.0, 153.5, 136.8, 135.1, 134.9, 129.03, 129.02, 124.1, 105.3, 61.0, 56.3, 33.0, 31.1 ppm.

**HRMS (ESI-TOF):** calc'd for $C_{20}H_{20}NO_7$ $[M+H]^+$ 386.1234; found 386.1234.

**Compound S31**




***1-(tert-butyl) 3-(1,3-dioxoisoindolin-2-yl) piperidine-1,3-dicarboxylate***

Following General Procedure A on 5.0 mmol scale with 1-(*tert*-butoxycarbonyl)piperidine-3-carboxylic acid. Purification by flash column chromatography (silica, 2:1 hexanes:EtOAc) afforded 1.42 g (76%) of the title compound **S31**.

**Physical State**: white solid.

**m.p.:** 135 – 137 ºC.

$R_f$ = 0.30 (1:1 hexanes:EtOAc).

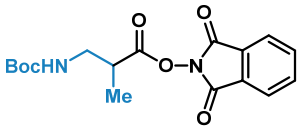
**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.88 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.51 – 4.14 (m, 1H), 3.95 (d, *J* = 13.3 Hz, 1H), 3.29 – 3.02 (m, 1H), 2.94 – 2.80 (m, 2H), 2.33 – 2.19 (m, 1H),

1.88 – 1.72 (m, 2H), 1.61 – 1.50 (m, 1H), 1.47 (s, 9H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 169.6, 161.9, 154.6, 134.9, 129.0, 124.1, 80.2, 45.4 (br), 43.5 (br), 39.2, 28.5, 27.6, 24.1 (br) ppm.

**HRMS (ESI-TOF):** calc'd for $C_{19}H_{23}N_2O_6$ $[M+H]^+$ 375.1551; found 375.1546.

**Compound S32**




***1,3-dioxoisoindolin-2-yl 3-((tert-butoxycarbonyl)amino)-2-methylpropanoate***

Following General Procedure A on 2.0 mmol scale with 3-((*tert*-butoxycarbonyl)amino)-2-methylpropanoic acid. Purification by flash column chromatography (silica, 4:1 hexanes:EtOAc) afforded 501 mg (72%) of the title compound **S32**.

**Physical State**: white solid.

**m.p.:** 77 – 80 ºC.

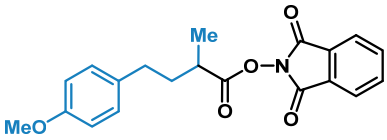
$R_f$ = 0.25 (4:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 5.27 (t, *J* = 6.5 Hz, 1H), 3.57 – 3.52 (m, 1H), 3.37 – 3.32 (m, 1H), 3.12 – 3.08 (m, 1H), 1.43 (s, 9H), 1.34 (d, *J* = 7.1 Hz, 3H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 171.7, 162.1, 156.2, 135.0, 129.0, 124.2, 79.7, 43.5, 38.5, 28.5, 14.3 ppm.

**HRMS (ESI-TOF):** calc'd for $C_{17}H_{21}N_2O_6$ $[M+H]^+$ 349.1394; found 349.1392.

**Compound S33**




Following General Procedure A on 6.0 mmol scale with 4-(4-methoxyphenyl)-2-methylbutanoic acid. Purification by flash column chromatography (silica, 6:1 hexanes:EtOAc) afforded 1.80 g (85%) of the title compound **S33**.

**Physical State**: white solid.

**m.p.:** 54 – 55 ºC.

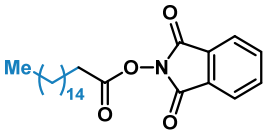
$R_f$ = 0.40 (4:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.89 – 2.81 (m, 1H), 2.80 – 2.67 (m, 2H), 2.17 – 2.09 (m, 1H), 1.92 – 1.84 (m, 1H), 1.38 (d, *J* = 7.0 Hz, 3H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 172.8, 162.2, 158.1, 134.9, 133.3, 129.6, 129.1, 124.1, 114.0, 55.4, 36.6, 35.9, 32.2, 17.2 ppm.

**HRMS (ESI-TOF):** calc'd for $C_{20}H_{20}NO_5$ $[M+H]^+$ 354.1336; found 354.1325.

**Compound S34**




***1,3-dioxoisoindolin-2-yl heptadecanoate***

Following General Procedure A on 1.5 mmol scale with heptadecanoic acid. Purification by flash column chromatography (silica, 8:1 hexanes:EtOAc) afforded 433 mg of the title compound **S34** (70%).

**Physical State**: white fluffy solid.

**m.p.:** 62 – 63 ºC.

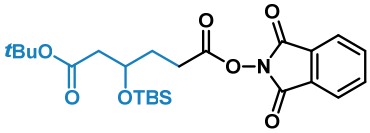
$R_f$ = 0.51 (4:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.91 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.81 (dd, *J* = 5.5, 3.1 Hz, 2H), 2.68 (t, *J* = 7.5 Hz, 2H), 1.81 (p, *J* = 7.5 Hz, 2H), 1.52 – 1.40 (m, 2H), 1.40 – 1.24 (m, 24H), 0.90 (t, *J* = 7.0 Hz, 3H) ppm .

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 169.7, 162.0, 134.7, 129.0, 123.9, 31.9, 31.0, 29.71, 29.70, 29.69, 29.68, 29.67, 29.64, 29.58, 29.39, 29.37, 29.1, 28.8, 24.7, 22.7, 14.1 ppm.

**HRMS (ESI-TOF):** calc'd for $C_{25}H_{38}NO_4$ $[M+H]^+$ 416.2795; found 416.2787.

**Compound 45**




Following General Procedure A on 10.0 mmol scale with **4**. Purification by flash column chromatography (silica, 8:1 hexanes:EtOAc) afforded 4.25 g of the title compound **45** (89%).

**Physical State**: white solid.

**m.p.:** 69 – 70 ºC.

$R_f$ = 0.54 (3:1 hexanes:EtOAc).

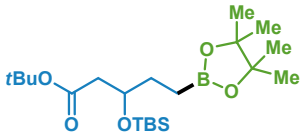
**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.88 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.22 (tdd, *J* = 6.9, 5.6, 4.2 Hz, 1H), 2.85 – 2.66 (m, 2H), 2.47 (dd, *J* = 14.9, 5.7 Hz, 1H), 2.35 (dd, *J* = 14.9, 6.9 Hz, 1H), 2.09 – 2.01 (m, 1H), 1.97 – 1.89 (m, 1H), 1.45 (s, 9H), 0.90 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 170.3, 169.8, 162.0, 134.9, 129.1, 124.1, 80.9, 67.9, 43.7, 31.8, 28.3, 26.7, 26.0, 18.1, -4.5, -4.6 ppm.

**HRMS (ESI-TOF):** calc'd for $C_{24}H_{36}NO_7Si$ $[M+H]^+$ 478.2254; found 478.2256.

**Experimental Procedures and Characterization Data for Borylation Products**

**Compound 2**




***Tert-butyl***

***3-((tert-butyldimethylsilyl)oxy)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate***

Following General Procedure B on 0.1 mmol scale with redox-active ester **45**, $Cu(acac)_2$ (20 mol%) and $B_2pin_2$ (1.5 equiv) in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 20:1 hexanes:$Et_2O$) afforded 26.6 mg (64%) of the title compound **2**.

**Physical State**: colorless oil.

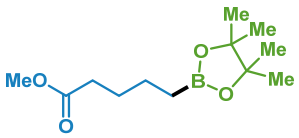
$R_f$ = 0.54 (8:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 4.04 (p, *J* = 5.9 Hz, 1H), 2.33 (dd, *J* = 6.1, 2.0 Hz, 2H), 1.66 – 1.56 (m, 2H), 1.44 (s, 9H), 1.24 (s, 12H), 0.87 (s, 9H), 0.78 (ddd, *J* = 11.6, 9.6, 6.4 Hz, 2H), 0.07 (s, 3H), 0.05 (s, 3H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 171.3, 83.1, 80.3, 70.8, 43.6, 31.6, 28.3, 26.7, 25.0, 18.2, -4.3, -4.5 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

**HRMS (ESI-TOF):** calc'd for $C_{21}H_{43}BNaO_5Si$ $[M+Na]^+$ 437.2865; found 437.2874.

**Compound 6**




Following General Procedure B on 0.2 mmol scale with redox-active ester **5** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, hexanes to 100:1 $CH_2Cl_2$:$Et_2O$) afforded 36.8 mg (76%) of the title compound **6**.

Following General Procedure B on 0.1 mmol scale with redox-active ester **5**, $Cu(acac)_2$ (20 mol%) and $B_2pin_2$ (1.5 equiv) in dioxane/DMF (4:1). Purification by flash column chromatography (silica, hexanes to 100:1 $CH_2Cl_2$:$Et_2O$) afforded 14.3 mg (59%) of the title compound **6**.

**Physical state:** colorless oil.

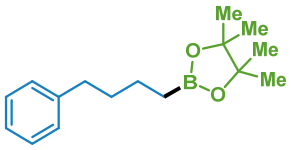
$R_f$ = 0.55 (silica gel, 6:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 3.65 (s, 3H), 2.30 (t, *J* = 7.6 Hz, 2H), 1.66 – 1.59 (m, 2H), 1.46 – 1.40 (m, 2H), 1.23 (s, 12H), 0.78 (t, *J* = 7.9 Hz, 2H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 174.4, 83.1, 51.6, 34.1, 27.7, 25.0, 23.8, 11.1 (br, C–B) ppm.

Spectroscopic data are in accordance with that reported in the literature.[5]

**Compound 11**




Following General Procedure B on 0.2 mmol scale with redox-active ester **S1** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 20:1 hexanes:$Et_2O$) afforded 36.5 mg (70%) of the title compound **11**.

**Physical state:** colorless oil.

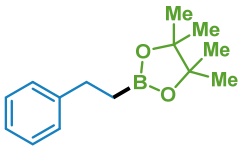
$\boldsymbol{R_f}$ = 0.50 (silica gel, 12:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.28 – 7.25 (m, 2H), 7.18 – 7.15 (m, 3H), 2.61 (t, *J* = 7.8 Hz, 2H), 1.66 – 1.61 (m, 2H), 1.50 – 1.45 (m, 2H), 1.24 (s, 12H), 0.82 (t, *J* = 7.8 Hz, 2H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 143.1, 128.5, 128.3, 125.6, 83.0, 35.9, 34.3, 25.0, 23.9 11.3 (br, C–B) ppm.

Spectroscopic data are in accordance with that reported in the literature.[5]

**Compound 12**




***4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S2** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 20:1 hexanes:$Et_2O$) afforded 33.3 mg (72%) of the title compound **12**.

**Physical State**: colorless oil.

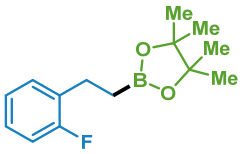
$\boldsymbol{R_f}$ = 0.50 (silica gel, 12:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.28 – 7.24 (m, 2H), 7.24 – 7.19 (m, 2H), 7.18 – 7.10 (m, 1H), 2.75 (t, *J* = 8.2 Hz, 2H), 1.22 (s, 12H), 1.15 (t, *J* = 8.3 Hz, 2H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 144.5, 128.3, 128.1, 125.6, 83.2, 30.1, 25.0, 13.2 (br, C–B) ppm.

Spectroscopic data are in accordance with that reported in the literature.[9]

**Compound 13**




***2-(2-fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S26** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 20:1 hexanes:$Et_2O$) afforded 30.2 mg (60%) of the title compound **13**.

**Physical State**: colorless oil.

$R_f$ = 0.51 (silica gel, 12:1 hexanes:EtOAc).

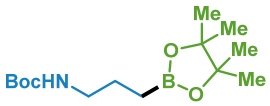
**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.23 (t, *J* = 7.7 Hz, 1H), 7.16 – 7.10 (m, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 7.00 – 6.91 (m, 1H), 2.77 (t, *J* = 8.2 Hz, 2H), 1.22 (s, 12H), 1.14 (t, *J* = 8.2 Hz, 2H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 161.2 (d, *J* = 244.6 Hz), 131.3 (d, *J* = 15.9 Hz), 130.2 (d, *J* = 5.2 Hz), 127.3 (d, *J* = 8.2 Hz), 123.9 (d, *J* = 3.5 Hz), 115.2 (d, *J* = 22.3 Hz), 25.0, 23.3 (d, *J* = 3.0 Hz), 11.8 (br, C–B) ppm.

**$^{19}$F NMR (376 MHz, $CDCl_3$):** δ -119.1.

Spectroscopic data are in accordance with that reported in the literature.[9]

**Compound 14**




***tert-butyl (3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)carbamate***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S3** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 20:1 hexanes:acetone) afforded 31.4 mg (55%) of the title compound **14**.

**Physical State**: colorless oil.

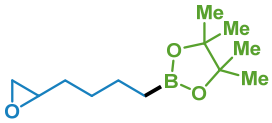
$R_f$ = 0.54 (8:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 4.73 (br s, 0.86H), 4.38 (br s, 0.14H), 3.17 – 2.95 (m, 2H), 1.63 – 1.53 (m, 2H), 1.42 (s, 9H), 1.24 (s, 12H), 0.78 (t, *J* = 7.7 Hz, 2H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 156.1, 83.3, 79.0, 42.8, 28.6, 25.0, 24.3, 8.6 (br, C–B) ppm.

**HRMS (ESI-TOF):** calc'd for $C_{14}H_{28}BNNaO_4$ $[M+Na]^+$ 308.2004; found 308.2015.

**Compound 15**



***4,4,5,5-tetramethyl-2-(4-(oxiran-2-yl)butyl)-1,3,2-dioxaborolane***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S4** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 15:1 hexanes:EtOAc) afforded 31.0 mg (69%) of the title compound **15**.

**Physical State**: colorless oil.

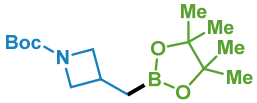
$R_f$ = 0.4 (10:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 2.92 – 2.88 (m, 1H), 2.75 – 2.71 (m, 1H), 2.45 (dd, *J* = 5.1, 2.7 Hz, 1H), 1.58 – 1.40 (m, 6H), 1.24 (s, 12H), 0.81 – 0.77 (m, 2H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 83.1, 52.5, 47.3, 32.4, 28.7, 25.0, 24.0, 11.4 (br, C–B) ppm.

**HRMS (ESI-TOF):** calc'd for $C_{12}H_{24}BO_3$ $[M+H]^+$ 227.1813; found: 227.1815.

**Compound 16**



***tert-butyl 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)azetidine-1-carboxylate***

Following General Procedure B on 0.144 mmol scale with redox-active ester **S27** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 10:1 hexanes: EtOAc) afforded 24.0 mg (56%) of the title compound **16**.

**Physical State**: colorless oil.

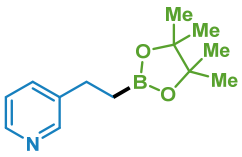
$R_f$ = 0.2 (10:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 4.05 – 3.98 (m, 2H), 3.51 (dd, *J* = 8.5, 5.7 Hz, 2H), 2.70 – 2.65 (m, 1H), 1.43 (s, 9H), 1.22 (s, 12H), 1.10 (d, *J* = 7.9 Hz, 2H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 156.6, 83.4, 79.1, 56.6 (br), 28.6, 25.3, 24.9 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

**HRMS (ESI-TOF):** calc'd for $C_{15}H_{28}BNO_4Na$ $[M+Na]^+$ 320.2004; found: 320.2010.

**Compound 17**



***3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)pyridine***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S5** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 10:1 hexanes:acetone) afforded 18.6 mg (40%) of the title compound **17**.

**Physical State**: colorless oil.

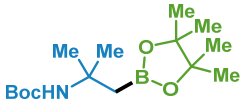
$R_f$ = 0.48 (4:1 hexanes:acetone).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 8.48 (s, 1H), 8.41 (d, *J* = 4.8 Hz, 1H), 7.55 (dt, *J* = 7.8, 1.9 Hz, 1H), 7.20 (dd, *J* = 7.8, 4.8 Hz, 1H), 2.75 (t, *J* = 8.0 Hz, 2H), 1.21 (s, 12H), 1.14 (t, *J* = 8.0 Hz, 2H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 149.6, 146.9, 139.8, 135.9, 123.4, 83.4, 27.3, 25.0 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

Spectroscopic data are in accordance with that reported in the literature.[6]

**Compound 18**




***tert-butyl (2-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)carbamate***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S28** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 15:1 hexanes: EtOAc) afforded 42.1 mg (70%) of the title compound **18**.

**Physical State**: colorless oil.

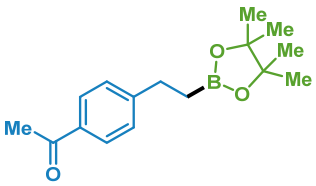
$R_f$ = 0.4 (10:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 4.75 (s, 1H), 1.41 (s, 9H), 1.34 (s, 6H), 1.23 (s, 2H), 1.22 (s, 12H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 154.8, 83.2, 78.4, 51.6, 29.3, 28.6, 26.3 (br, C–B), 24.9 ppm.

**HRMS (ESI-TOF):** calc'd for $C_{15}H_{30}BNO_4Na$ $[M+Na]^+$ 322.2160; found 322.2172.

**Compound 19**




***1-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)ethan-1-one***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S29** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 15:1 hexanes: EtOAc) afforded 35.1 mg (64%) of the title compound **19**.

**Physical State**: colorless oil.

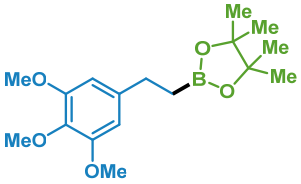
$R_f$ = 0.3 (10:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 2.83 – 2.77 (m, 2H), 2.57 (s, 3H), 1.22 (s, 12H), 1.18 – 1.12 (m, 2H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 198.1, 150.5, 135.0, 128.6, 128.4, 83.4, 30.2, 26.7 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

**HRMS (ESI-TOF):** calc'd for $C_{16}H_{24}BO_3$ $[M+H]^+$ 275.1813; found 275.1828.

**Compound 20**




***4,4,5,5-tetramethyl-2-(3,4,5-trimethoxyphenethyl)-1,3,2-dioxaborolane***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S30** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 15:1 hexanes:$Et_2O$) afforded 41.9 mg (65%) of the title compound **20**.

**Physical State**: white solid.

**m.p.:** 45 – 47 ºC.

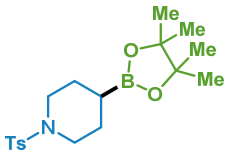
$R_f$ = 0.50 (silica gel, 6:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 6.45 (s, 2H), 3.84 (s, 6H), 3.81 (s, 3H), 2.70 – 2.67 (m, 2H), 1.22 (s, 12H), 1.16 – 1.12 (m, 2H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ153.1, 140.4, 136.0, 105.0, 83.3, 61.0, 56.1, 30.5, 25.0, 13.2 (br, C–B) ppm.

**HRMS (ESI-TOF):** calc'd for $C_{17}H_{27}BNaO_5$ $[M+Na]^+$ 345.1844; found 345.1854.

**Compound 21**




***4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylpiperidine***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S6** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 5:1 hexanes: EtOAc) afforded 48.2 mg (66%) of the title compound **21**.

**Physical State**: white solid.

**m.p.:** 102 – 104 ºC.

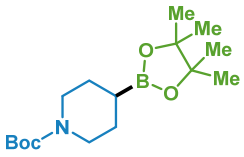
$R_f$ = 0.2 (4:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.36 (dt, *J* = 10.3, 4.3 Hz, 2H), 2.51 (td, *J* = 9.9, 3.1 Hz, 2H), 2.41 (s, 3H), 1.76 – 1.70 (m, 2H), 1.67 – 1.59 (m, 2H), 1.15 (s, 12H), 0.89 (tt, *J* = 10.2, 4.0 Hz, 1H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 143.3, 133.2, 129.6, 127.9, 83.4, 47.2, 26.6, 24.8, 21.6, 18.9 (br, C–B) ppm.

**HRMS (ESI-TOF):** calc'd for $C_{18}H_{29}BN_4S$ $[M+H]^+$ 366.1905; found 366.1919.

**Compound 22**




***tert-butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine-1-carboxylate***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S7** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 5:2:1 hexanes:$CH_2Cl_2$:EtOAc) afforded 42.5 mg (68%) of the title compound **22**.

**Physical State**: colorless oil.

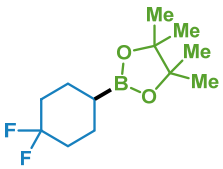
$R_f$ = 0.46 (4:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 3.89 – 3.65 (m, 2H), 3.01 – 2.84 (m, 2H), 1.66 – 1.57 (m, 2H), 1.51 – 1.44 (m, 2H), 1.44 (s, 9H), 1.22 (s, 12H), 1.09 (tt, *J* = 10.5, 3.6 Hz, 1H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 155.0, 83.3, 79.1, 45.5 (br), 44.5 (br), 28.6, 27.1, 24.9, 20.0 (br, C–B) ppm.

Spectroscopic data are in accordance with that reported in the literature.[6]

**Compound 23**




***2-(4,4-difluorocyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane***

Following General Procedure B on 0.1 mmol scale with redox-active ester **S8** in dioxane/DMF (6:1). Purification by flash column chromatography (silica, 20:1 hexanes: EtOAc) afforded 18.5 mg (75%) of the title compound **23**.

**Physical state:** colorless oil.

$R_f$ = 0.45 (silica gel, 9:1 hexanes:EtOAc).

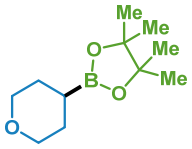
**$^1$H NMR (600 MHz, $CDCl_3$):** δ 2.02 – 1.91 (m, 2H), 1.83 – 1.75 (m, 2H), 1.75 – 1.55 (m, 4H), 1.22 (s, 12H), 1.02 – 0.92 (m, 1H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 123.9 (t, *J* = 240.5 Hz), 83.4, 34.5 (t, *J* = 23.3 Hz), 24.9, 24.4 (t, *J* = 4.9 Hz) 19.9 (br, C–B) ppm.

**$^{19}$F NMR (376 MHz, $CDCl_3$):** δ -91.8 (d, *J* = 235.5 Hz), -99.0 (d, *J* = 235.4 Hz).

Spectroscopic data are in accordance with that reported in the literature.[5]

**Compound 24**




***4,4,5,5-tetramethyl-2-(tetrahydro-2H-pyran-4-yl)-1,3,2-dioxaborolane***

Following General Procedure B on 0.1 mmol scale with redox-active ester **S9** in dioxane/DMF (6:1). Purification by flash column chromatography (silica, 15:1 hexanes: EtOAc) afforded 13.9 mg (66%) of the title compound **24**.

**Physical state:** colorless oil.

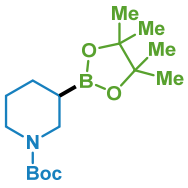
$R_f$ = 0.4 (silica gel, 10:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 3.83 (dt, *J* = 11.2, 4.0 Hz, 2H), 3.49 – 3.44 (m, 2H), 1.64 – 1.59 (m, 4H), 1.24 (s, 12H), 1.22 – 1.18 (m, 1H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 83.3, 69.0, 27.8, 24.9 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

Spectroscopic data are in accordance with that reported in the literature.[6]

**Compound 25**




***tert-butyl (R)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine-1-carboxylate***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S31** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 5:2:1 hexanes:$CH_2Cl_2$:EtOAc) afforded 38.6 mg (62%) of the title compound **25**.

**Physical State**: colorless oil.

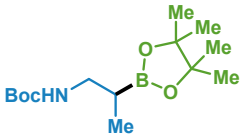
$R_f$ = 0.46 (4:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 3.96 – 3.77 (m, 2H), 3.01 – 2.82 (m, 2H), 1.84 – 1.73 (m, 1H), 1.45 (s, 9H), 1.44 – 1.39 (m, 2H), 1.22 (s, 12H), 1.16 – 1.10 (m, 2H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 155.0, 83.3, 79.2, 45.8 (br), 44.7 (br), 28.7, 26.21, 26.17, 24.93, 24.86, 22.0 (br, C–B) ppm.

**HRMS (ESI-TOF):** calc'd for $C_{16}H_{30}BNNaO_4$ $[M+Na]^+$ 334.2160; found 334.2167.

**Compound 26**




***tert-butyl (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)carbamate***

Following General Procedure B on 0.1 mmol scale with redox-active ester **S32** in dioxane/DMF (6:1). Purification by flash column chromatography (silica, 10:1 hexanes: EtOAc) afforded 16.0 mg (56%) of the title compound **26**.

**Physical State**: colorless oil.

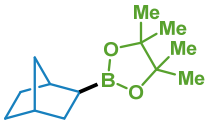
$R_f$ = 0.4 (10:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 4.78 (br s, 1H), 3.21 – 3.04 (m, 2H), 1.42 (s, 9H), 1.24 – 1.19 (m, 1H), 1.22 (s, 12H), 0.96 (d, $J$ = 7.6 Hz, 3H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 156.2, 83.4, 78.9, 43.6, 28.6, 24.9, 24.8, 18.4 (br, C–B), 13.2 ppm.

**HRMS (ESI-TOF):** calc'd for $C_{14}H_{28}BNO_4Na$ $[M+Na]^+$ 308.2004; found 308.2016.

**Compound 27**




***2-(bicyclo[2.2.1]heptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane***

Following General Procedure B on 0.1 mmol scale with redox-active ester **S10** in dioxane/DMF (6:1). Purification by flash column chromatography (silica, 25:1 hexanes:EtOAc) afforded 13.1 mg (59%) of the title compound **27** with 10:1 *dr* as determined by crude $^1$H NMR.

**Physical state:** colorless oil.

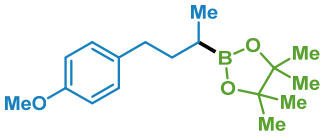
$R_f$ = 0.38 (silica gel, 19:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 2.38 – 2.17 (m, 2H), 1.57 – 1.42 (m, 3H), 1.38 – 1.31 (m, 1H), 1.26 – 1.12 (m, 18H), 0.91 – 0.81 (m, 1H) ppm. (mixture of exo and endo isomers)

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 82.9, 38.9, 38.3, 36.8, 32.4, 32.3, 29.4, 24.9 ppm (exo); 83.0, 41.1, 39.1, 37.2, 32.0, 30.0, 28.0, 25.1, 25.0 ppm (endo). The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

Spectroscopic data are in accordance with that reported in the literature.[5]

**Compound 28**




***(R)-2-(4-(4-methoxyphenyl)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S33** in dioxane/DMF (2:1). Purification by flash column chromatography (silica, 15:1 hexanes:$Et_2O$) afforded 37.8 mg (65%) of the title compound **28**.

**Physical State**: colorless oil.

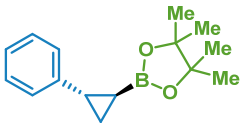
$R_f$ = 0.47 (12:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.17 – 7.04 (m, 2H), 6.88 – 6.74 (m, 2H), 3.78 (s, 3H), 2.56 (ddd, *J* = 9.6, 6.5, 2.9 Hz, 2H), 1.82 – 1.68 (m, 1H), 1.63 – 1.48 (m, 1H), 1.25 (s, 12H), 1.10 – 1.04 (m, 1H), 1.01 (d, *J* = 7.0 Hz, 3H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 157.7, 135.3, 129.4, 113.8, 83.0, 55.4, 35.7, 34.5, 24.94, 24.90, 15.6 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

**GCMS (EI):** m/z (%) 290 (21), 121 (100).

**Compound 29**




***4,4,5,5-tetramethyl-2-(2-phenylcyclopropyl)-1,3,2-dioxaborolane***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S11** in MTBE/DMF (6:1). Purification by flash column chromatography (silica, 20:1 hexanes:$Et_2O$) afforded 20.5 mg (42%) of the title compound **29** with >20:1 *dr* as determined by $^1$H NMR.

**Physical State**: colorless oil.

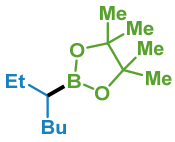
$R_f$ = 0.48 (silica gel, 9:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.26 – 7.22 (m, 2H), 7.15 – 7.11 (m, 1H), 7.10 – 7.06 (m, 2H), 2.11 (dt, *J* = 8.1, 5.4 Hz, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.16 (ddd, *J* = 8.1, 6.8, 3.7 Hz, 1H), 1.01 (ddd, *J* = 9.9, 5.3, 3.7 Hz, 1H), 0.31 (ddd, *J* = 9.8, 6.8, 5.5 Hz, 1H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 143.5, 128.4, 125.8, 125.7, 83.3, 24.9, 24.8, 22.0, 15.2 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

Spectroscopic data are in accordance with that reported in the literature.[5]

**Compound 30**




***(R)-2-(heptan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S12** in dioxane/DMF (1:2). Purification by flash column chromatography (silica, 20:1 hexanes:$Et_2O$) afforded 31.0 mg (69%) of the title compound **30**.

**Physical state:** colorless oil.

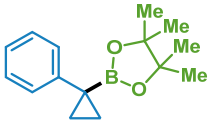
$R_f$ = 0.52 (silica gel, 12:1 EtOAc:hexanes).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 1.46 – 1.20 (m, 8H), 1.24 (s, 12H), 0.90 – 0.86 (m, 7H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 82.9, 31.7, 31.0, 25.0, 24.96, 24.94, 24.4, 23.1, 14.3, 13.9 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

Spectroscopic data are in accordance with that reported in the literature.[5]

**Compound 31**




***4,4,5,5-tetramethyl-2-(1-phenylcyclopropyl)-1,3,2-dioxaborolane***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S13** in dioxane/DMF (2:1). Purification by flash column chromatography (silica, 20:1 hexanes:$Et_2O$) afforded 41.7 mg (85%) of the title compound **31**.

**Physical State**: white solid.

**m.p.:** 46 – 47 ºC.

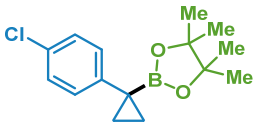
$R_f$ = 0.54 (8:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.31 – 7.28 (m, 2H), 7.28 – 7.24 (m, 2H), 7.17 – 7.13 (m, 1H), 1.24 (s, 12H), 1.15 – 1.12 (m, 2H), 0.97 – 0.91 (m, 2H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 144.9, 129.0, 128.1, 125.3, 83.4, 24.7, 13.5 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

Spectroscopic data are in accordance with that reported in the literature.[6]

**Compound 32**



***2-(1-(4-chlorophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S14** in dioxane/DMF (2:1). Purification by flash column chromatography (silica, 50:1 hexanes:$Et_2O$) afforded 43.8 mg (76%) of the title compound **32**.

**Physical State**: white solid.

**m.p.:** 83 – 85 °C.

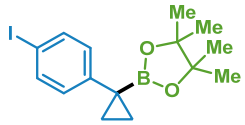
$R_f$ = 0.50 (silica gel, 12:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.19 (s, 4H), 1.21 (s, 12H), 1.11 (dd, *J* = 6.0, 3.6 Hz, 2H), 0.87 (dd, *J* = 6.0 Hz, 3.6 Hz, 2H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 143.5, 131.0, 130.5, 128.2, 83.6, 24.7, 13.6 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

Spectroscopic data are in accordance with that reported in the literature.[5]

**Compound 33**




***2-(1-(4-iodophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S15** in MTBE/DMF (6:1). Purification by flash column chromatography (silica, 100:1 hexanes:$Et_2O$) afforded 28.0 mg (38%) of the title compound **33**.

**Physical State**: white solid.

**m.p.:** 90 – 91 ºC.

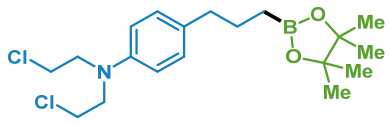
$R_f$ = 0.50 (8:1 hexanes:$Et_2O$).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 1.23 (s, 12H), 1.15 – 1.12 (m, 2H), 0.90 – 0.87 (m, 2H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 144.2, 136.5, 130.7, 89.9, 83.0, 24.1, 13.0 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

**GCMS (EI):** m/z (%) 370 (40), 143 (61), 101 (100).

**Compound 34**




***N,N-bis(2-chloroethyl)-4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)aniline***

Following General Procedure B on 0.225 mmol scale with redox-active ester **S16** in dioxane/DMF

(4:1). Purification by flash column chromatography (silica, 20:1 hexanes:EtOAc) afforded 49 mg (57%) of the title compound **34**.

**Physical State**: colorless oil.

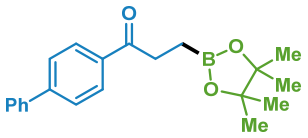
$R_f$ = 0.30 (silica gel, 20:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.07 (d, *J* = 8.6 Hz, 2H), 6.62 (d, *J* = 8.7 Hz, 2H), 3.69 (t, *J* = 6.9 Hz, 4H), 3.63 – 3.60 (m, 4H), 2.54 – 2.50 (m, 2H), 1.68 (p, *J* = 7.6 Hz, 2H), 1.24 (s, 12H), 0.81 (t, *J* = 7.9 Hz, 2H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 144.1, 132.2, 129.9, 112.2, 83.0, 53.8, 40.7, 37.5, 26.5, 25.0, 11.00 (br, C–B) ppm.

Spectroscopic data are in accordance with that reported in the literature.[5]

**Compound 35**




***1-([1,1'-biphenyl]-4-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S17** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 12:1 hexanes:$Et_2O$) afforded 30.2 mg (45%) of the title compound **35**.

**Physical State**: white solid.

**m.p.:** 92 – 94 ºC.

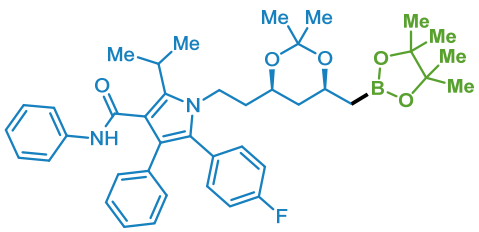
$R_f$ = 0.44 (6:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 8.05 (d, *J* = 8.5 Hz, 2H), 7.70 – 7.64 (m, 2H), 7.64 – 7.60 (m, 2H), 7.50 – 7.44 (m, 2H), 7.42 – 7.37 (m, 1H), 3.19 (t, *J* = 7.0 Hz, 2H), 1.27 (s, 12H), 1.10 (t, *J* = 7.0 Hz, 2H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 200.3, 145.6, 140.2, 135.8, 129.1, 128.7, 128.3, 127.4, 127.3, 83.3, 33.9, 24.9 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

Spectroscopic data are in accordance with that reported in the literature.[6]

**Compound 36**



***1-(2-((4R,6S)-2,2-dimethyl-6-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1,3-dioxan-4-yl) ethyl)-5-(4-fluorophenyl)-2-isopropyl-N,4-diphenyl-1H-pyrrole-3-carboxamide***

Following General Procedure B on 0.025 mmol scale with redox-active ester **S20** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 6:1 hexanes:EtOAc) afforded 9.0 mg (52%) of the title compound **36**.

**Physical State**: white foam.

$R_f$ = 0.52 (silica gel, 4:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.22 – 7.12 (m, 9H), 7.10 – 7.03 (m, 2H), 7.02 – 6.94 (m, 3H), 6.85 (br s, 1H), 4.09 – 4.02 (m, 1H), 4.01 – 3.95 (m, 1H), 3.86 – 3.79 (m, 1H), 3.70 – 3.64 (m, 1H), 3.62 – 3.53 (m, 1H), 1.69 – 1.63 (m, 2H), 1.53 (d, *J* = 7.1 Hz, 3H), 1.52 (d, *J* = 7.1 Hz, 3H), 1.36 – 1.32 (m, 1H), 1.34 (s, 3H), 1.29 (s, 3H), 1.23 (s, 12H), 1.08 – 1.00 (m, 2H), 0.96 (dd, *J* = 15.2, 7.9 Hz, 1H) ppm.

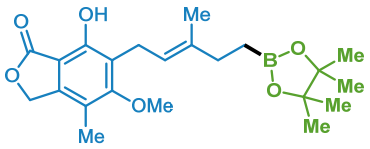
**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 165.0, 162.4 (d, *J* = 247.6 Hz), 141.7, 138.6, 134.8, 133.3 (d, *J* = 8.1 Hz), 130.7, 128.9, 128.8, 128.5, 128.4 (d, *J* = 3.6 Hz), 126.7, 123.6, 121.9, 119.7, 115.43 (d, *J* = 21.4 Hz), 115.37, 98.6, 83.3, 66.73, 66.68, 41.0, 38.4, 38.3, 30.3, 26.2, 24.91, 24.87, 21.9, 21.7, 20.0 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

**$^{19}$F NMR (376 MHz, $CDCl_3$):** δ -114.1 ppm.

**$[\alpha]_D^{20}$** = +3.9 (c 1.0, $CHCl_3$).

Spectroscopic data are in accordance with that reported in the literature.[5]

**Compound 37**




***(E)-7-hydroxy-5-methoxy-4-methyl-6-(3-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent -2-en-1-yl)isobenzofuran-1(3H)-one***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S18** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, hexanes to 7:6:1 hexanes:$CH_2Cl_2$:EtOAc) afforded 54.6 mg (68%) of the title compound **37**.

**Physical State**: white solid.

**m.p.:** 122 – 124 °C.

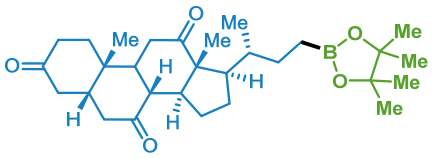
$R_f$ = 0.40 (silica gel, 2:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.65 (s, 1H), 5.22 – 5.19 (m, 1H), 5.19 (s, 2H), 3.75 (s, 3H), 3.37 (d, *J* = 6.6 Hz, 2H), 2.14 (s, 3H), 2.09 (t, *J* = 7.8 Hz, 2H), 1.78 (s, 3H), 1.18 (s, 12H), 0.86 (t, *J* = 7.8 Hz, 2H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 173.1, 163.9, 153.9, 143.9, 137.9, 122.8, 120.6, 116.8, 106.4, 83.0, 70.2, 61.1, 33.6, 24.9, 22.7, 16.3, 11.7, 9.8 (br, C–B) ppm.

Spectroscopic data are in accordance with that reported in the literature.[5]

**Compound 38**




***(5S,8R,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)dodecahydro-3H-cyclopenta[a]phenanthrene-3,7,12(2H,4H)-trione***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S21** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 5:1 to 2:1 hexanes:EtOAc) afforded 66.9 mg (69%) of the title compound **38**.

**Physical State**: white solid.

$R_f$ = 0.36 (silica gel, 2:1 hexanes:EtOAc).

**m.p.:** 230 – 232 °C.

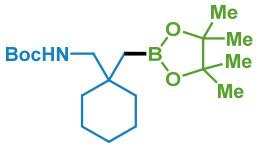
**$^{1}$H NMR (600 MHz, $CDCl_3$):** δ 2.94 – 2.79 (m, 3H), 2.36 – 2.16 (m, 6H), 2.16 – 2.07 (m, 2H), 2.06 – 1.92 (m, 4H), 1.83 (td, $J$ = 11.4, 7.1 Hz, 1H), 1.63 – 1.54 (m, 2H), 1.39 (s, 3H), 1.34 – 1.13 (m, 16 H), 1.05 (s, 3H), 0.87 – 0.78 (m, 4H), 0.69 – 0.61 (m, 1H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 212.1, 209.2, 208.9, 83.0, 57.1, 51.9, 49.2, 47.0, 45.8, 45.7, 45.1, 42.9, 38.8, 38.2, 36.6, 36.1, 35.4, 29.4, 27.8, 25.4, 25.0, 24.9, 22.1, 18.6, 12.0, 8.1 (br, C–B) ppm.

**$[\alpha]_D^{20}$** = +11.3 (c 1.0, $CHCl_3$).

Spectroscopic data are in accordance with that reported in the literature.[5]

**Compound 39**




***tert-butyl ((1-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclohexyl)methyl)carbamate***

Following General Procedure B on 0.123 mmol scale with redox-active ester **S19** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 15:1 hexanes:EtOAc) afforded 36.0 mg (83%) of the title compound **39**.

**Physical State**: white solid.

**m.p.:** 92 – 96 °C.

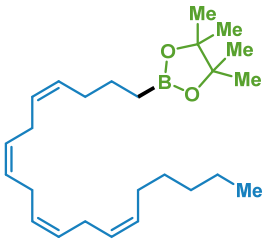
$R_f$ = 0.28 (silica gel, 20:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 5.32 (br s, 1H), 3.12 – 3.00 (m, 2H), 1.52 – 1.41 (m, 4H), 1.43 (s, 9H), 1.38 – 1.34 (m, 2H), 1.33 – 1.28 (m, 4H), 1.25 (s, 12H), 0.80 (s, 2H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 156.5, 83.4, 78.7, 50.0, 36.7, 36.3, 28.6, 26.4, 25.0, 21.9 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

Spectroscopic data are in accordance with that reported in the literature.[5]

**Compound 40**




***4,4,5,5-tetramethyl-2-((4Z,7Z,10Z,13Z)-nonadeca-4,7,10,13-tetraen-1-yl)-1,3,2-dioxaborolane***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S23** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 20:1 hexanes:$Et_2O$) afforded 27.0 mg (35%) of the title compound **40**.

**Physical State**: colorless oil.

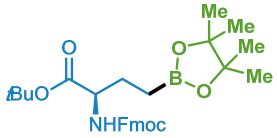
$R_f$ = 0.52 (12:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 5.49 – 5.26 (m, 8H), 2.88 – 2.77 (m, 6H), 2.12 – 1.99 (m, 4H), 1.48 (p, *J* = 7.7 Hz, 2H), 1.39 – 1.26 (m, 6H), 1.24 (s, 12H), 0.89 (t, *J* = 6.9 Hz, 3H), 0.80 (t, *J* = 7.9 Hz, 2H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 130.6, 130.3, 128.7, 128.6, 128.1, 128.1, 128.0, 127.7, 83.0, 31.7, 30.0, 29.5, 27.4, 25.8, 25.0, 24.2, 22.7, 14.2, 11.0 (br, C–B) ppm.

Spectroscopic data are in accordance with that reported in the literature.[6]

**Compound 41**




***tert-butyl (R)-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S22** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 8:1 hexanes:EtOAc) afforded 43.3 mg (43%) of the title compound **41**.

**Physical state:** white foam.

$R_f$ = 0.49 (silica gel, 4:1 hexanes:EtOAc).

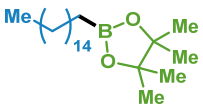
**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.61 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 5.54 (d, *J* = 8.2 Hz, 0.87H), 5.23 (br s, 0.13H), 4.44 – 4.30 (m, 2H), 4.26 – 4.07 (m, 2H), 2.00 – 1.86 (m, 1H), 1.86 – 1.72 (m, 1H), 1.47 (s, 9H), 1.23 (s, 12H), 0.91 – 0.72 (m, 2H).

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 171.9, 156.2, 144.2, 144.1, 141.41, 141.42, 127.8, 127.2, 125.3, 120.1, 83.5, 81.9, 67.0, 56.0, 47.4, 28.2, 27.0, 25.0, 24.9, 6.9 (br, C–B) ppm;

**$[\alpha]_D^{20}$** = +0.75 (c 0.66, $CHCl_3$).

Spectroscopic data are in accordance with that reported in the literature.[5]

**Compound 42**




***2-hexadecyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S34** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 20:1 hexanes:$Et_2O$) afforded 54.2 mg (77%) of the title compound **42**.

**Physical State**: colorless oil.

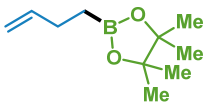
$R_f$ = 0.47 (10:1 hexanes:$Et_2O$).

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 1.43 – 1.34 (m, 2H), 1.34 – 1.17 (m, 38H), 0.88 (t, *J* = 7.0 Hz, 3H), 0.76 (t, *J* = 7.8 Hz, 2H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 82.9, 32.6, 32.1, 29.9, 29.82, 29.81, 29.75, 29.6, 29.5, 24.9, 24.2, 22.8, 14.3, 11.4 (br, C–B) ppm.

**GCMS (EI):** m/z (%) 352 (0.2), 337 (39), 129 (100).

**Compound 48**




***2-(but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane***

Following General Procedure B on 0.2 mmol scale with redox-active ester **S24** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 20:1 pentane:$Et_2O$) afforded 17.1 mg (47%) of the title compound **48**.

**Physical State**: colorless oil.

$R_f$ = 0.47 (19:1 pentane:$Et_2O$).

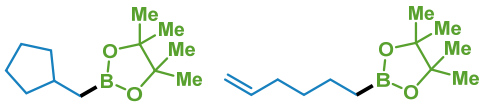
**$^1$H NMR (600 MHz, $CDCl_3$):** δ 5.88 (ddt, *J* = 17.2, 10.2, 6.2 Hz, 1H), 4.99 (dq, *J* = 17.1, 1.8 Hz, 1H), 4.90 (ddt, *J* = 10.2, 2.0, 1.3 Hz, 1H), 2.17 (tdt, *J* = 7.8, 6.3, 1.5 Hz, 2H), 1.24 (s, 12H), 0.88 (t, *J* = 7.9 Hz,

2H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 140.8, 113.3, 83.2, 28.1, 25.0 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

Spectroscopic data are in accordance with that reported in the literature.[6]

**Mixture 49**




3.6 : 1 mixture

Following General Procedure B on 0.2 mmol scale with redox-active ester **S25** in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 20:1 hexanes:$Et_2O$) afforded an inseparable mixture **49** (23.5 mg, 56%) containing cyclized and noncyclized products in 3.6:1 ratio.

**Physical State**: colorless oil.

$R_f$ = 0.52 (12:1 hexanes:EtOAc).

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 5.80 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 0.22H), 4.98 (dq, *J* = 17.1, 1.7 Hz, 0.22H), 4.91 (ddt, *J* = 10.2, 2.4, 1.2 Hz, 0.22H), 2.04 (tdd, *J* = 6.7, 5.3, 1.4 Hz, 0.44H), 1.95 (tt, *J* = 8.9, 7.3 Hz, 0.78H), 1.83 – 1.72 (m, 1.56H), 1.65 – 1.55 (m, 1.56H), 1.54 – 1.45 (m, 1.56H), 1.44 – 1.35 (m, 0.88H), 1.24 (s, 12H), 1.11 – 0.99 (m, 1.56H), 0.83 (d, *J* = 7.5 Hz, 1.56H), 0.77 (t, *J* = 7.5 Hz, 0.44H) ppm. (Data in red color belong to cyclized product)

**$^{13}$C NMR (151 MHz, $CDCl_3$):** δ 139.3, 114.2, 83.01, 82.95, 36.3, 35.2, 33.7, 31.8, 25.3, 25.0, 23.7 ppm. (Data in red color belong to cyclized product). The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

Spectroscopic data are in accordance with that reported in the literature.[6]

**X-Ray Crystallographic Data for Compound 35**

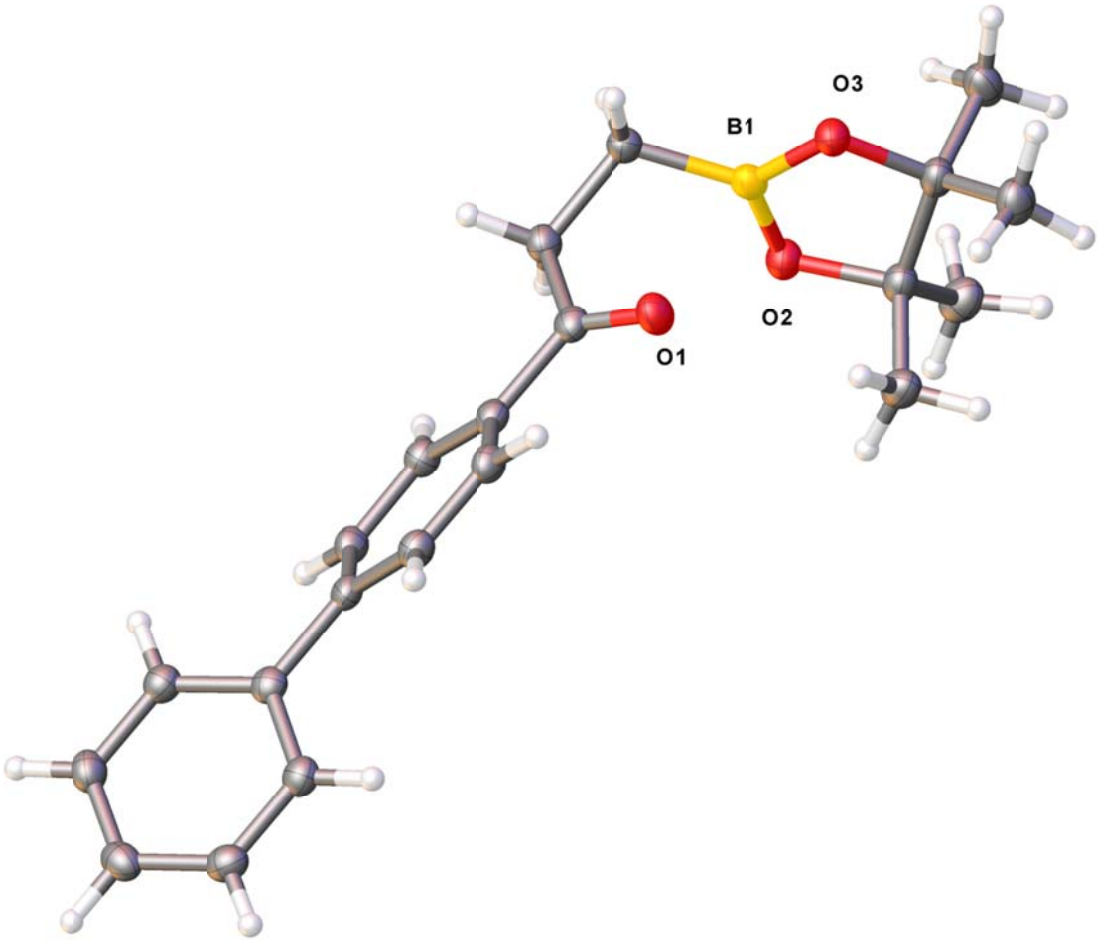



**Figure S3.** X-Ray Crystallographic Data for Compound **35**

X-ray information for compound **35** can be obtained free of charge from The Cambridge Crystallographic Data center with number CCDC 1862648.

Table 1. Crystal data and structure refinement for Baran676.

| | |
|---|---|
| Report date | 2018-07-30 |
| Identification code | jie4-065-3 |
| Empirical formula | C21 H25 B O3 |
| Molecular formula | C21 H25 B O3 |
| Formula weight | 336.22 |
| Temperature | 100.0 K |
| Wavelength | 1.54178 Å |
| Crystal system | Triclinic |
| Space group | P-1 |

| | | |
|---|---|---|
| Unit cell dimensions | a = 5.9378(3) Å | α= 72.769(2)°. |
| | b = 14.5346(7) Å | β= 89.933(3)°. |
| | c = 21.5395(11) Å | γ = 89.866(3)°. |
| Volume | 1775.50(15) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.258 $Mg/m^3$ | |
| Absorption coefficient | 0.644 $mm^{-1}$ | |
| F(000) | 720 | |
| Crystal size | 0.276 x 0.043 x 0.038 $mm^3$ | |
| Crystal color, habit | Colorless Needle | |
| Theta range for data collection | 2.147 to 68.490°. | |
| Index ranges | -6<=h<=7, -17<=k<=17, -25<=l<=25 | |
| Reflections collected | 54888 | |
| Independent reflections | 6407 [R(int) = 0.0352, R(sigma) = 0.0168] | |
| Completeness to theta = 68.000° | 98.5 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.3201 and 0.2347 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 6407 / 0 / 459 | |
| Goodness-of-fit on $F^2$ | 1.041 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0370, wR2 = 0.0892 | |
| R indices (all data) | R1 = 0.0421, wR2 = 0.0920 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.315 and -0.215 $e.Å^{-3}$ | |

Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for Baran676. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 6747(2) | 3260(1) | 2323(1) | 28(1) |
| O(2) | 9735(2) | 5206(1) | 1642(1) | 25(1) |
| O(3) | 7806(2) | 4692(1) | 889(1) | 25(1) |
| C(1) | 10682(2) | 3494(1) | 1611(1) | 24(1) |
| C(2) | 10733(2) | 3062(1) | 2351(1) | 23(1) |
| C(3) | 8410(2) | 2946(1) | 2650(1) | 22(1) |
| C(4) | 8177(2) | 2432(1) | 3359(1) | 21(1) |
| C(5) | 6151(2) | 1974(1) | 3597(1) | 23(1) |
| C(6) | 5890(2) | 1490(1) | 4250(1) | 22(1) |
| C(7) | 7639(2) | 1463(1) | 4690(1) | 21(1) |
| C(8) | 9656(2) | 1923(1) | 4448(1) | 22(1) |
| C(9) | 9936(2) | 2393(1) | 3793(1) | 22(1) |
| C(10) | 7398(2) | 954(1) | 5394(1) | 21(1) |
| C(11) | 5420(2) | 1015(1) | 5731(1) | 24(1) |
| C(12) | 5235(3) | 553(1) | 6392(1) | 26(1) |
| C(13) | 7020(3) | 14(1) | 6731(1) | 27(1) |
| C(14) | 8987(2) | -56(1) | 6400(1) | 26(1) |
| C(15) | 9177(2) | 408(1) | 5740(1) | 23(1) |
| C(16) | 8048(2) | 5948(1) | 1376(1) | 25(1) |
| C(17) | 7283(2) | 5716(1) | 744(1) | 24(1) |
| C(18) | 6190(3) | 5797(1) | 1886(1) | 30(1) |
| C(19) | 9150(3) | 6927(1) | 1264(1) | 33(1) |
| C(20) | 4790(2) | 5858(1) | 599(1) | 31(1) |
| C(21) | 8635(3) | 6231(1) | 143(1) | 32(1) |
| B(1) | 9340(3) | 4466(1) | 1383(1) | 23(1) |
| O(1') | 2152(2) | 1721(1) | 7630(1) | 31(1) |
| O(2') | 5095(2) | -151(1) | 8297(1) | 26(1) |
| O(3') | 3091(2) | 363(1) | 9041(1) | 27(1) |
| C(1') | 6014(3) | 1560(1) | 8344(1) | 26(1) |
| C(2') | 6067(2) | 2045(1) | 7608(1) | 25(1) |
| C(3') | 3756(2) | 2126(1) | 7309(1) | 24(1) |
| C(4') | 3456(2) | 2667(1) | 6606(1) | 22(1) |
| C(5') | 1404(2) | 2589(1) | 6307(1) | 23(1) |

| | | | | |
|---|---|---|---|---|
| C(6') | 1078(2) | 3038(1) | 5654(1) | 23(1) |
| C(7') | 2801(2) | 3579(1) | 5269(1) | 21(1) |
| C(8') | 4833(2) | 3666(1) | 5571(1) | 23(1) |
| C(9') | 5162(2) | 3220(1) | 6229(1) | 23(1) |
| C(10') | 2503(2) | 4040(1) | 4561(1) | 22(1) |
| C(11') | 510(2) | 4514(1) | 4311(1) | 24(1) |
| C(12') | 250(2) | 4946(1) | 3649(1) | 26(1) |
| C(13') | 1966(2) | 4903(1) | 3221(1) | 26(1) |
| C(14') | 3954(2) | 4423(1) | 3463(1) | 25(1) |
| C(15') | 4224(2) | 4001(1) | 4126(1) | 23(1) |
| C(16') | 3417(2) | -899(1) | 8561(1) | 26(1) |
| C(17') | 2582(2) | -658(1) | 9186(1) | 26(1) |
| C(18') | 1614(3) | -773(1) | 8041(1) | 32(1) |
| C(19') | 4567(3) | -1871(1) | 8684(1) | 34(1) |
| C(20') | 88(3) | -807(1) | 9321(1) | 35(1) |
| C(21') | 3902(3) | -1170(1) | 9797(1) | 34(1) |
| B(1') | 4652(3) | 592(1) | 8553(1) | 24(1) |

Table 3. Bond lengths [Å] and angles [°] for Baran676.

| | |
|---|---|
| O(1)-C(3) | 1.2201(16) |
| O(2)-C(16) | 1.4585(16) |
| O(2)-B(1) | 1.3701(19) |
| O(3)-C(17) | 1.4608(16) |
| O(3)-B(1) | 1.3651(18) |
| C(1)-C(2) | 1.5316(18) |
| C(1)-B(1) | 1.568(2) |
| C(2)-C(3) | 1.510(2) |
| C(3)-C(4) | 1.4943(18) |
| C(4)-C(5) | 1.398(2) |
| C(4)-C(9) | 1.3918(19) |
| C(5)-C(6) | 1.3825(19) |
| C(6)-C(7) | 1.3989(19) |
| C(7)-C(8) | 1.396(2) |
| C(7)-C(10) | 1.4839(18) |
| C(8)-C(9) | 1.3831(19) |
| C(10)-C(11) | 1.397(2) |
| C(10)-C(15) | 1.3961(19) |
| C(11)-C(12) | 1.387(2) |
| C(12)-C(13) | 1.388(2) |
| C(13)-C(14) | 1.387(2) |
| C(14)-C(15) | 1.3859(19) |
| C(16)-C(17) | 1.565(2) |
| C(16)-C(18) | 1.525(2) |
| C(16)-C(19) | 1.520(2) |
| C(17)-C(20) | 1.514(2) |
| C(17)-C(21) | 1.5179(19) |
| O(1')-C(3') | 1.2215(17) |
| O(2')-C(16') | 1.4619(17) |
| O(2')-B(1') | 1.3743(19) |
| O(3')-C(17') | 1.4554(17) |
| O(3')-B(1') | 1.3672(19) |
| C(1')-C(2') | 1.5334(18) |
| C(1')-B(1') | 1.571(2) |
| C(2')-C(3') | 1.506(2) |
| C(3')-C(4') | 1.4959(18) |

| | |
|---|---|
| C(4')-C(5') | 1.399(2) |
| C(4')-C(9') | 1.395(2) |
| C(5')-C(6') | 1.3789(19) |
| C(6')-C(7') | 1.4022(19) |
| C(7')-C(8') | 1.3953(19) |
| C(7')-C(10') | 1.4842(18) |
| C(8')-C(9') | 1.3854(19) |
| C(10')-C(11') | 1.3944(19) |
| C(10')-C(15') | 1.398(2) |
| C(11')-C(12') | 1.3855(19) |
| C(12')-C(13') | 1.387(2) |
| C(13')-C(14') | 1.391(2) |
| C(14')-C(15') | 1.3850(19) |
| C(16')-C(17') | 1.568(2) |
| C(16')-C(18') | 1.5207(19) |
| C(16')-C(19') | 1.518(2) |
| C(17')-C(20') | 1.513(2) |
| C(17')-C(21') | 1.524(2) |

| | |
|---|---|
| B(1)-O(2)-C(16) | 107.44(11) |
| B(1)-O(3)-C(17) | 107.51(11) |
| C(2)-C(1)-B(1) | 112.89(11) |
| C(3)-C(2)-C(1) | 112.70(11) |
| O(1)-C(3)-C(2) | 121.10(12) |
| O(1)-C(3)-C(4) | 120.25(13) |
| C(4)-C(3)-C(2) | 118.65(11) |
| C(5)-C(4)-C(3) | 119.62(12) |
| C(9)-C(4)-C(3) | 121.64(12) |
| C(9)-C(4)-C(5) | 118.74(12) |
| C(6)-C(5)-C(4) | 120.85(13) |
| C(5)-C(6)-C(7) | 120.65(13) |
| C(6)-C(7)-C(10) | 121.72(12) |
| C(8)-C(7)-C(6) | 118.05(12) |
| C(8)-C(7)-C(10) | 120.22(12) |
| C(9)-C(8)-C(7) | 121.44(12) |
| C(8)-C(9)-C(4) | 120.24(13) |
| C(11)-C(10)-C(7) | 121.57(12) |
| C(15)-C(10)-C(7) | 120.31(12) |

| | |
|---|---|
| C(15)-C(10)-C(11) | 118.12(12) |
| C(12)-C(11)-C(10) | 120.94(13) |
| C(11)-C(12)-C(13) | 120.32(13) |
| C(14)-C(13)-C(12) | 119.23(13) |
| C(15)-C(14)-C(13) | 120.50(13) |
| C(14)-C(15)-C(10) | 120.88(13) |
| O(2)-C(16)-C(17) | 102.48(10) |
| O(2)-C(16)-C(18) | 106.32(11) |
| O(2)-C(16)-C(19) | 108.36(12) |
| C(18)-C(16)-C(17) | 113.14(12) |
| C(19)-C(16)-C(17) | 114.87(12) |
| C(19)-C(16)-C(18) | 110.86(12) |
| O(3)-C(17)-C(16) | 102.79(10) |
| O(3)-C(17)-C(20) | 108.51(12) |
| O(3)-C(17)-C(21) | 106.57(11) |
| C(20)-C(17)-C(16) | 114.43(12) |
| C(20)-C(17)-C(21) | 109.77(12) |
| C(21)-C(17)-C(16) | 114.11(12) |
| O(2)-B(1)-C(1) | 121.86(13) |
| O(3)-B(1)-O(2) | 113.43(12) |
| O(3)-B(1)-C(1) | 124.57(13) |
| B(1')-O(2')-C(16') | 107.28(11) |
| B(1')-O(3')-C(17') | 107.88(11) |
| C(2')-C(1')-B(1') | 113.91(12) |
| C(3')-C(2')-C(1') | 112.17(12) |
| O(1')-C(3')-C(2') | 120.40(12) |
| O(1')-C(3')-C(4') | 120.04(13) |
| C(4')-C(3')-C(2') | 119.49(12) |
| C(5')-C(4')-C(3') | 118.61(12) |
| C(9')-C(4')-C(3') | 122.83(12) |
| C(9')-C(4')-C(5') | 118.52(12) |
| C(6')-C(5')-C(4') | 120.87(13) |
| C(5')-C(6')-C(7') | 120.89(13) |
| C(6')-C(7')-C(10') | 121.56(12) |
| C(8')-C(7')-C(6') | 117.99(12) |
| C(8')-C(7')-C(10') | 120.45(12) |
| C(9')-C(8')-C(7') | 121.26(13) |
| C(8')-C(9')-C(4') | 120.46(13) |

| | |
|---|---|
| C(11')-C(10')-C(7') | 121.26(12) |
| C(11')-C(10')-C(15') | 118.26(12) |
| C(15')-C(10')-C(7') | 120.48(12) |
| C(12')-C(11')-C(10') | 120.90(13) |
| C(11')-C(12')-C(13') | 120.42(13) |
| C(12')-C(13')-C(14') | 119.26(13) |
| C(15')-C(14')-C(13') | 120.30(13) |
| C(14')-C(15')-C(10') | 120.85(13) |
| O(2')-C(16')-C(17') | 102.65(11) |
| O(2')-C(16')-C(18') | 106.34(11) |
| O(2')-C(16')-C(19') | 107.97(12) |
| C(18')-C(16')-C(17') | 113.66(12) |
| C(19')-C(16')-C(17') | 115.04(12) |
| C(19')-C(16')-C(18') | 110.36(12) |
| O(3')-C(17')-C(16') | 102.91(11) |
| O(3')-C(17')-C(20') | 108.95(12) |
| O(3')-C(17')-C(21') | 106.46(11) |
| C(20')-C(17')-C(16') | 114.67(12) |
| C(20')-C(17')-C(21') | 109.38(12) |
| C(21')-C(17')-C(16') | 113.87(12) |
| O(2')-B(1')-C(1') | 122.05(13) |
| O(3')-B(1')-O(2') | 113.32(13) |
| O(3')-B(1')-C(1') | 124.34(13) |

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Baran676. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| O(1) | 25(1) | 31(1) | 24(1) | -4(1) | -4(1) | 4(1) |
| O(2) | 26(1) | 23(1) | 25(1) | -6(1) | -2(1) | 3(1) |
| O(3) | 28(1) | 24(1) | 22(1) | -6(1) | -2(1) | 5(1) |
| C(1) | 25(1) | 24(1) | 22(1) | -6(1) | 1(1) | 2(1) |
| C(2) | 24(1) | 23(1) | 22(1) | -6(1) | -2(1) | 3(1) |
| C(3) | 26(1) | 18(1) | 23(1) | -8(1) | -3(1) | 2(1) |
| C(4) | 23(1) | 18(1) | 23(1) | -8(1) | -1(1) | 3(1) |
| C(5) | 22(1) | 22(1) | 26(1) | -8(1) | -4(1) | 3(1) |
| C(6) | 20(1) | 21(1) | 26(1) | -7(1) | 0(1) | 1(1) |
| C(7) | 23(1) | 18(1) | 23(1) | -7(1) | -1(1) | 4(1) |
| C(8) | 22(1) | 22(1) | 23(1) | -8(1) | -4(1) | 3(1) |
| C(9) | 21(1) | 20(1) | 25(1) | -7(1) | 0(1) | 0(1) |
| C(10) | 23(1) | 17(1) | 24(1) | -8(1) | 0(1) | -1(1) |
| C(11) | 25(1) | 20(1) | 27(1) | -7(1) | -1(1) | 2(1) |
| C(12) | 29(1) | 23(1) | 27(1) | -9(1) | 5(1) | -1(1) |
| C(13) | 37(1) | 22(1) | 22(1) | -6(1) | 0(1) | -2(1) |
| C(14) | 29(1) | 23(1) | 26(1) | -6(1) | -6(1) | 3(1) |
| C(15) | 23(1) | 22(1) | 25(1) | -8(1) | 0(1) | 1(1) |
| C(16) | 26(1) | 22(1) | 26(1) | -4(1) | 2(1) | 4(1) |
| C(17) | 24(1) | 22(1) | 24(1) | -3(1) | 2(1) | 4(1) |
| C(18) | 36(1) | 26(1) | 27(1) | -6(1) | 6(1) | 3(1) |
| C(19) | 35(1) | 25(1) | 38(1) | -9(1) | 6(1) | -1(1) |
| C(20) | 26(1) | 32(1) | 33(1) | -5(1) | -1(1) | 4(1) |
| C(21) | 30(1) | 35(1) | 25(1) | -1(1) | 3(1) | 5(1) |
| B(1) | 21(1) | 26(1) | 20(1) | -4(1) | 4(1) | -1(1) |
| O(1') | 29(1) | 33(1) | 25(1) | -2(1) | 2(1) | -3(1) |
| O(2') | 29(1) | 24(1) | 26(1) | -7(1) | 0(1) | -2(1) |
| O(3') | 32(1) | 23(1) | 25(1) | -6(1) | 0(1) | -2(1) |
| C(1') | 30(1) | 26(1) | 24(1) | -7(1) | -3(1) | -1(1) |
| C(2') | 28(1) | 24(1) | 23(1) | -5(1) | 0(1) | -1(1) |
| C(3') | 30(1) | 18(1) | 23(1) | -7(1) | 2(1) | 1(1) |
| C(4') | 25(1) | 19(1) | 23(1) | -8(1) | 1(1) | 2(1) |
| C(5') | 22(1) | 22(1) | 26(1) | -7(1) | 4(1) | 0(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(6') | 21(1) | 23(1) | 26(1) | -9(1) | 0(1) | 2(1) |
| C(7') | 24(1) | 18(1) | 23(1) | -7(1) | 1(1) | 2(1) |
| C(8') | 24(1) | 20(1) | 24(1) | -6(1) | 3(1) | -2(1) |
| C(9') | 23(1) | 21(1) | 24(1) | -8(1) | -1(1) | 0(1) |
| C(10') | 23(1) | 18(1) | 24(1) | -8(1) | -1(1) | -2(1) |
| C(11') | 23(1) | 22(1) | 27(1) | -10(1) | 1(1) | -1(1) |
| C(12') | 27(1) | 21(1) | 29(1) | -7(1) | -6(1) | 1(1) |
| C(13') | 34(1) | 21(1) | 22(1) | -5(1) | -2(1) | -4(1) |
| C(14') | 28(1) | 24(1) | 24(1) | -9(1) | 4(1) | -4(1) |
| C(15') | 22(1) | 21(1) | 25(1) | -8(1) | -1(1) | -1(1) |
| C(16') | 27(1) | 23(1) | 27(1) | -5(1) | -3(1) | -3(1) |
| C(17') | 29(1) | 22(1) | 26(1) | -4(1) | -2(1) | -3(1) |
| C(18') | 37(1) | 28(1) | 30(1) | -6(1) | -9(1) | -1(1) |
| C(19') | 36(1) | 27(1) | 39(1) | -10(1) | -8(1) | 2(1) |
| C(20') | 30(1) | 35(1) | 37(1) | -8(1) | -1(1) | -3(1) |
| C(21') | 36(1) | 35(1) | 26(1) | -3(1) | -5(1) | -3(1) |
| B(1') | 26(1) | 26(1) | 21(1) | -5(1) | -6(1) | 4(1) |

Table 5. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for Baran676.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 9986 | 3024 | 1417 | 28 |
| H(1B) | 12247 | 3606 | 1447 | 28 |
| H(2A) | 11480 | 2424 | 2462 | 28 |
| H(2B) | 11639 | 3483 | 2540 | 28 |
| H(5) | 4937 | 1995 | 3306 | 27 |
| H(6) | 4510 | 1173 | 4402 | 27 |
| H(8) | 10863 | 1913 | 4739 | 27 |
| H(9) | 11335 | 2690 | 3638 | 26 |
| H(11) | 4183 | 1379 | 5505 | 29 |
| H(12) | 3879 | 604 | 6615 | 31 |
| H(13) | 6896 | -302 | 7184 | 32 |
| H(14) | 10214 | -426 | 6627 | 32 |
| H(15) | 10536 | 354 | 5520 | 28 |
| H(18A) | 5529 | 5156 | 1958 | 45 |
| H(18B) | 5021 | 6289 | 1733 | 45 |
| H(18C) | 6825 | 5848 | 2294 | 45 |
| H(19A) | 9556 | 7016 | 1683 | 49 |
| H(19B) | 8094 | 7434 | 1037 | 49 |
| H(19C) | 10509 | 6962 | 1000 | 49 |
| H(20A) | 4454 | 5715 | 191 | 47 |
| H(20B) | 4375 | 6527 | 557 | 47 |
| H(20C) | 3927 | 5424 | 954 | 47 |
| H(21A) | 10247 | 6140 | 241 | 47 |
| H(21B) | 8275 | 6920 | 13 | 47 |
| H(21C) | 8256 | 5964 | -211 | 47 |
| H(1'A) | 5341 | 2013 | 8557 | 32 |
| H(1'B) | 7581 | 1429 | 8503 | 32 |
| H(2'A) | 6722 | 2697 | 7519 | 30 |
| H(2'B) | 7051 | 1668 | 7402 | 30 |
| H(5') | 219 | 2221 | 6558 | 28 |
| H(6') | -333 | 2980 | 5461 | 27 |
| H(8') | 6013 | 4039 | 5322 | 27 |

| | | | | |
|---|---|---|---|---|
| H(9') | 6559 | 3291 | 6424 | 27 |
| H(11') | -687 | 4541 | 4598 | 28 |
| H(12') | -1112 | 5274 | 3488 | 31 |
| H(13') | 1786 | 5199 | 2767 | 31 |
| H(14') | 5133 | 4384 | 3173 | 30 |
| H(15') | 5595 | 3680 | 4286 | 27 |
| H(18D) | 938 | -131 | 7951 | 48 |
| H(18E) | 446 | -1263 | 8195 | 48 |
| H(18F) | 2294 | -843 | 7643 | 48 |
| H(19D) | 5023 | -1962 | 8269 | 51 |
| H(19E) | 3520 | -2383 | 8907 | 51 |
| H(19F) | 5900 | -1894 | 8956 | 51 |
| H(20D) | -290 | -644 | 9719 | 52 |
| H(20E) | -295 | -1482 | 9376 | 52 |
| H(20F) | -767 | -391 | 8955 | 52 |
| H(21D) | 5519 | -1080 | 9709 | 51 |
| H(21E) | 3549 | -1860 | 9928 | 51 |
| H(21F) | 3485 | -901 | 10148 | 51 |

## Unsuccessful or Challenging Substrates

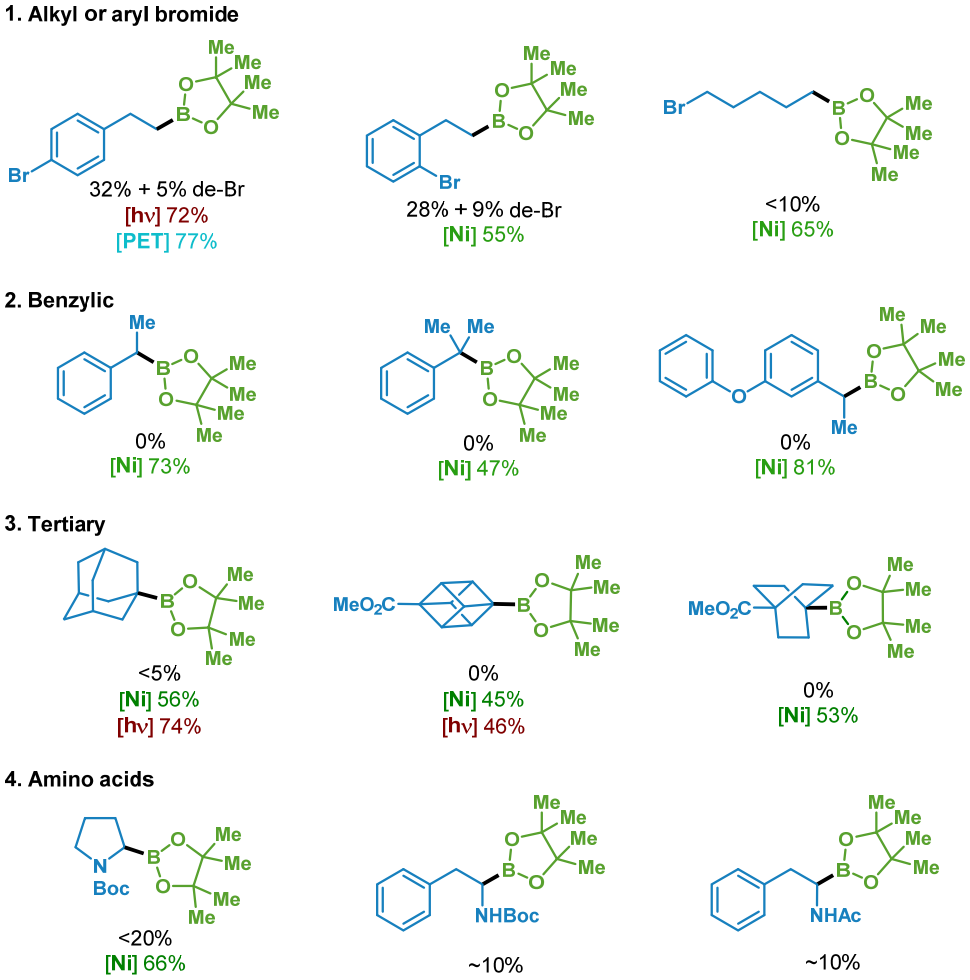



**Figure S4.** Unsuccessful or challenging substrates.

## Cost Calculations

### Price and Vendor of Reagents

**Table S8.** Price and vendor of reagents

| Reagents | CAS No. | Mw/Conc. | Vender | Price listed ($) | Price/mol ($) |
|---|---|---|---|---|---|
| $B_2pin_2$ | 73183-34-3 | 253.9 | Combi-Blocks | 360/1 kg | 91.4 |
| $B_2cat_2$ | 13826-27-2 | 237.8 | Combi-Blocks | 480/100 g | 1141.4 |
| $B_2(NMe_2)_4$ | 1630-79-1 | 197.9 | Combi-Blocks | 599/500 g | 237.1 |
| Catechol | 120-80-9 | 110.1 | Sigma-Aldrich | 292/5 kg | 6.4 |
| $B_2cat_2$ | 72% yield (2.2 eq catechol)[10] | | | | 348.9 |
| $LiOH•H_2O$ | 1310-66-3 | 42.0 | Sigma-Aldrich | 215/2 kg | 4.5 |
| $Cu(acac)_2$ | 13395-16-9 | 261.8 | Combi-Blocks | 250/1 kg | 65.5 |
| $MgCl_2$ | 7786-30-3 | 95.2 | Sigma-Aldrich | 164/5 kg | 3.1 |
| $NiCl_2•H_2O$ | 7791-20-0 | 237.7 | Sigma-Aldrich | 350/2 kg | 41.6 |
| *di*MeObipy | 17217-57-1 | 216.2 | Combi-Blocks | 360/25 g | 3113.3 |
| MeLi | 917-54-4 | 1.6 M in $Et_2O$ | Sigma-Aldrich | 1410/8 L | 110.2 |
| $MgBr_2•Et_2O$ | 29858-07-9 | 258.2 | Sigma-Aldrich | 135.3/100 g | 349.3 |
| Pinacol | 76-09-5 | 118.2 | Combi-Blocks | 250/1 kg | 29.6 |
| $Ir[(ppy)_2dtbpy]PF_6$ | 676525-77-2 | 914.0 | Sigma-Aldrich | 160/250 mg | 584960 |
| $IrCl_3•xH_2O$ | 14996-61-3 | >316.6 | Sigma-Aldrich | 1250/25 g | 15830 |
| 2-phenylpyridine | 1008-89-5 | 155.2 | Combi-Blocks | 900/1 kg | 139.7 |
| *t*Bubipy | 72914-19-3 | 268.4 | Oakwood | 210/25 g | 2254.6 |
| $NH_4PF_6$ | 16941-11-0 | 163.0 | Oakwood | 395/2.5 kg | 25.8 |
| $Ir[(ppy)_2dtbpy]PF_6$ | 1. 95% (2.5 eq PPy)[11], 2. 92% (2.5 eq *t*Bubipy, 10 eq $NH_4PF_6$)[12] | | | | 24918.8 |

**Cost Comparison**

**Table S9.** Cost comparison.

| **Reagents** | **Price/mol ($)** | **Ni** | **hv** | **PET** | **Cu** |
|---|---|---|---|---|---|
| $B_2pin_2$ | 91.4 | 3.3 eq | | 4 eq | 1.5 eq |
| $B_2cat_2$ | 1141.4[a] | | 1.25 eq[a] | | |
| $B_2cat_2$ | 348.9[b] | | 1.25 eq[b] | | |
| $LiOH•H_2O$ | 4.5 | | | | 15 eq |
| $Cu(acac)_2$ | 65.5 | | | | 0.2 eq |
| $MgCl_2$ | 3.1 | | | | 1.5 eq |
| $NiCl_2•H_2O$ | 41.6 | 0.1 eq | | | |
| *di*MeObipy | 3113.3 | 0.13 eq | | | |
| MeLi | 110.2 | 3.0 eq | | | |
| $MgBr_2•Et_2O$ | 349.3 | 1.5 eq | | | |
| Pinacol | 29.6 | | 4 eq | | |
| $Ir[(ppy)_2dtbpy]PF_6$ | 584960[a] | | | 0.01 eq[a] | |
| $Ir[(ppy)_2dtbpy]PF_6$ | 24918.8[b] | | | 0.01 eq[b] | |
| **Cost/mol ($)** | | 1565 | 1545[a]<br>555[b] | 6215[a]<br>615[b] | 222 |

[a]: Cost calculated based on price from commercial sources.

[b]: Cost calculated based on price of self-made reagents.

## Kinetic Studies

### General Method for Kinetic Studies

To a dry 1 dram vial equipped with a magnetic stir bar and a screw cap with septum was added 5-phenylvaleric NHPI ester (16.2 mg, 0.05 mmol), $LiOH•H_2O$ (31.5 mg, 0.75 mmol), $MgCl_2$ (anhydrous, 15.2 mg, 0.075 mmol) and $B_2pin_2$ (19 mg, 0.075 mmol). The screw joint of the vial was Teflon taped, the vial was closed and the atmosphere exchanged by 3 cycles of vacuum/$N_2$. The vial was placed in a 27 $^oC$ oil bath (stir speed 1000 rpm) and at time = 0, 0.35 mL of a mixed solution of $Cu(acac)_2$ (0.01 mmol) and 4,4'-di-*tert*-butylbiphenyl (0.005 mmol) was added. The mixture of $Cu(acac)_2$ (0.0286 M) and internal standard (0.0144 M) was prepared inert in a volumetric flask using a dry and inert solvent mixture of 1,4-dioxane and DMF (4:1). Aliquots (~20 μL) were removed from the reaction at the indicated times and directly injected into 0.4 mL MeCN in a filter vial without any further quench and subjected to analysis.

### Analysis

All samples were analyzed using a Waters I-Class (SM-FTN) instrument with Waters PDA diode array detector and Waters QDa mass spectrometer, equipped with a Waters Cortecs C18 column (2.1x55 mm, 1.6 micron). The analysis was taking place at 35 $^oC$ using a gradient based on (A) 0.1% formic acid in water and (B) acetonitrile (10-99% B over 2.5 minutes, hold at 99% B for 0.2 minutes).

Retention times for relevant species: RAE (**S1**) 1.836 minutes (detection wavelength 298 nm), product (**11**) 2.143 minutes (detection wavelength 228 nm), 5-phenylvaleric acid 1.211 minutes (detection wavelength 228 nm), 4,4'-di-*tert*-butyl biphenyl 2.614 minutes (detection wavelength 228 nm). Analyte concentrations were calculated against 4,4'-di-*tert*-butyl biphenyl as internal standard, and all analytes were calibrated separately using a series of six calibration solutions of different concentration with the highest concentration of the series being 5 mM.

**Results**

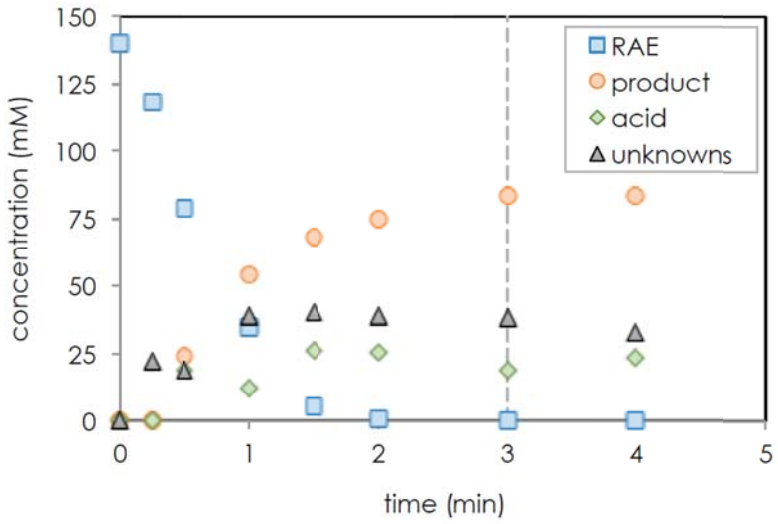



**Figure S5.** Time course of the borylation reaction under standard conditions: 140 mM RAE, 1.5 equiv $B_2pin_2$, 20 mol% $Cu(acac)_2$, 1.5 equiv $MgCl_2$, 15 equiv $LiOH•H_2O$.

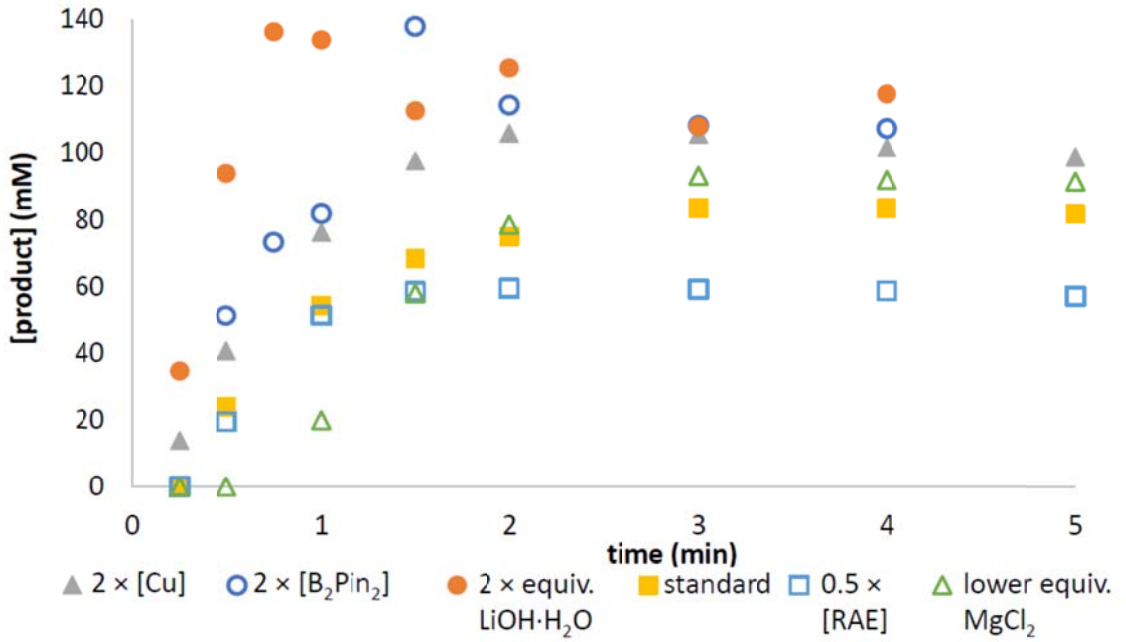



**Figure S6.** Time course of the borylation reaction with varying concentrations of reactants/reagents (cf Fig 3A in main article). Standard conditions: 140 mM RAE, 1.5 equiv $B_2pin_2$, 20 mol% $Cu(acac)_2$, 1.5 equiv $MgCl_2$, 15 equiv $LiOH•H_2O$. Low $MgCl_2$ = 28 mM (0.2 equiv)

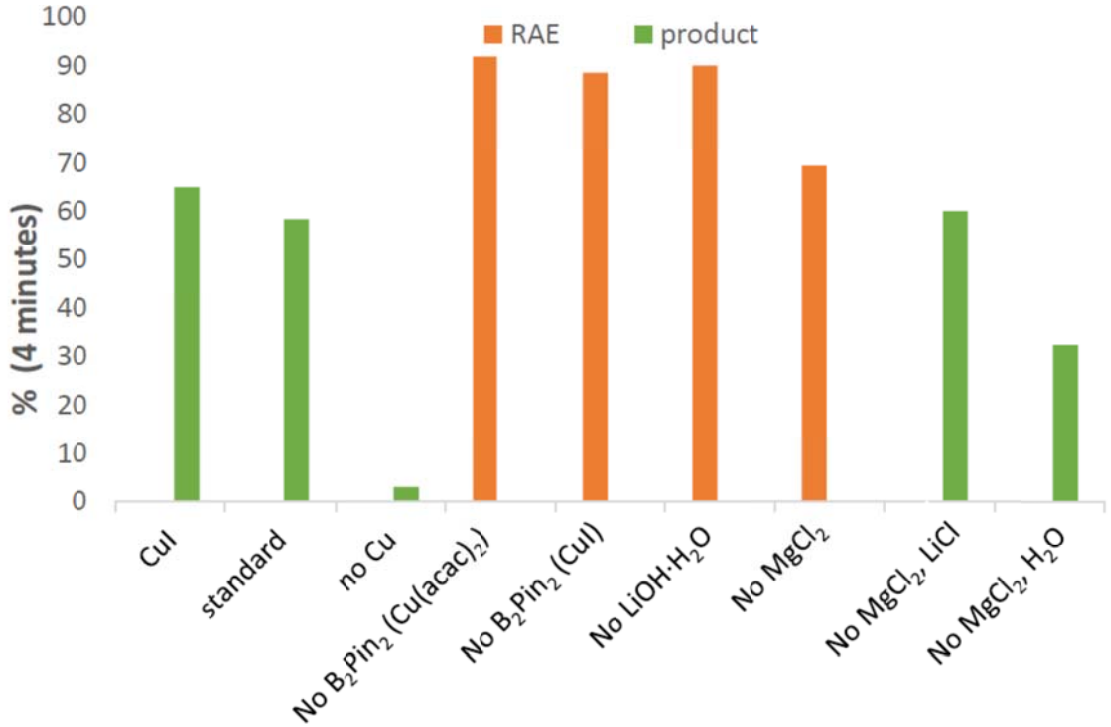



**Figure S7.** Yield of the borylation reaction after 4 minutes when one reaction component at a time has been removed or, in the case of Cu, exchanged (20 mol% $Cu(acac)_2$ for 20 mol% CuI). Standard conditions: 140 mM RAE, 1.5 equiv $B_2pin_2$, 20 mol% $Cu(acac)_2$, 1.5 equiv $MgCl_2$, 15 equiv $LiOH•H_2O$. Where applicable, [LiCl] = 210 mM (1.5 equiv) and [$H_2O$] = 2100 mM (15 equiv).

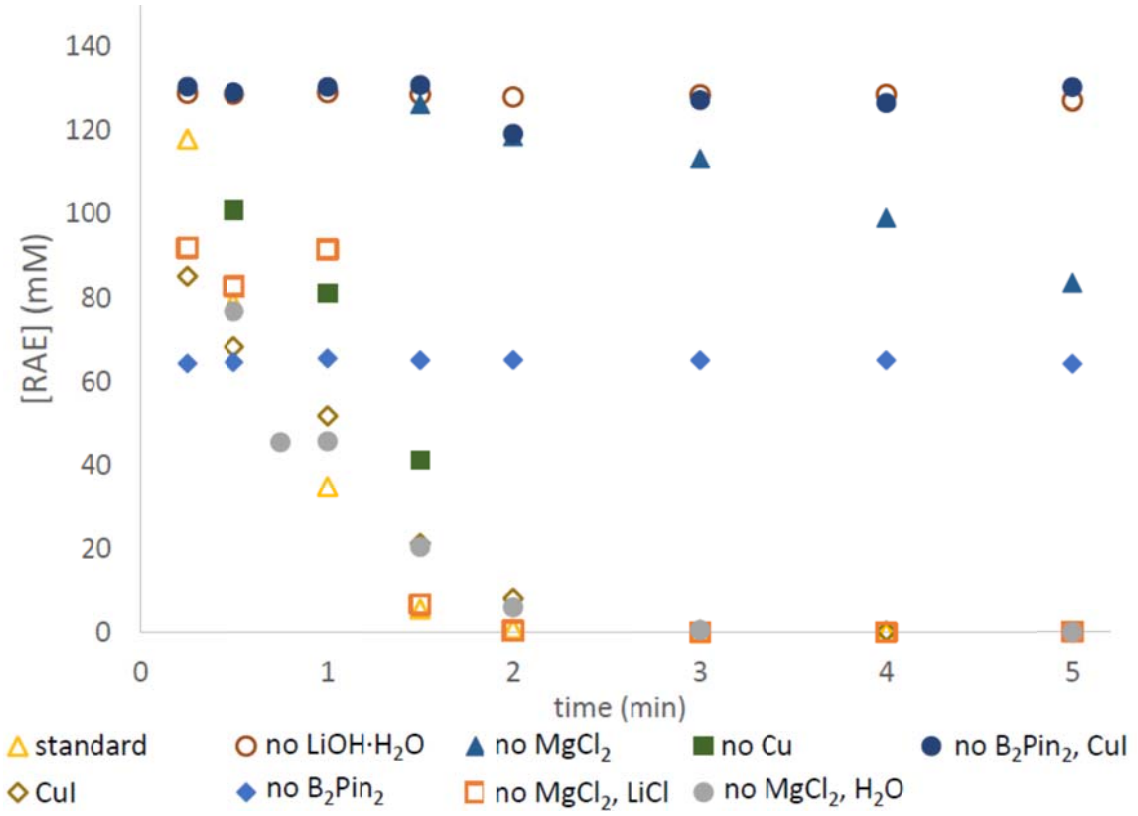



**Figure S8.** Time course data for the borylation reaction when one reaction component at a time has been removed or, in the case of Cu, exchanged (20 mol% $Cu(acac)_2$ for 20 mol% CuI). Standard conditions: 140 mM RAE, 1.5 equiv $B_2pin_2$, 20 mol% $Cu(acac)_2$, 1.5 equiv $MgCl_2$, 15 equiv $LiOH•H_2O$. Where applicable, [LiCl] = 210 mM (1.5 equiv) and [$H_2O$] = 2100 mM (15 equiv). For the no $B_2pin_2$ experiment, [RAE] = 70 mM.

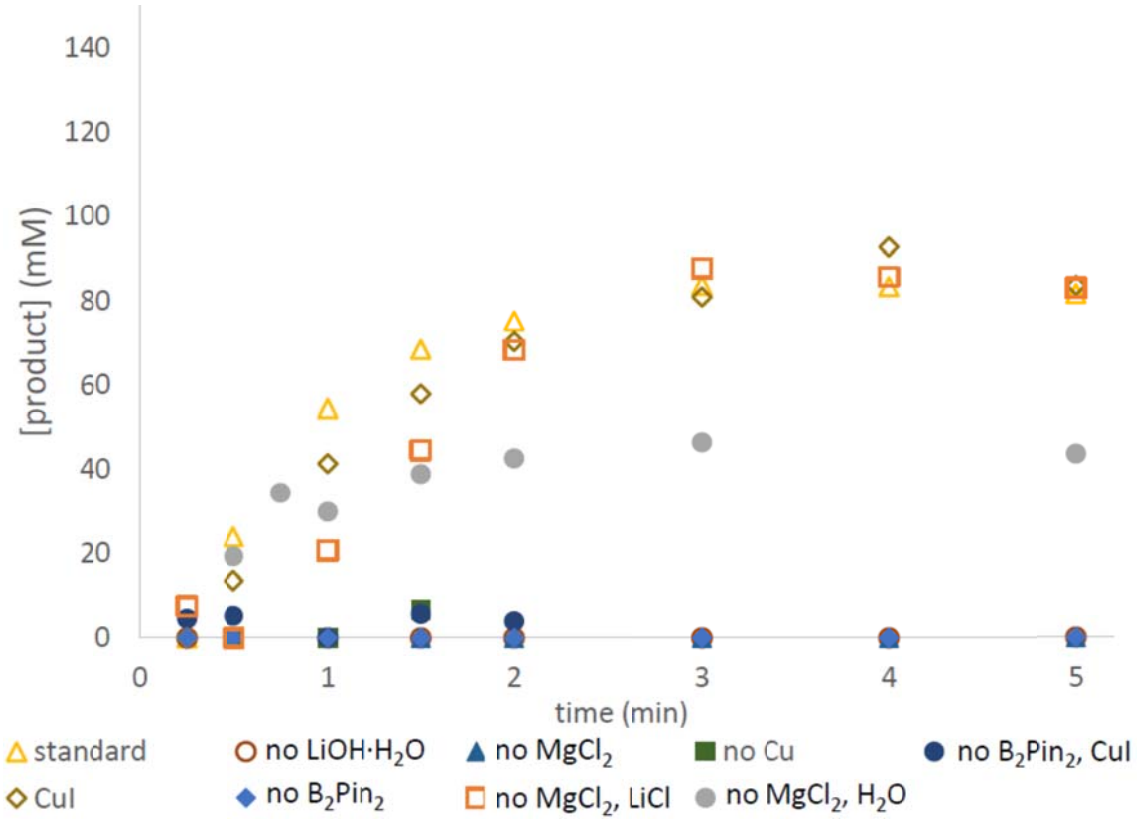



**Figure S9.** Time course data for the borylation reaction when one reaction component at a time has been removed or, in the case of Cu, exchanged (20 mol% $Cu(acac)_2$ for 20 mol% CuI). Standard conditions: 140 mM RAE, 1.5 equiv $B_2pin_2$, 20 mol% $Cu(acac)_2$, 1.5 equiv $MgCl_2$, 15 equiv $LiOH{\bullet}H_2O$. Where applicable, [LiCl] = 210 mM (1.5 equiv) and [$H_2O$] = 2100 mM (15 equiv). For the no $B_2pin_2$ experiment, [RAE] = 70 mM.

**Equations derived from Eq. 3 in the main article:**

$$\frac{d[product]}{d[RAE]} = \frac{1}{1+\frac{k\prime}{k}\cdot TON} \qquad \text{(S1)}$$

$$\text{TON} = \frac{[RAE]}{[Cu]} \qquad \text{(S2)}$$

$$\text{mol\%} = \frac{1}{TON} \cdot 100 \qquad \text{(S3)}$$

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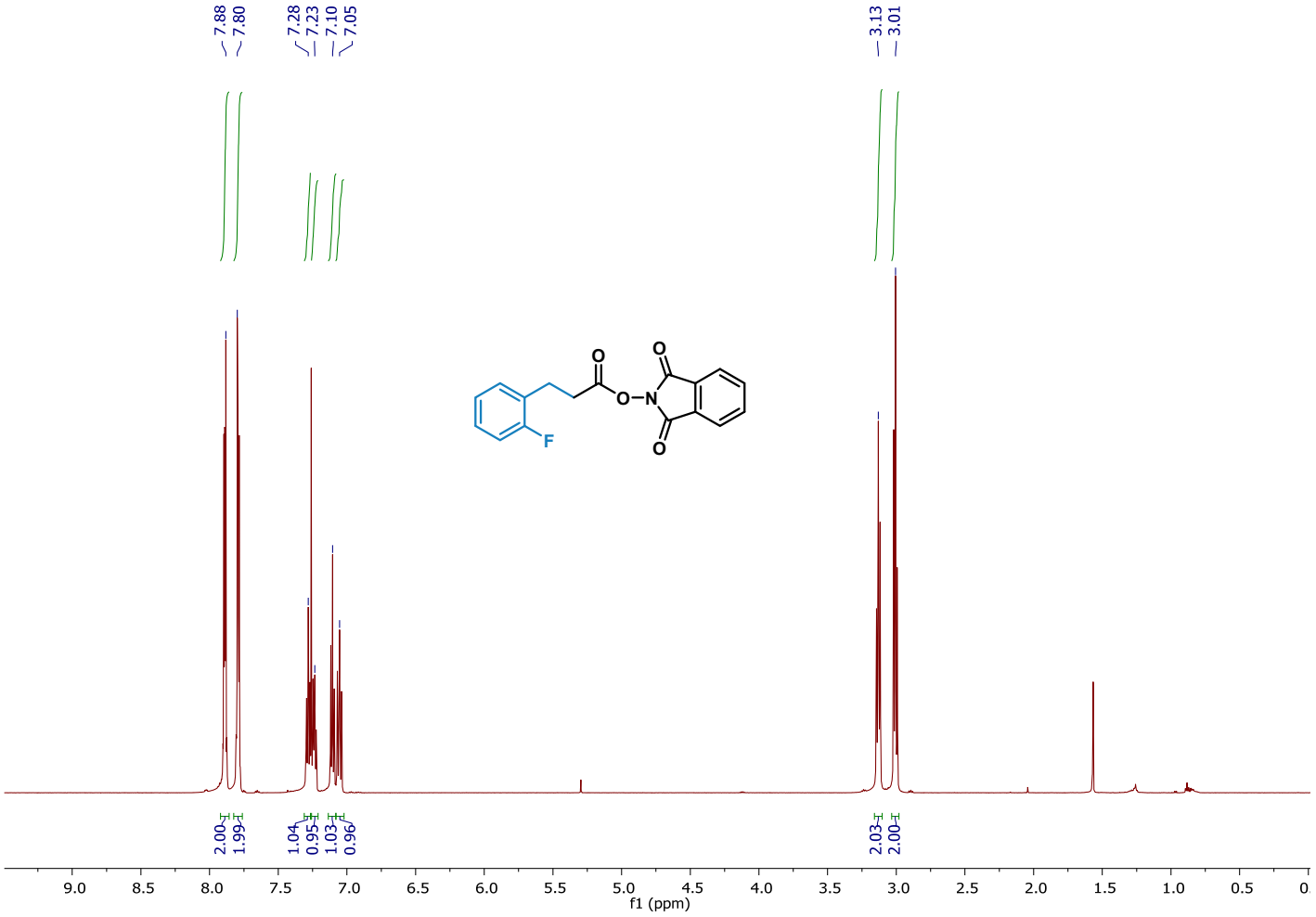
**NMR Spectra**

**Compound S26 $^{1}$H NMR**



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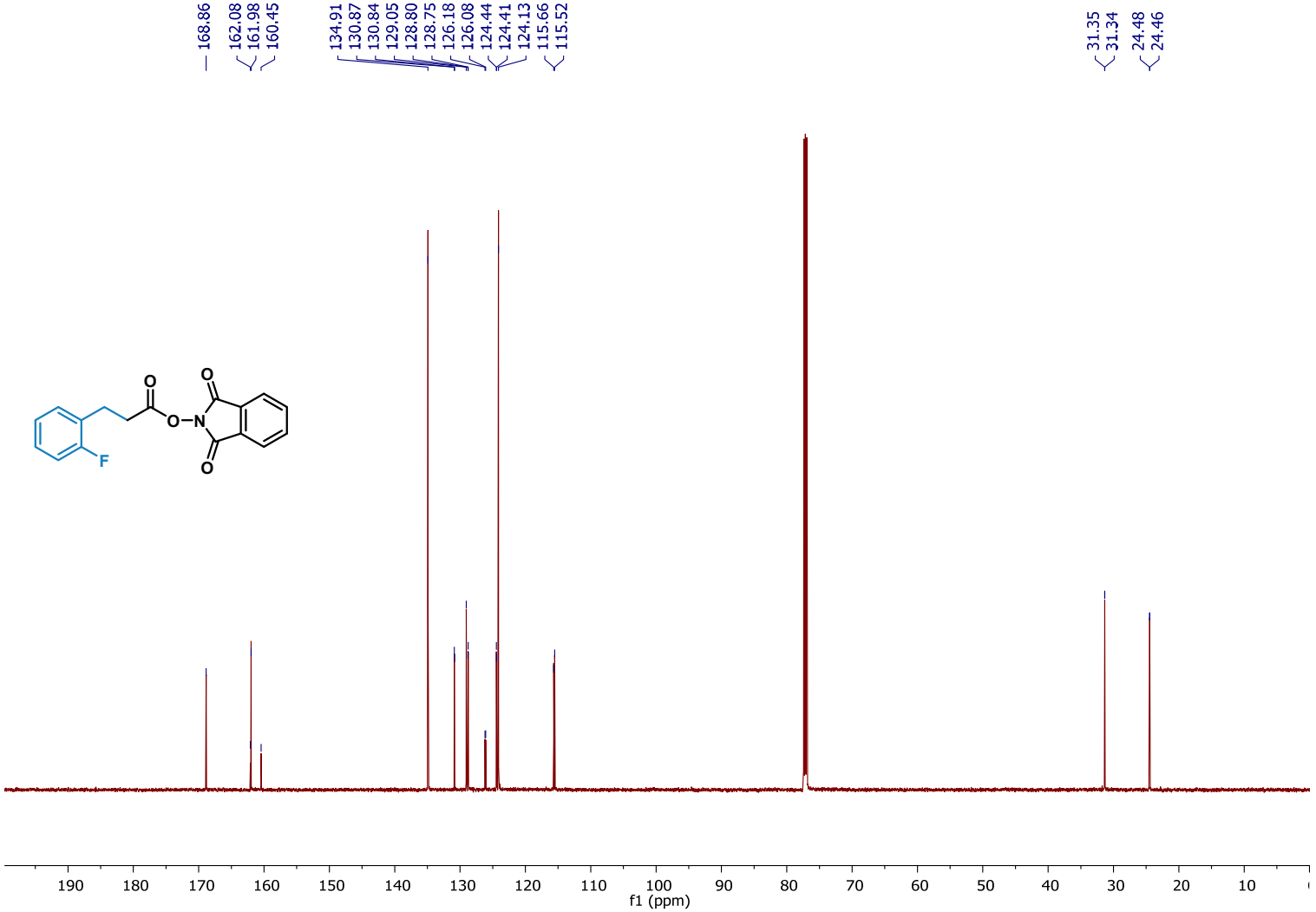
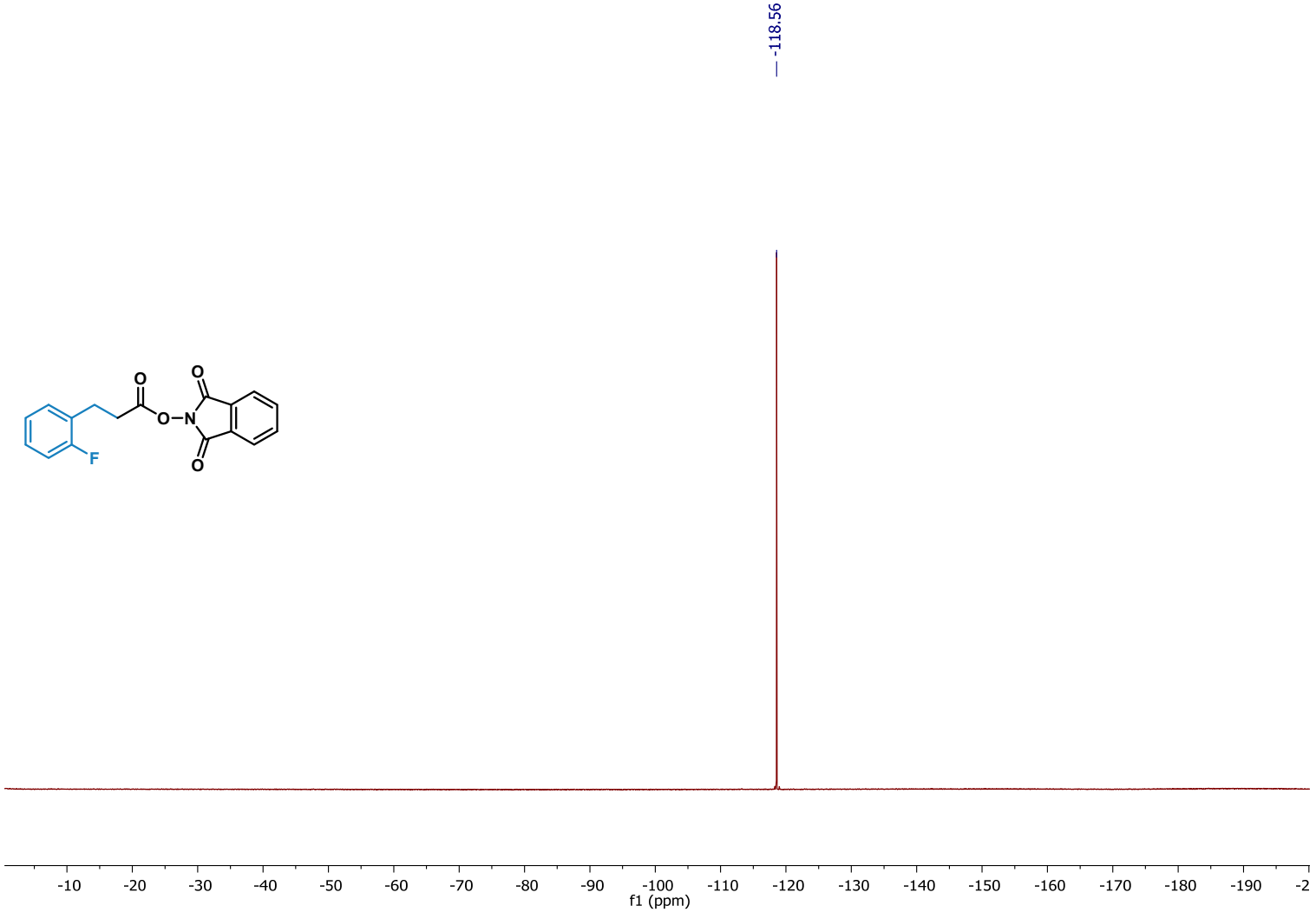


**Compound S26 $^{19}$F NMR**



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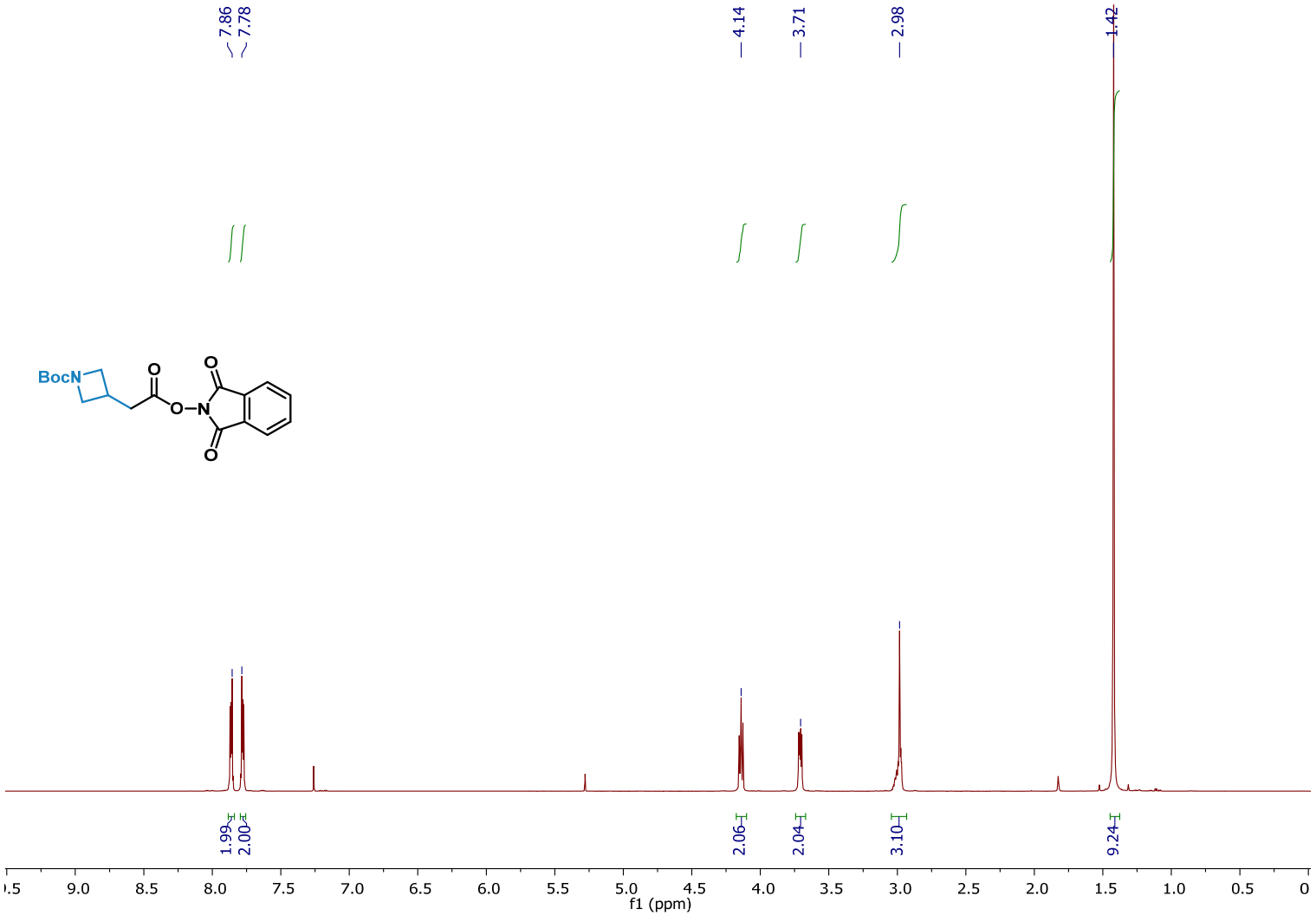

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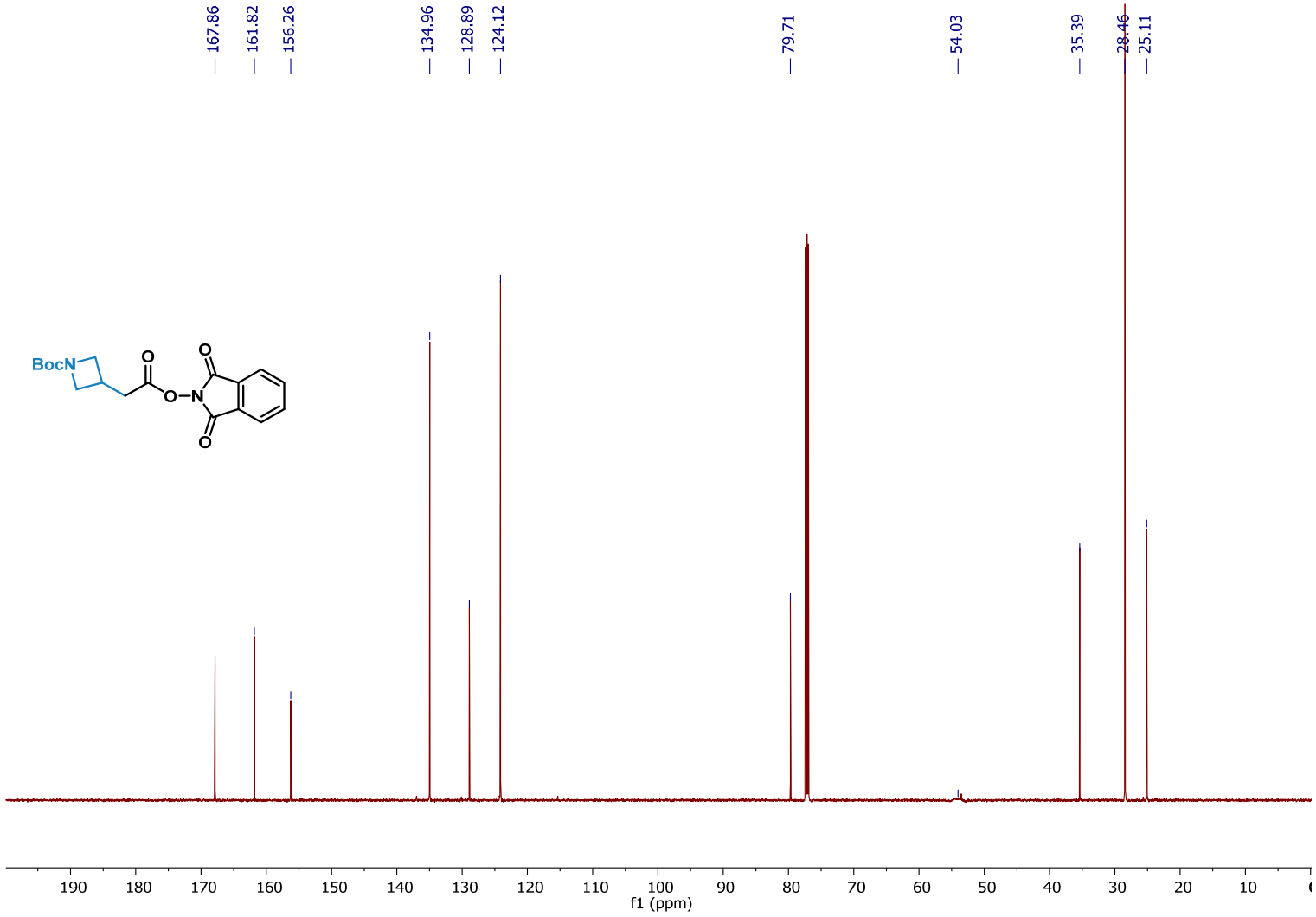

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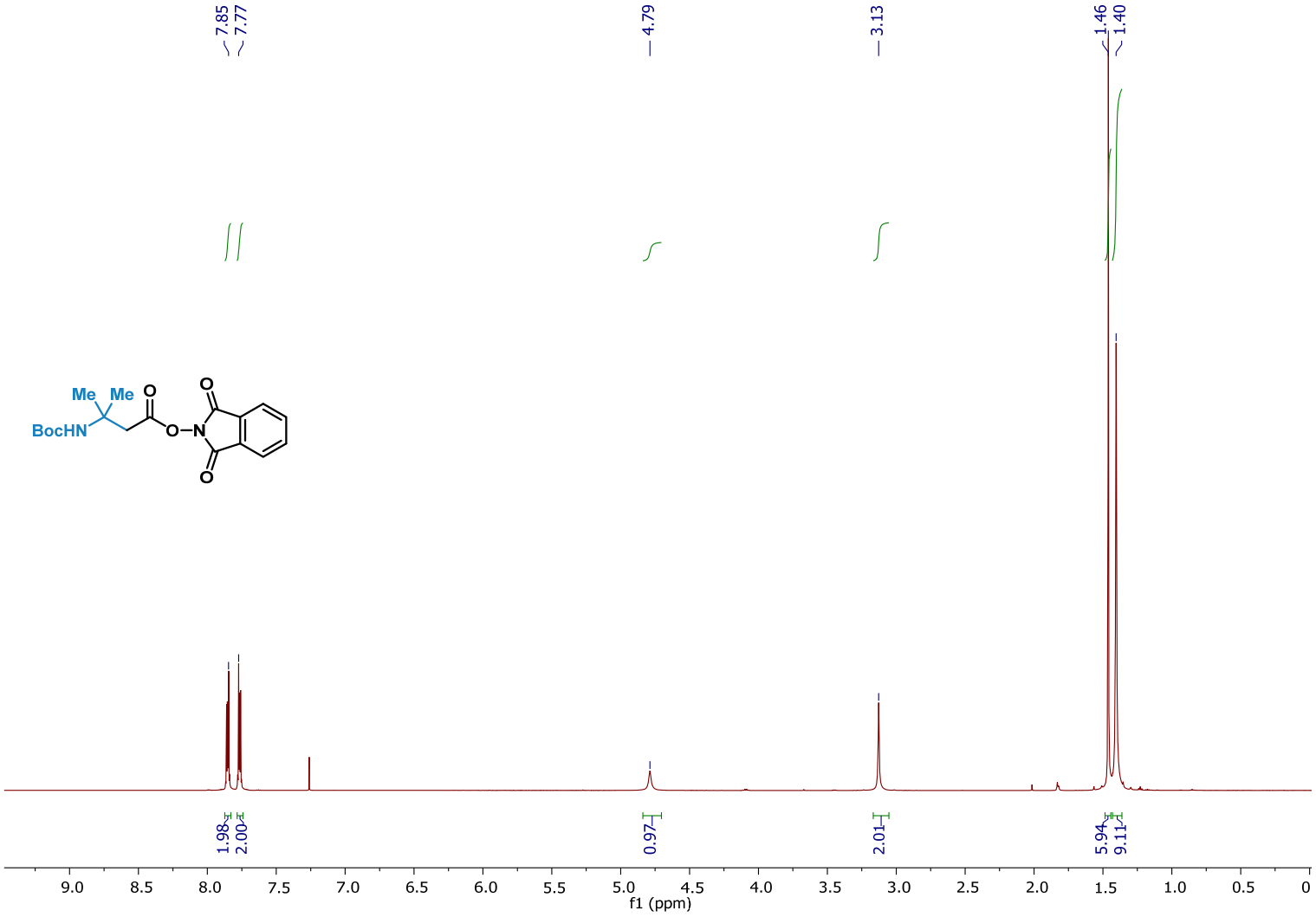

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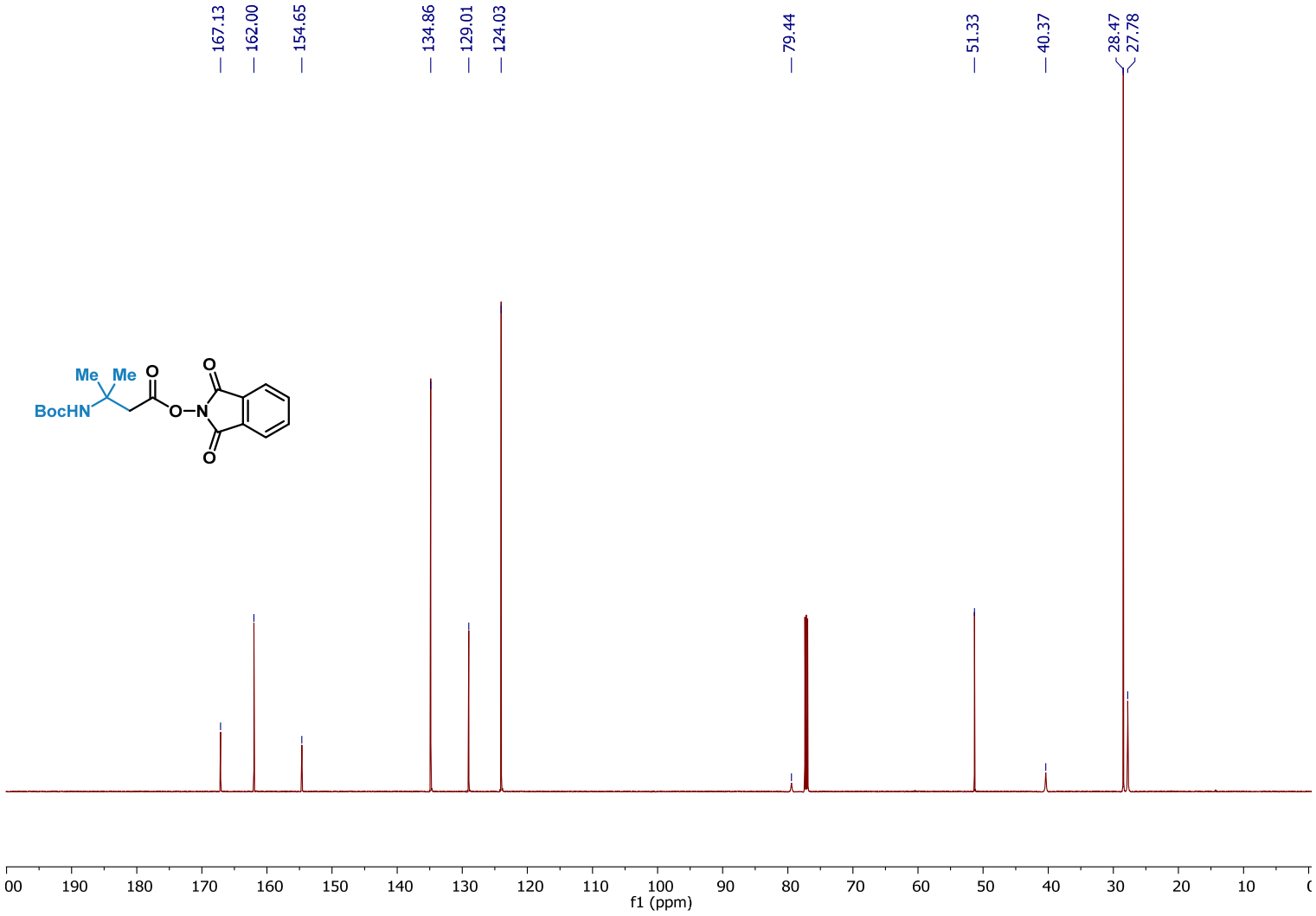

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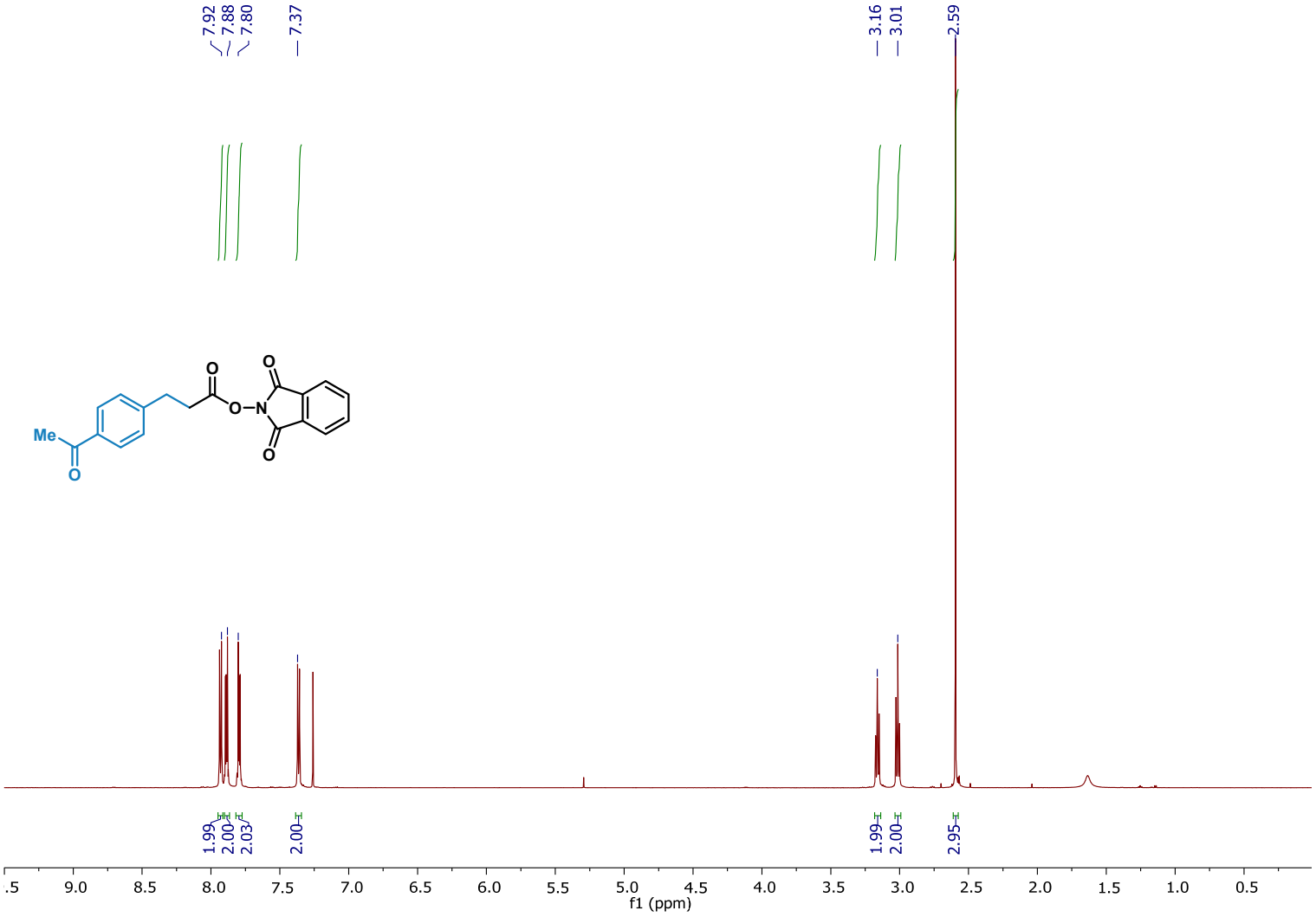

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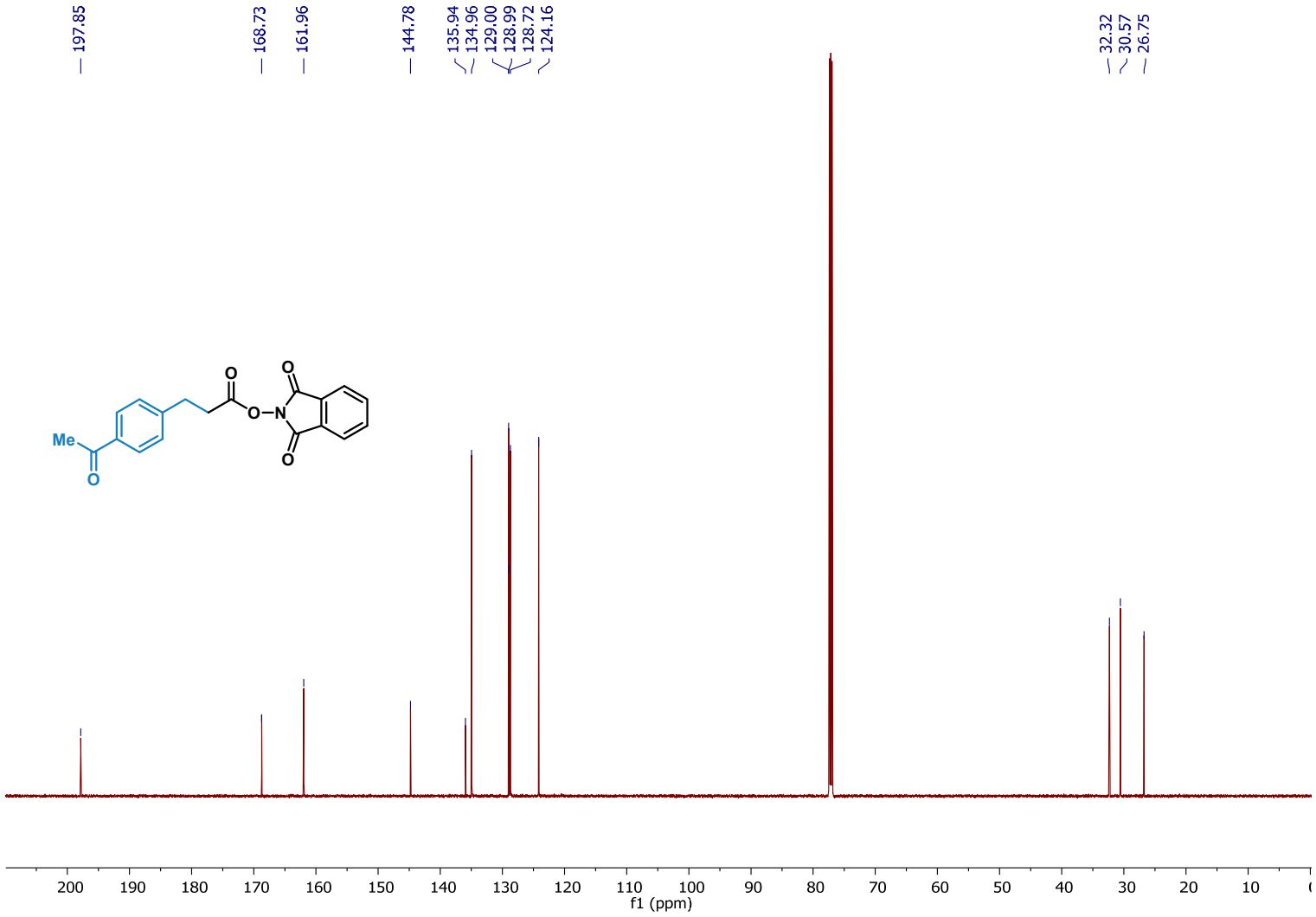

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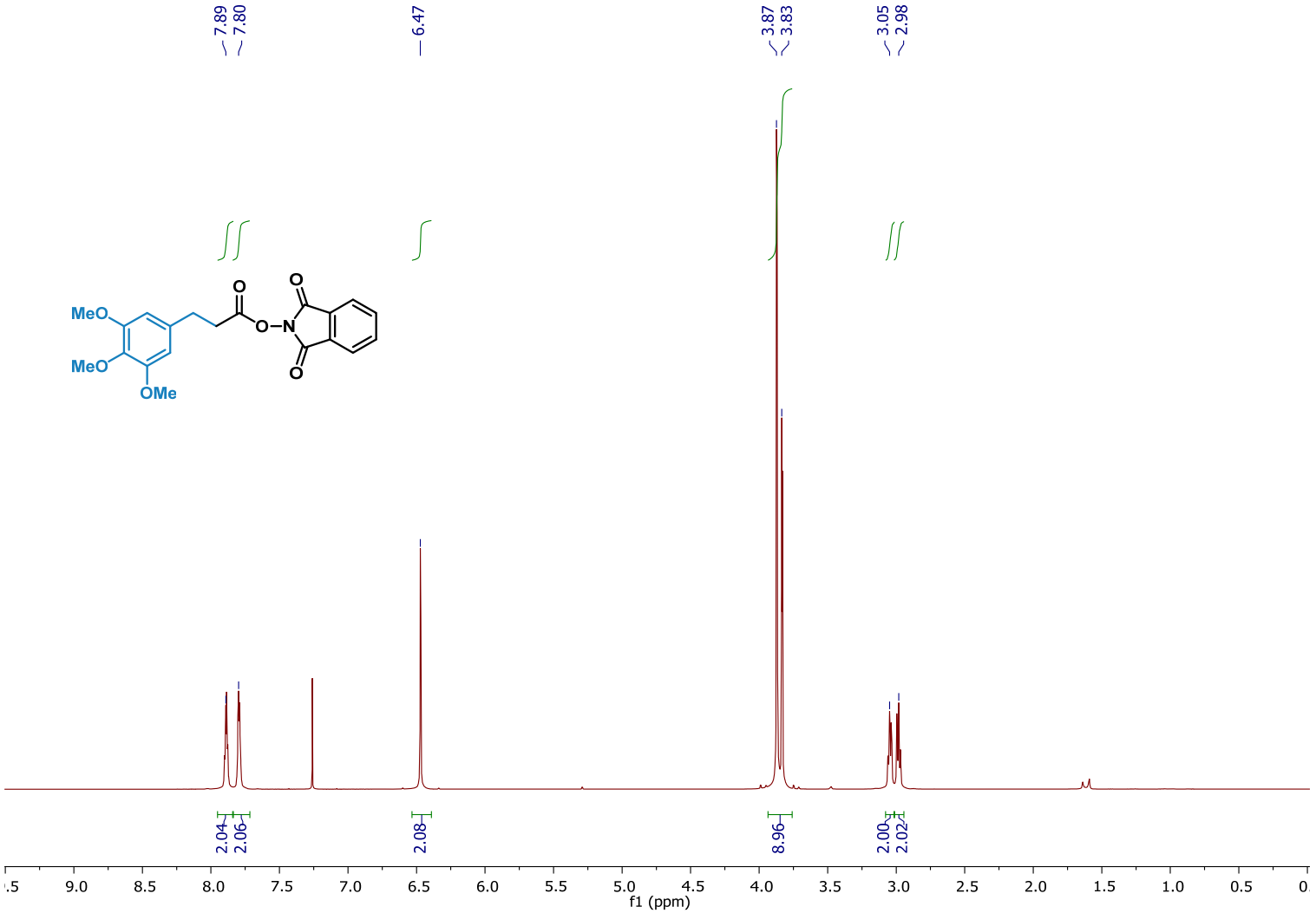

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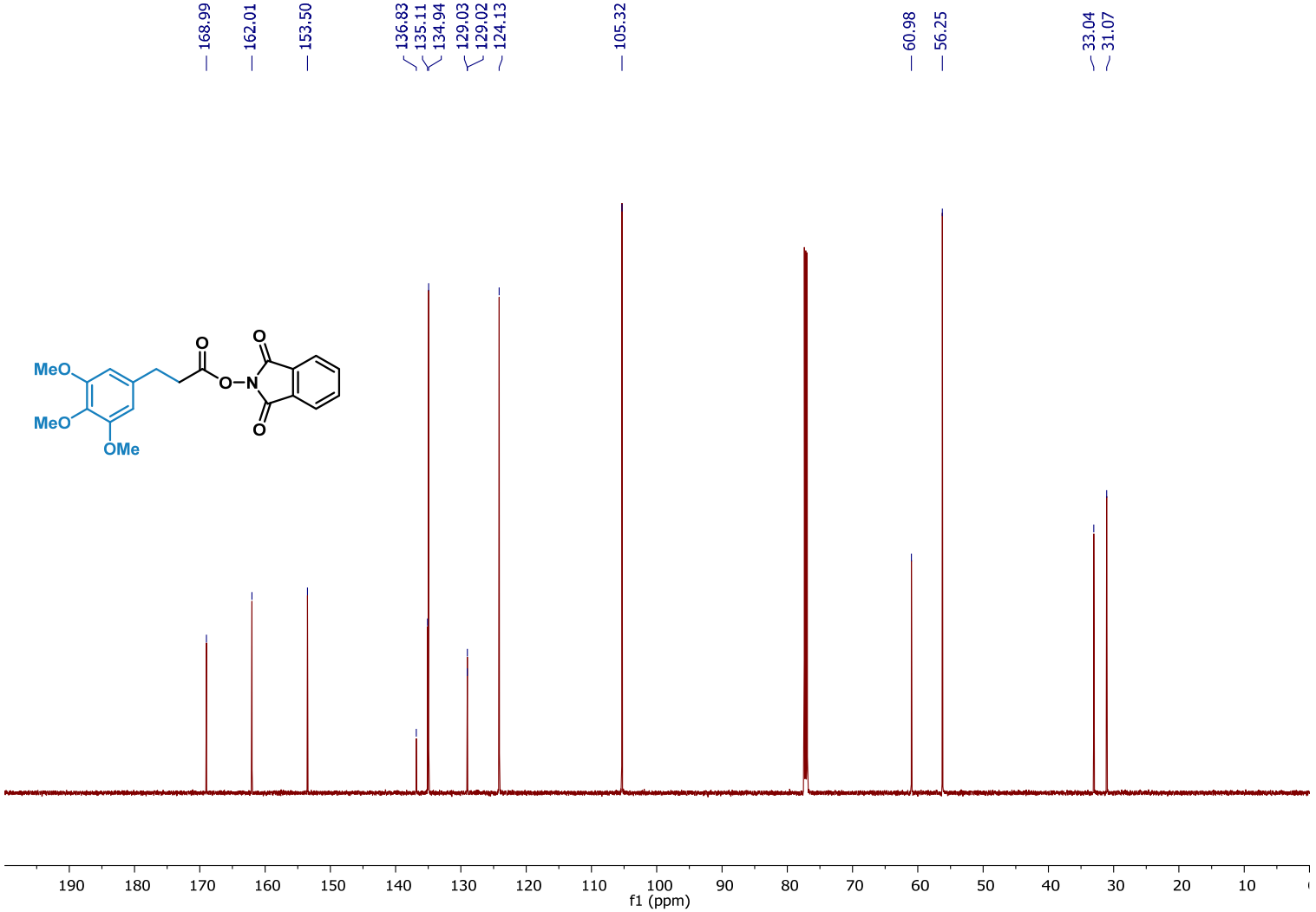

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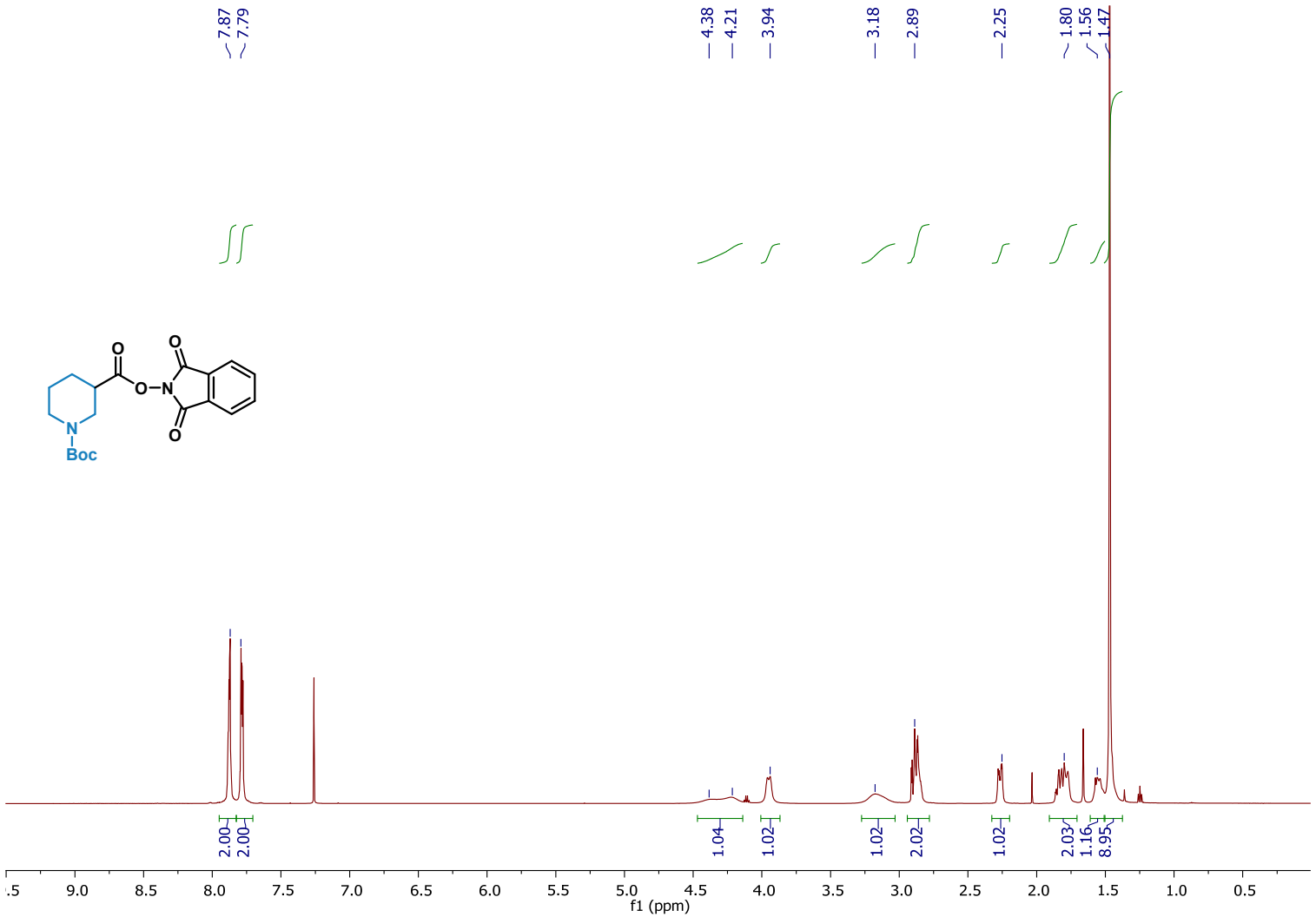

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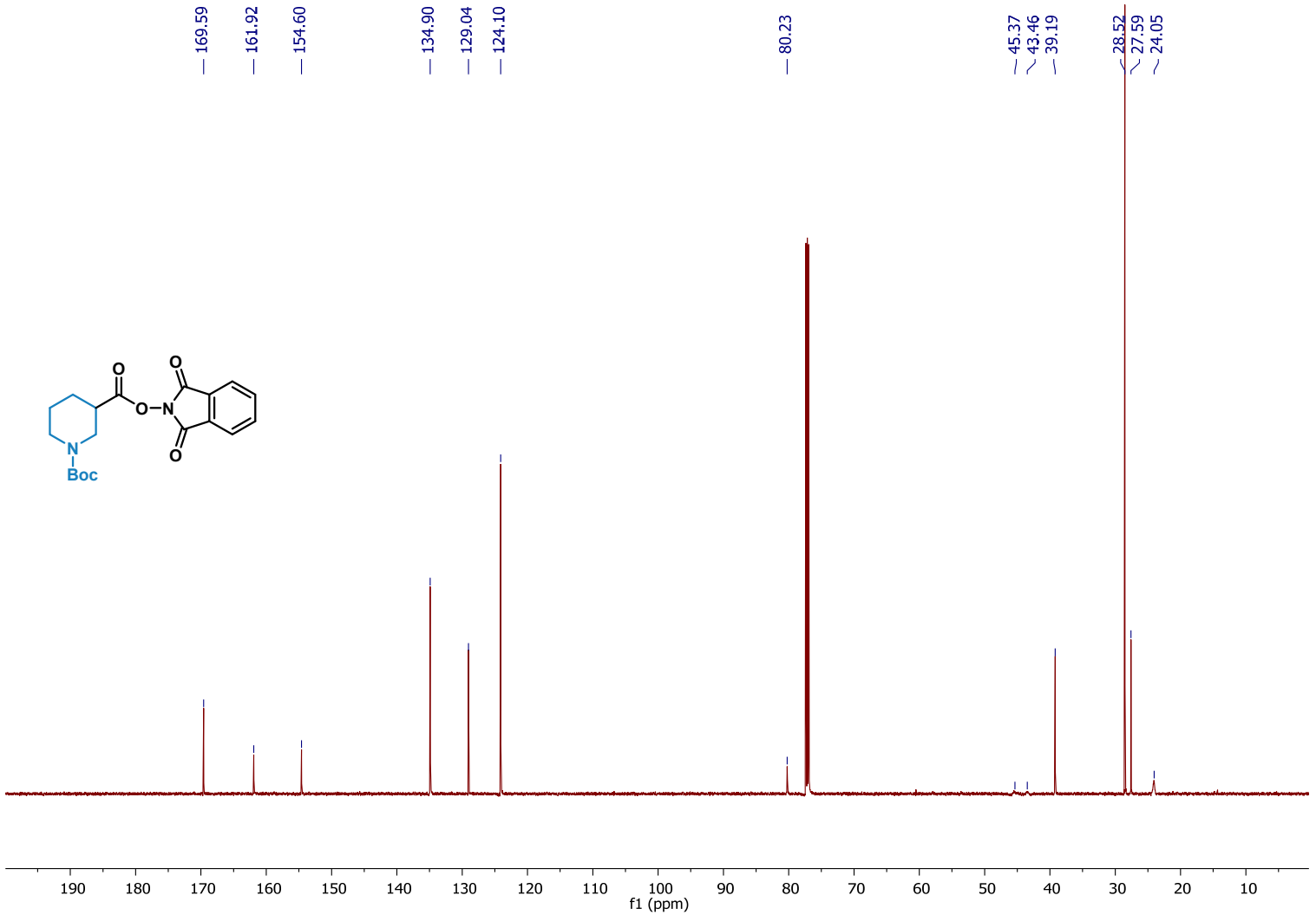

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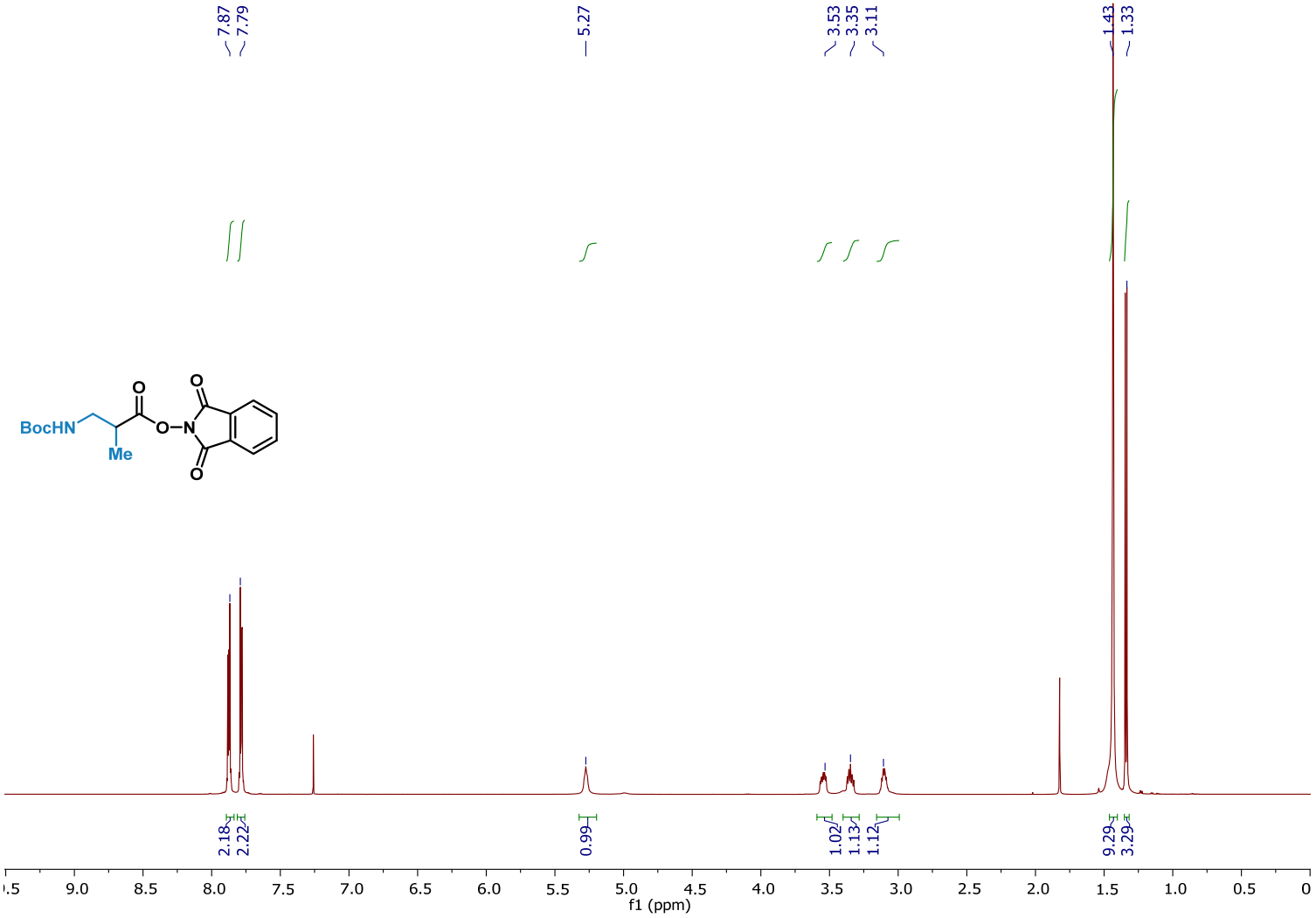

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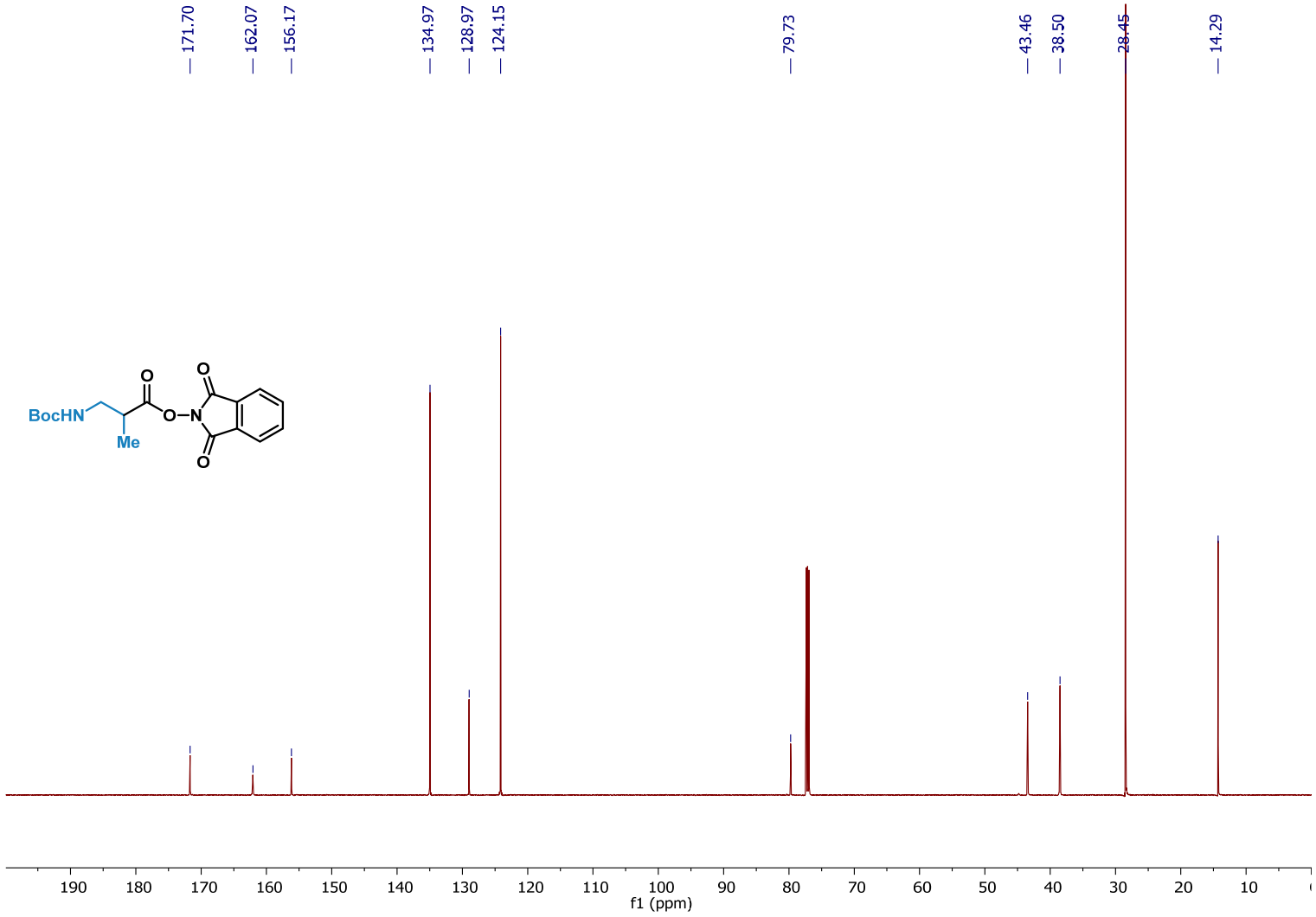

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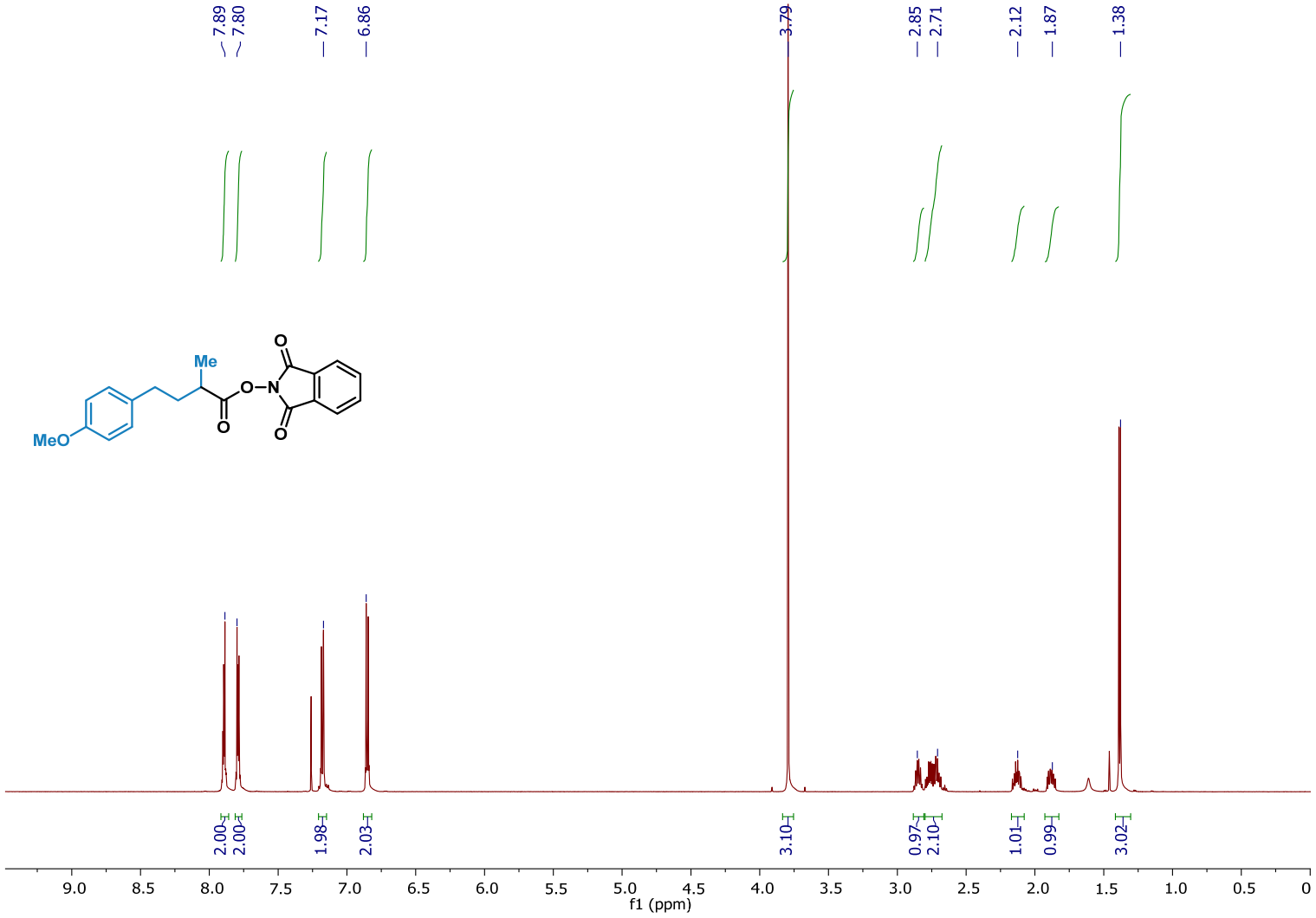

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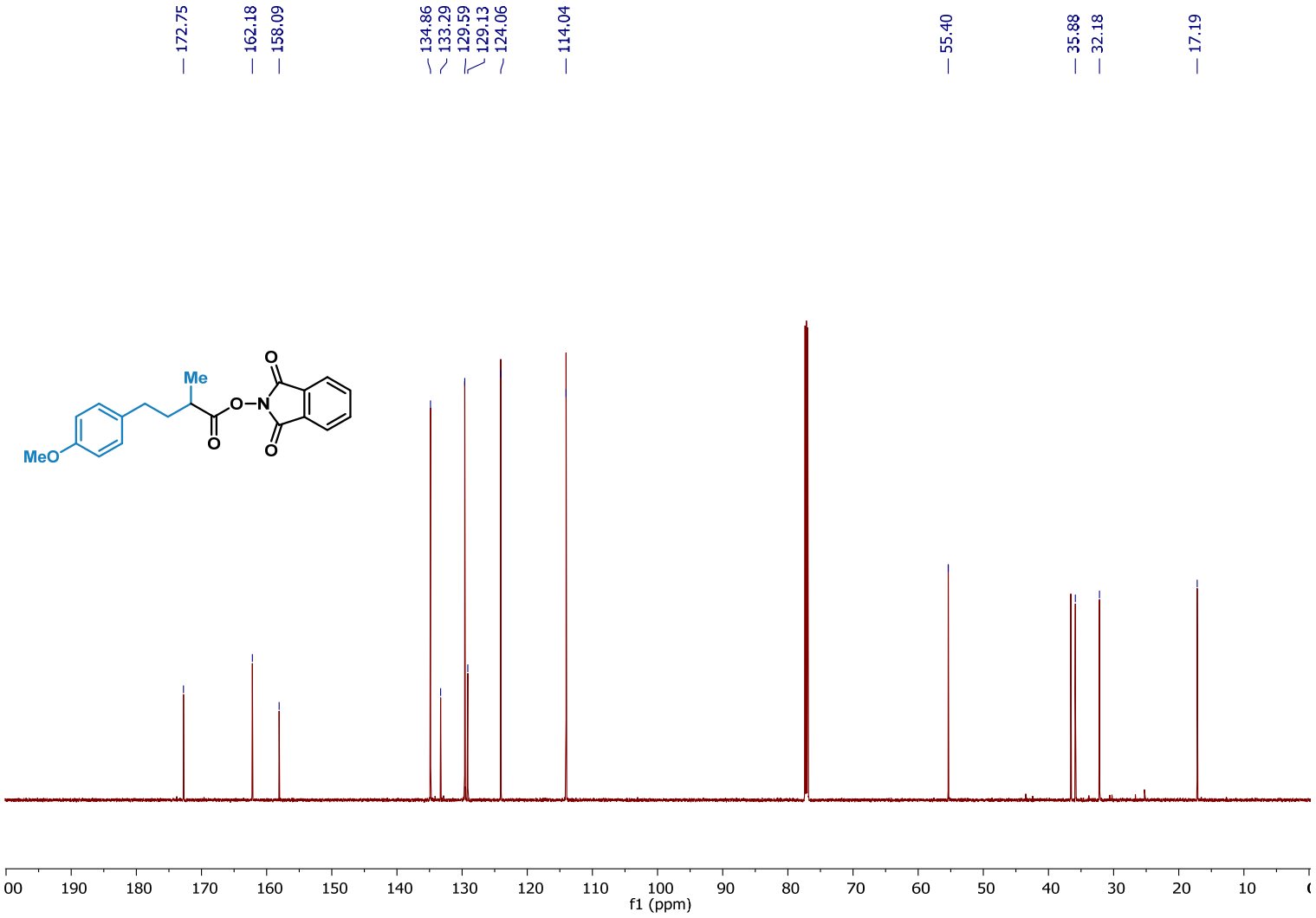

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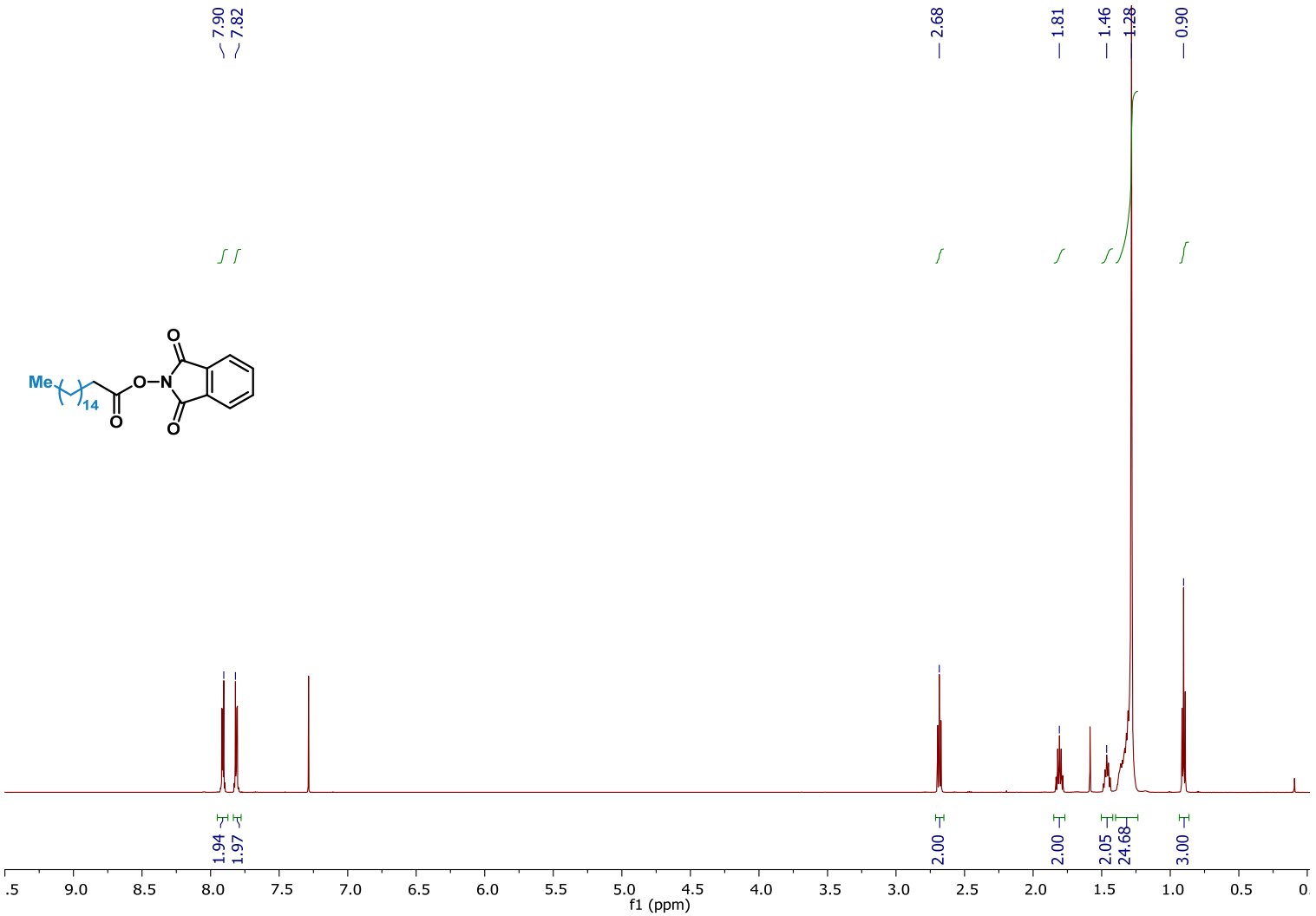

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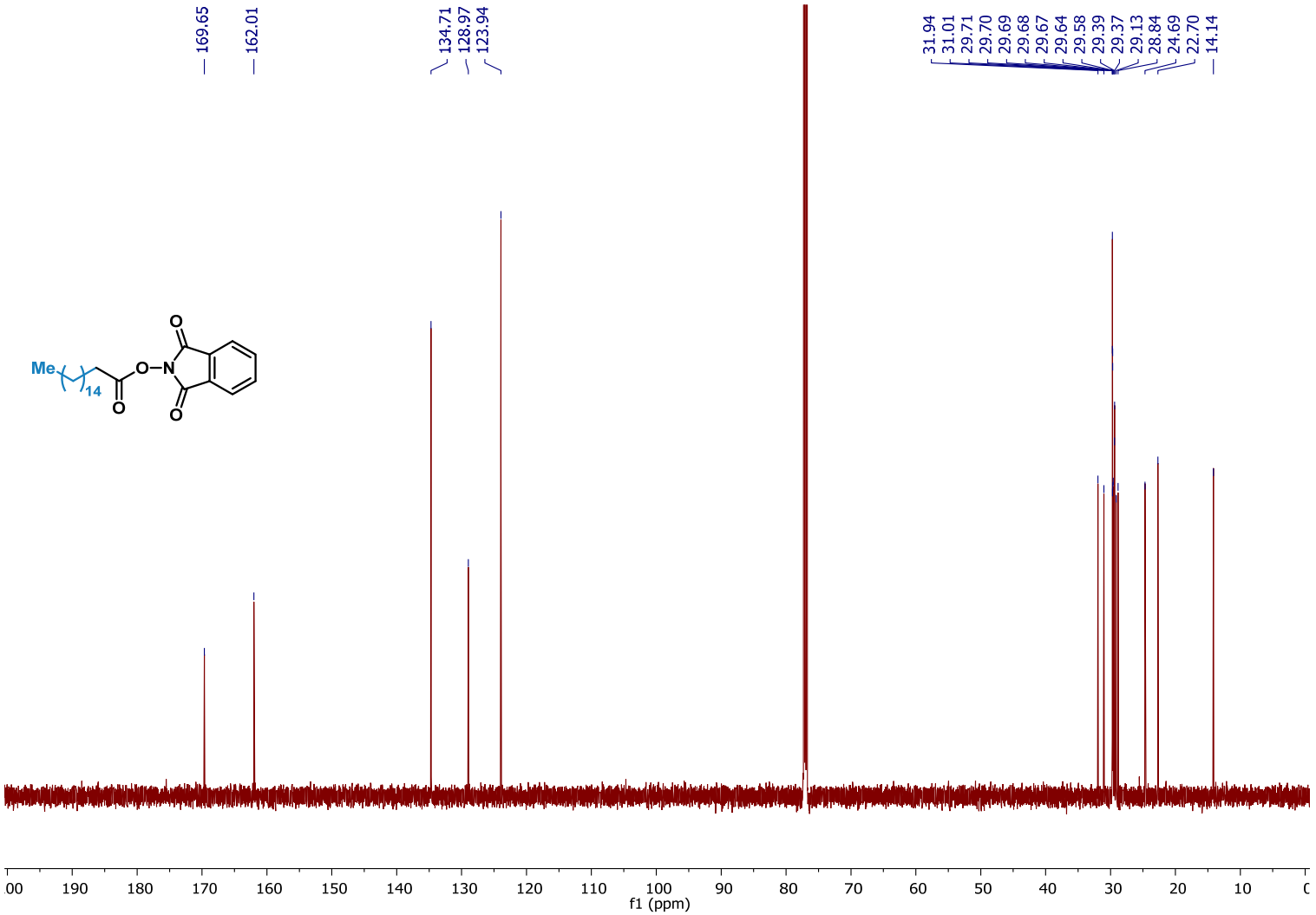
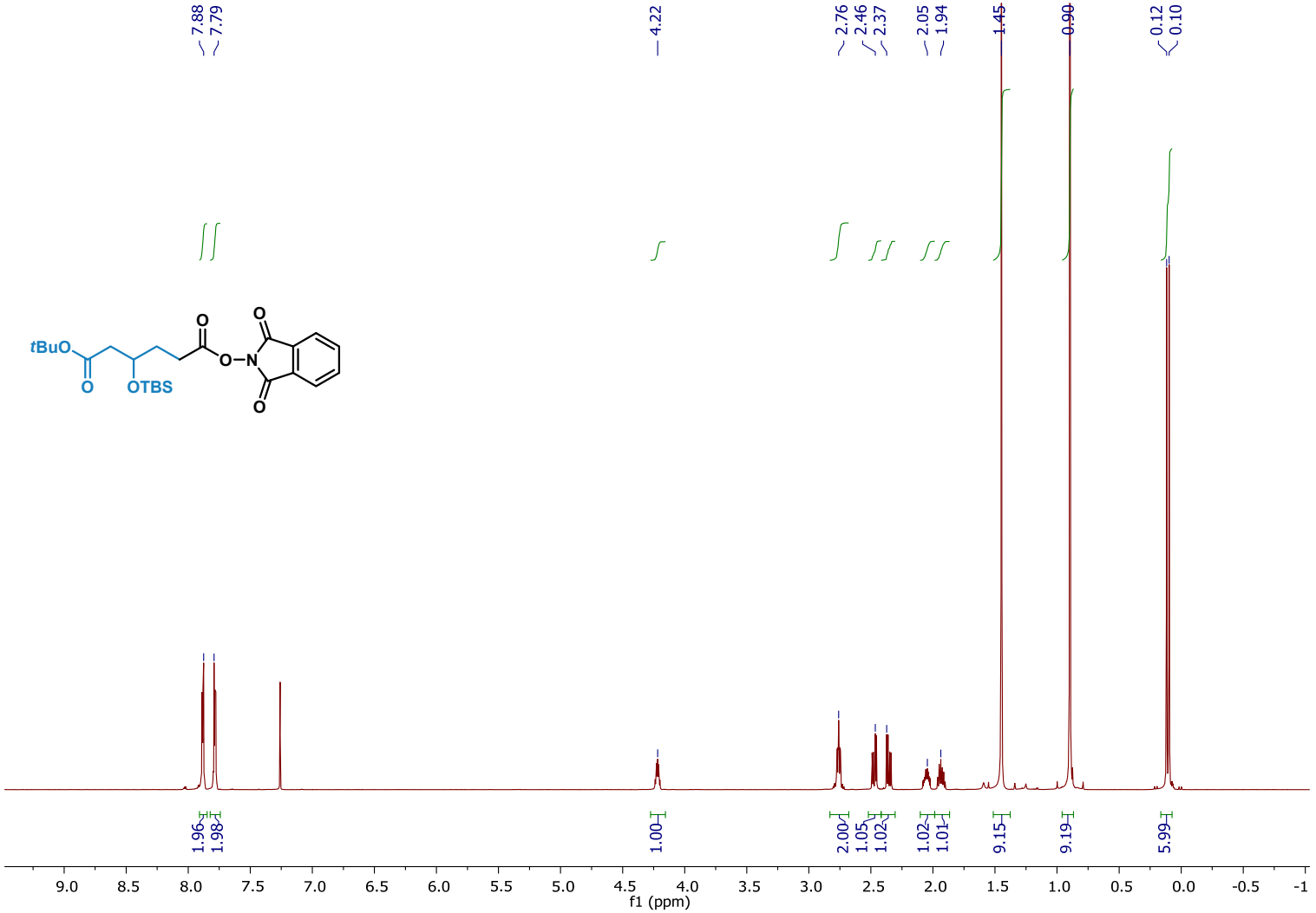


**Compound 45 $^{1}$H NMR**



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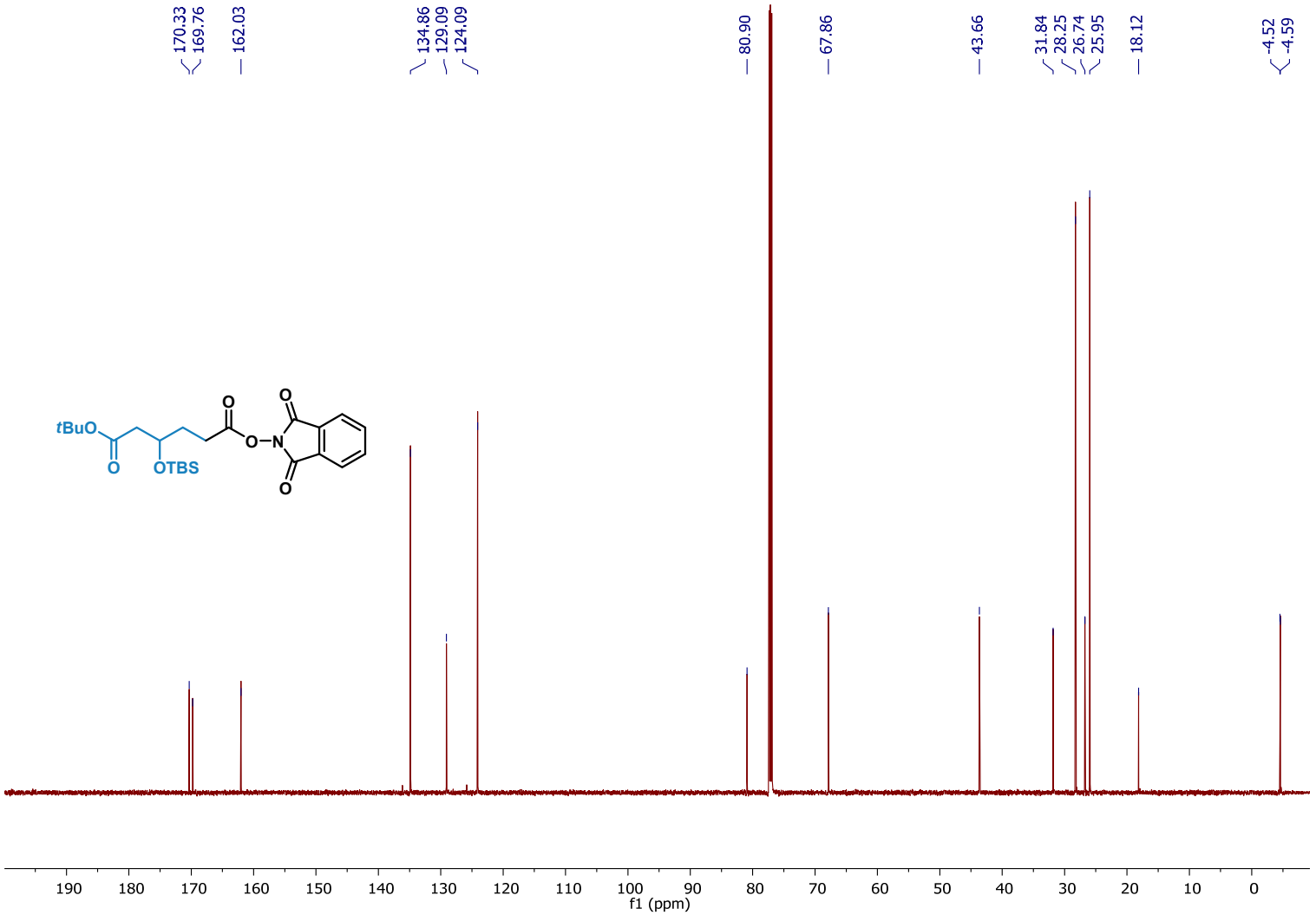
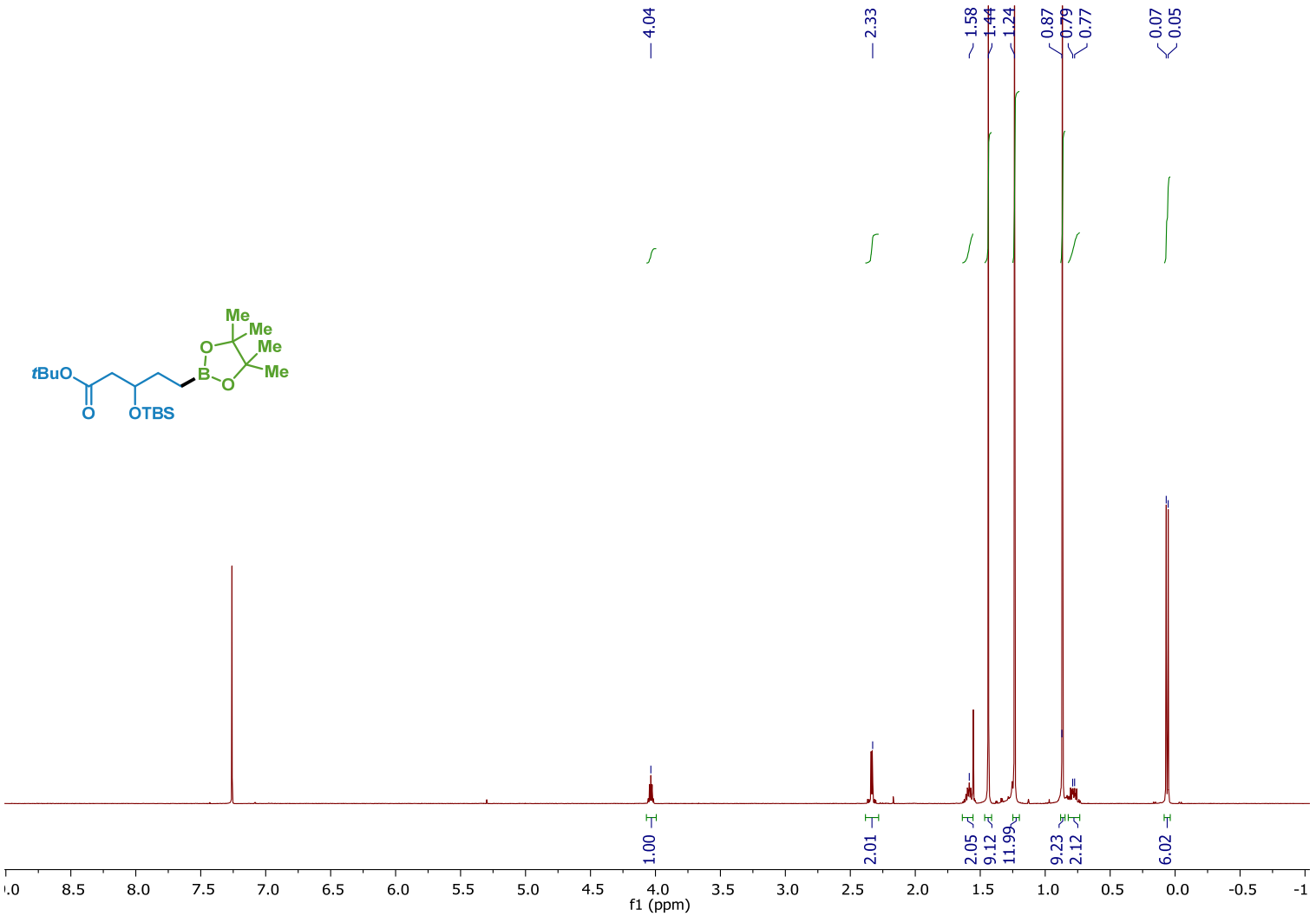
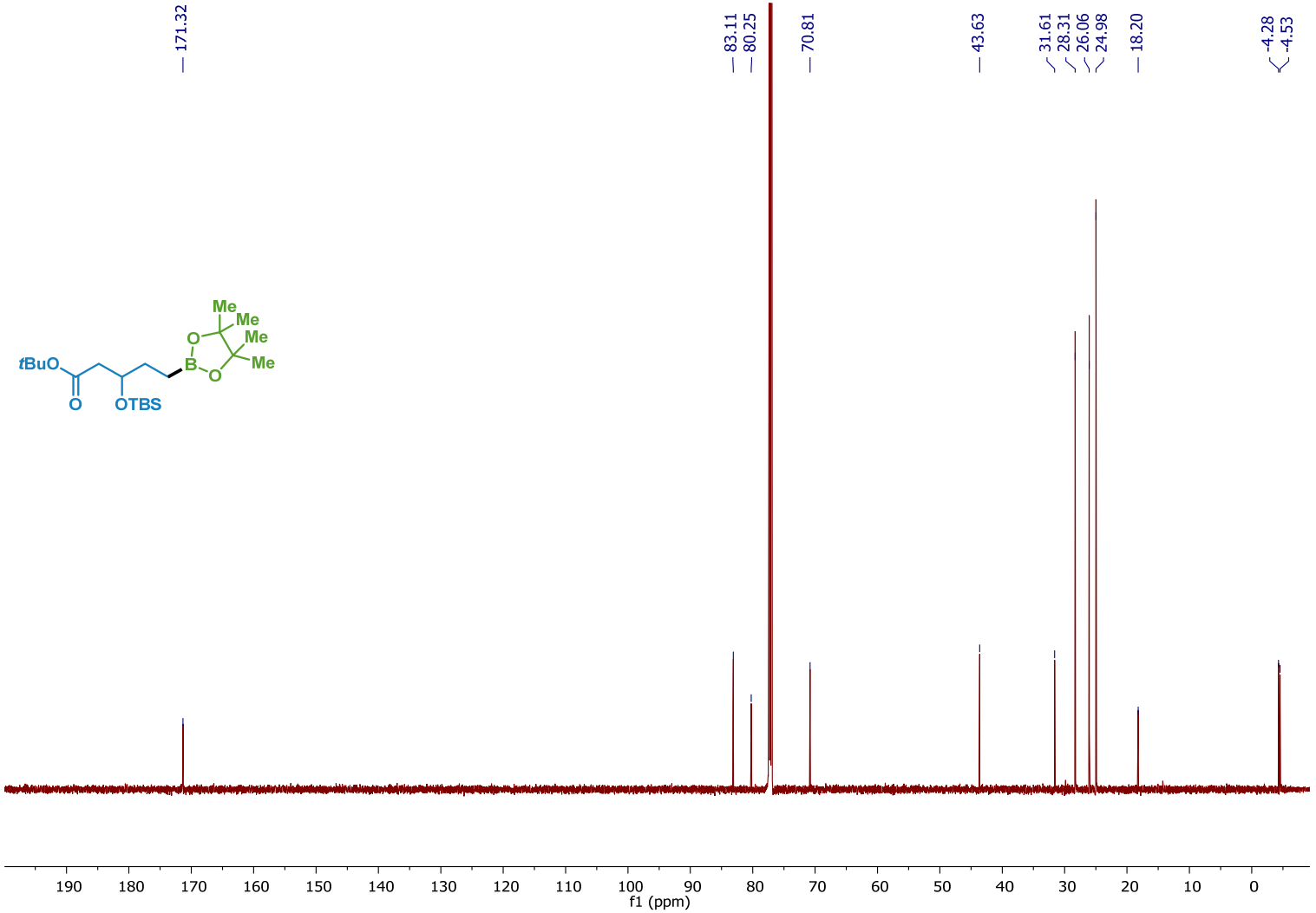


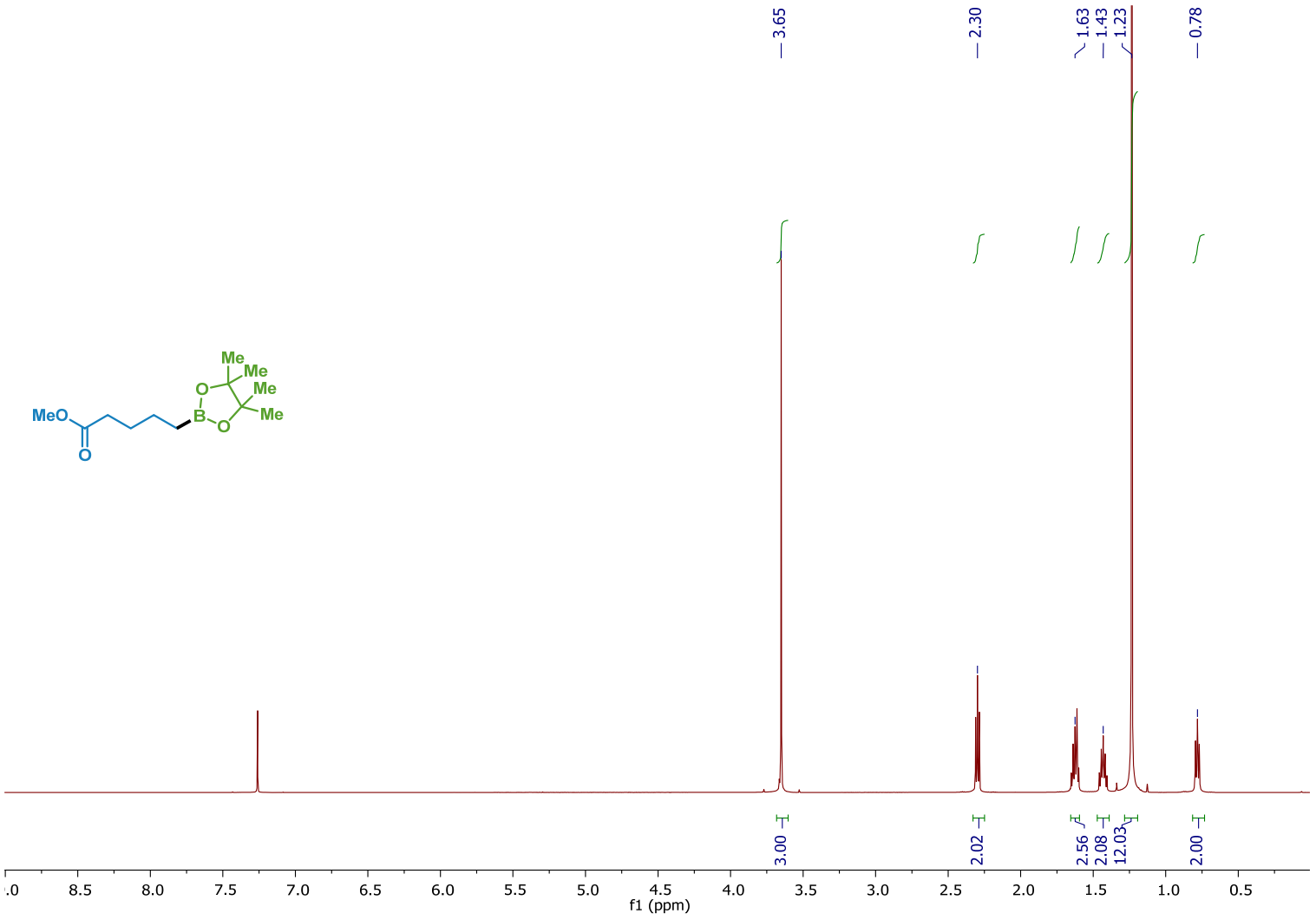
**Compound 2 $^{1}$H NMR**



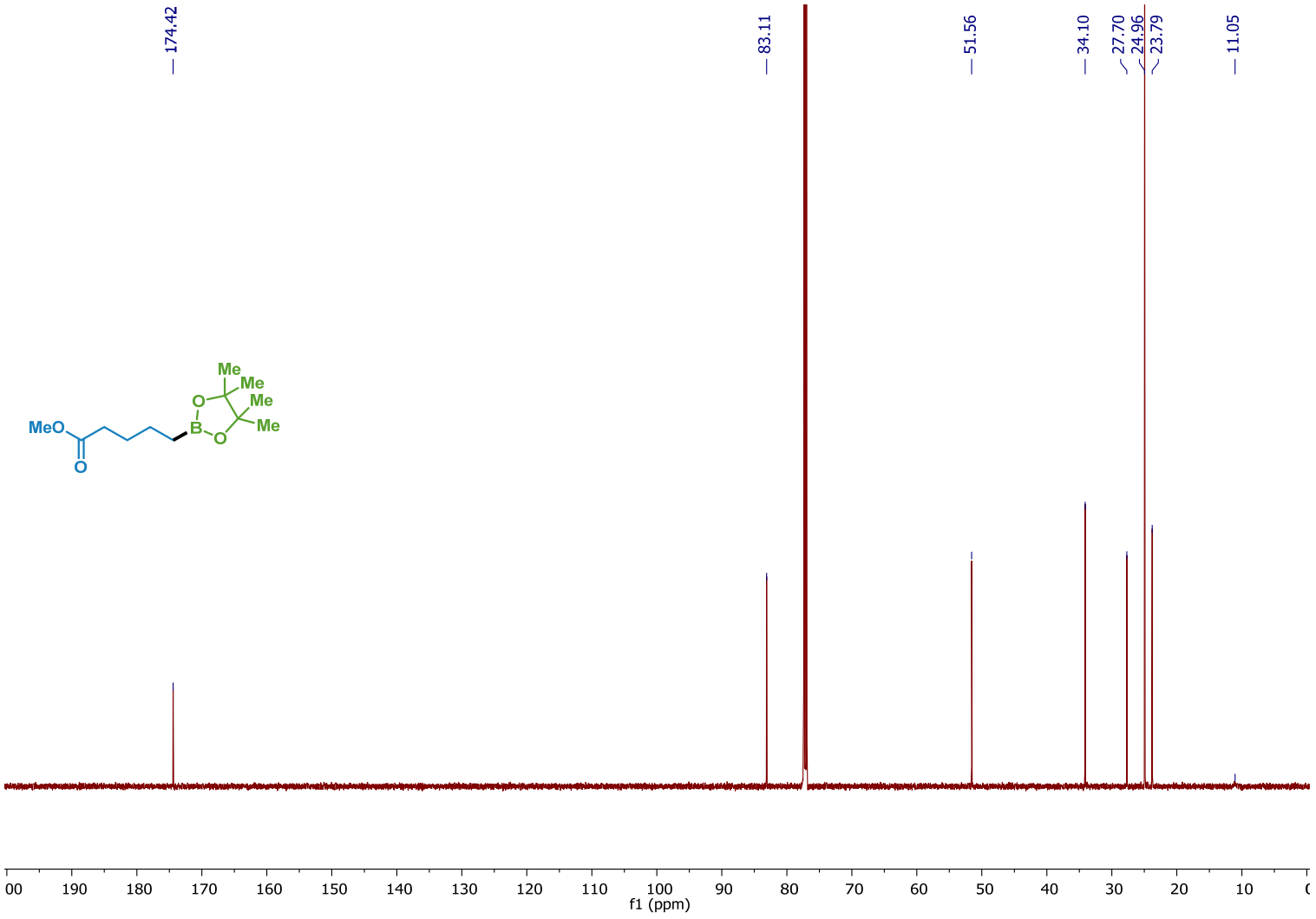
**Compound 2 $^{13}$C NMR**



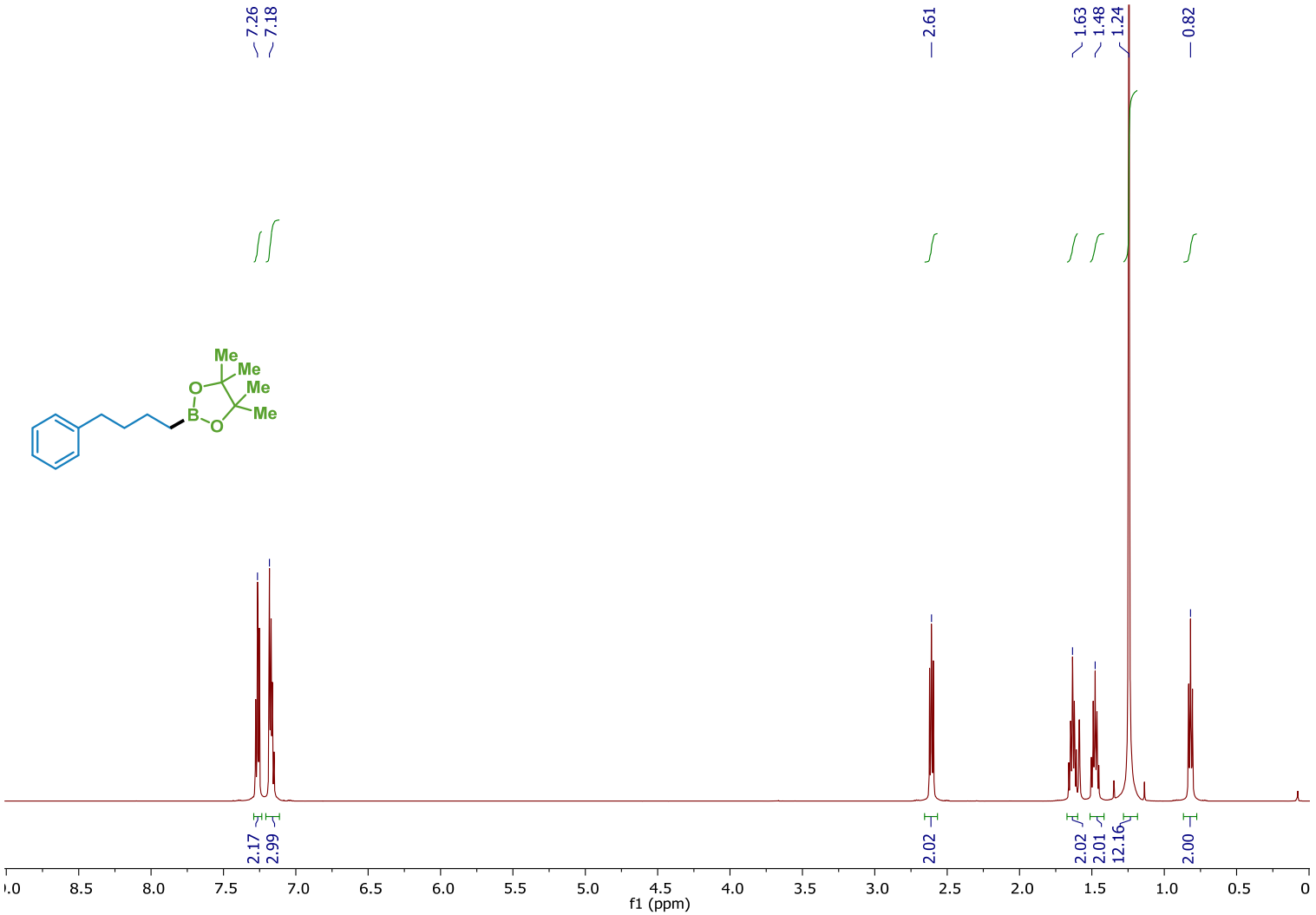
**Compound 6 $^{1}$H NMR**



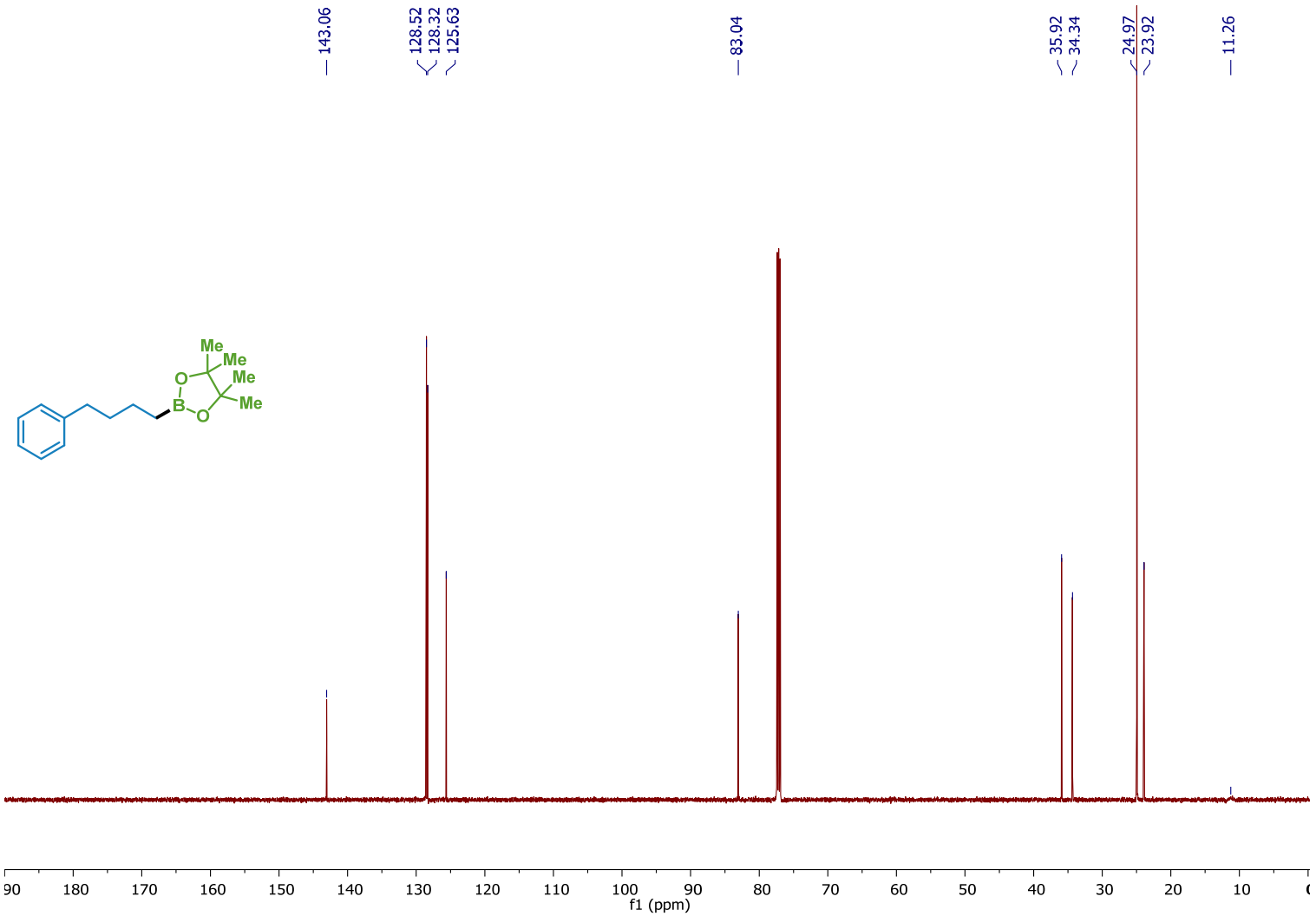
**Compound 6 $^{13}$C NMR**



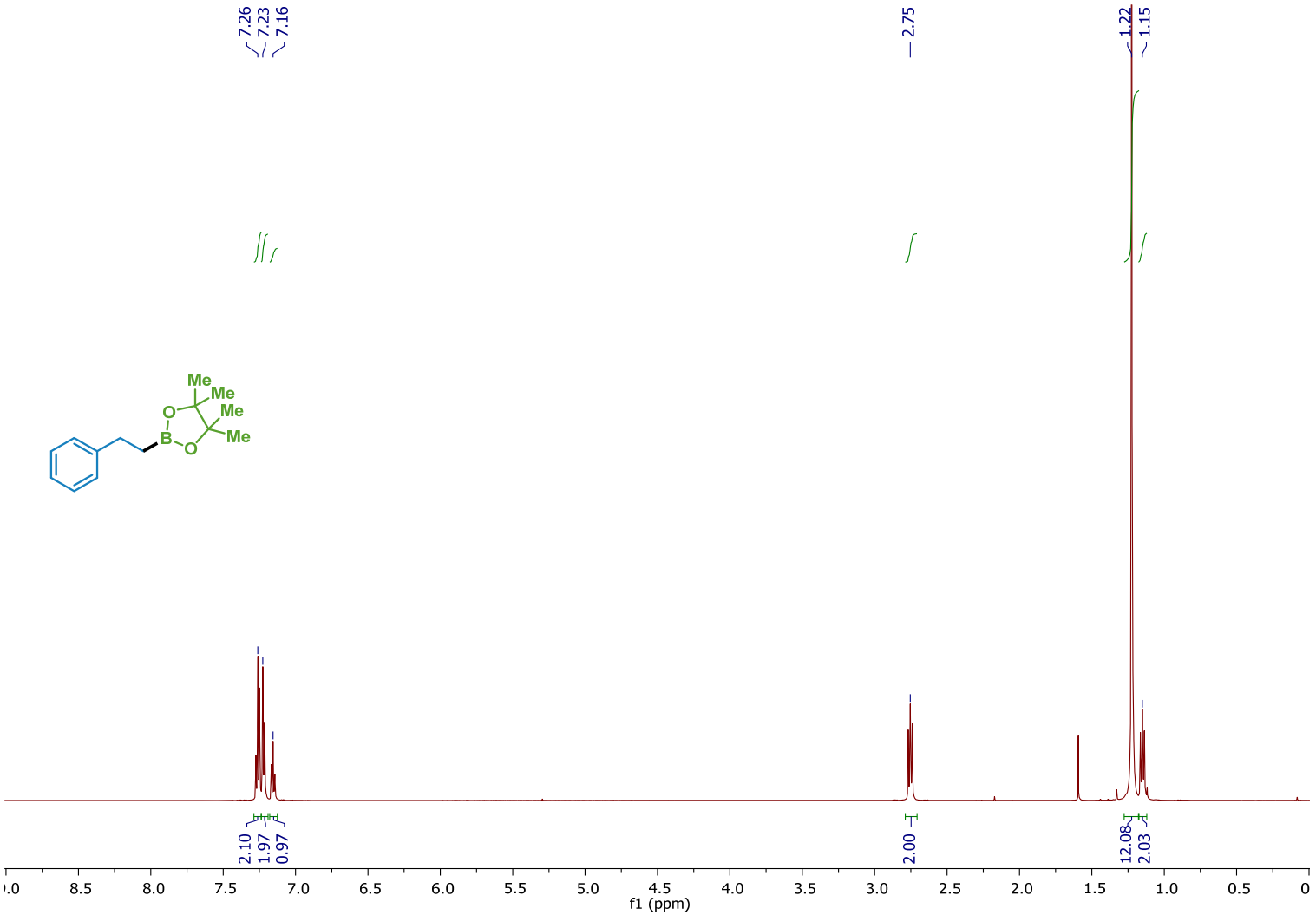
**Compound 11 $^{1}$H NMR**



**Compound 11 $^{13}$C NMR**



**Compound 12 $^{1}$H NMR**



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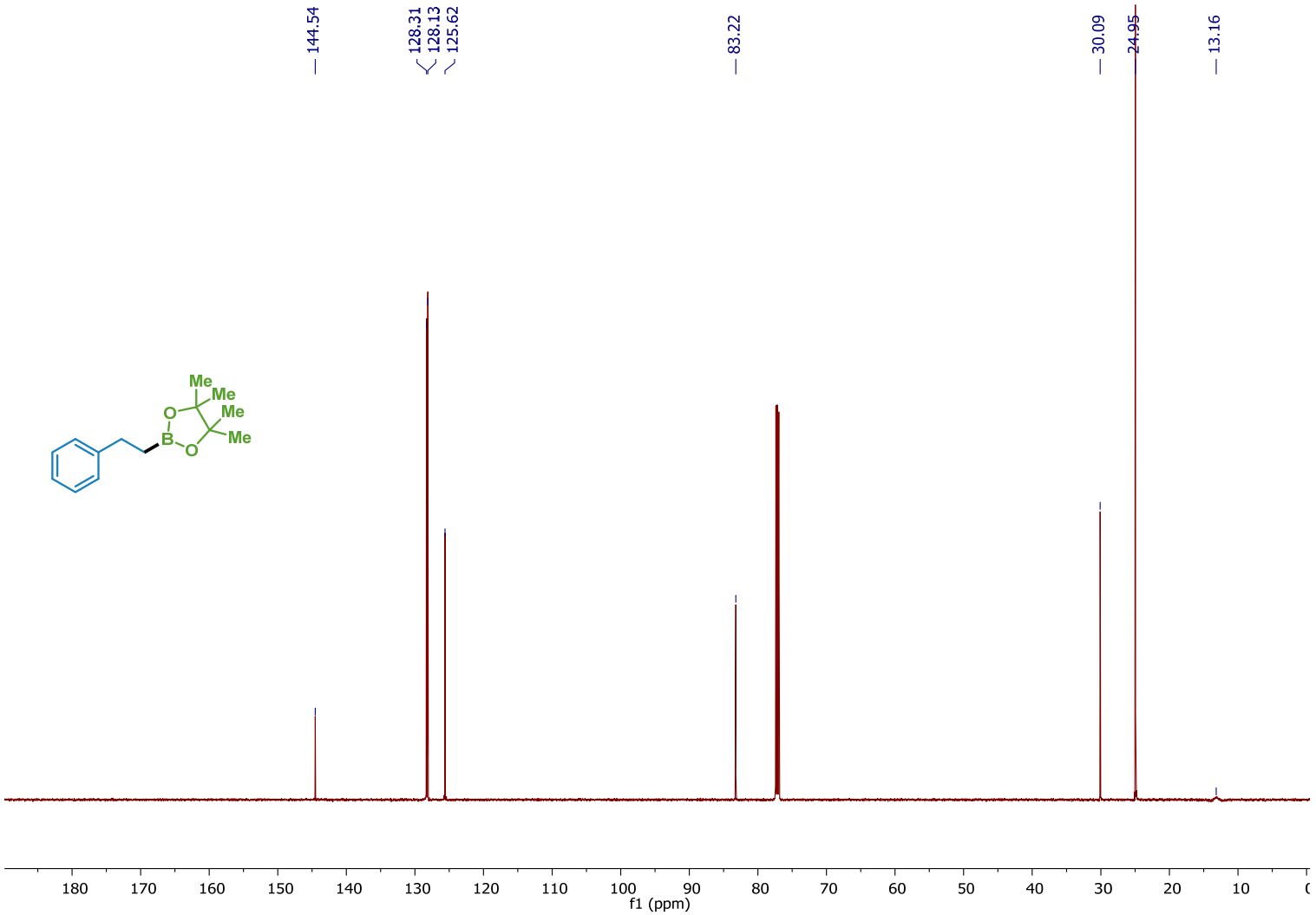

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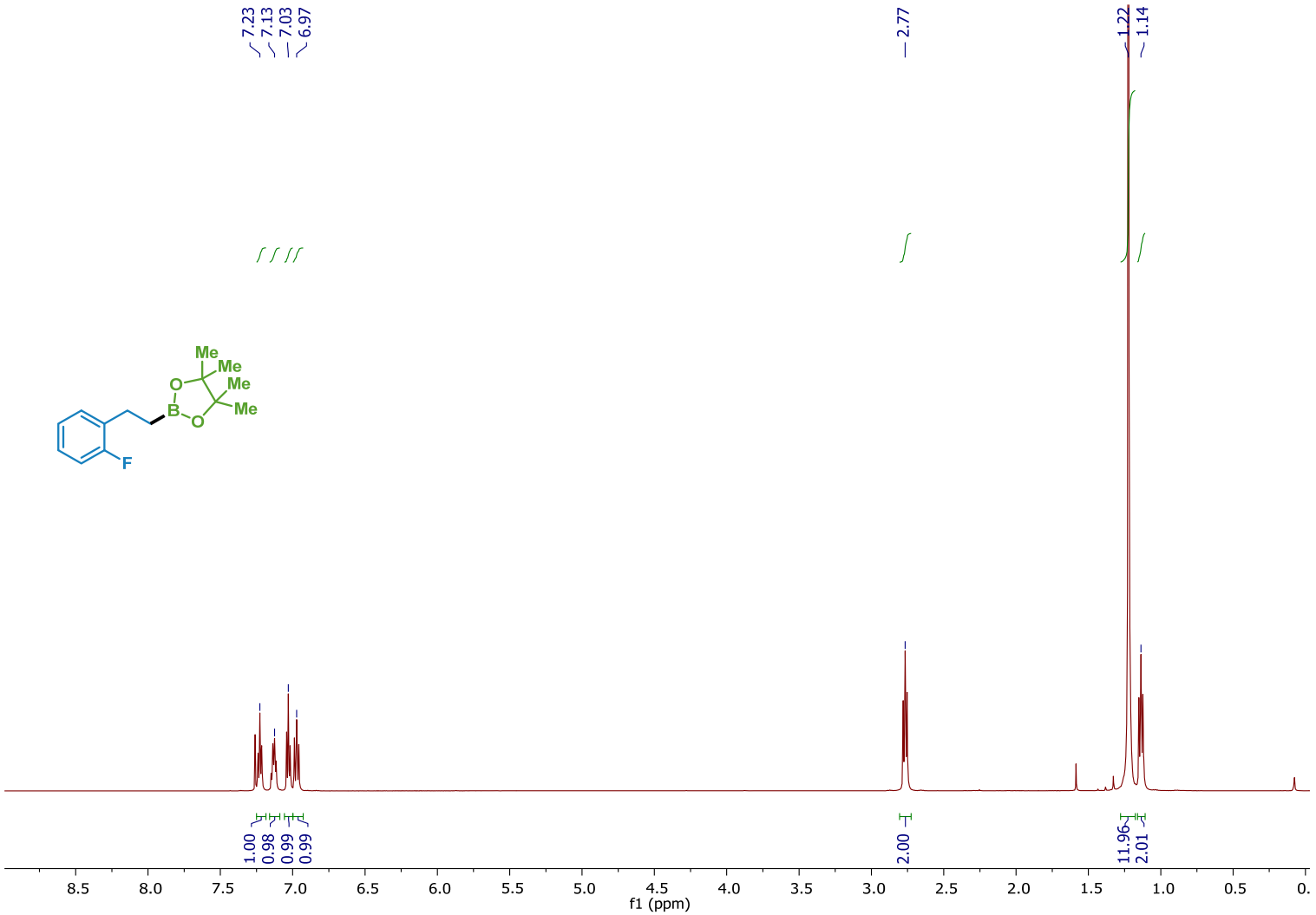
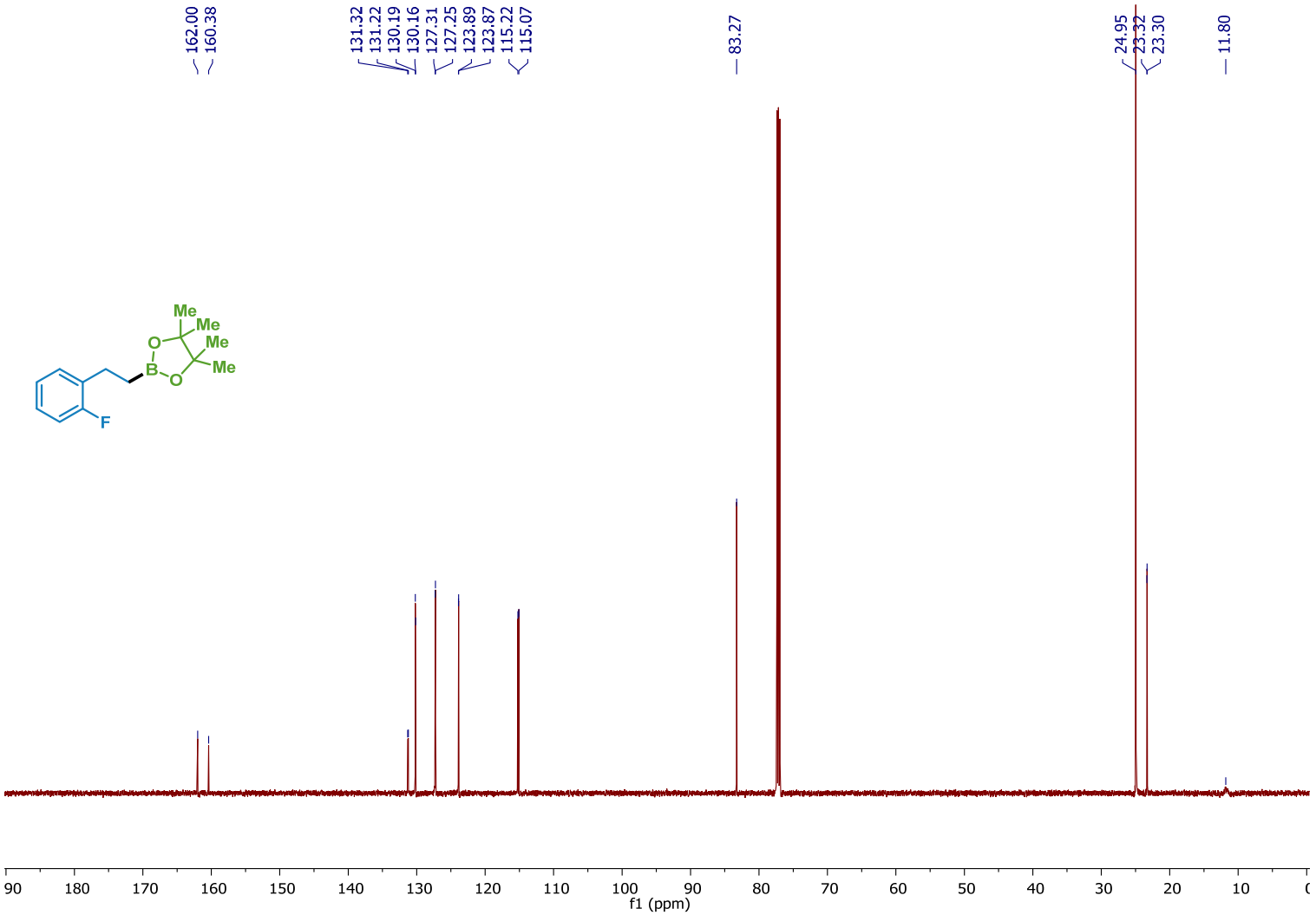
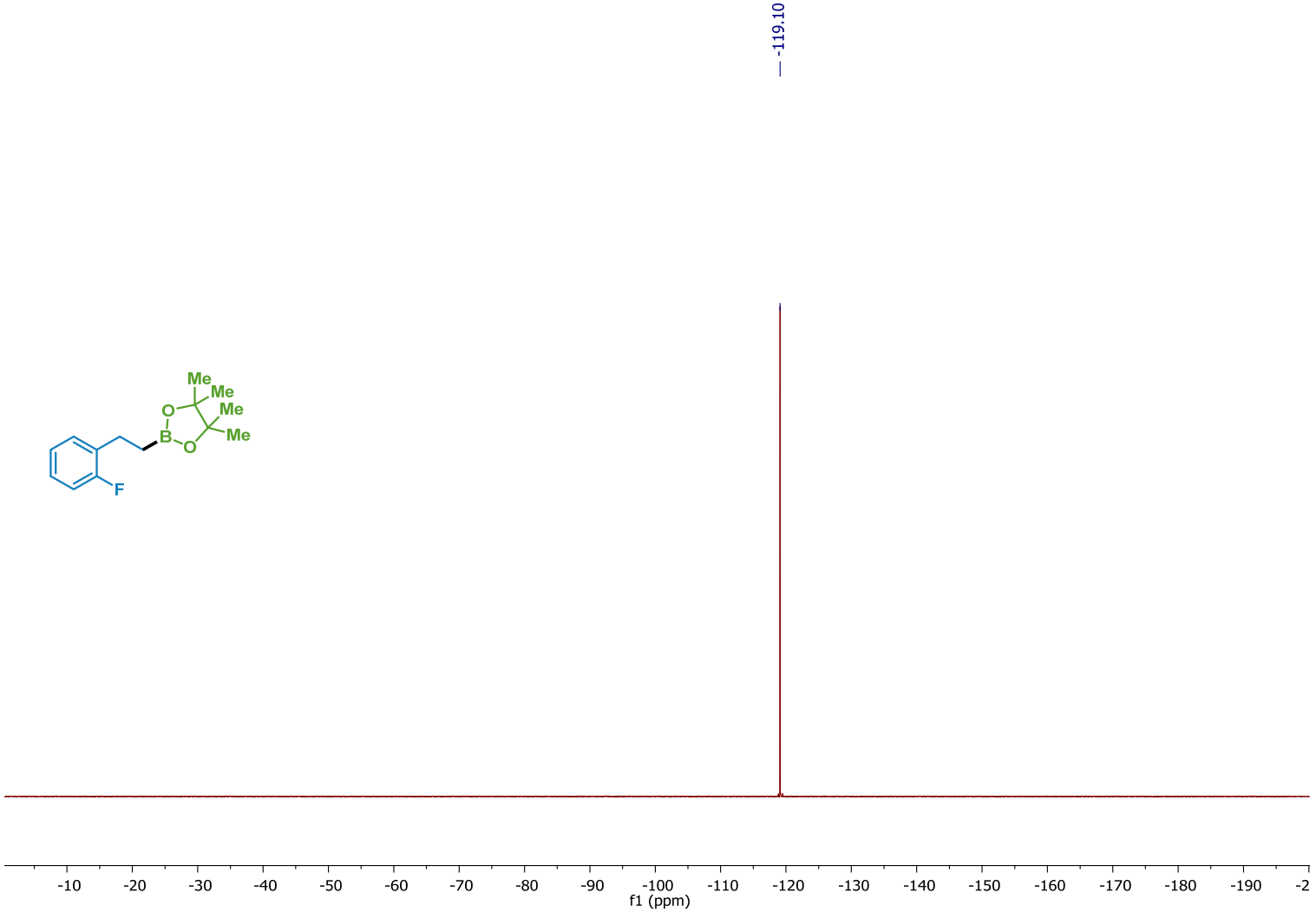


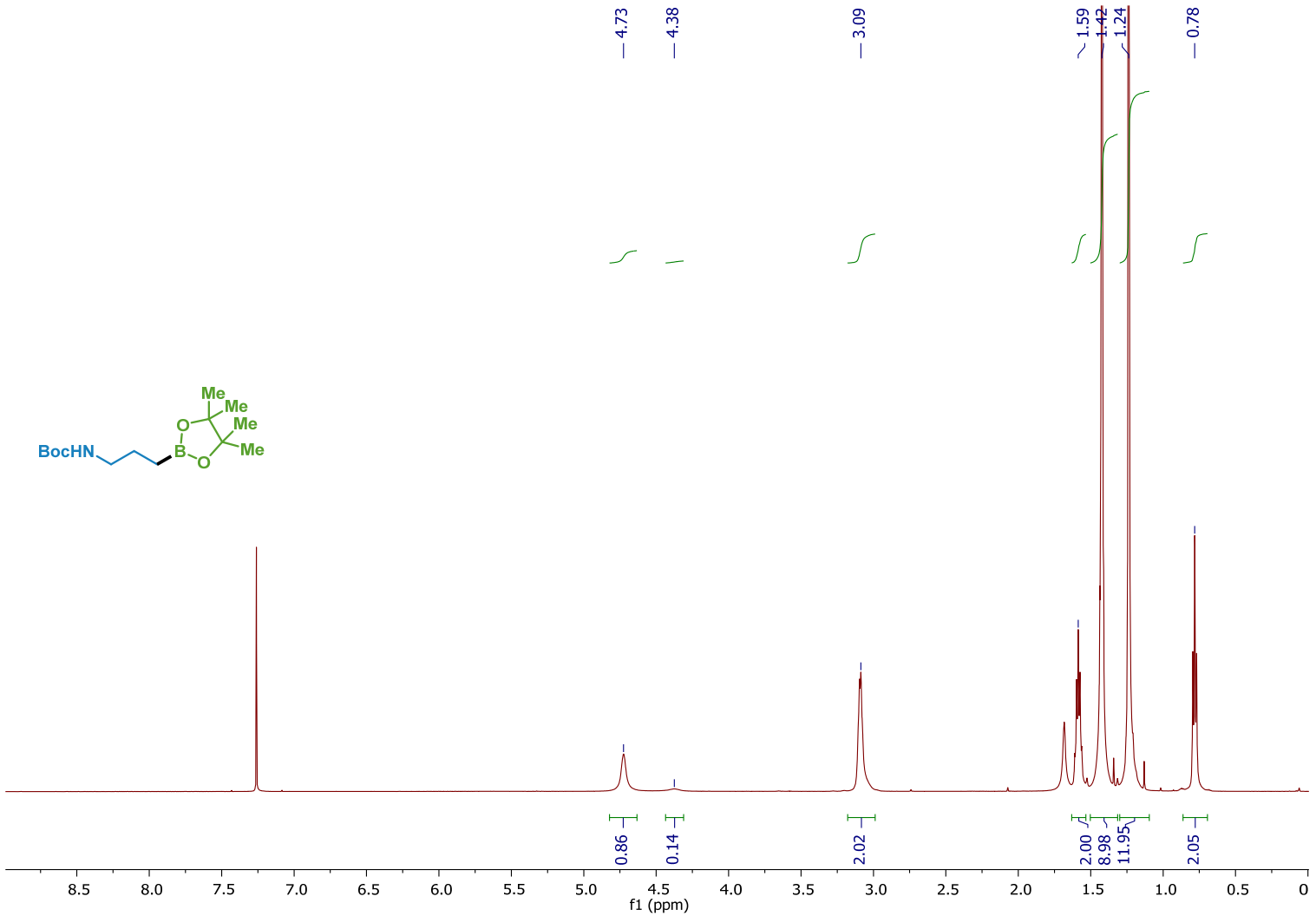
**Compound 13 $^{13}C$ NMR**



**Compound 13 $^{19}$F NMR**



**Compound 14 $^{1}$H NMR**



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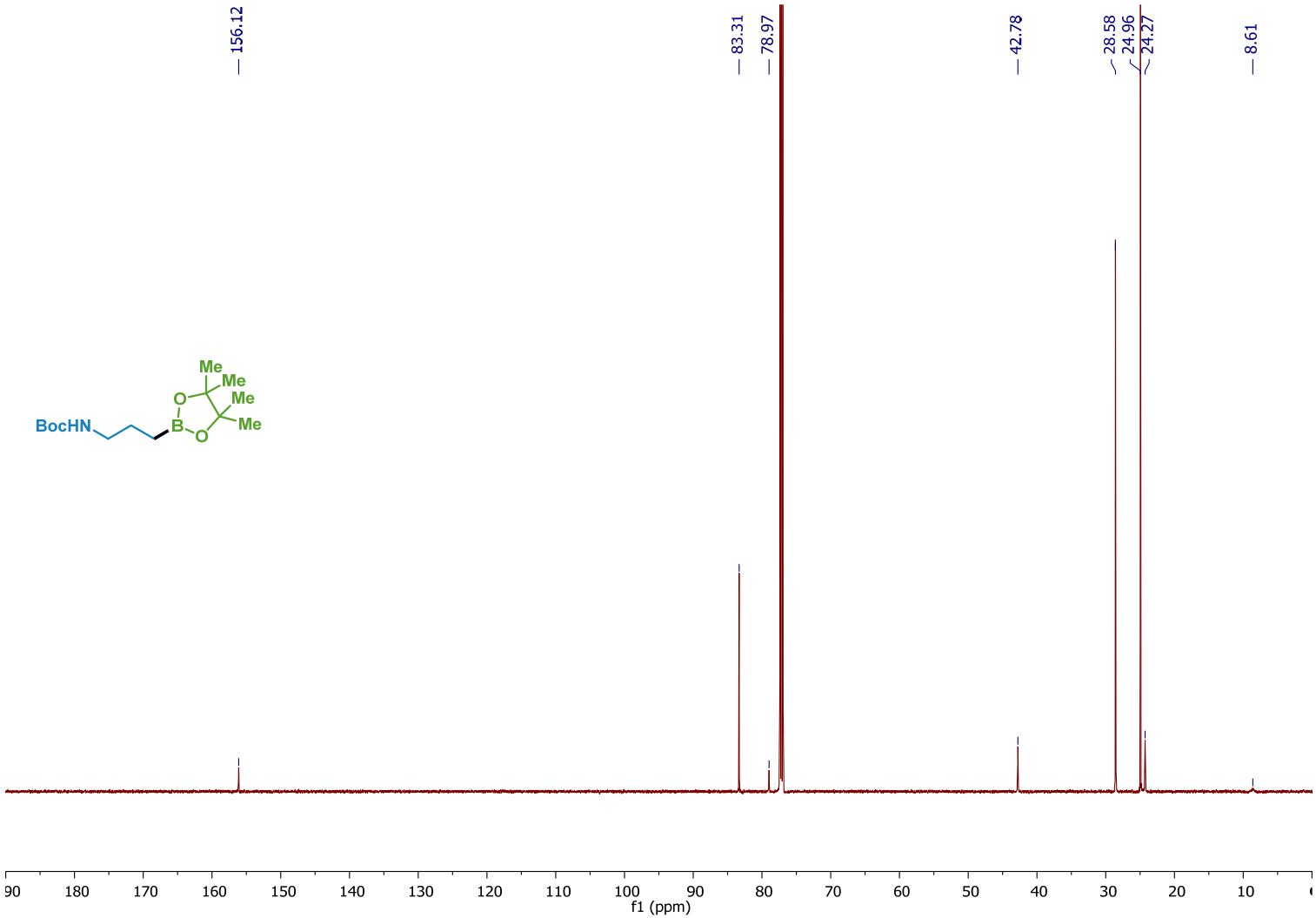

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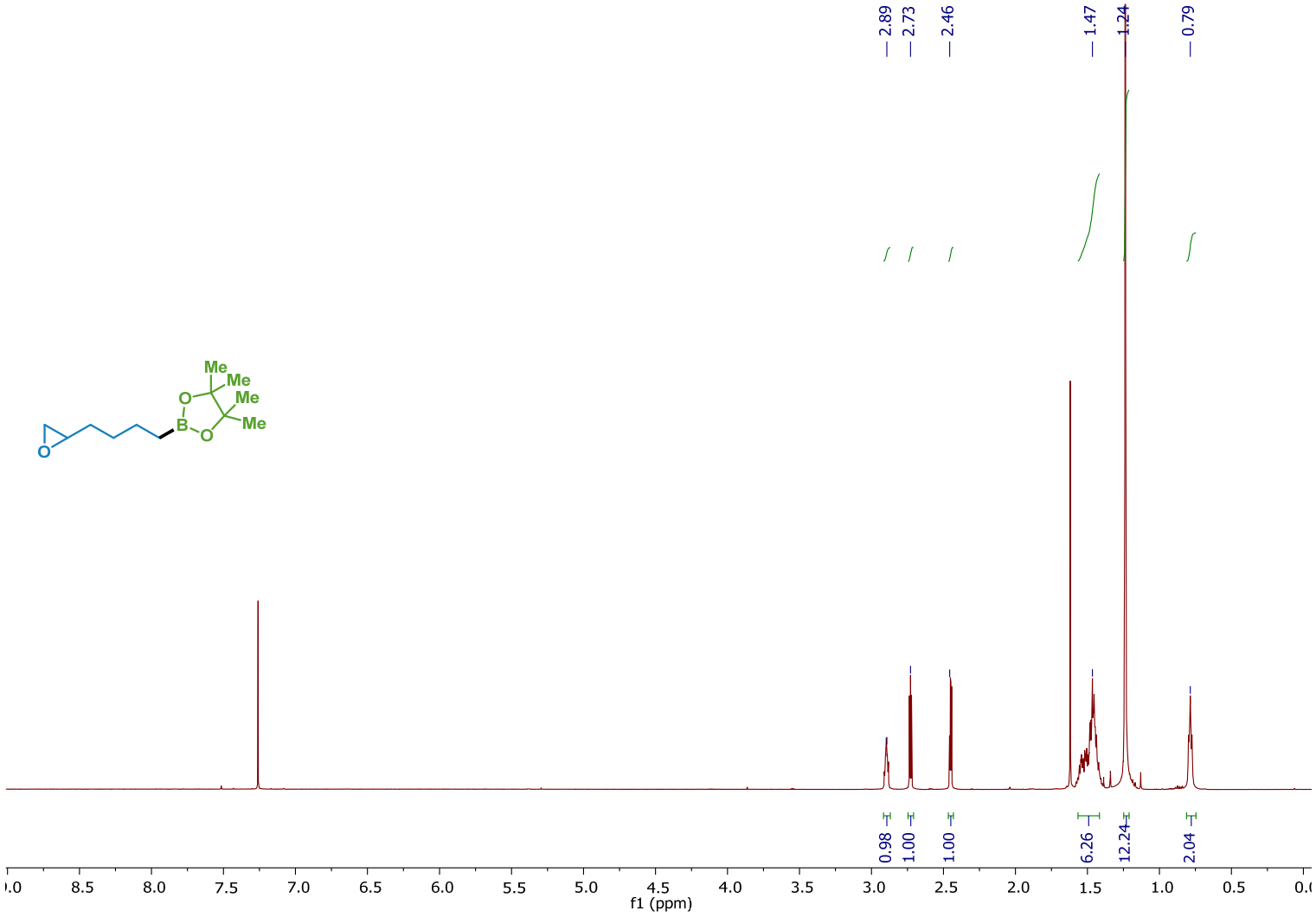
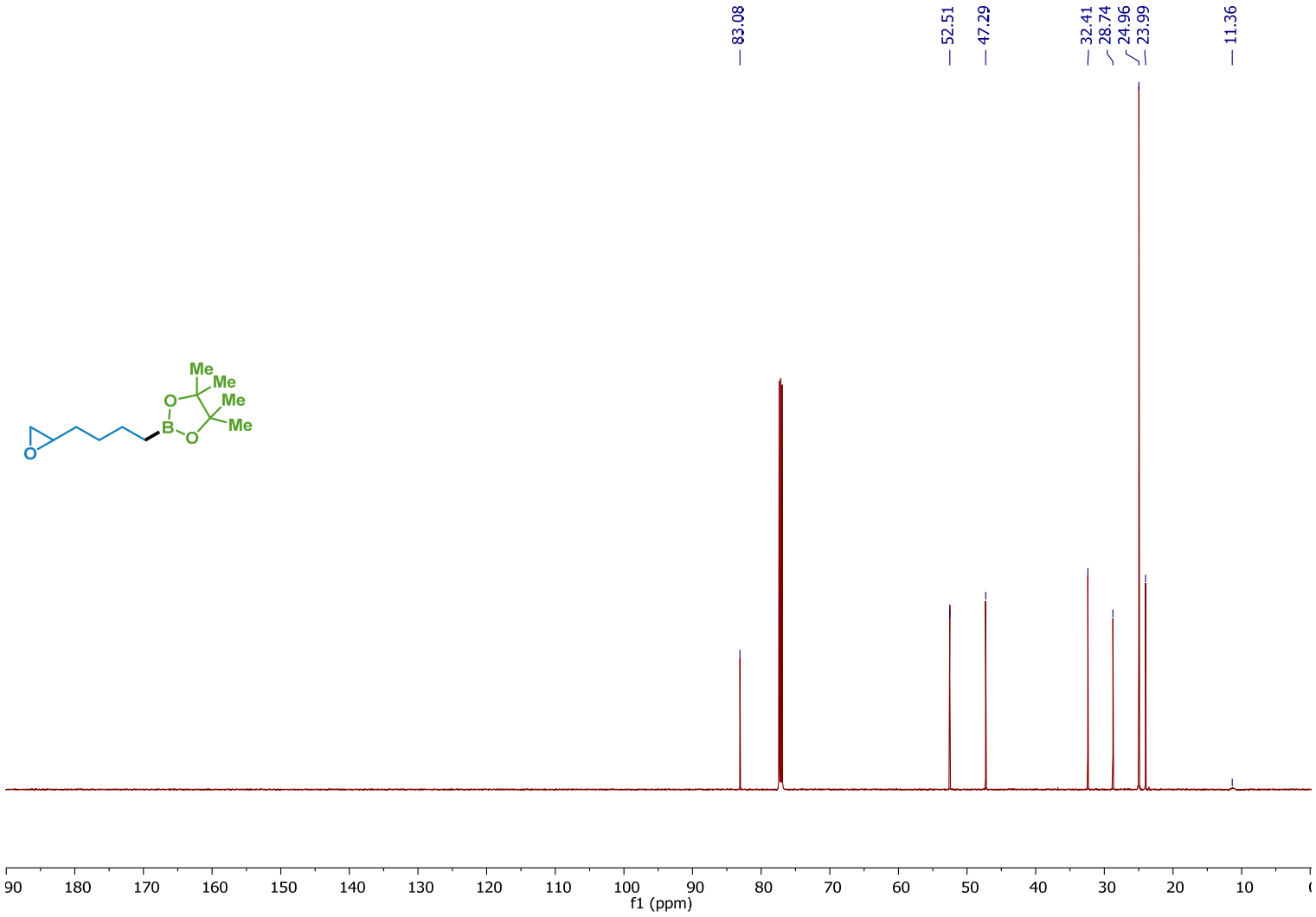


**Compound 15 $^{13}$C NMR**



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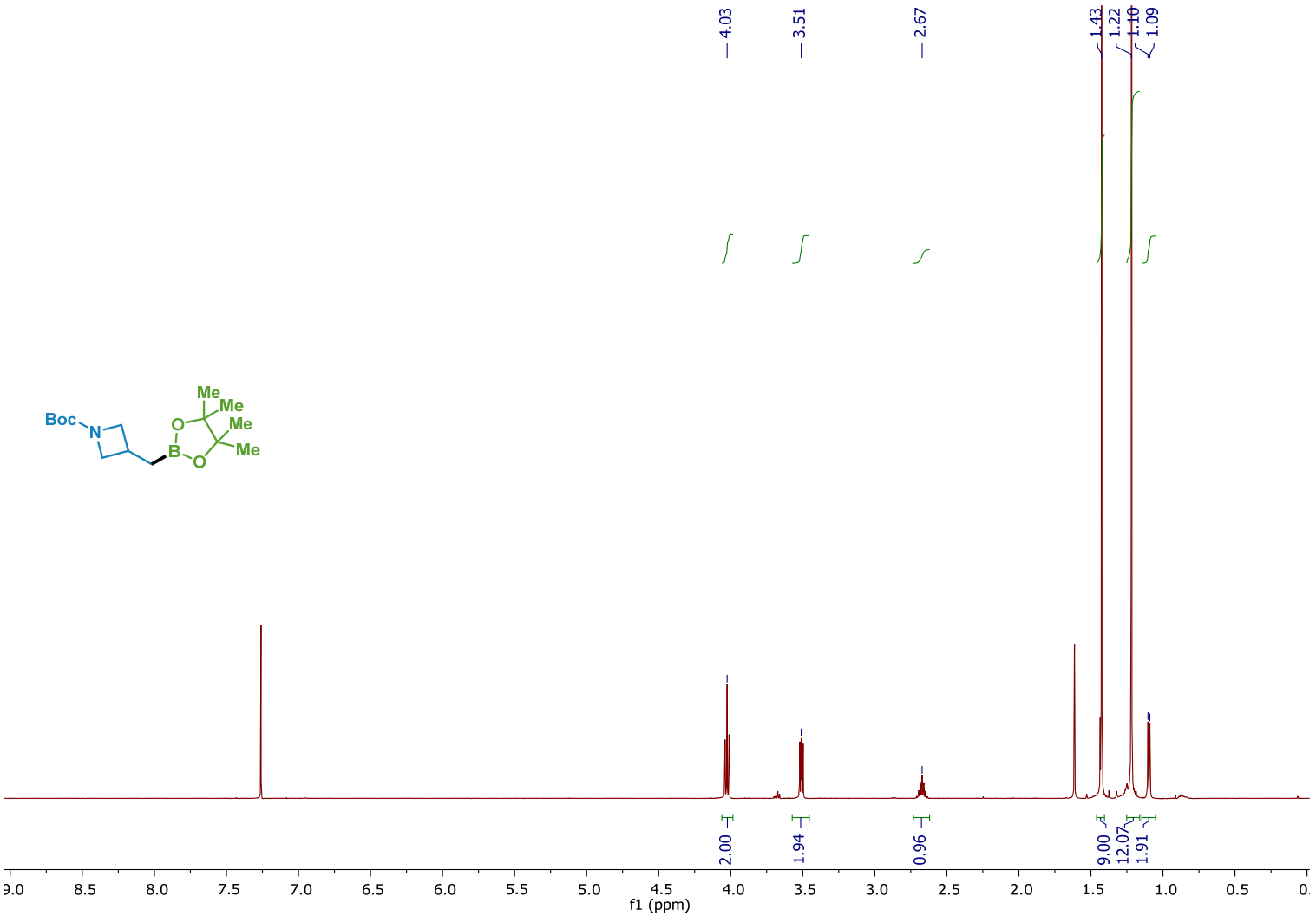

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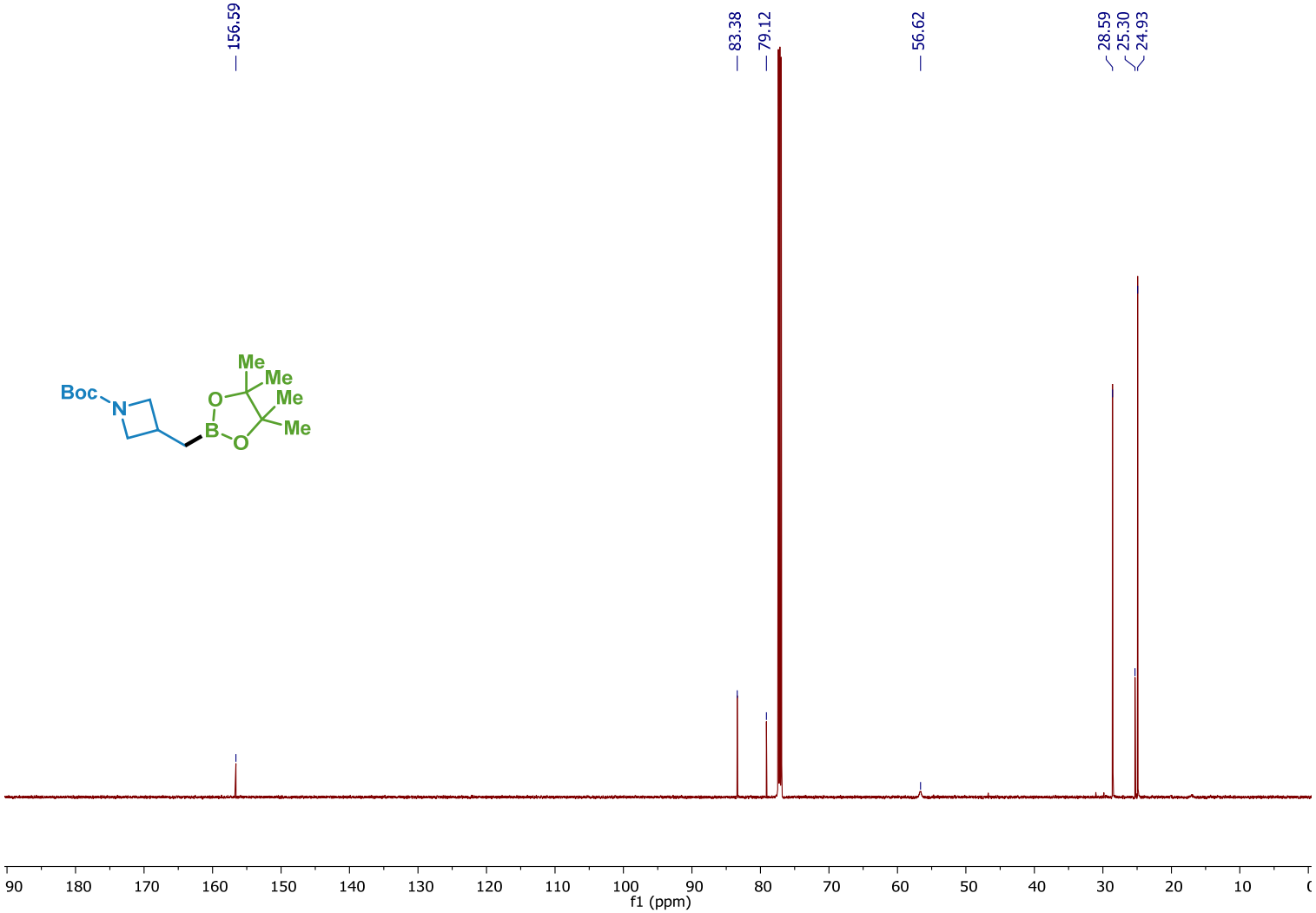
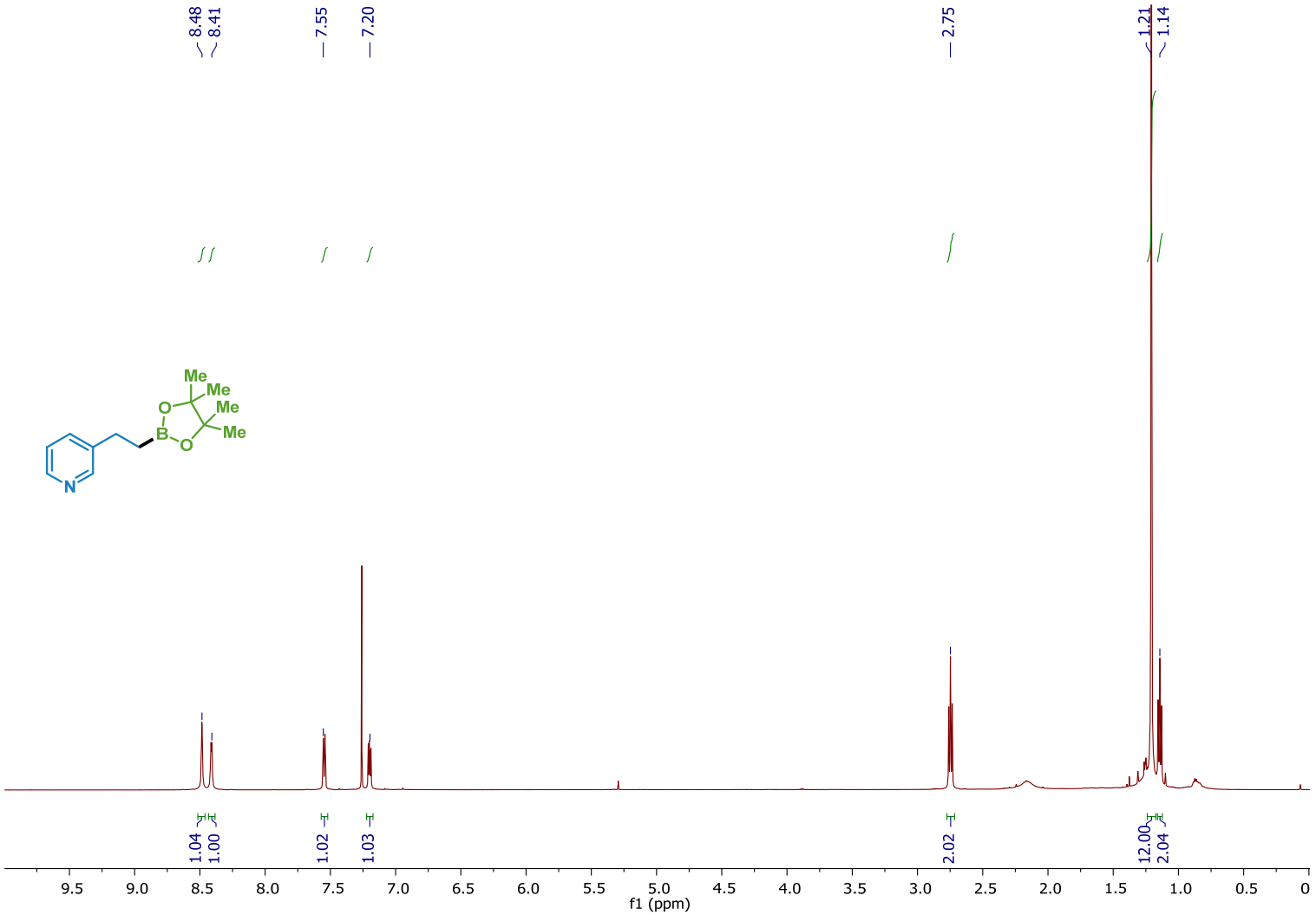
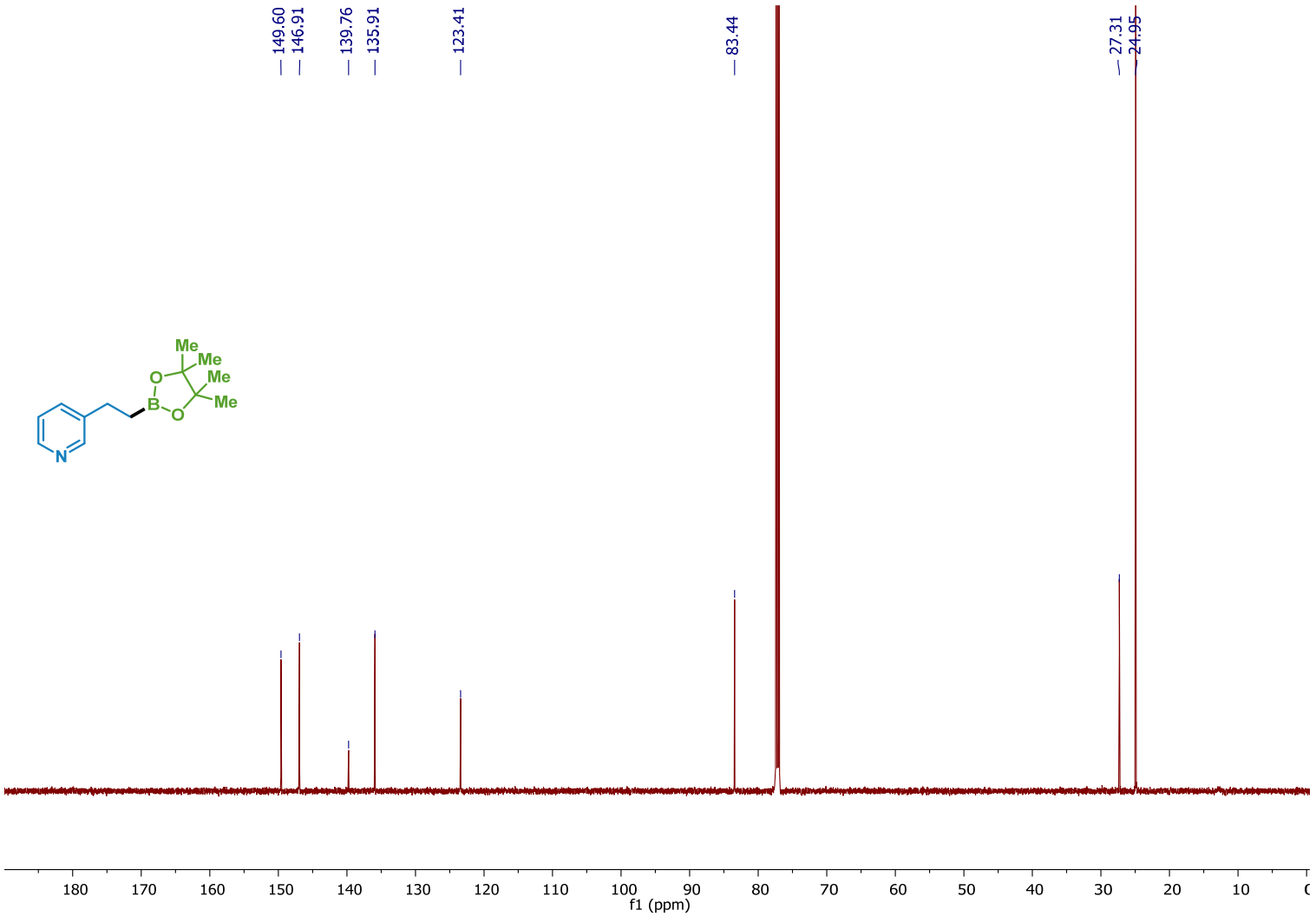


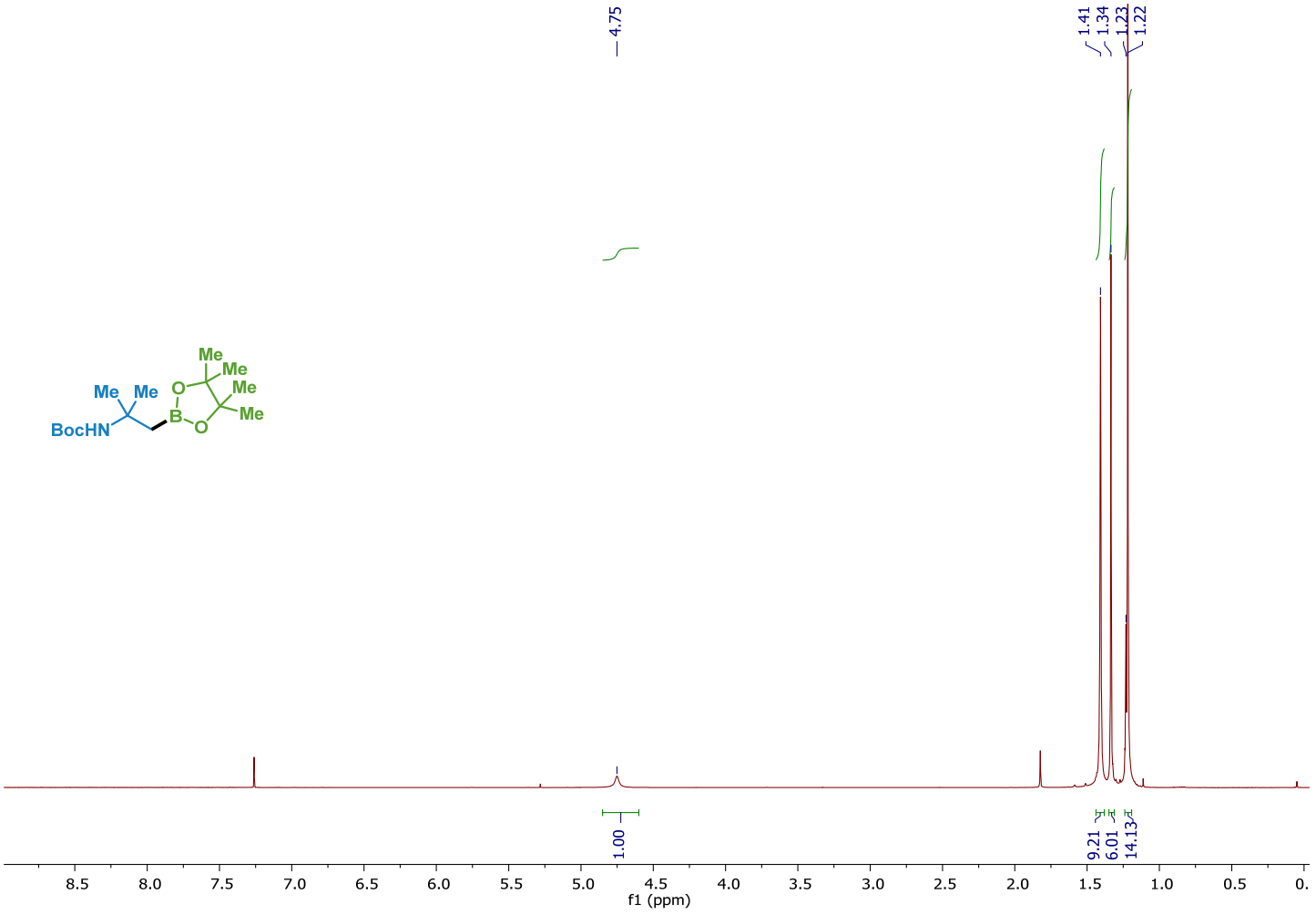
**Compound 17 $^{1}$H NMR**



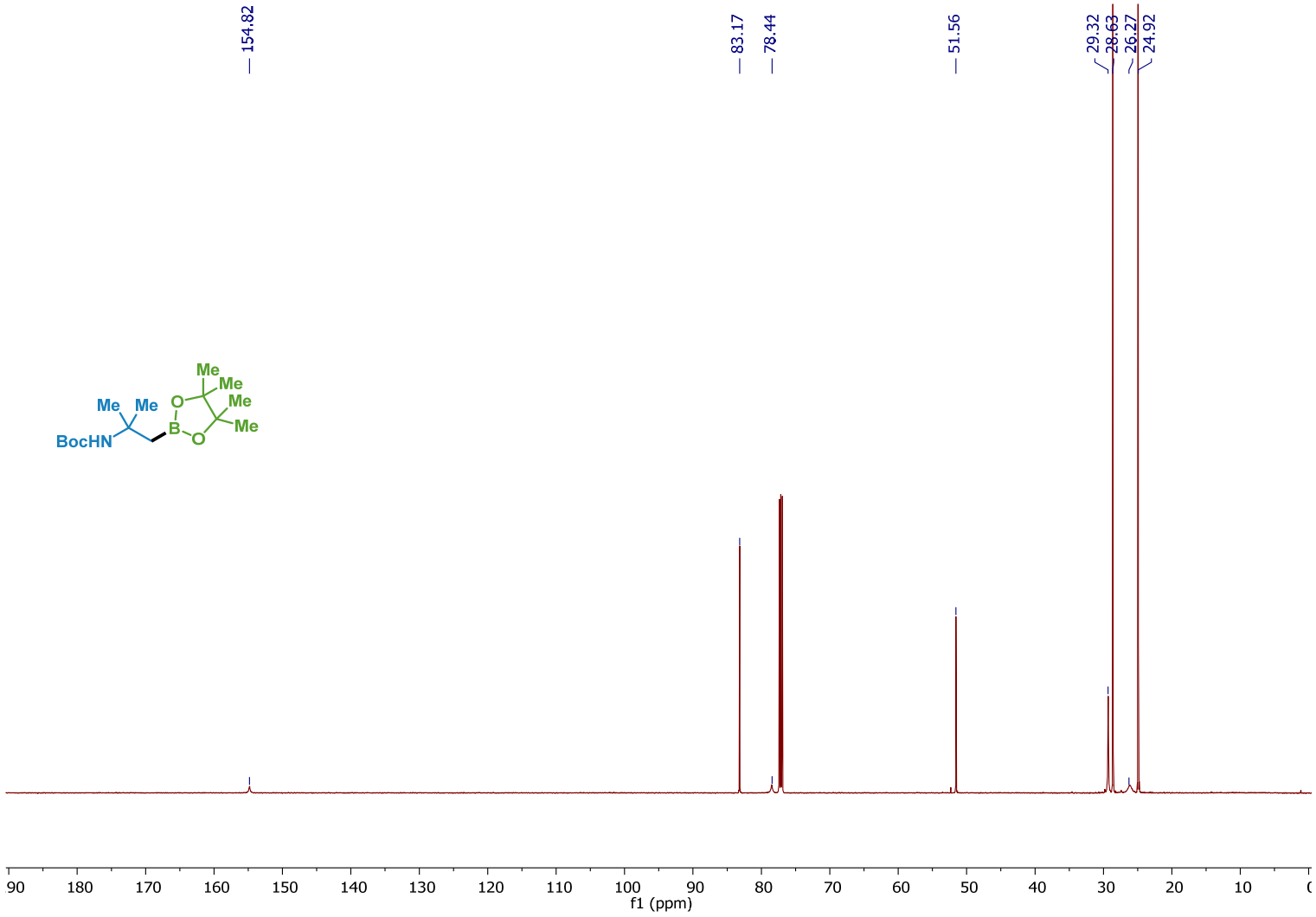
**Compound 17 $^{13}$C NMR**



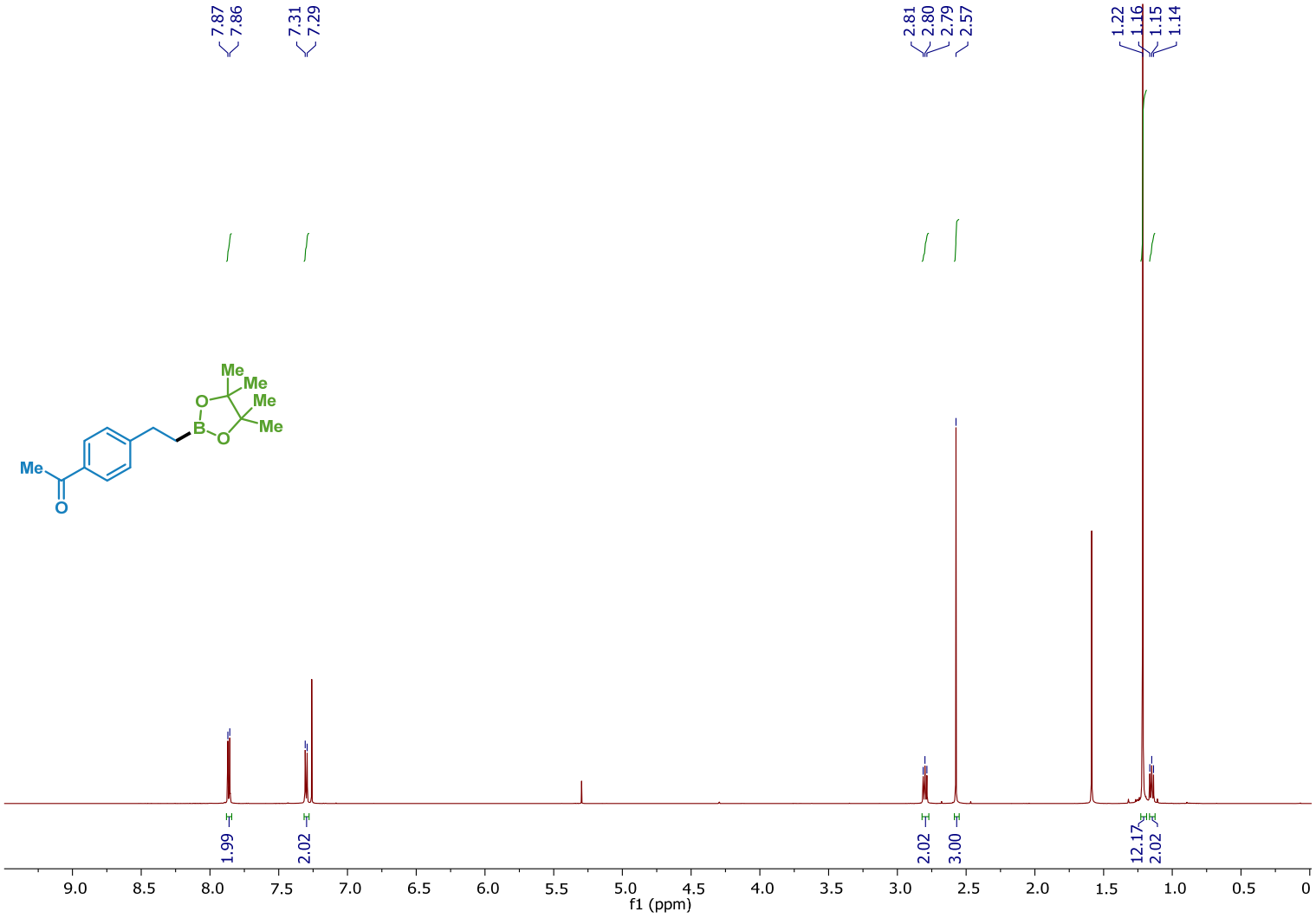
**Compound 18 $^{1}$H NMR**



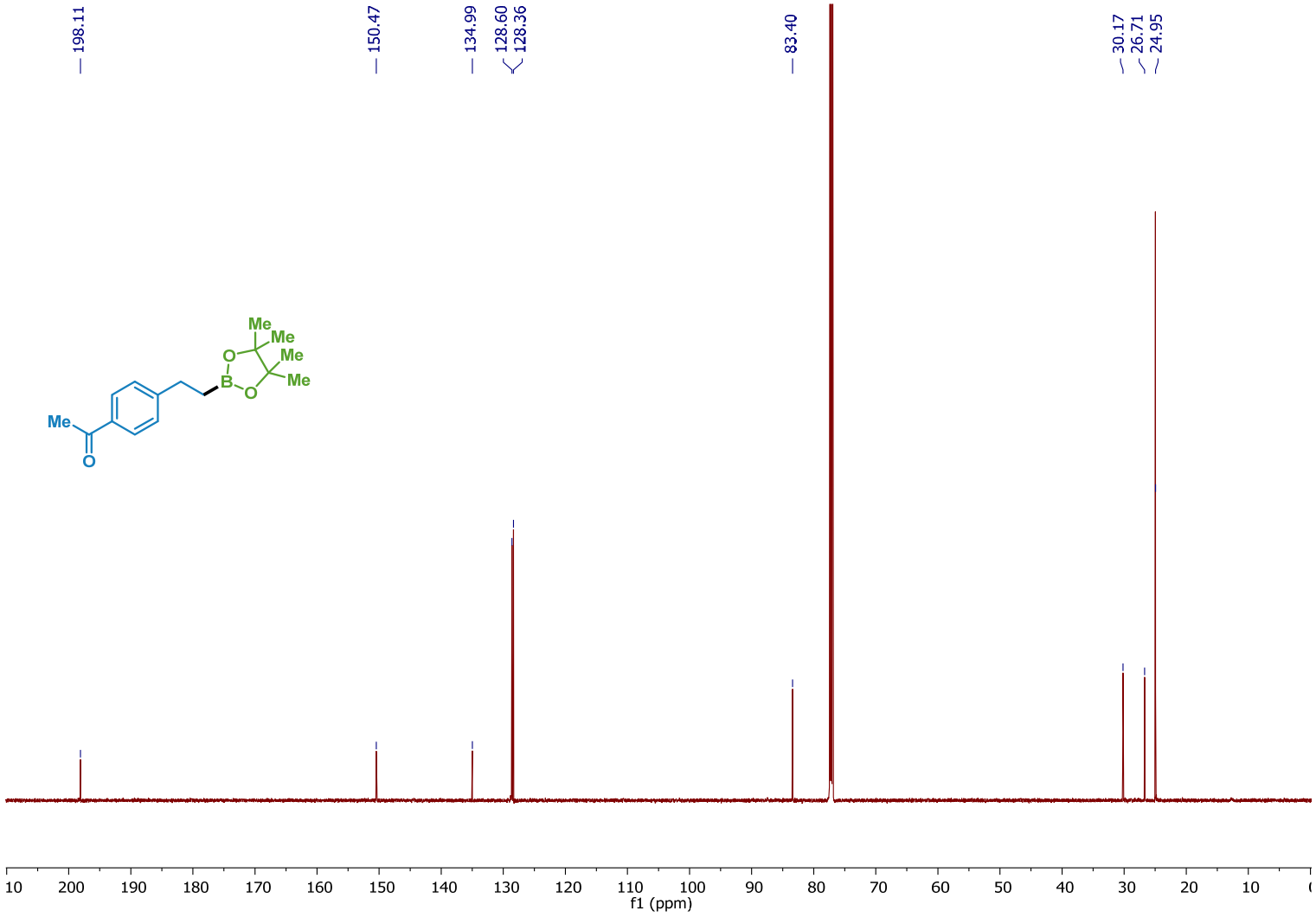
**Compound 18 $^{13}$C NMR**



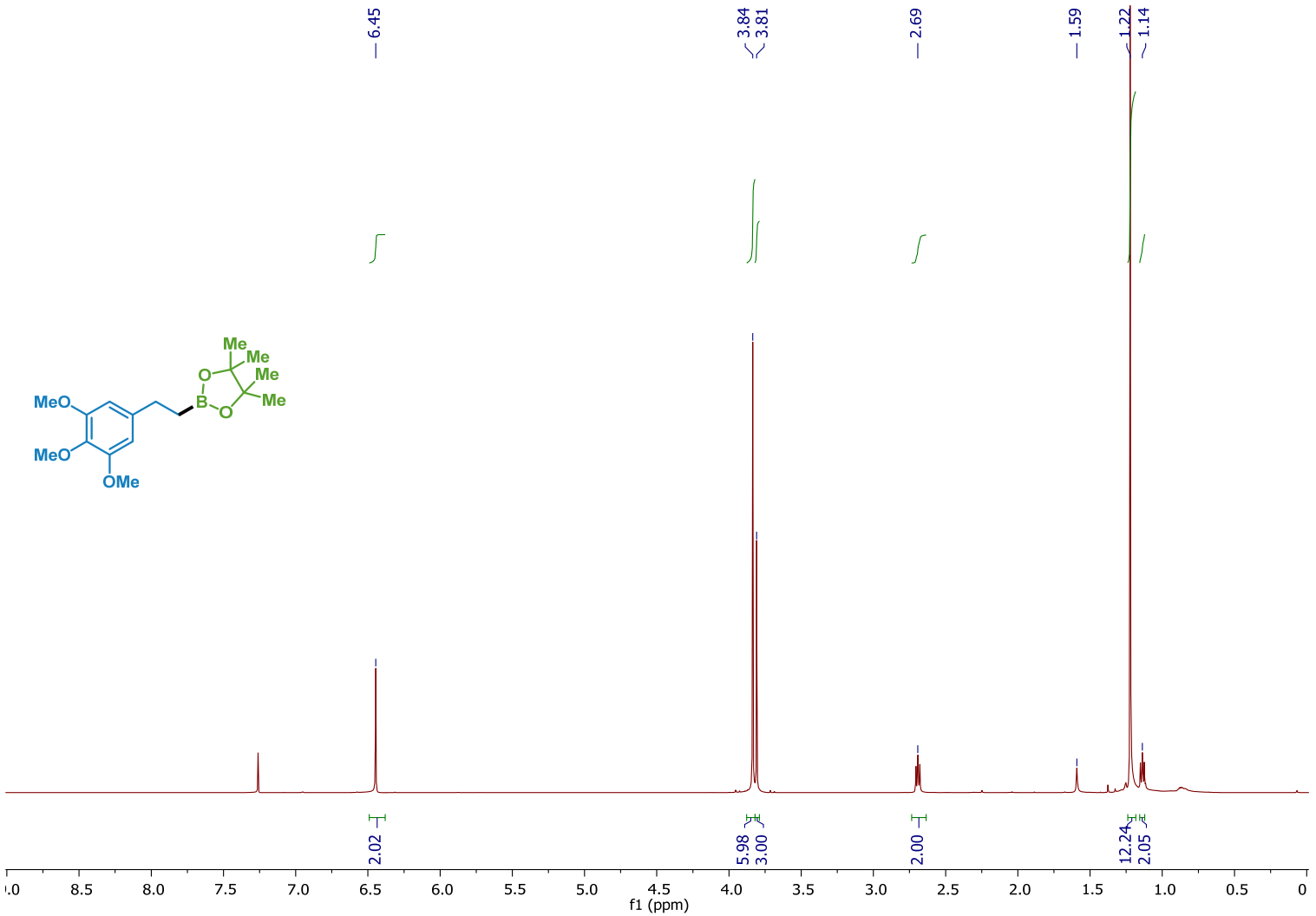
**Compound 19 $^{1}$H NMR**



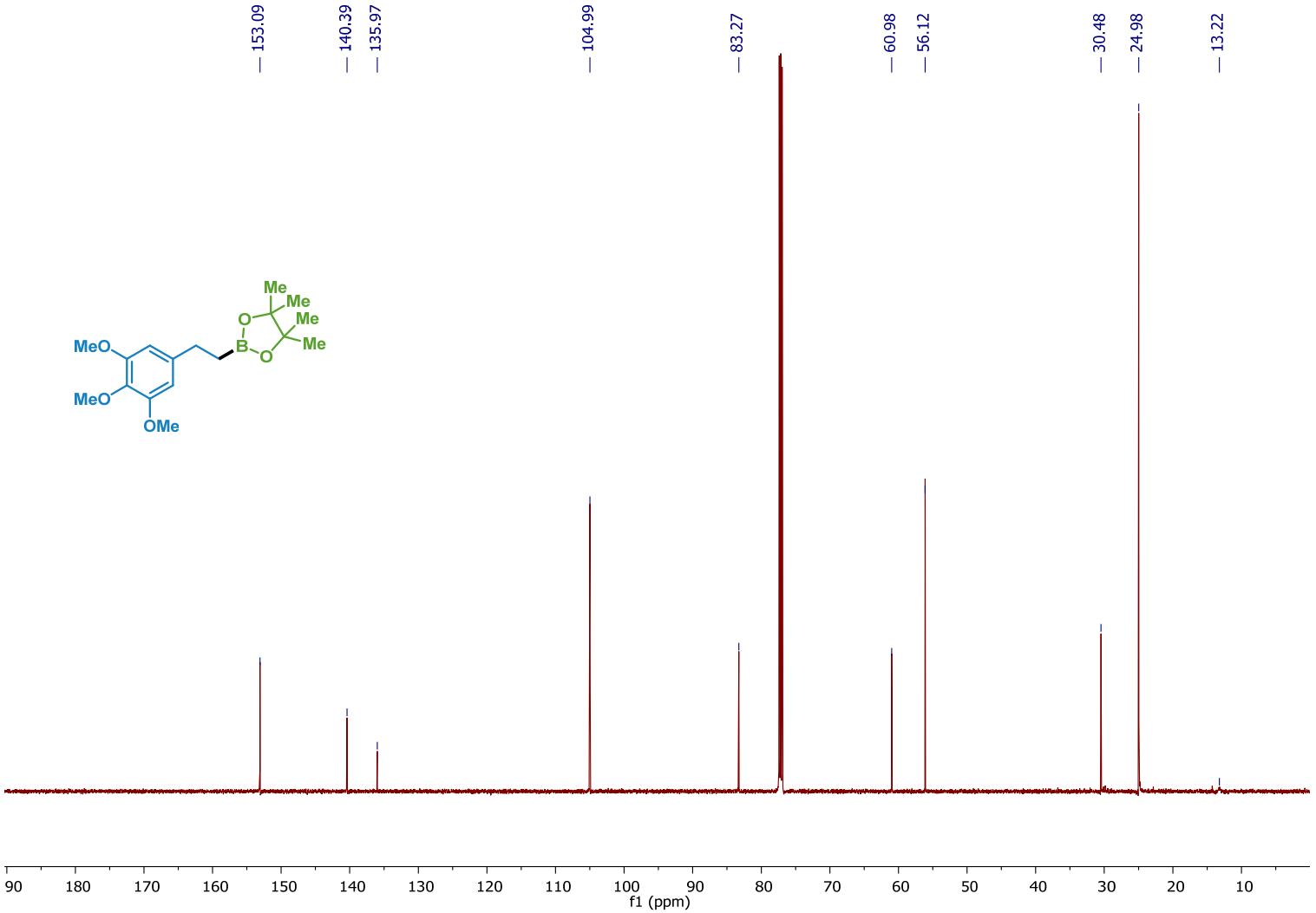
**Compound 19 $^{13}$C NMR**



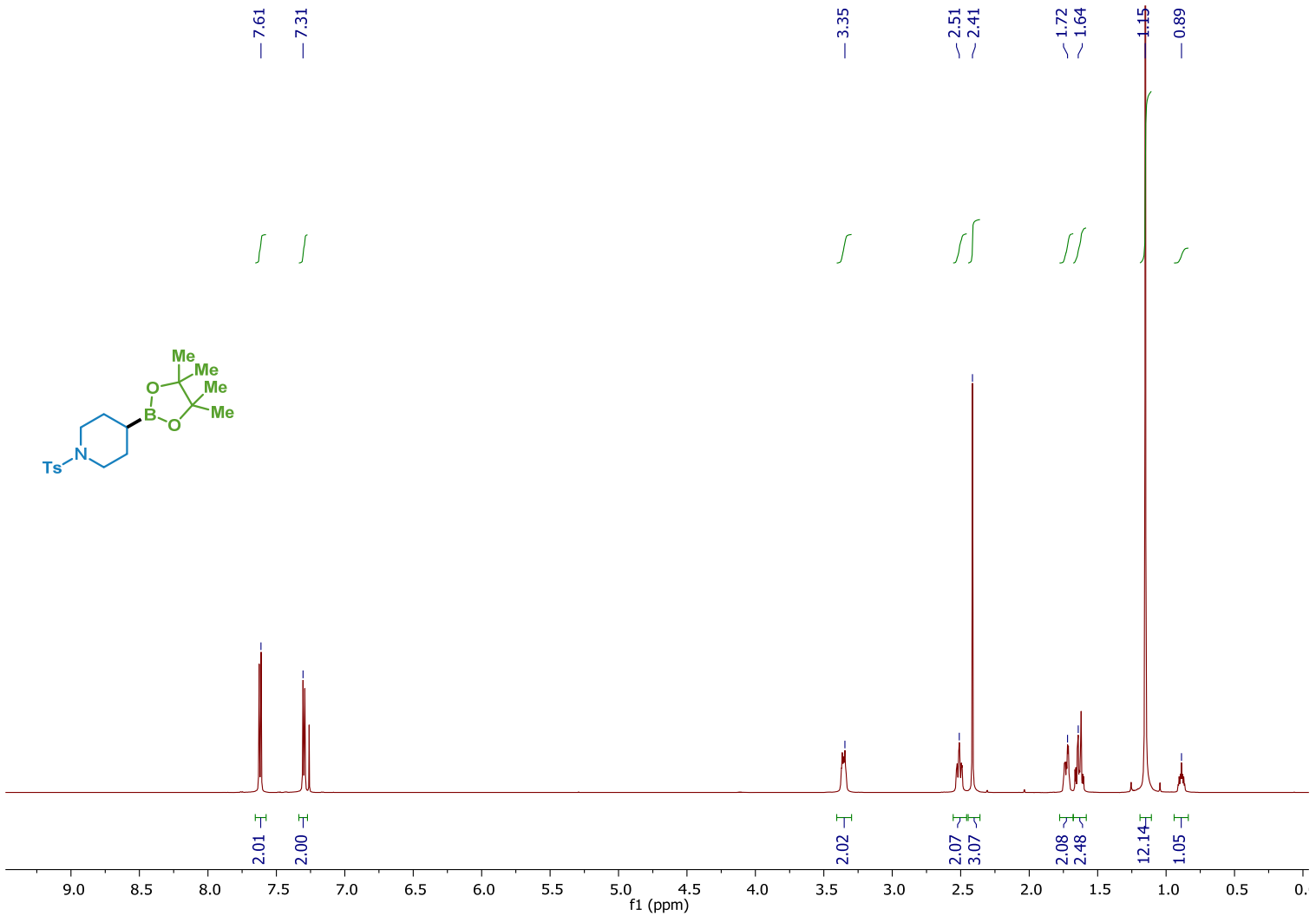
**Compound 20 $^{1}$H NMR**



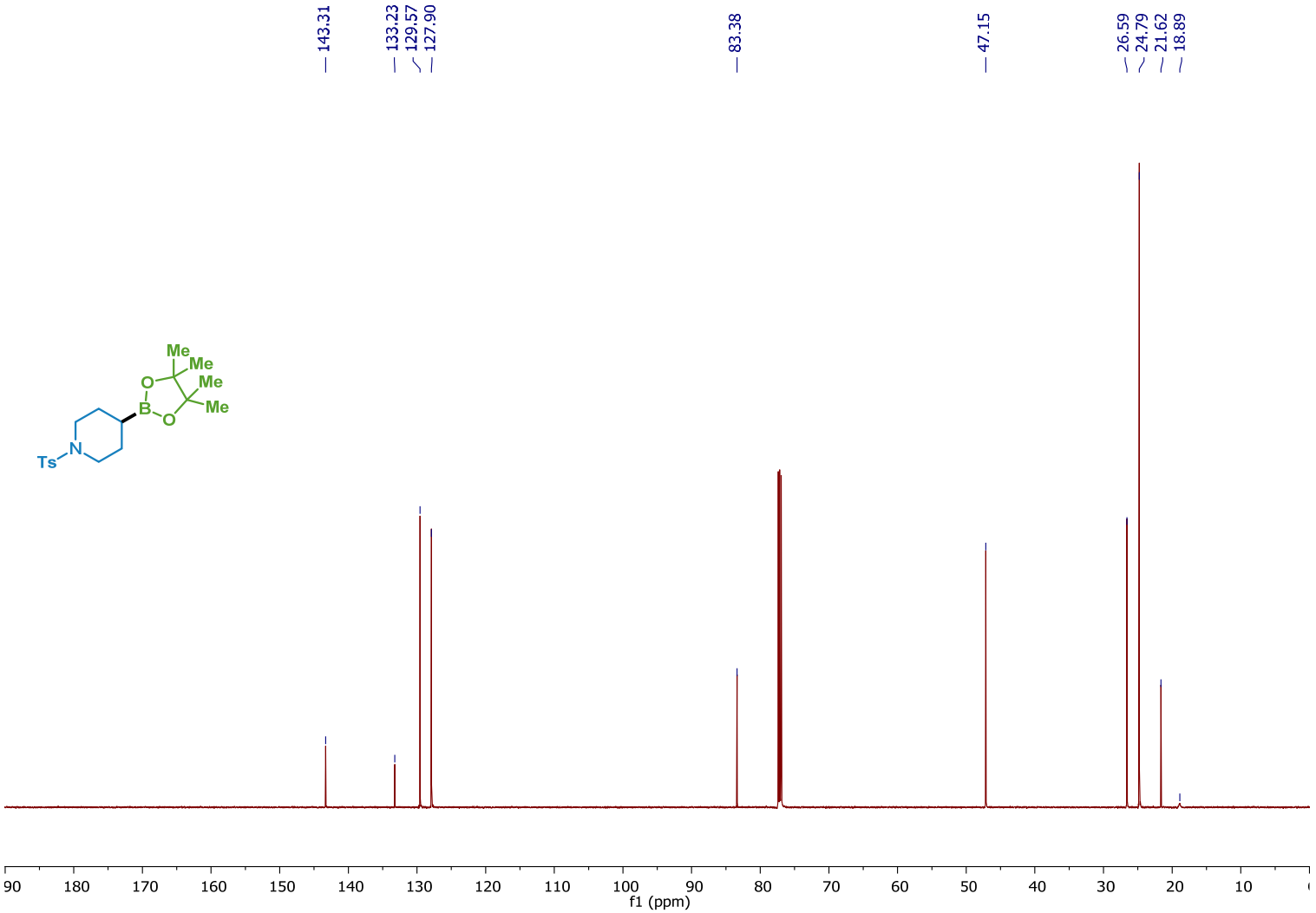
**Compound 20 $^{13}$C NMR**



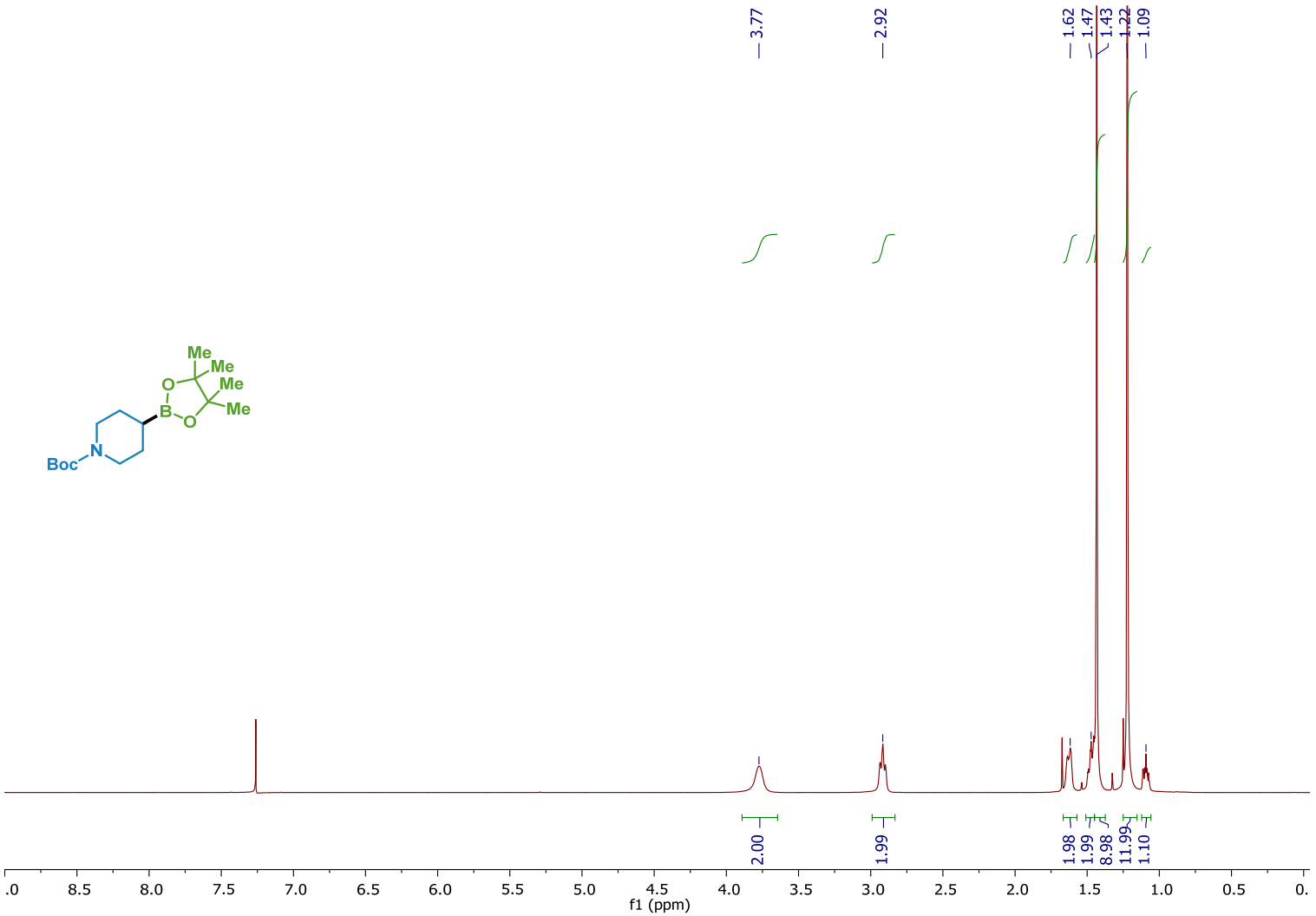
**Compound 21 $^{1}$H NMR**



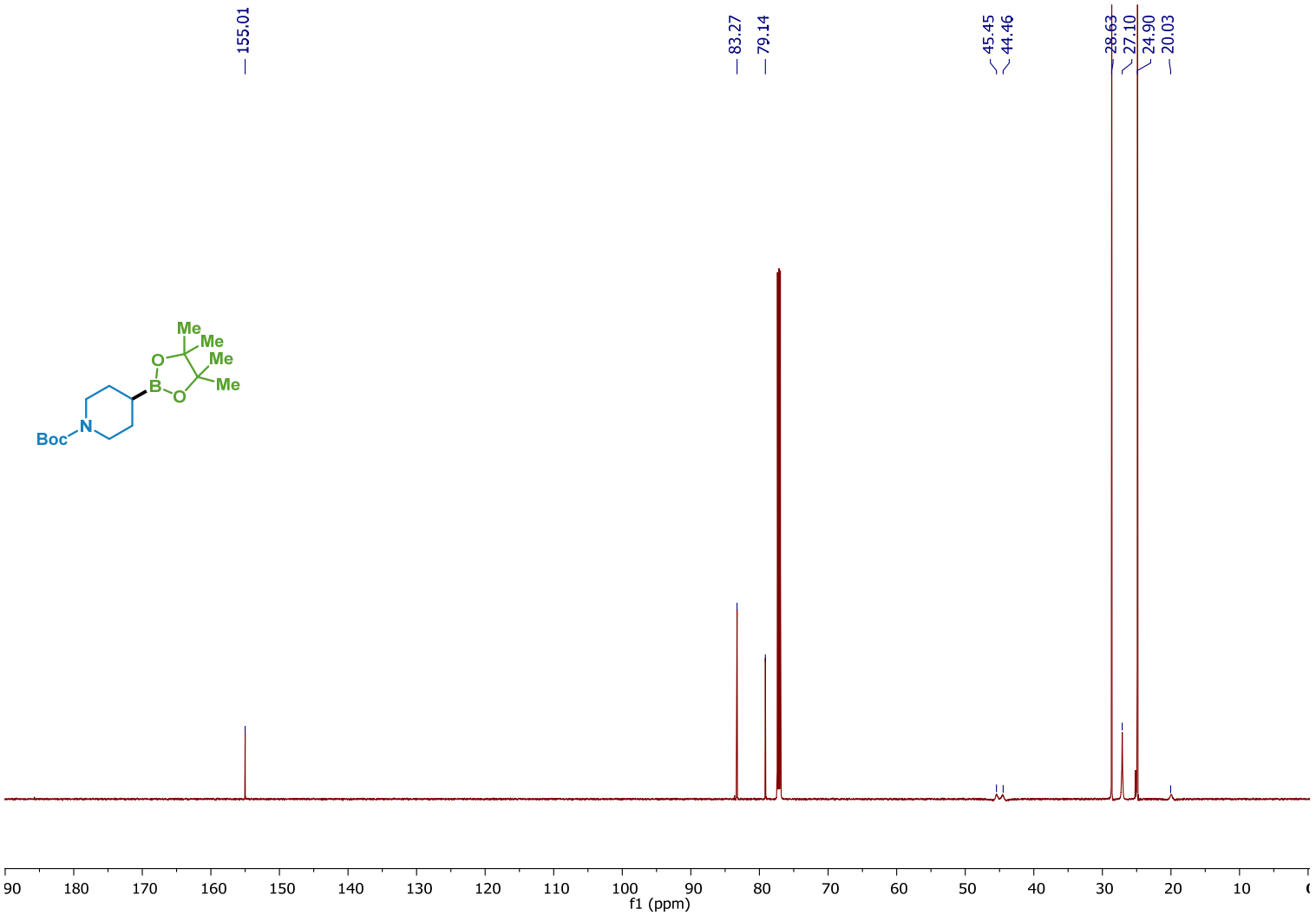
**Compound 21 $^{13}$C NMR**



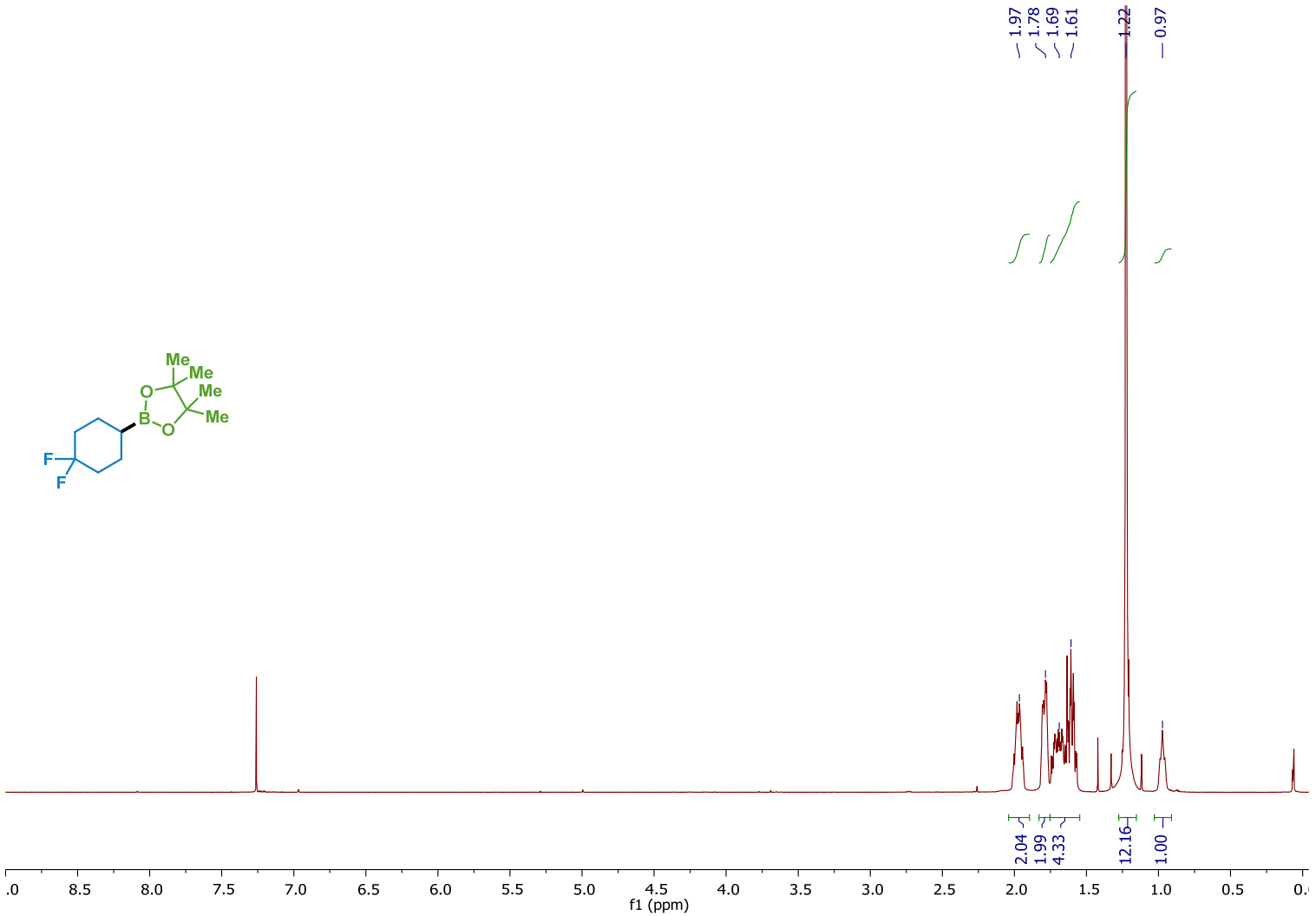
**Compound 22 $^{1}$H NMR**



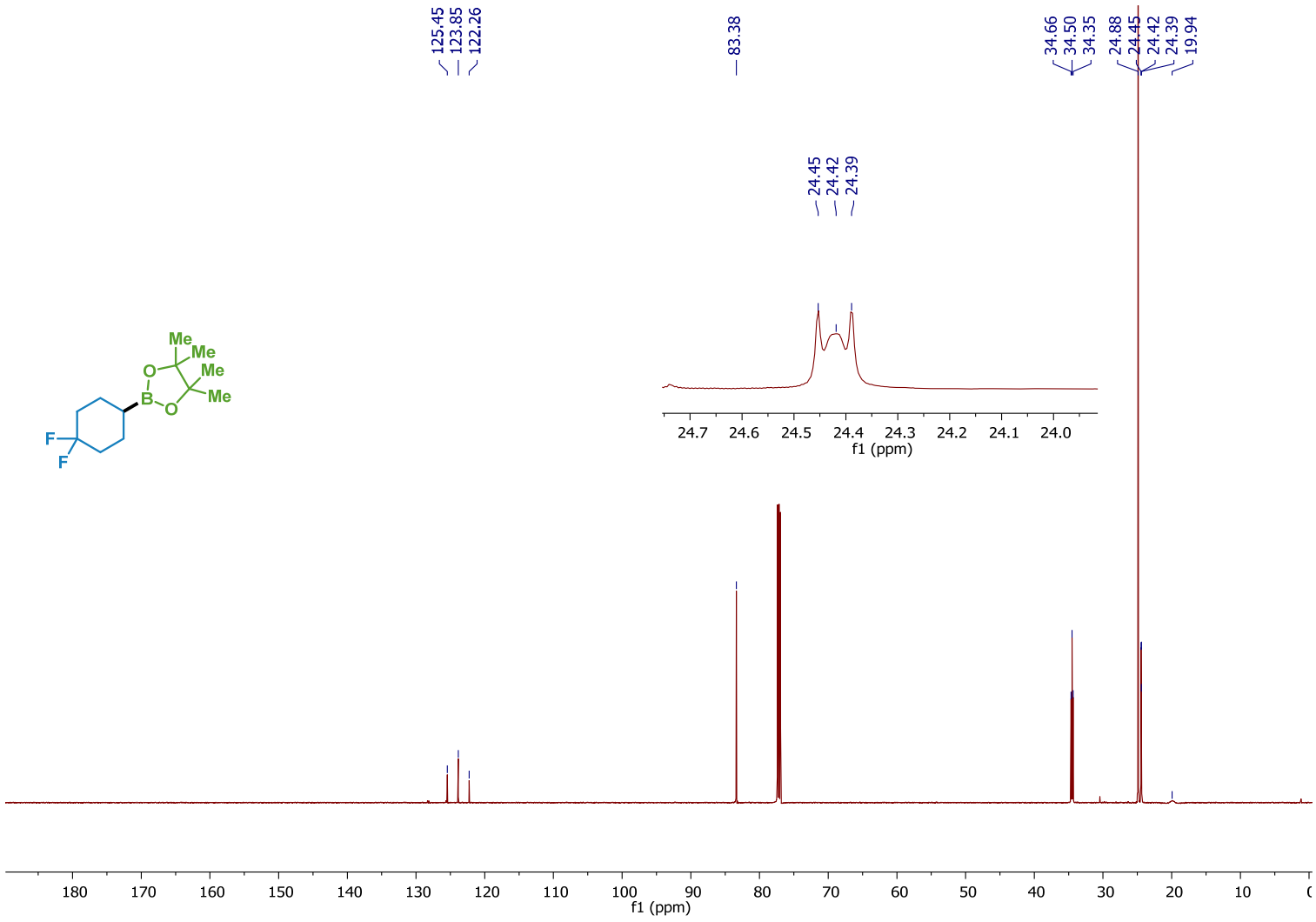
**Compound 22 $^{13}$C NMR**



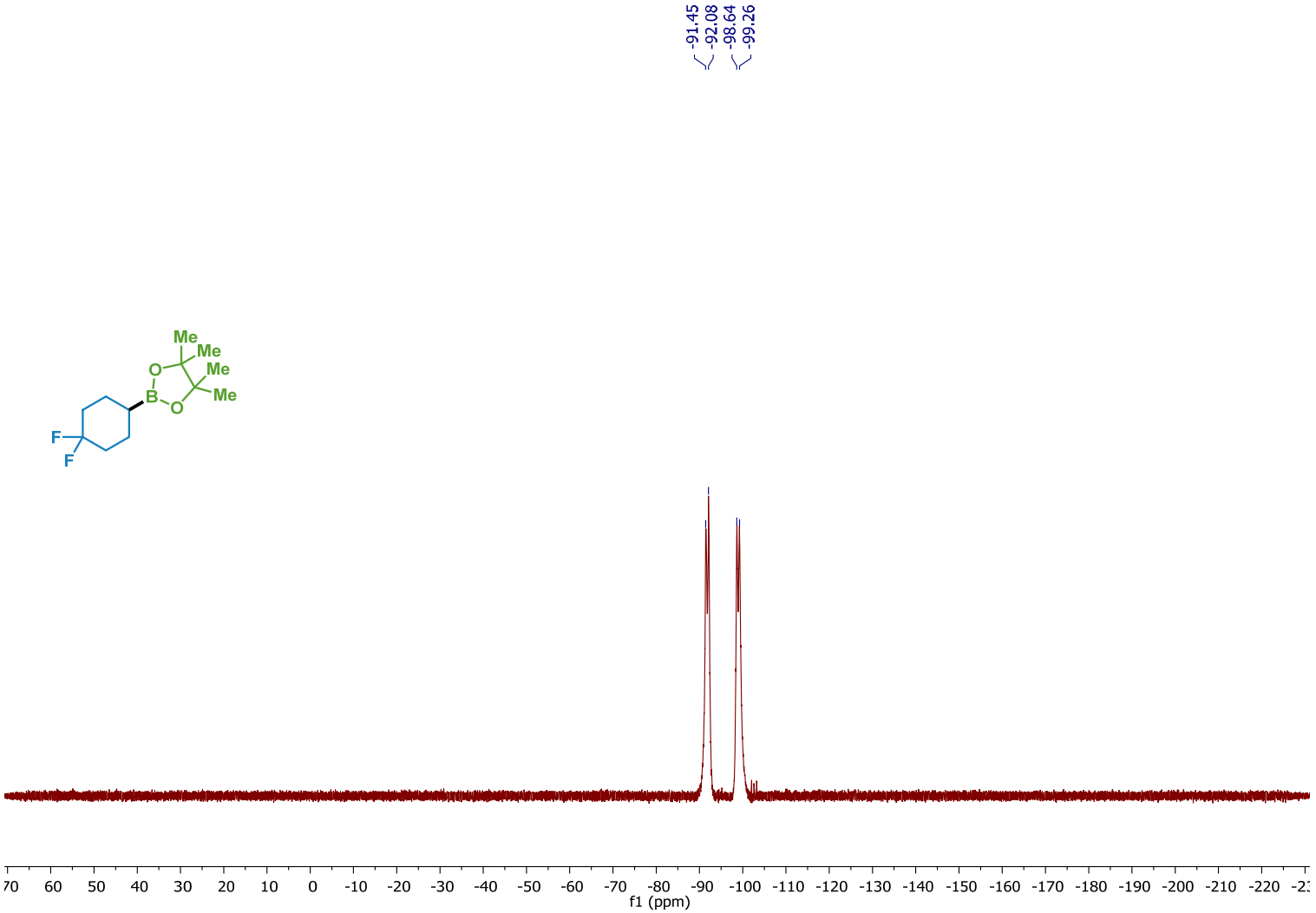
**Compound 23 $^{1}$H NMR**



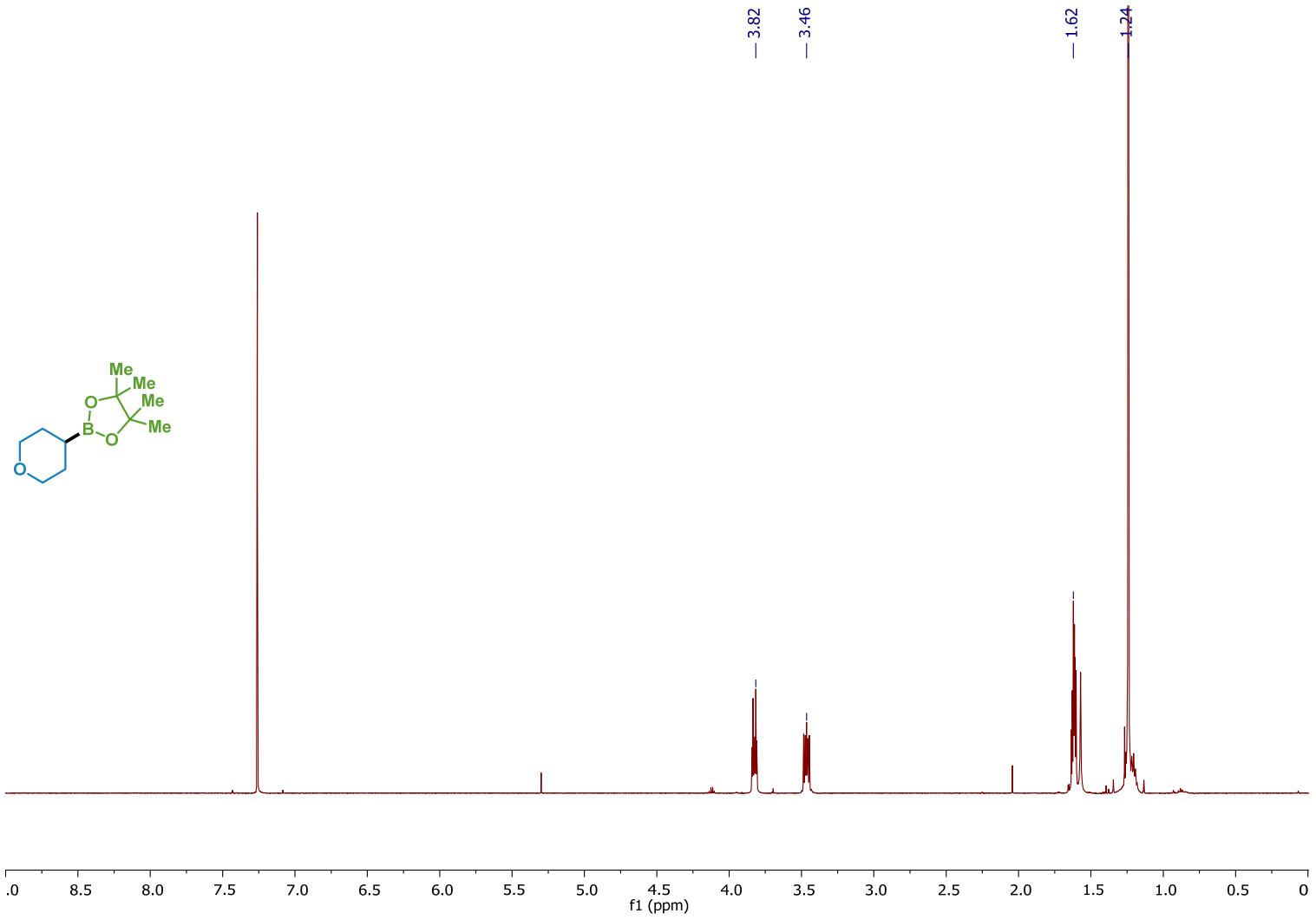
**Compound 23 $^{13}$C NMR**



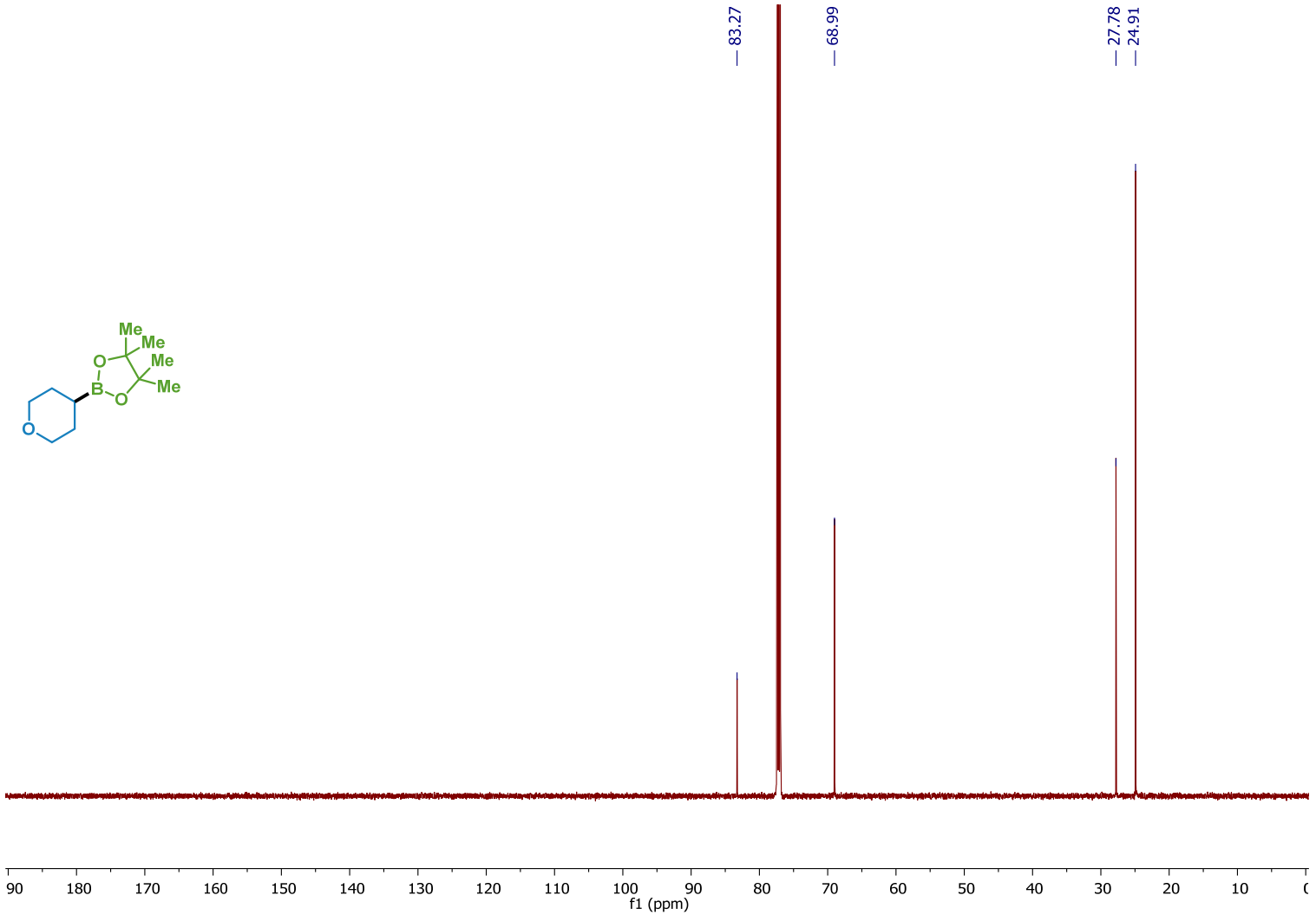
**Compound 23 $^{19}$F NMR**



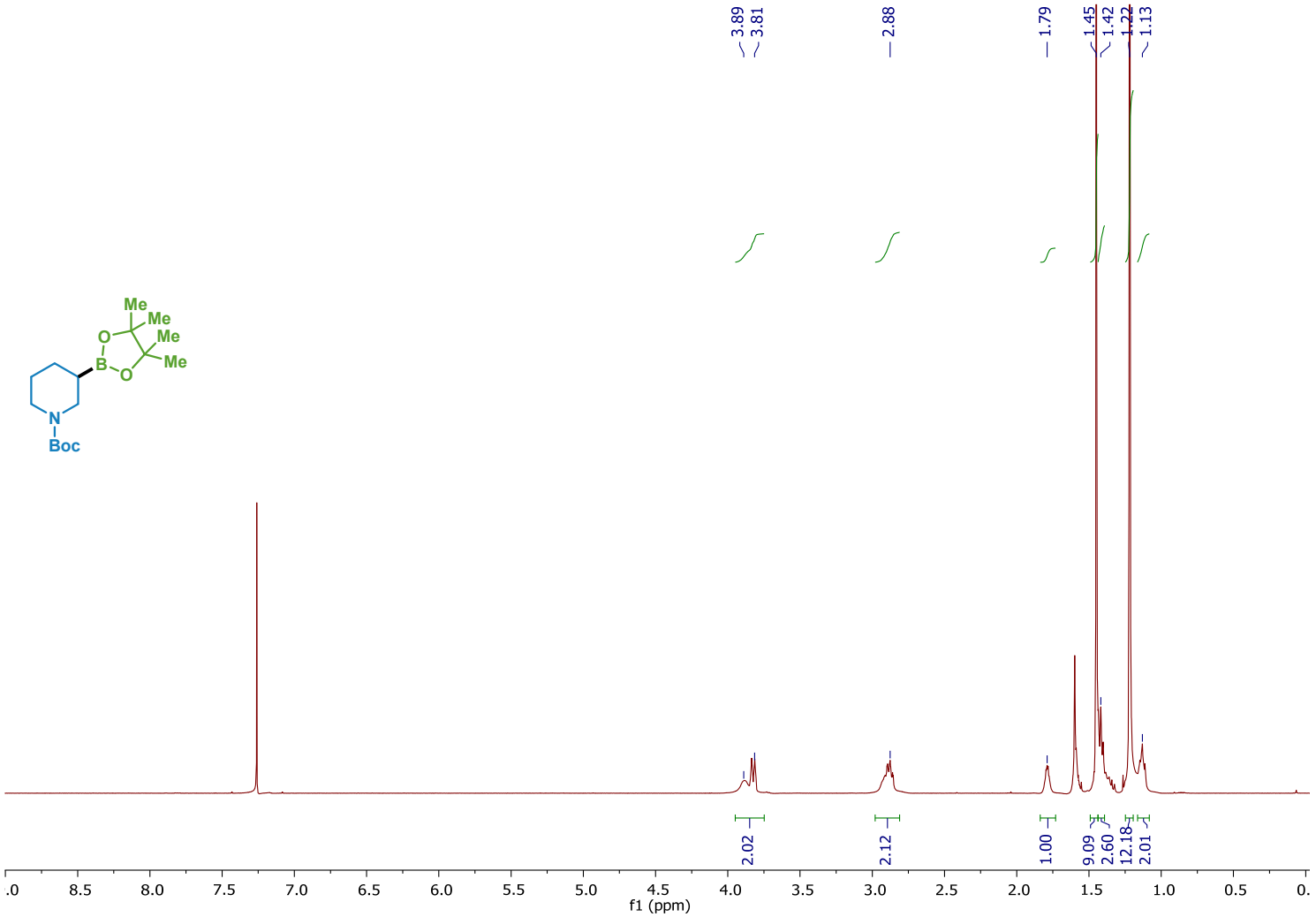
**Compound 24 $^{1}$H NMR**



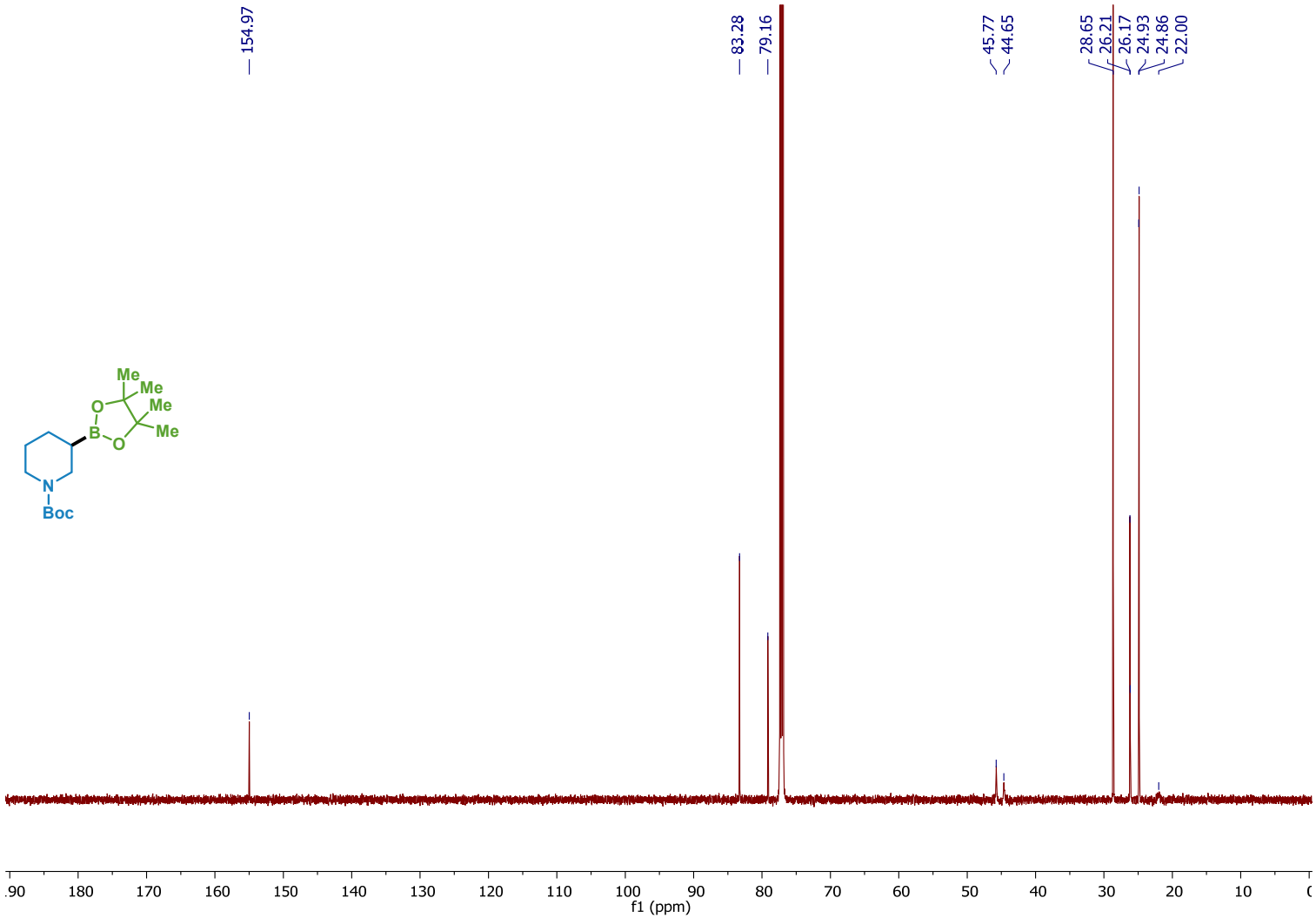
**Compound 24 $^{13}$C NMR**



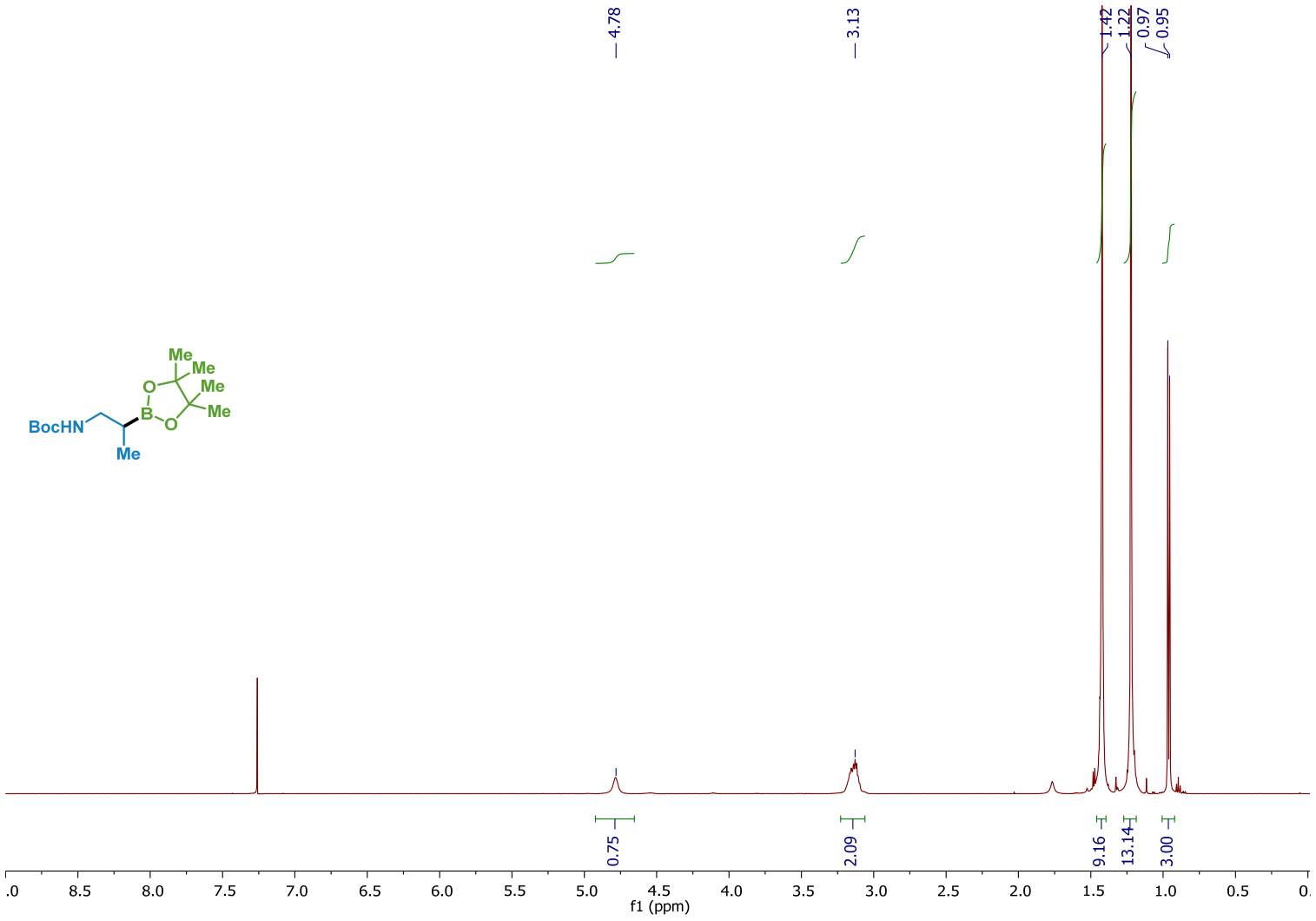
**Compound 25 $^{1}$H NMR**



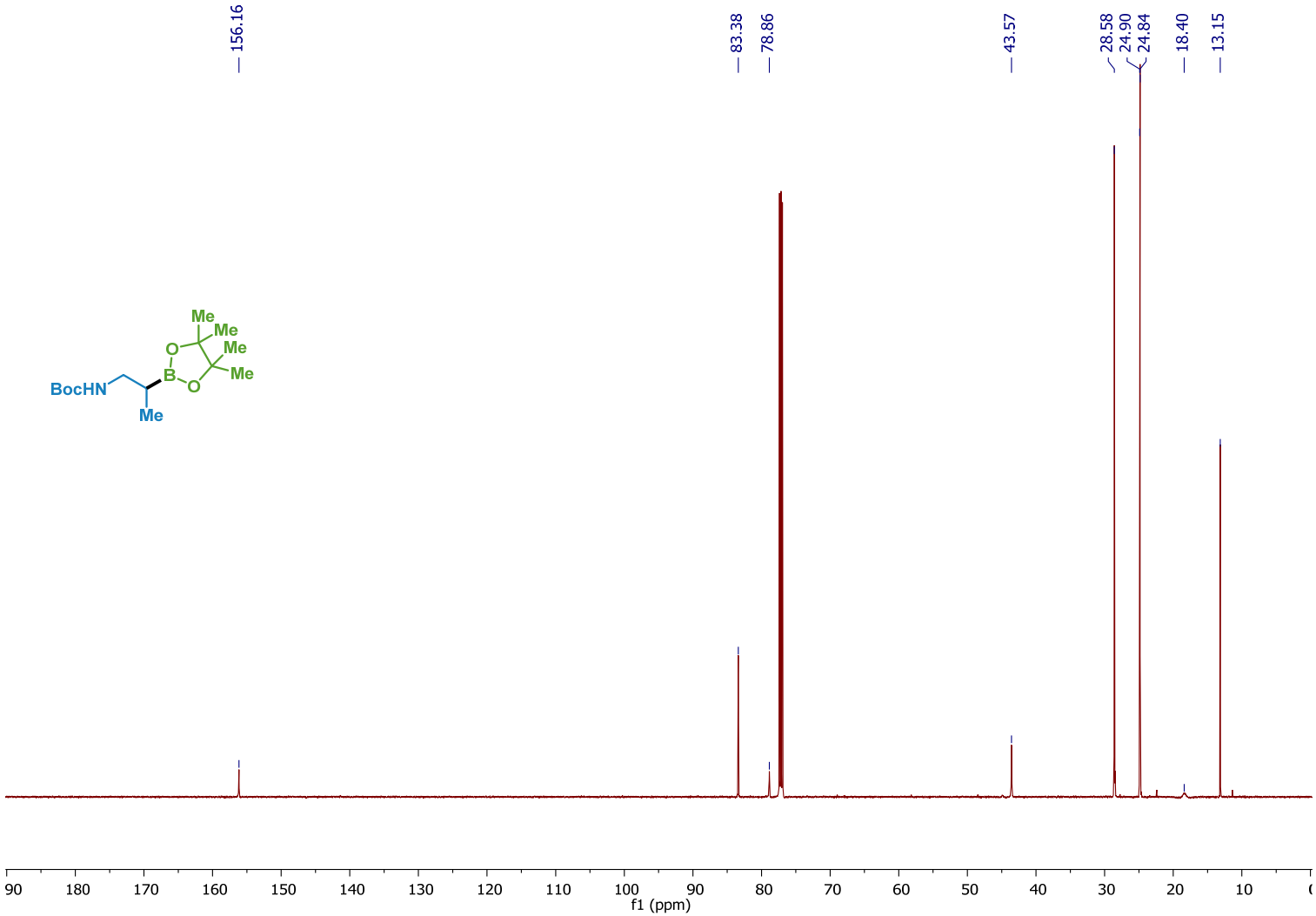
**Compound 25 $^{13}$C NMR**



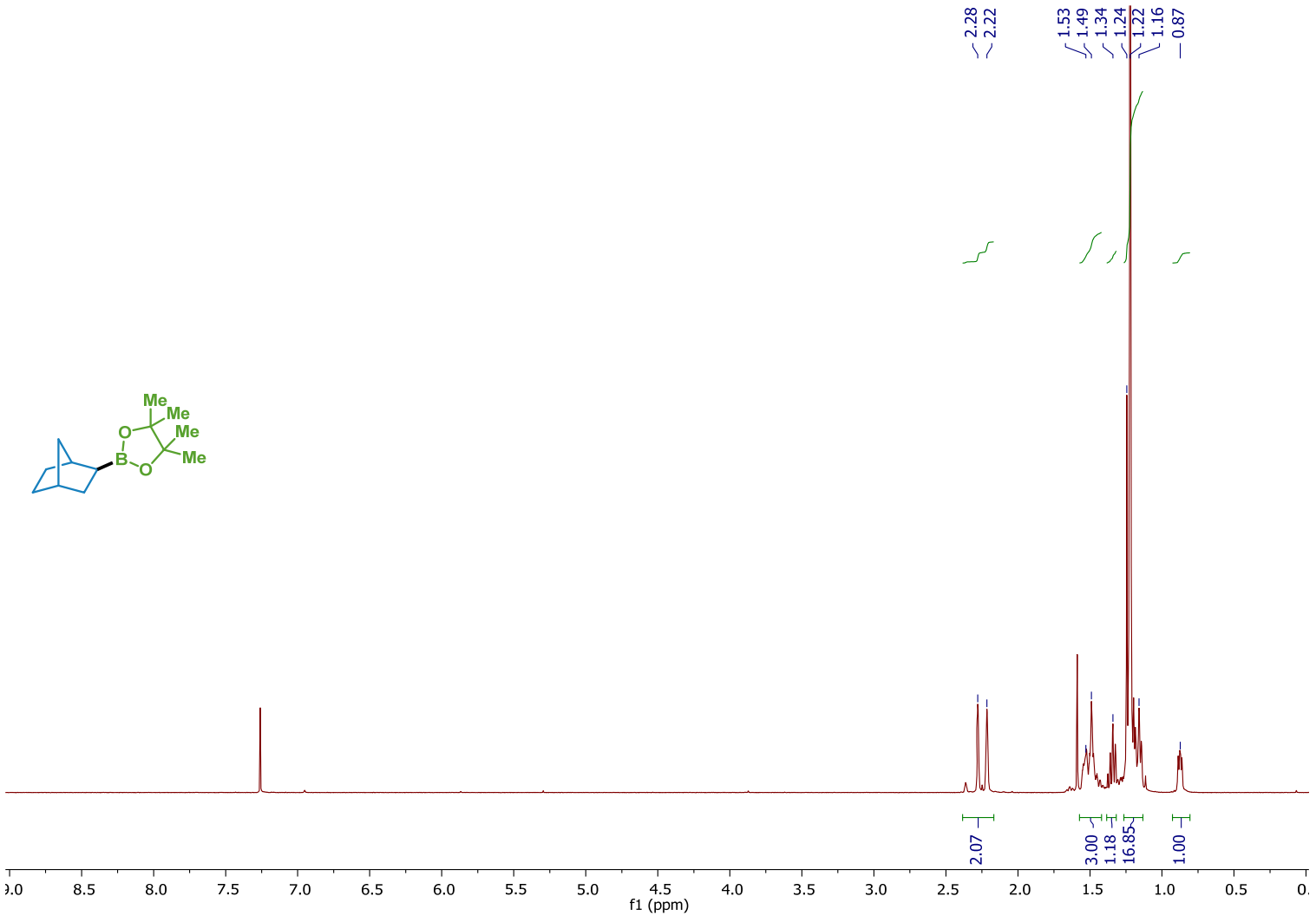
**Compound 26 $^{1}$H NMR**



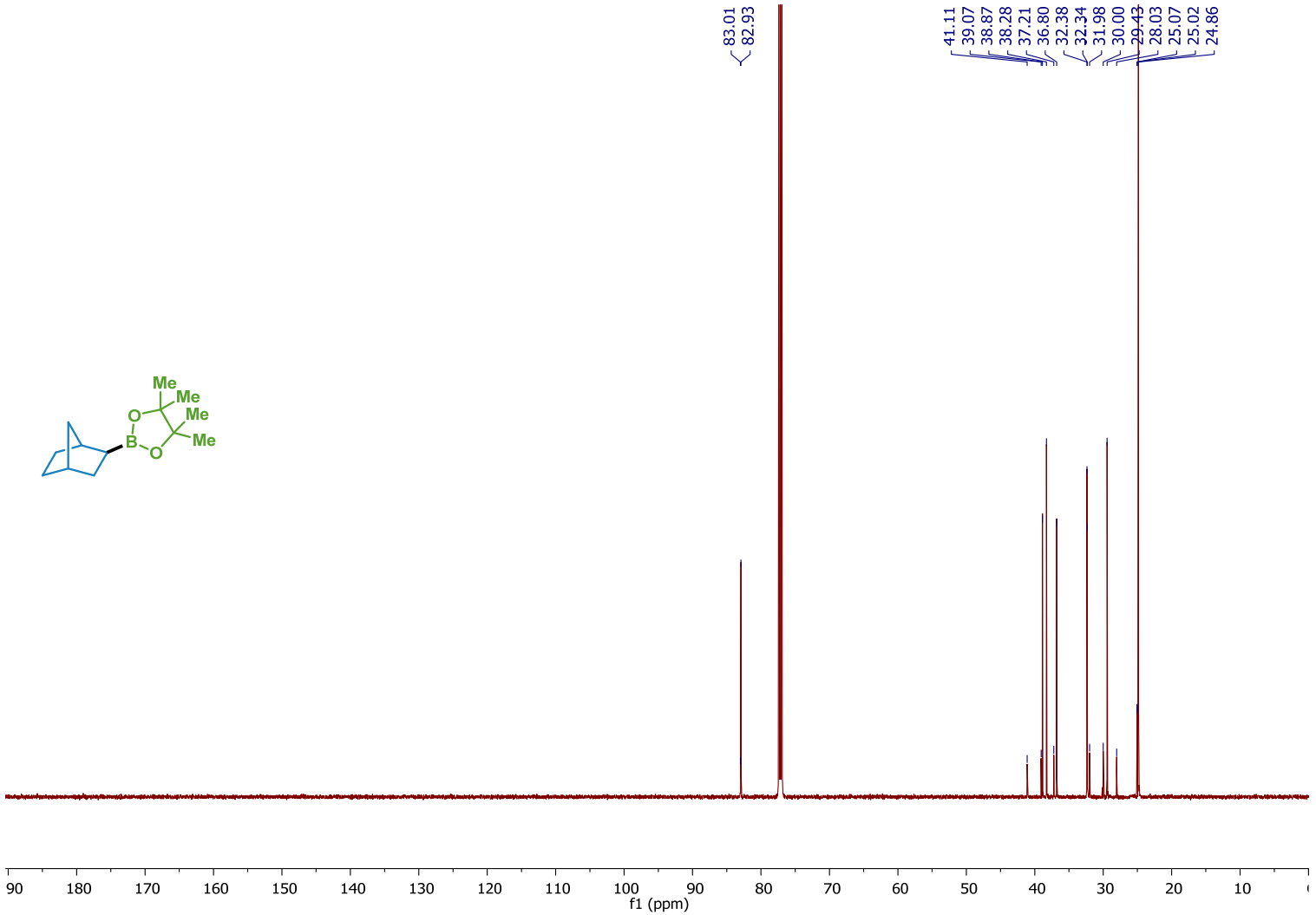
**Compound 26 $^{13}$C NMR**



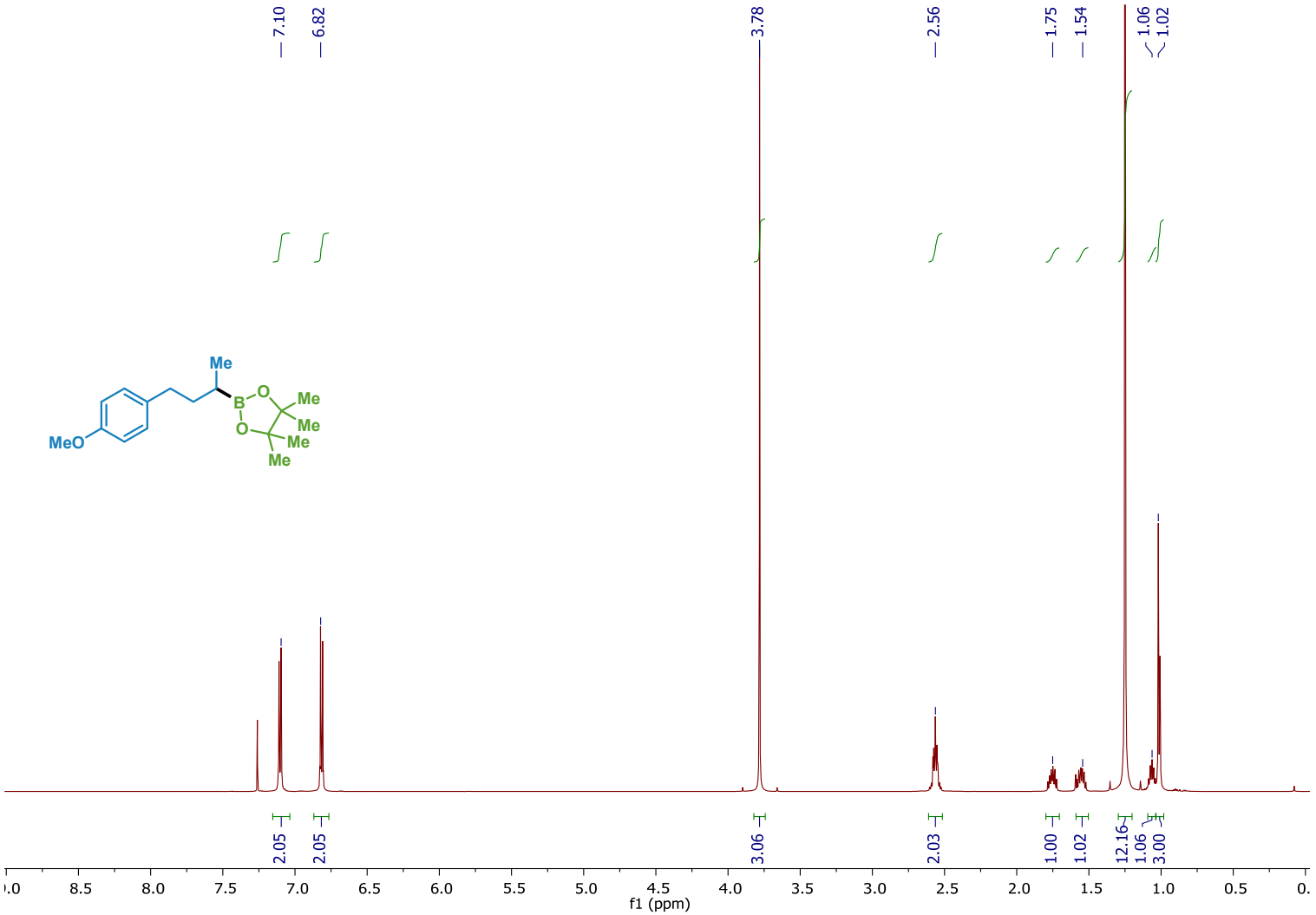
**Compound 27 $^{1}$H NMR**



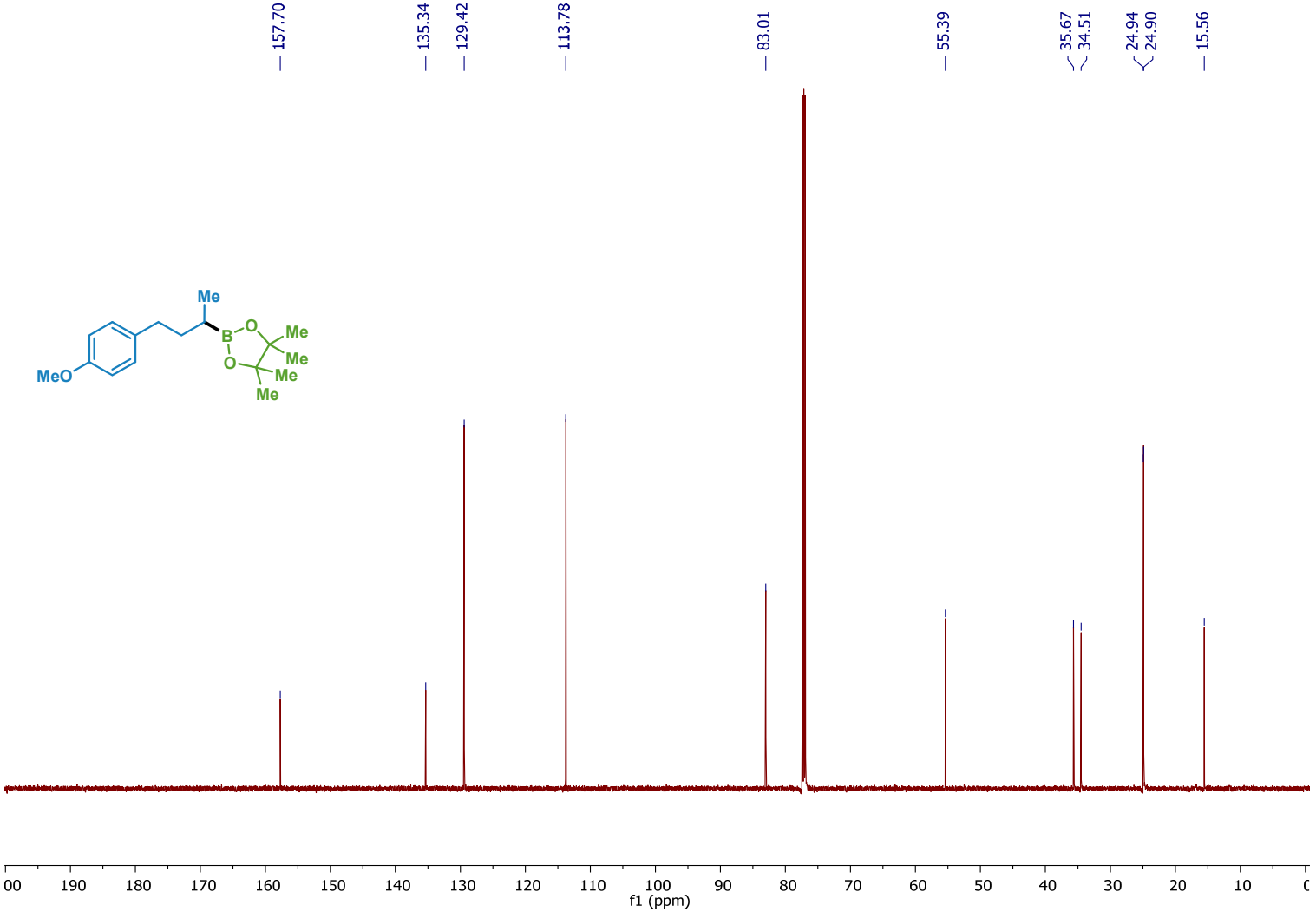
**Compound 27 $^{13}$C NMR**



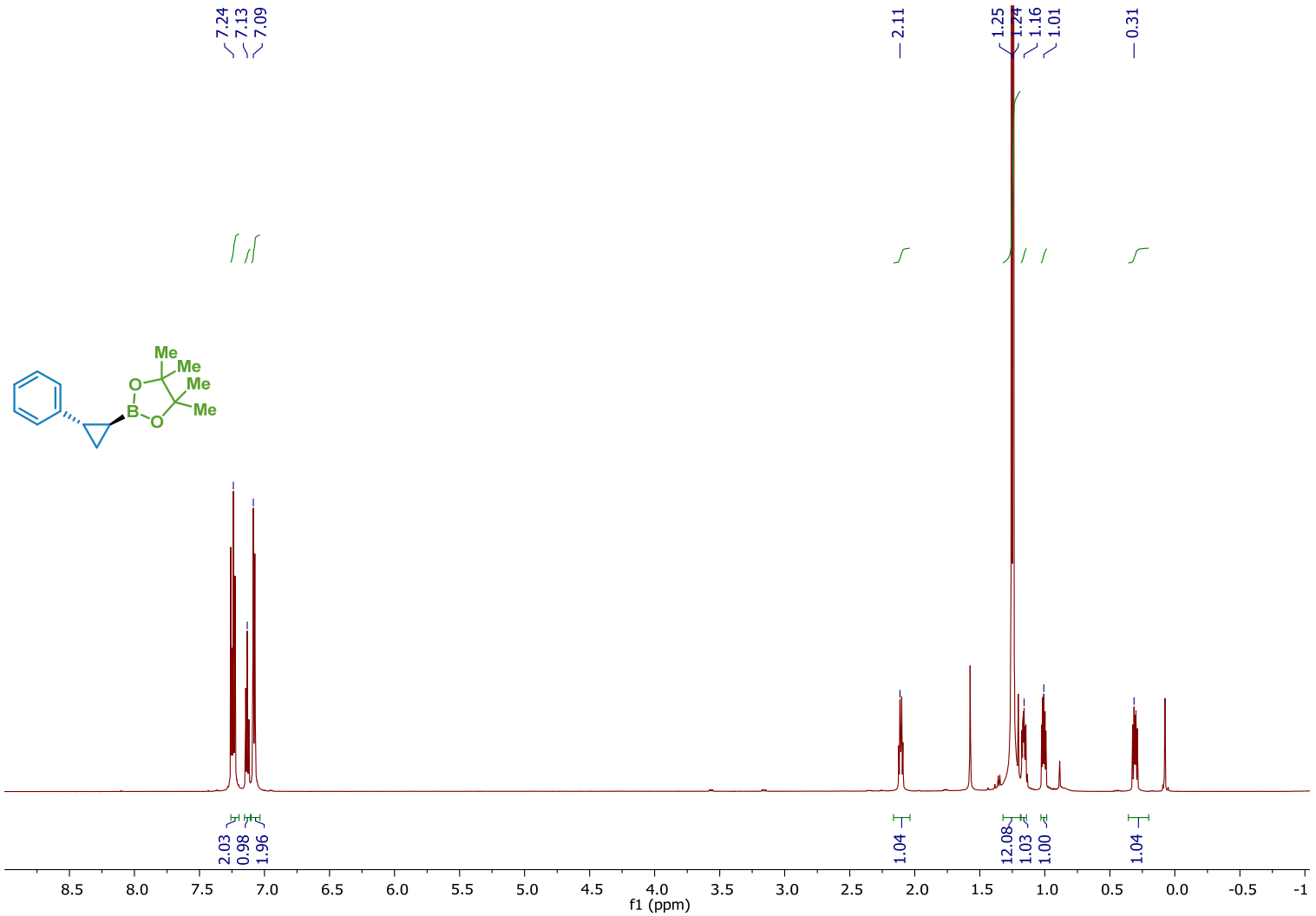
**Compound 28 $^{1}$H NMR**



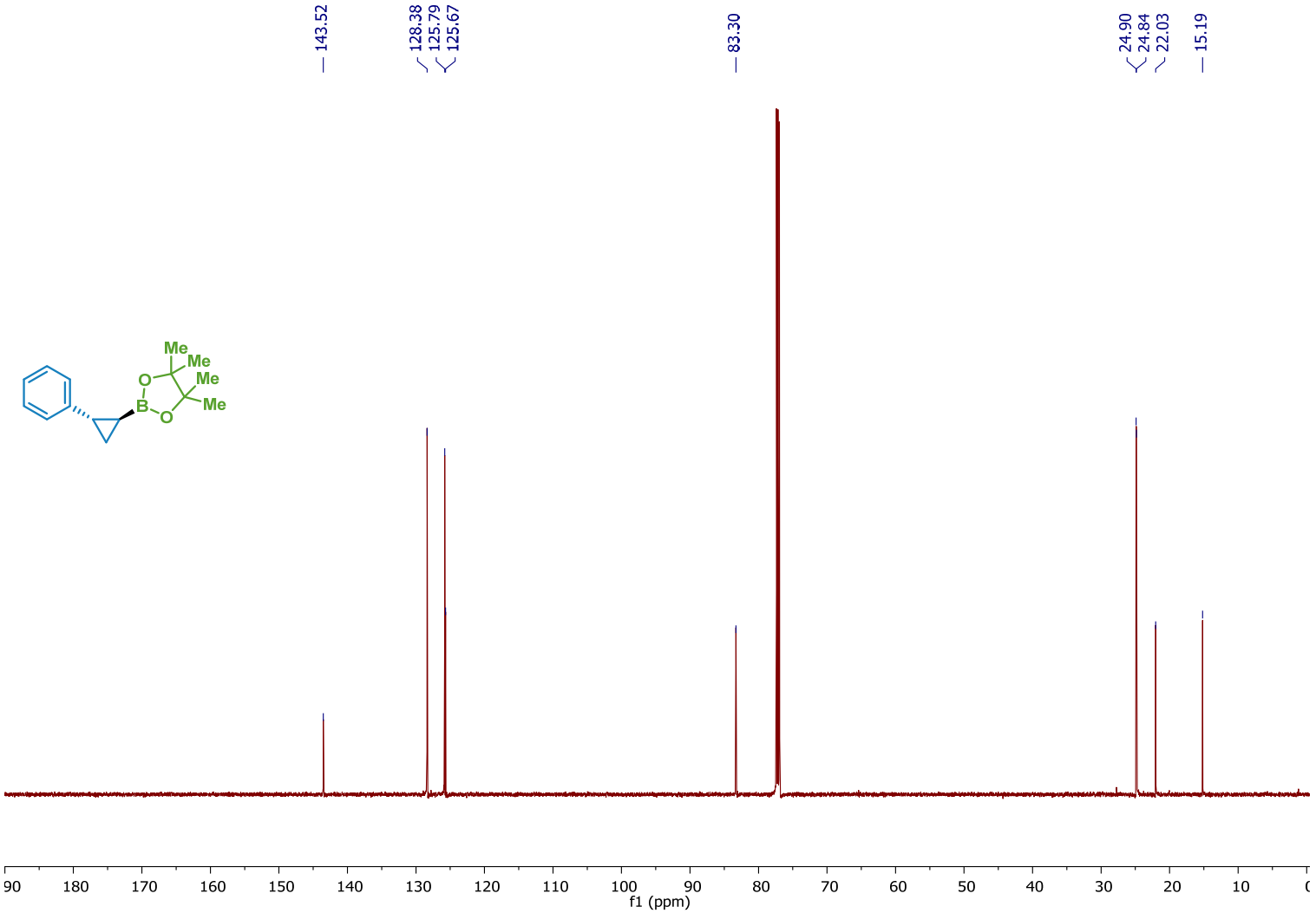
**Compound 28 $^{13}$C NMR**



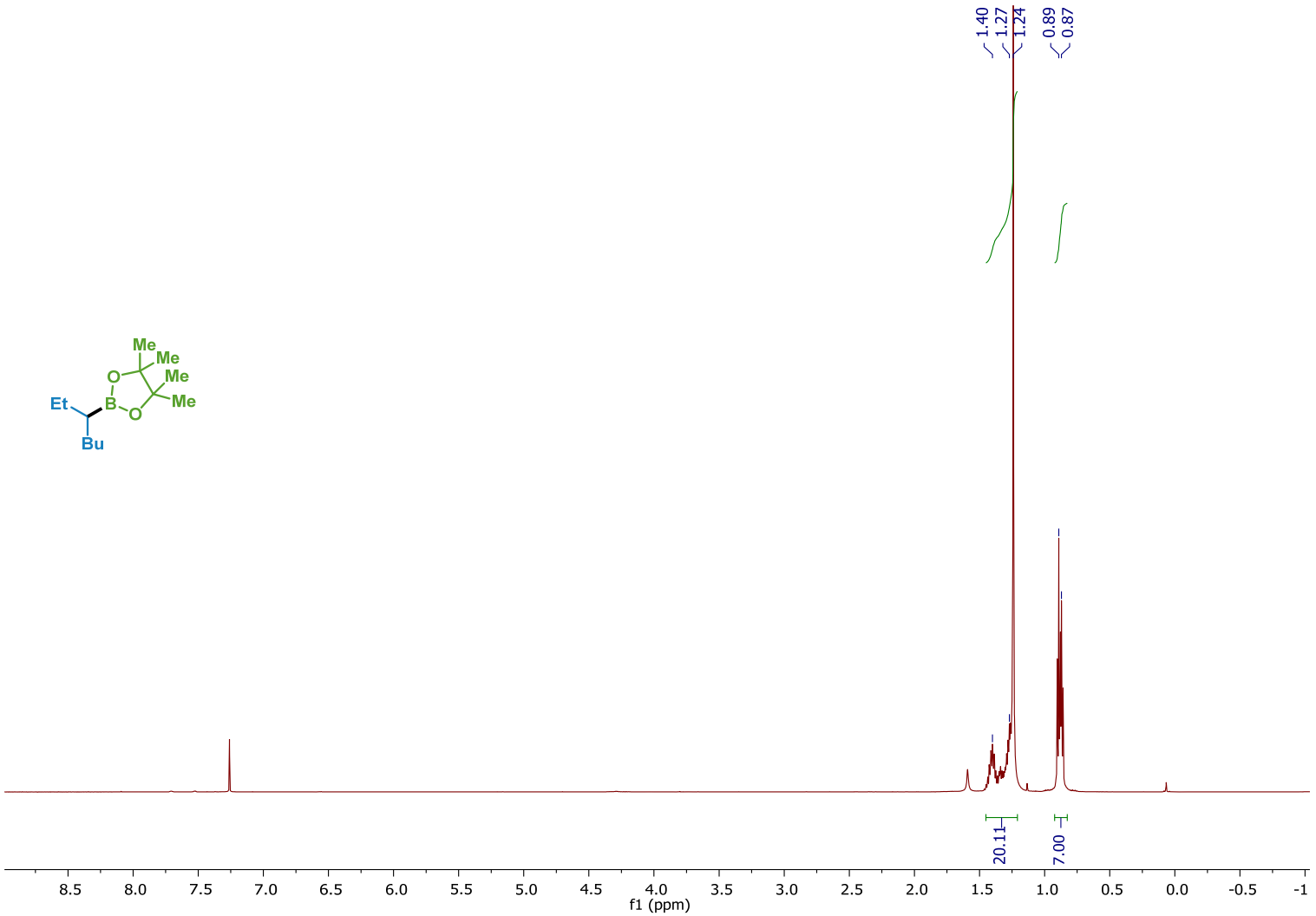
**Compound 29 $^{1}$H NMR**



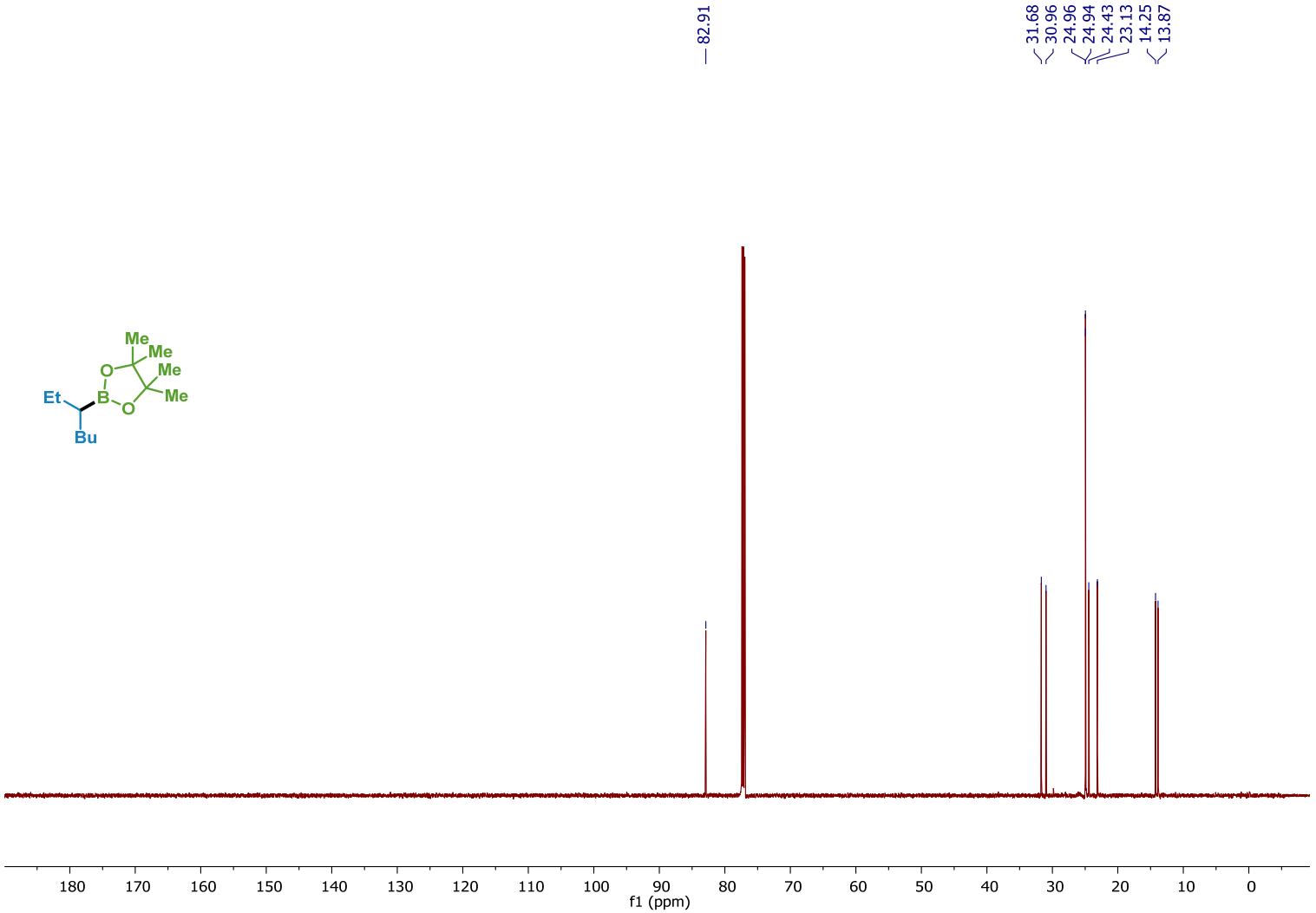
**Compound 29 $^{13}$C NMR**



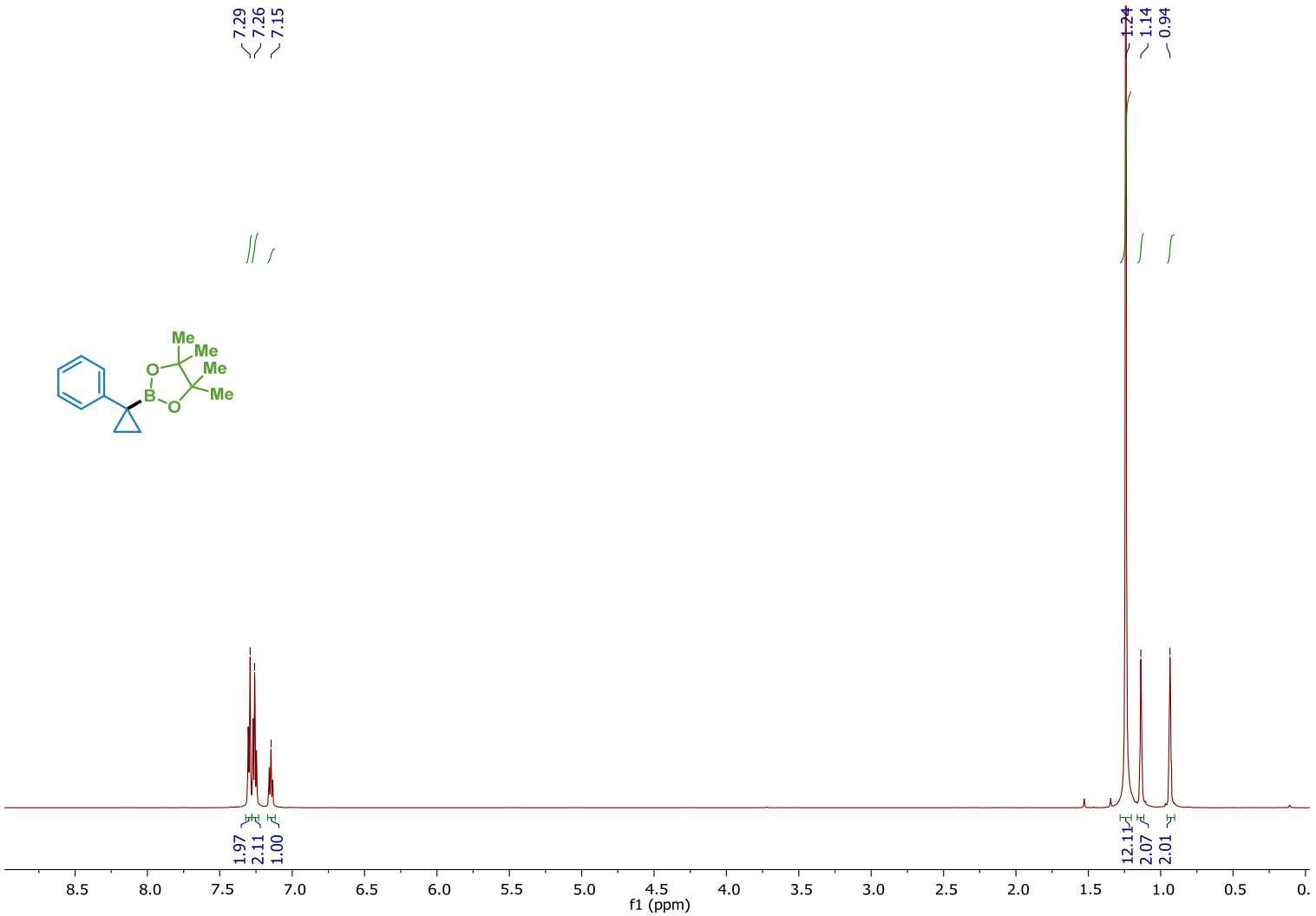
**Compound 30 $^{1}$H NMR**



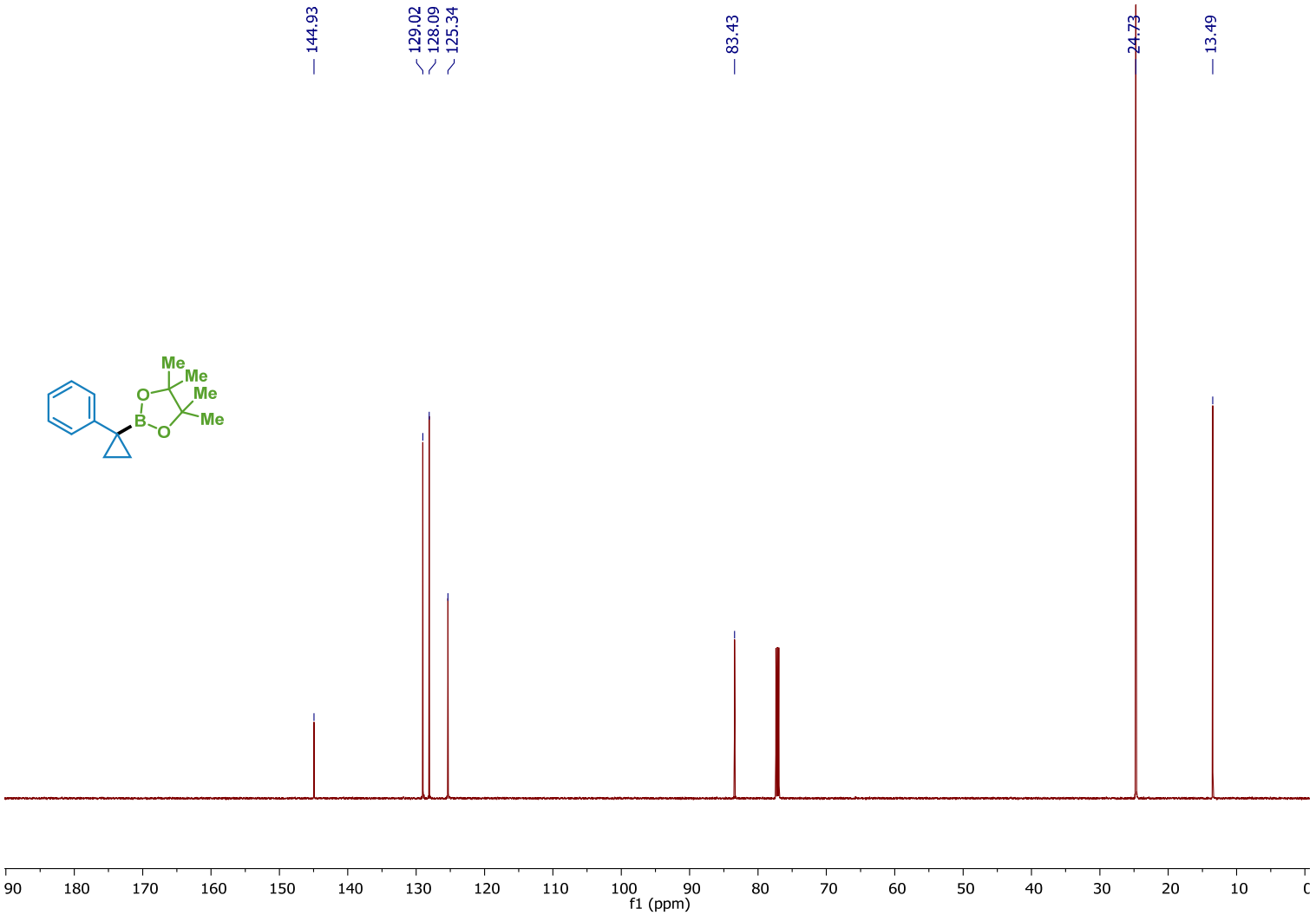
**Compound 30 $^{13}$C NMR**



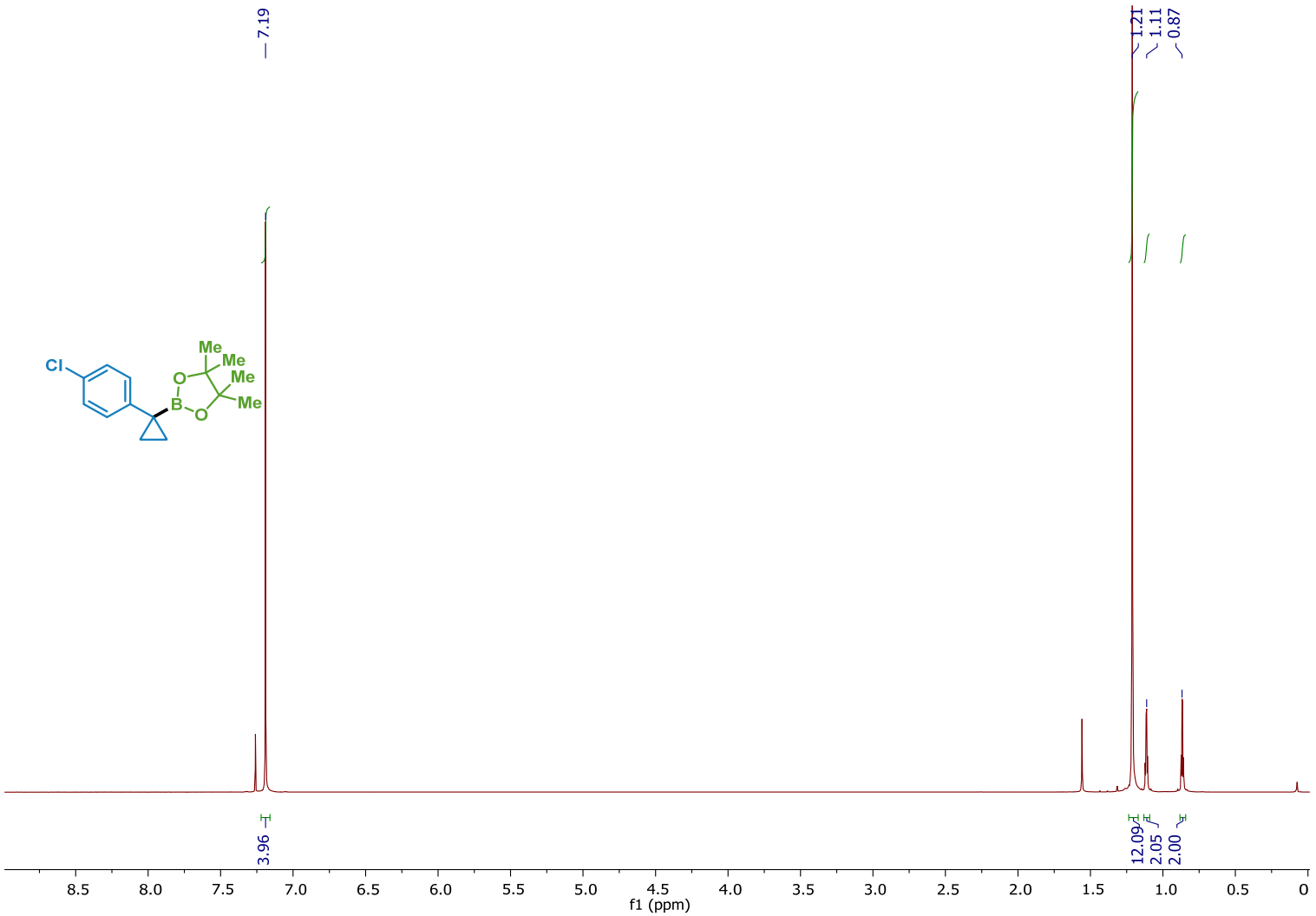
**Compound 31 $^{1}$H NMR**



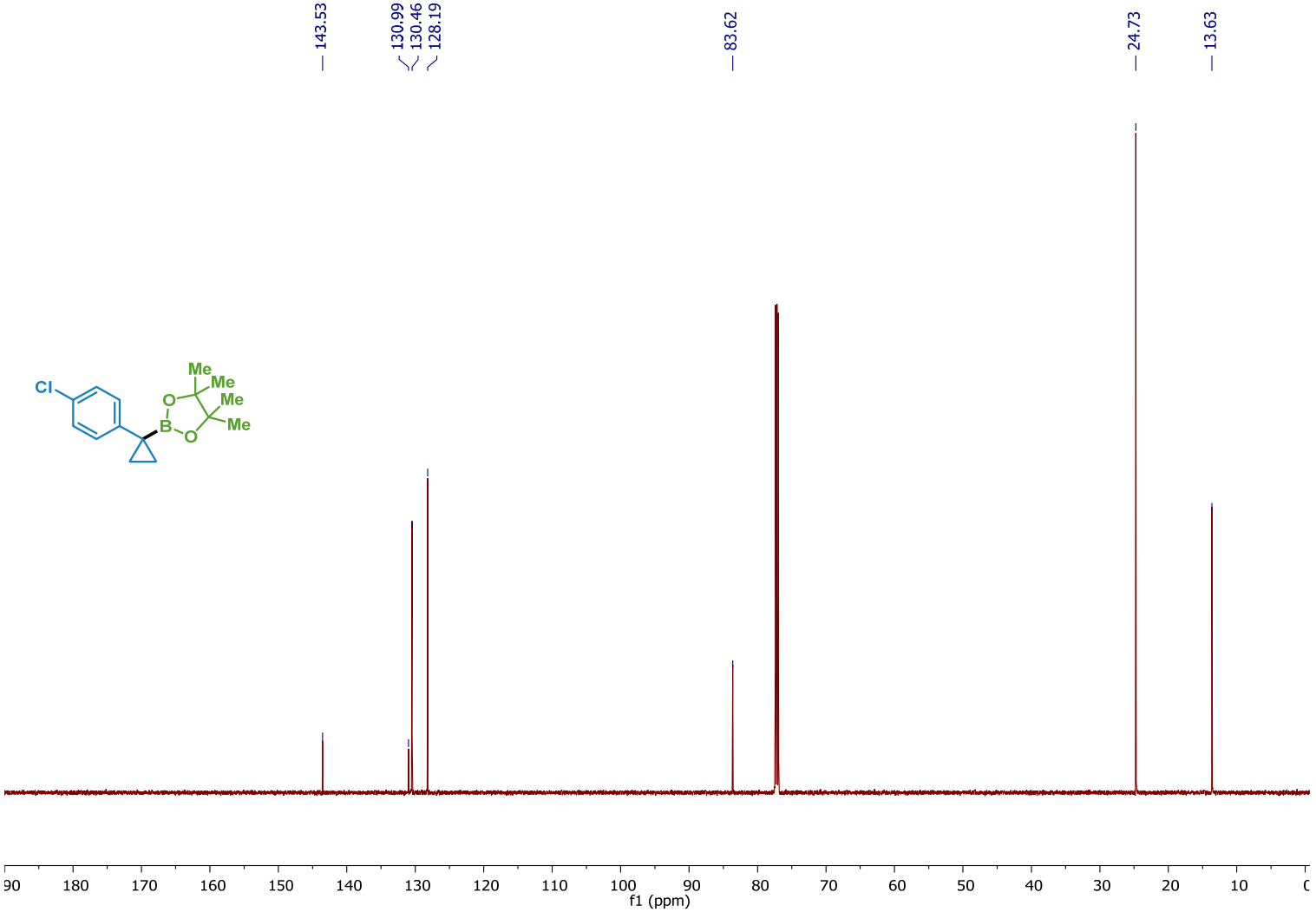
**Compound 31 $^{13}$C NMR**



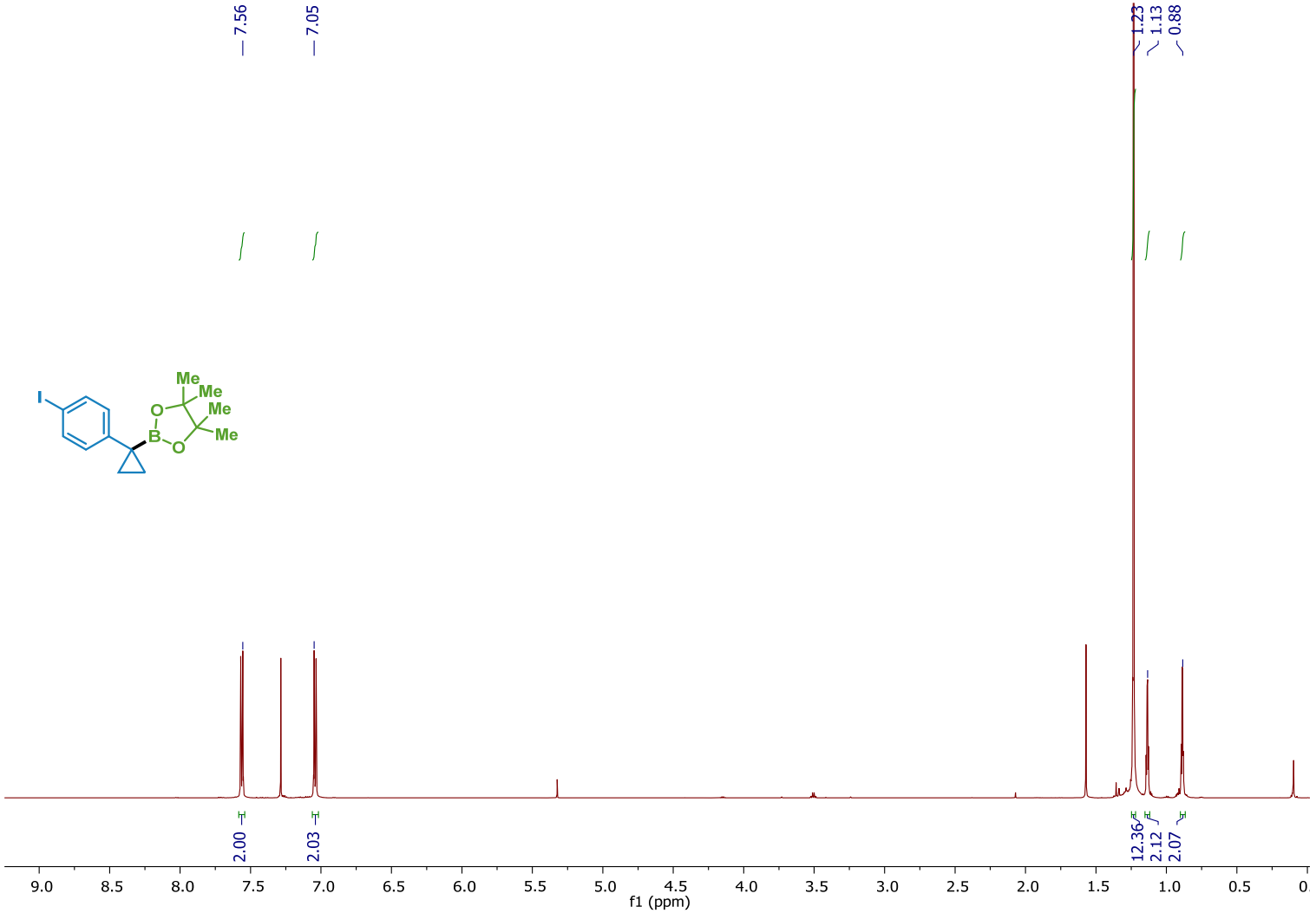
**Compound 32 $^{1}$H NMR**



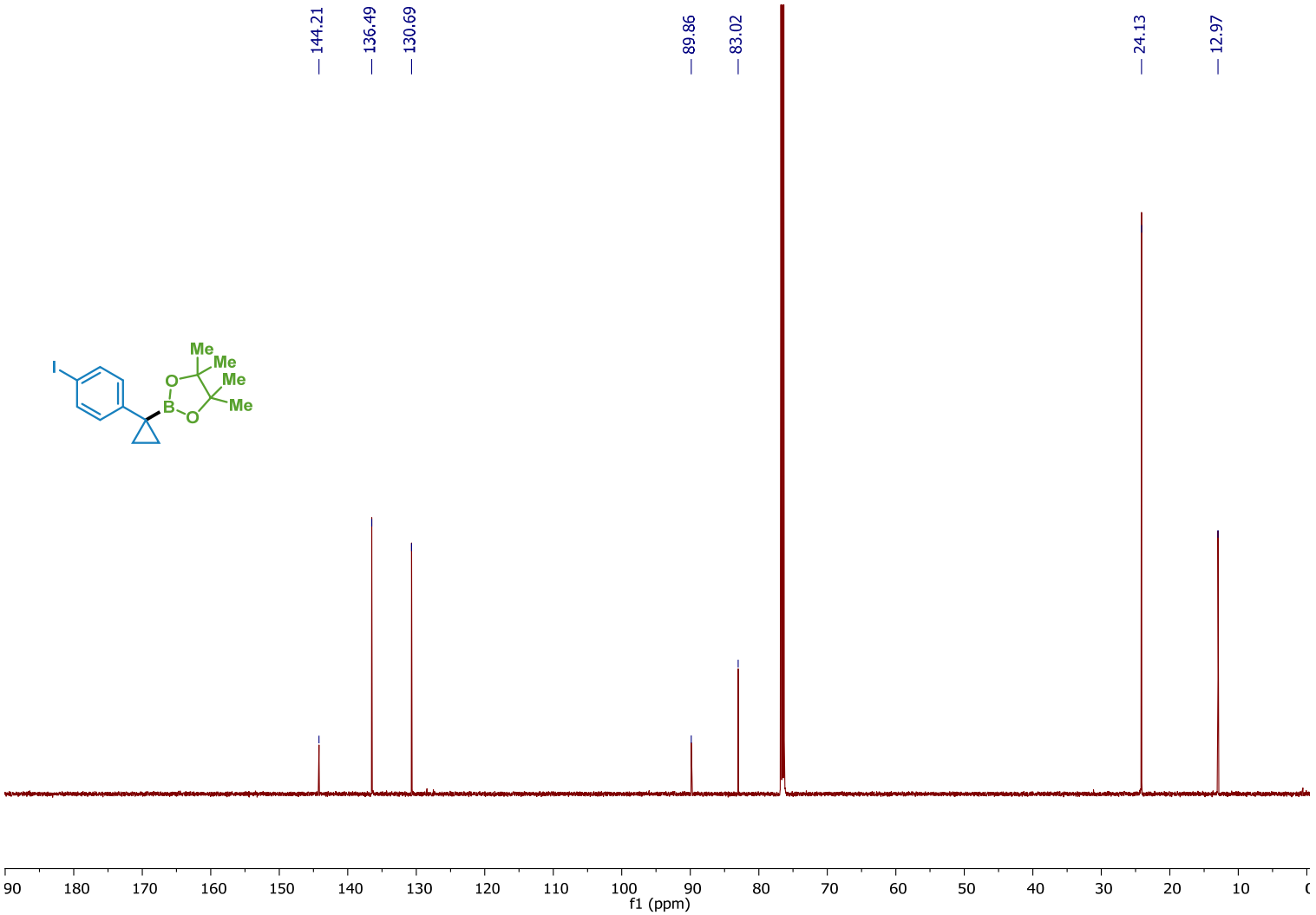
**Compound 32 $^{13}$C NMR**



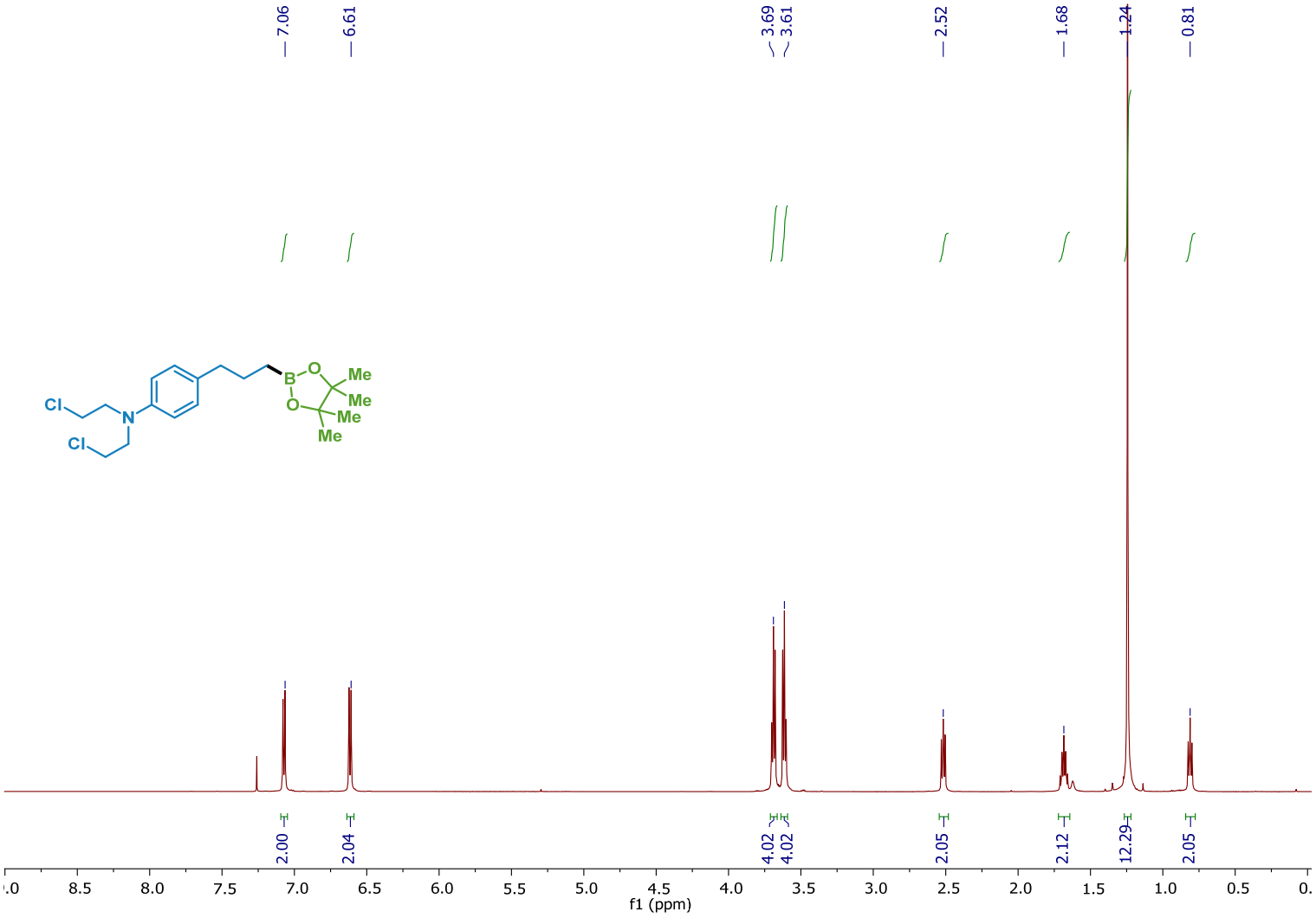
**Compound 33 $^{1}$H NMR**



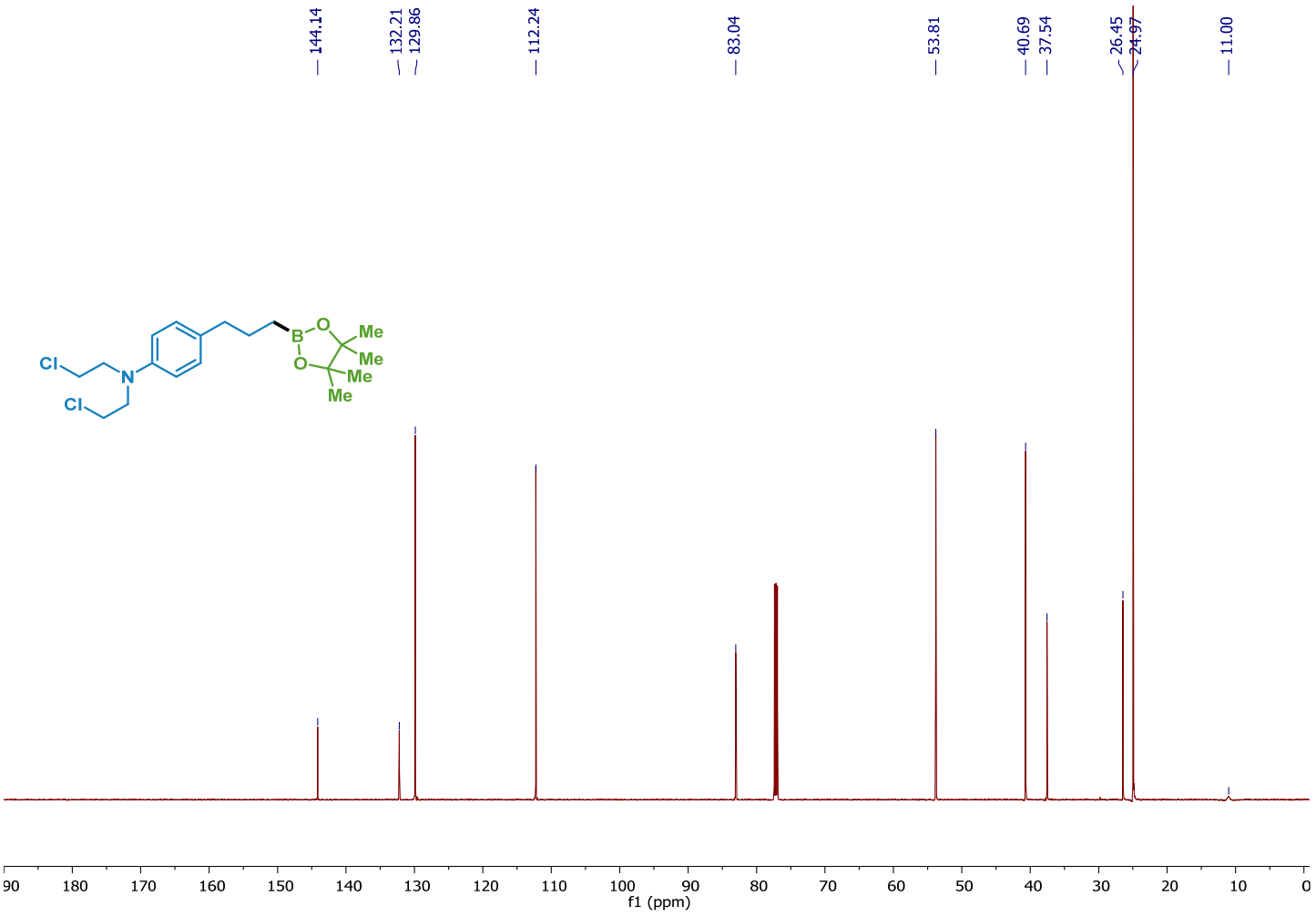
**Compound 33 $^{13}$C NMR**



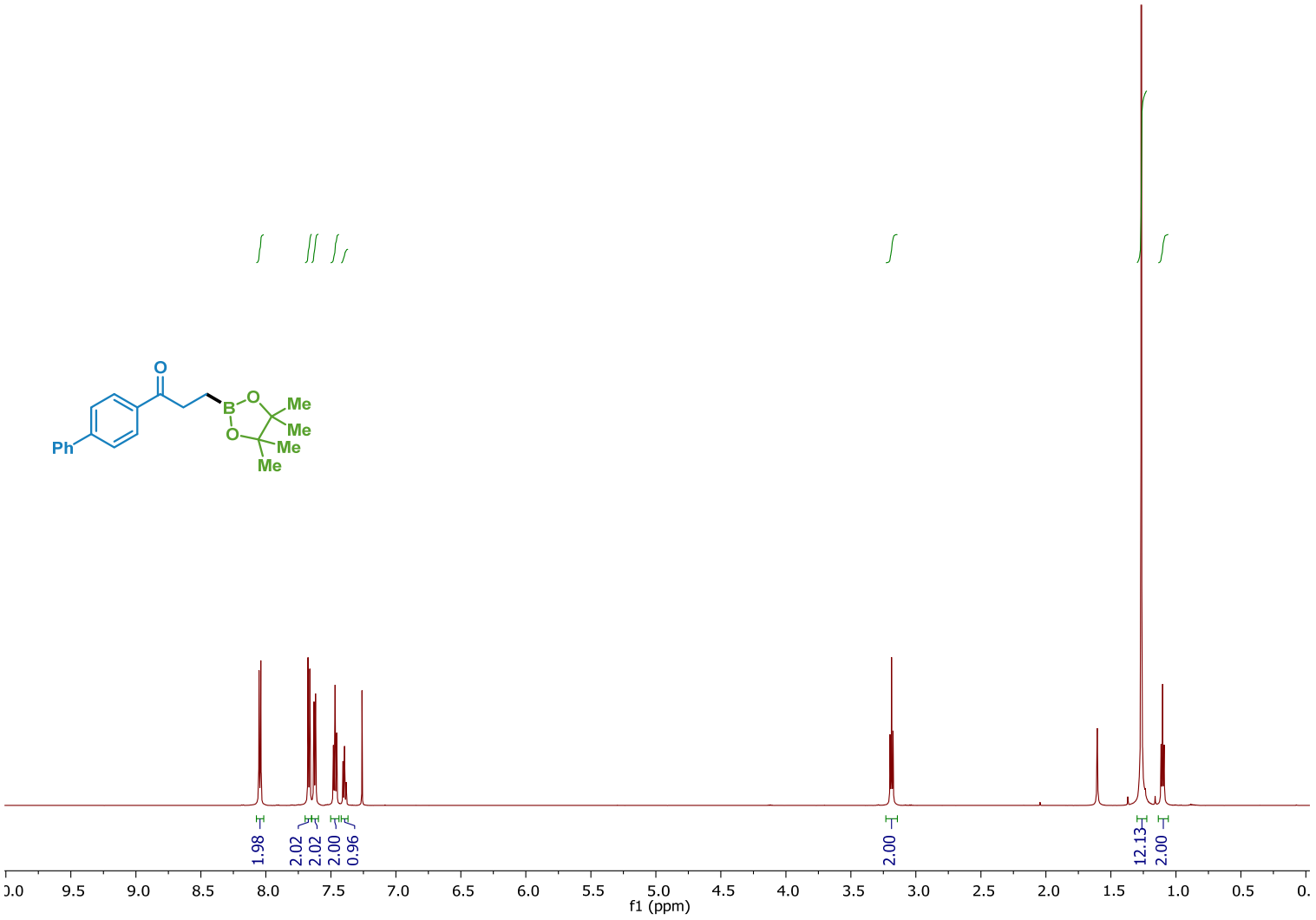
**Compound 34 $^{1}$H NMR**



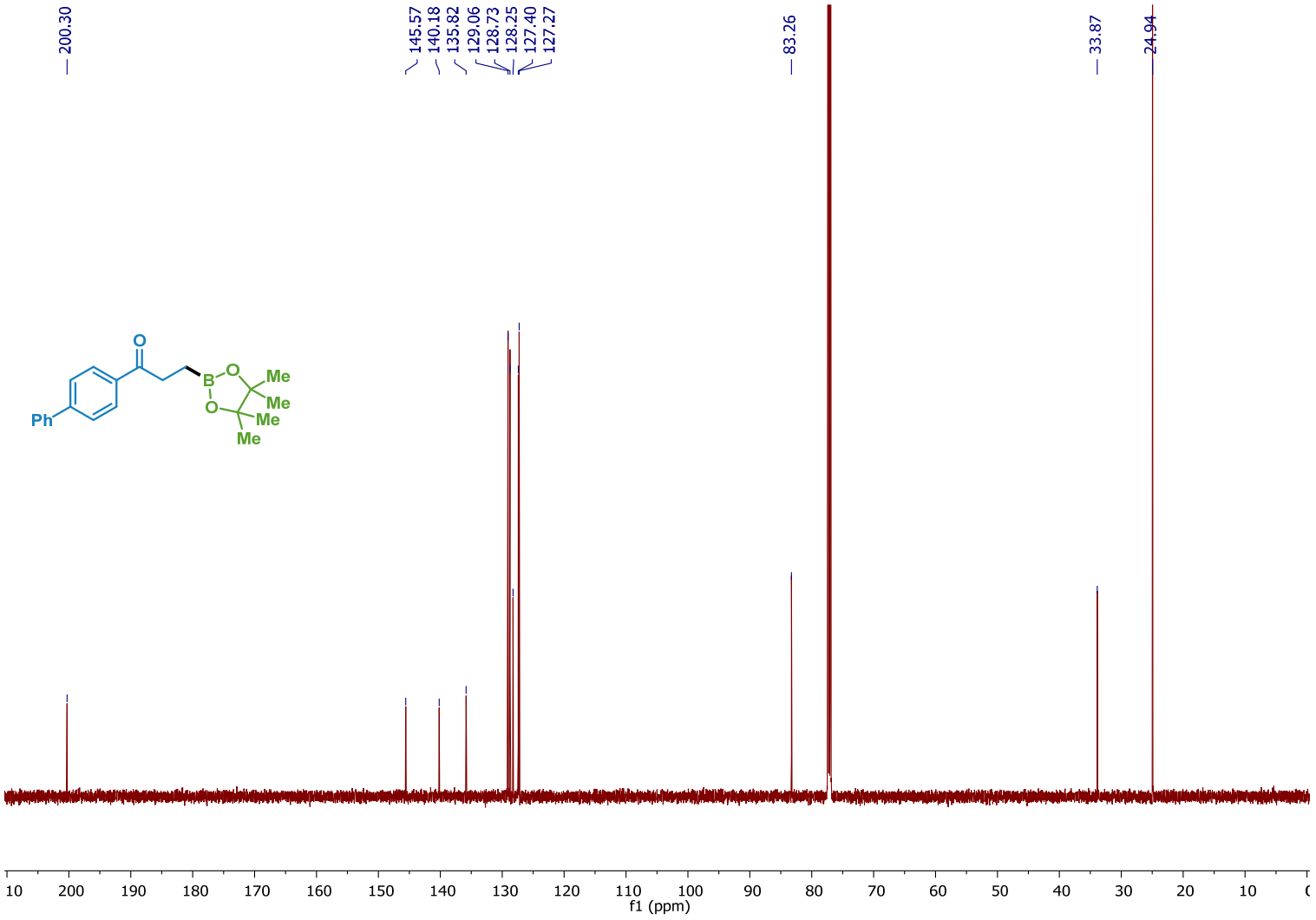
**Compound 34 $^{13}$C NMR**



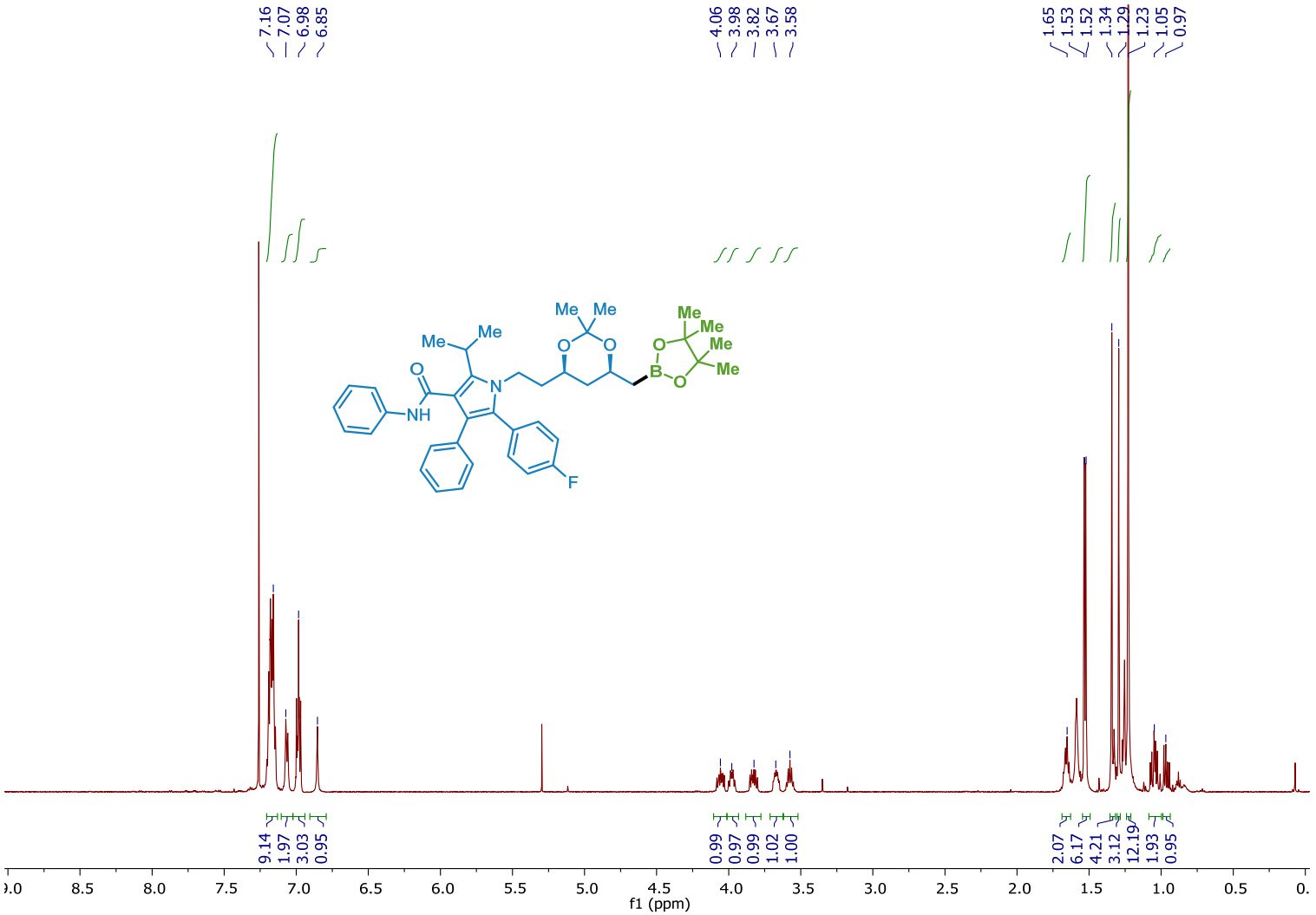
**Compound 35 $^{1}$H NMR**



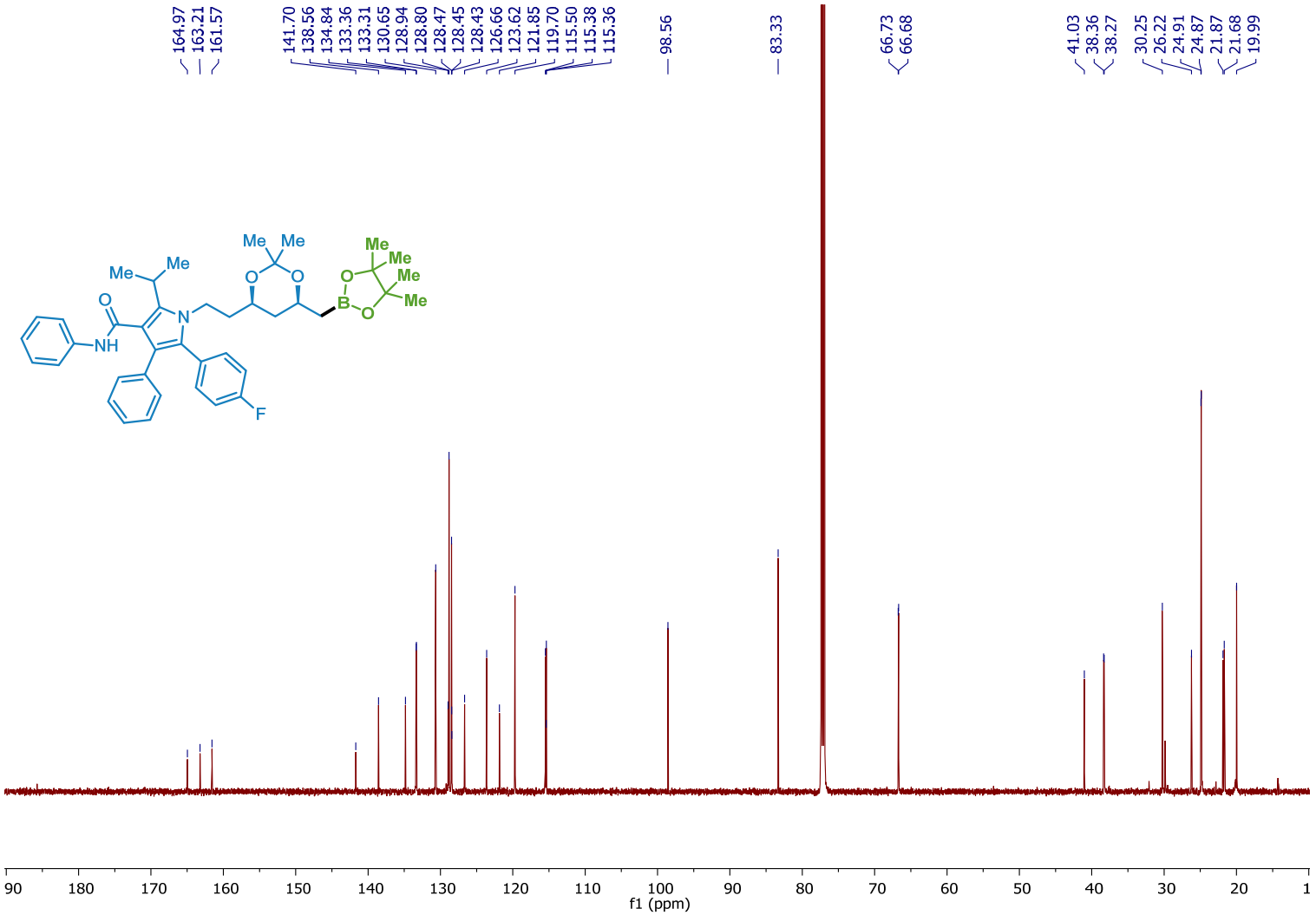
**Compound 35 $^{13}$C NMR**



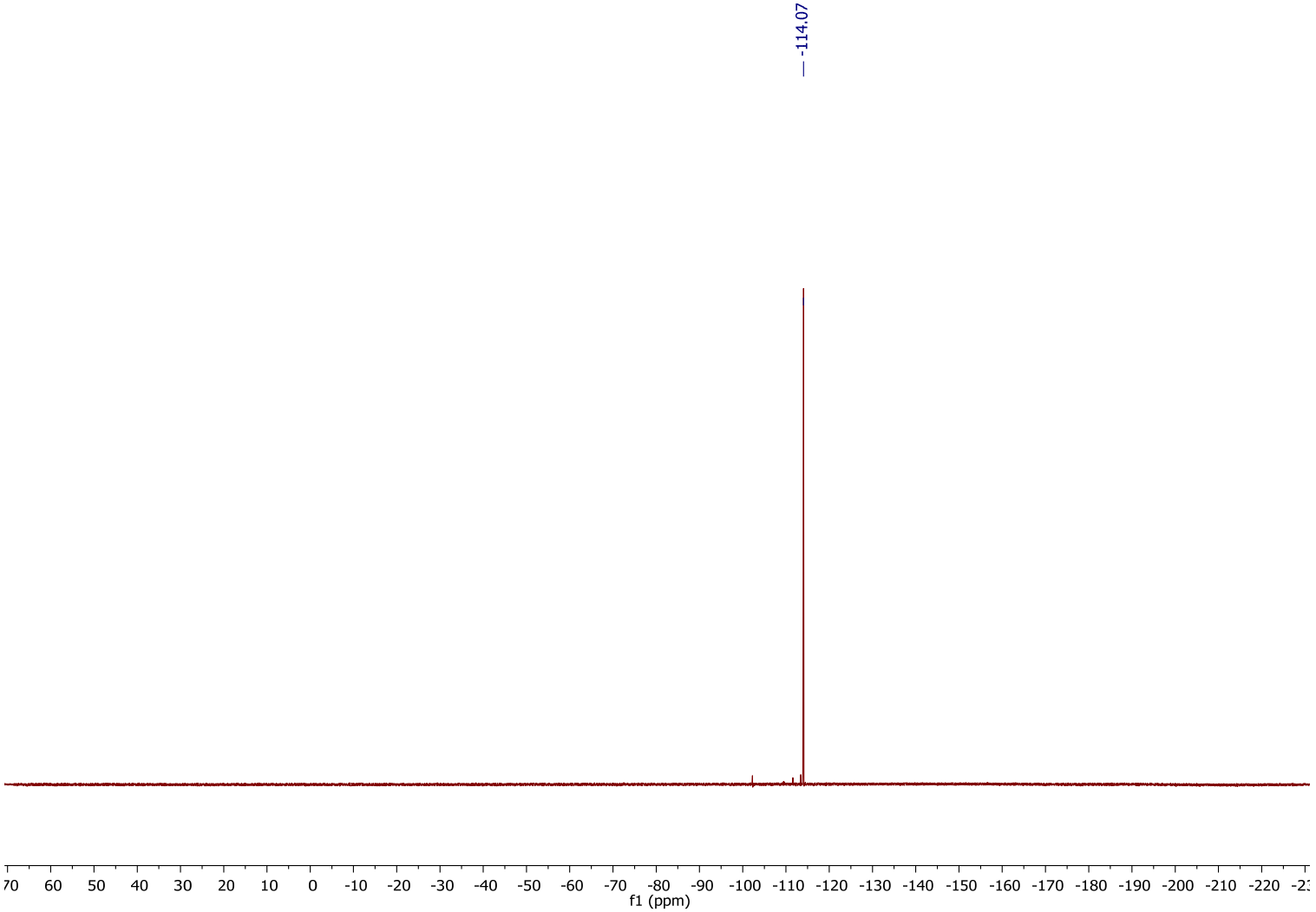
**Compound 36 $^{1}$H NMR**



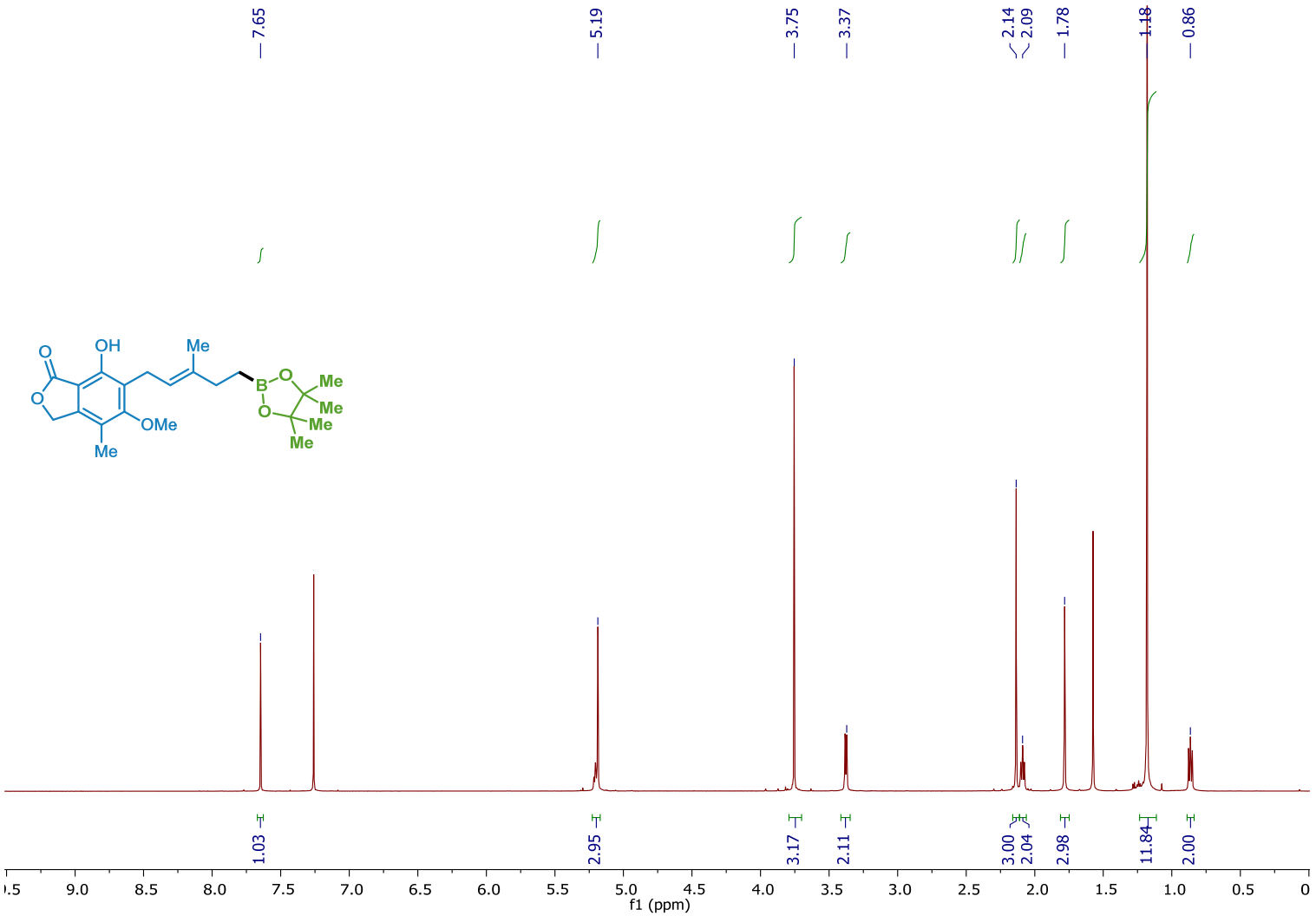
**Compound 36 $^{13}$C NMR**



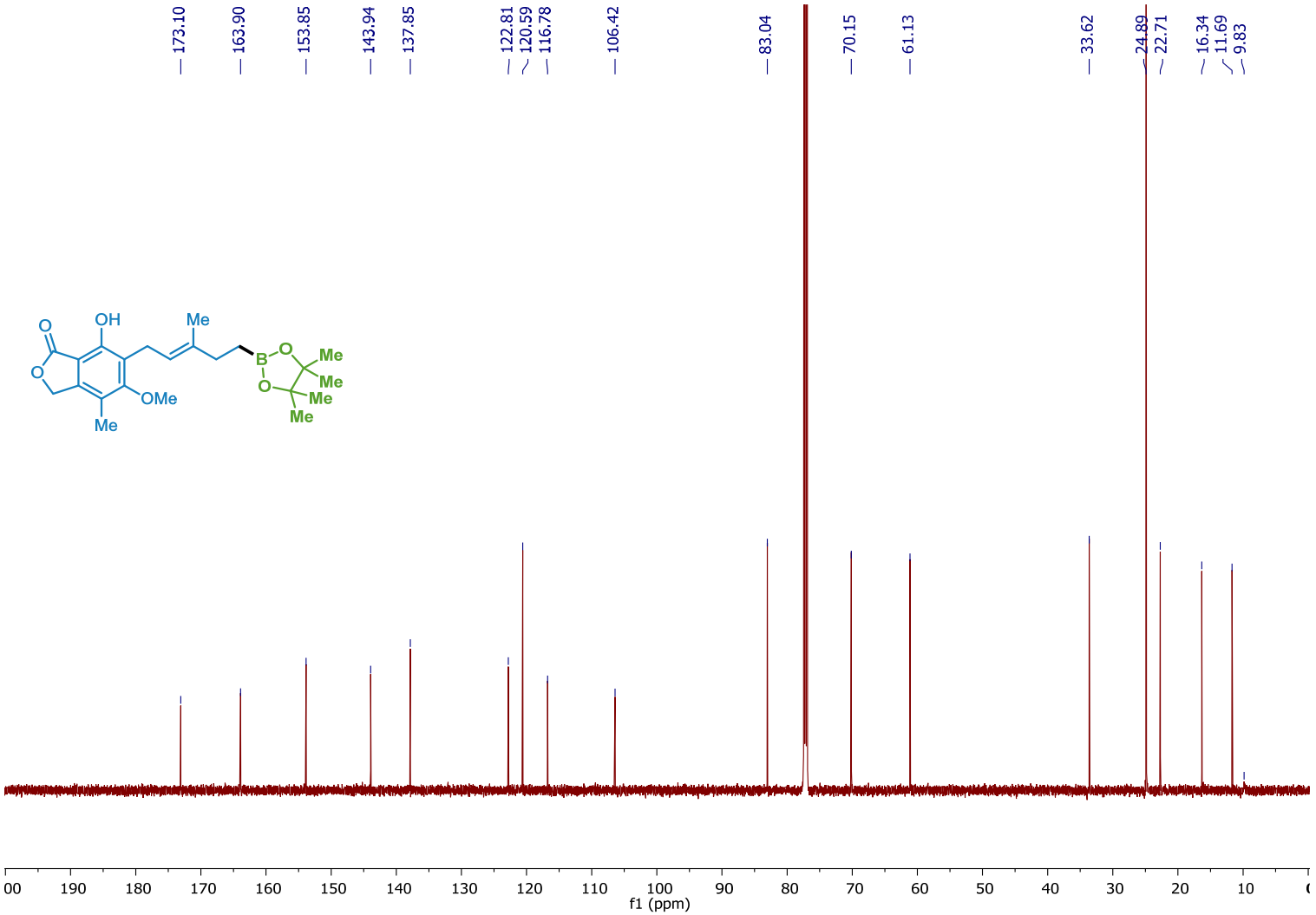
**Compound 36 $^{19}$F NMR**



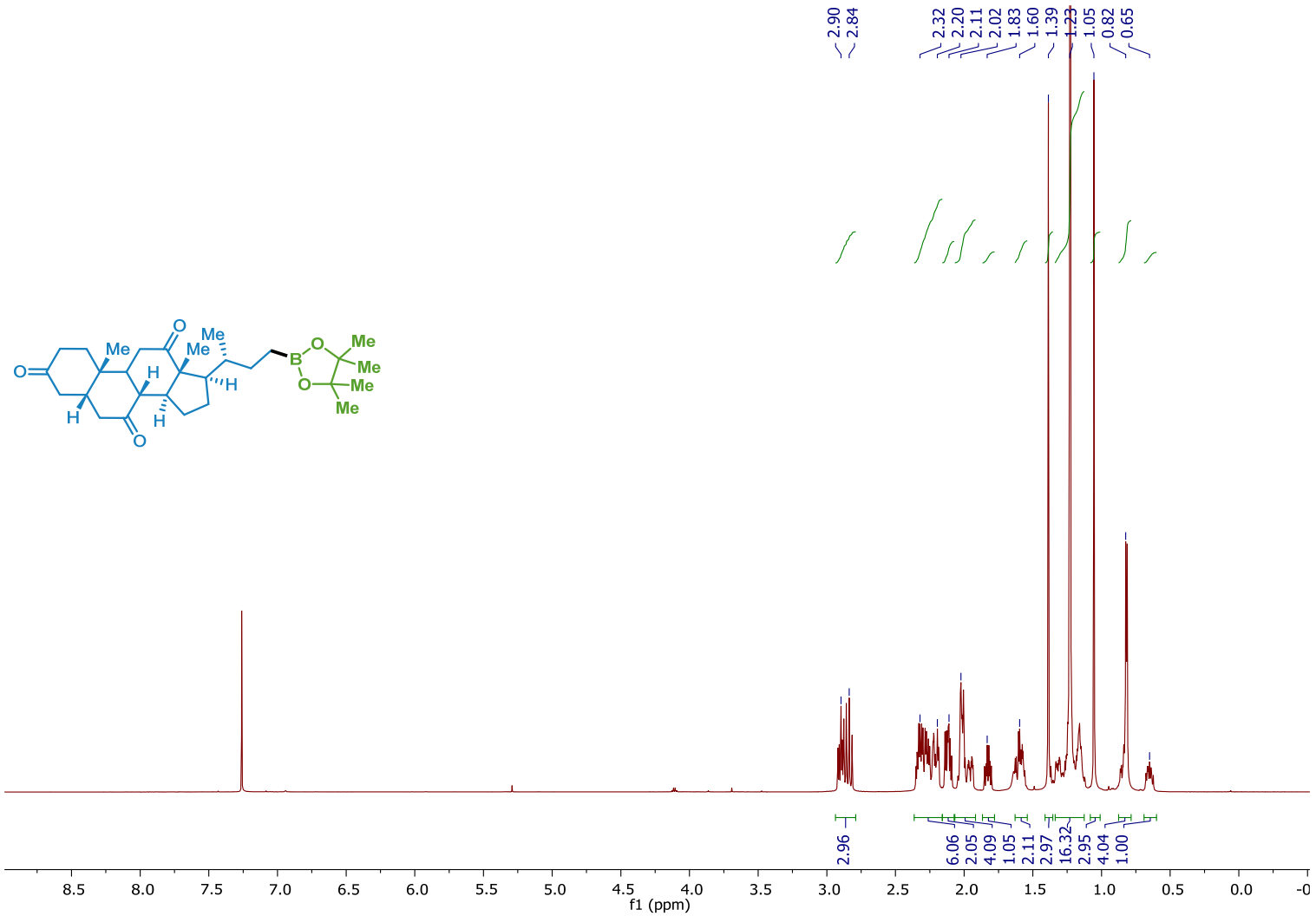
**Compound 37 $^{1}$H NMR**



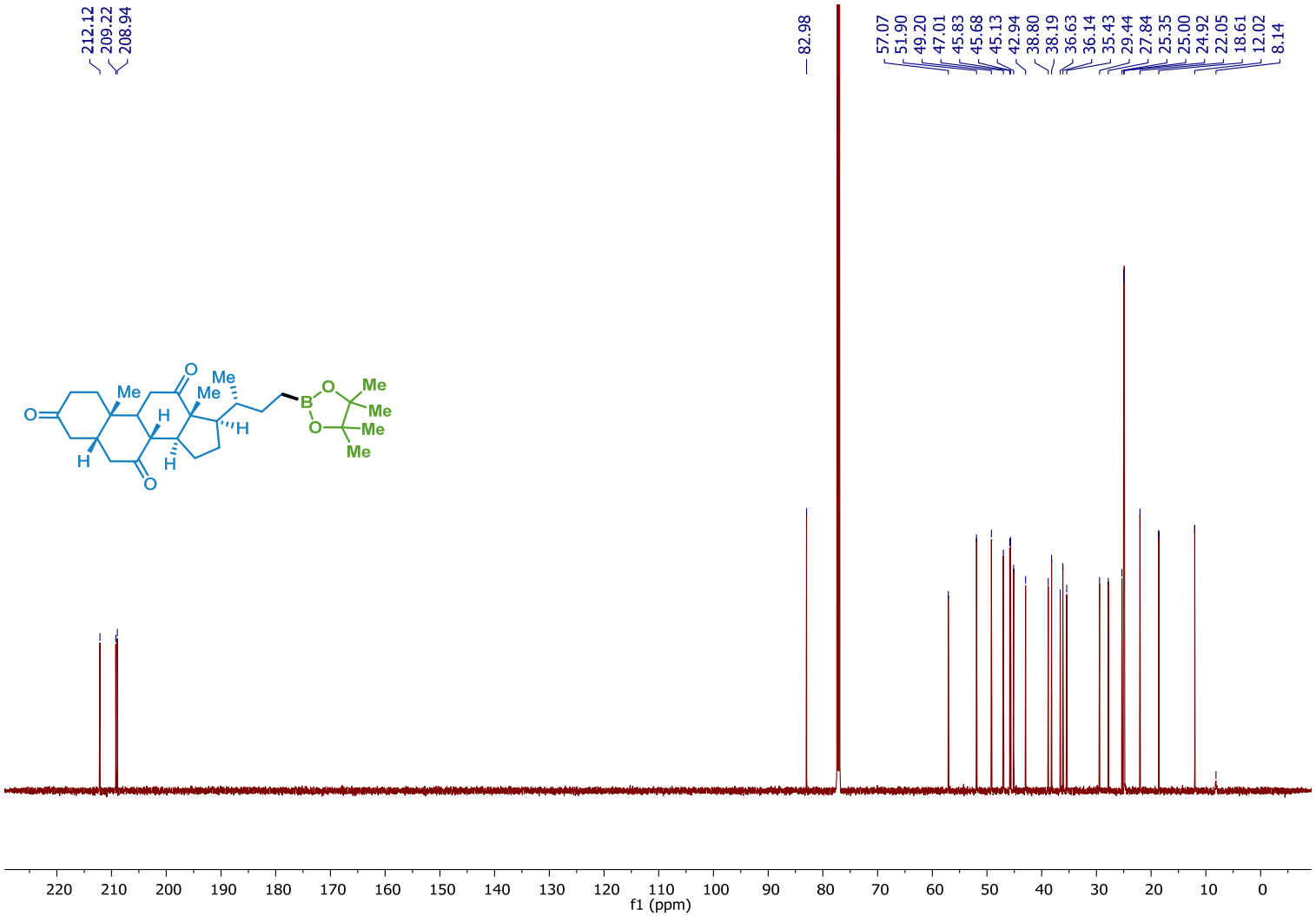
**Compound 37 $^{13}$C NMR**



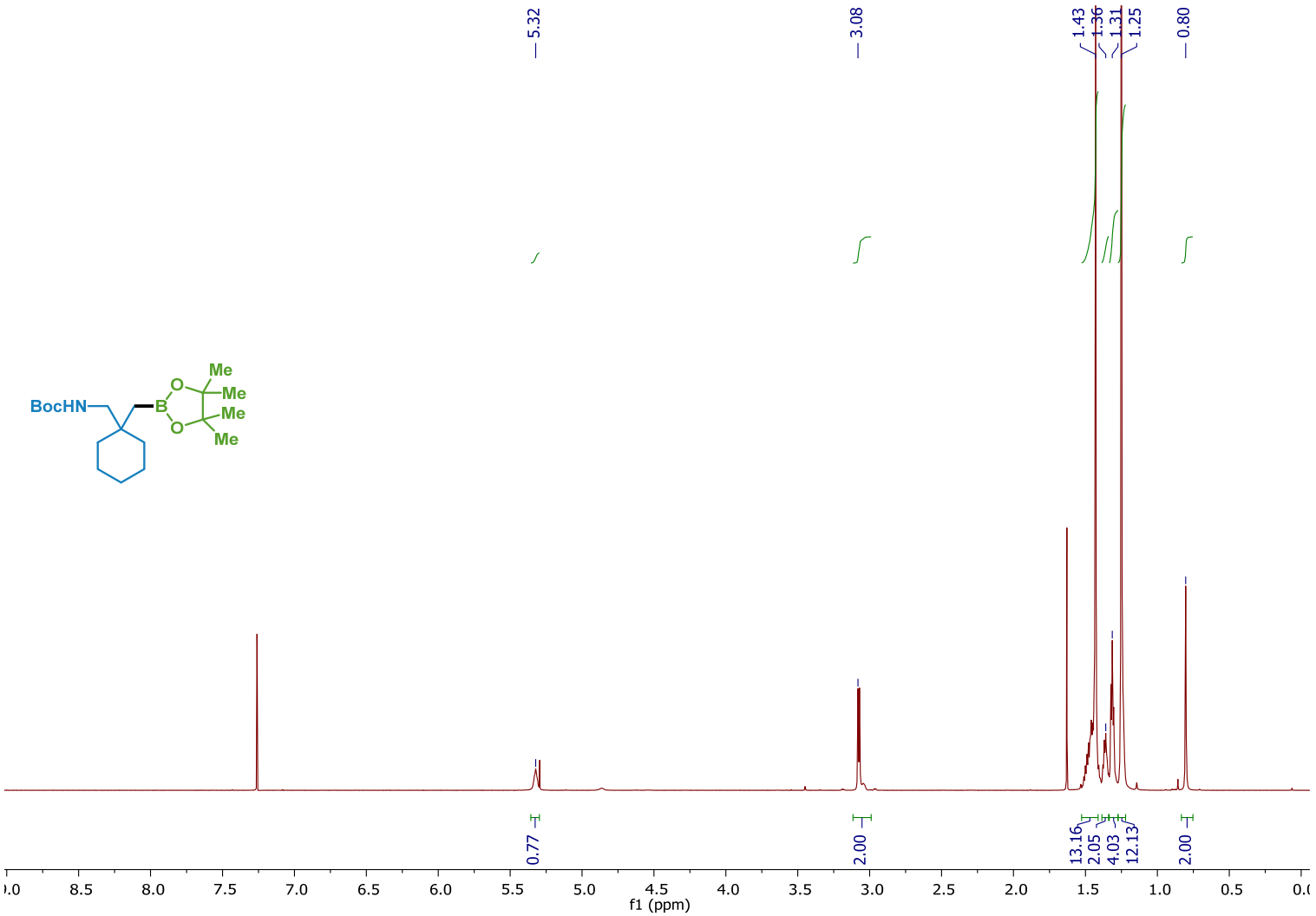
**Compound 38 $^{1}$H NMR**



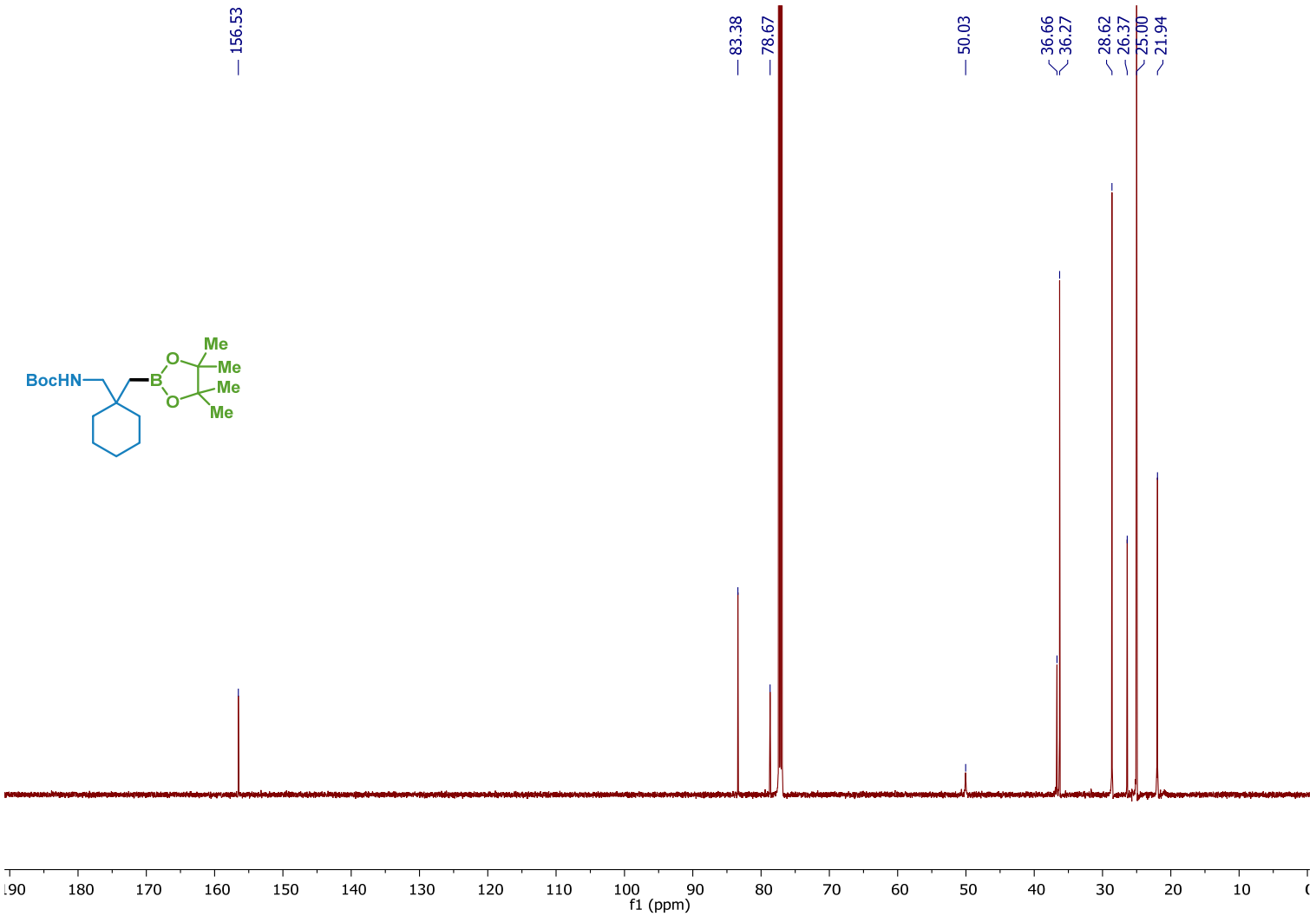
**Compound 38 $^{13}$C NMR**



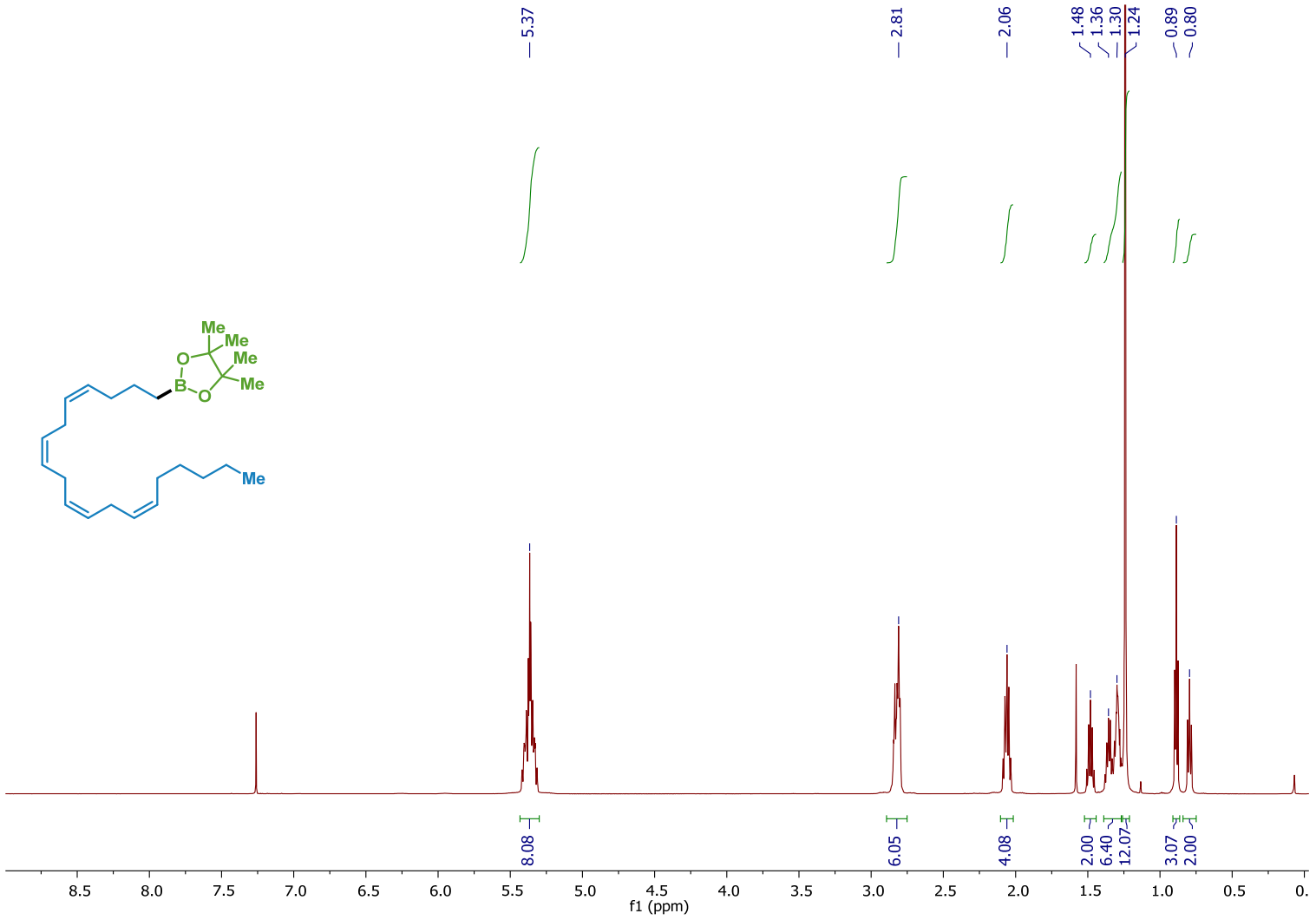
**Compound 39 $^{1}$H NMR**



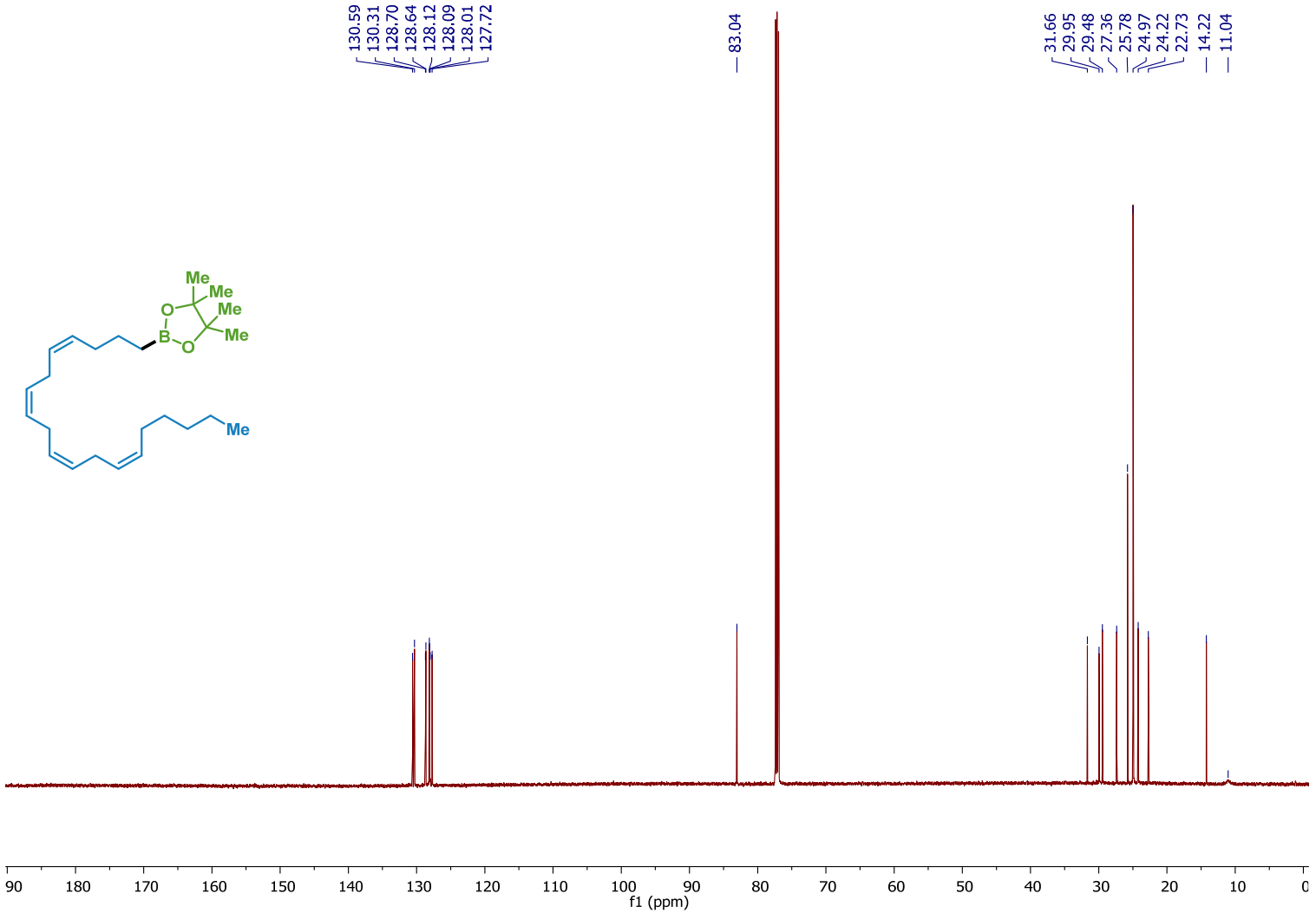
**Compound 39 $^{13}$C NMR**



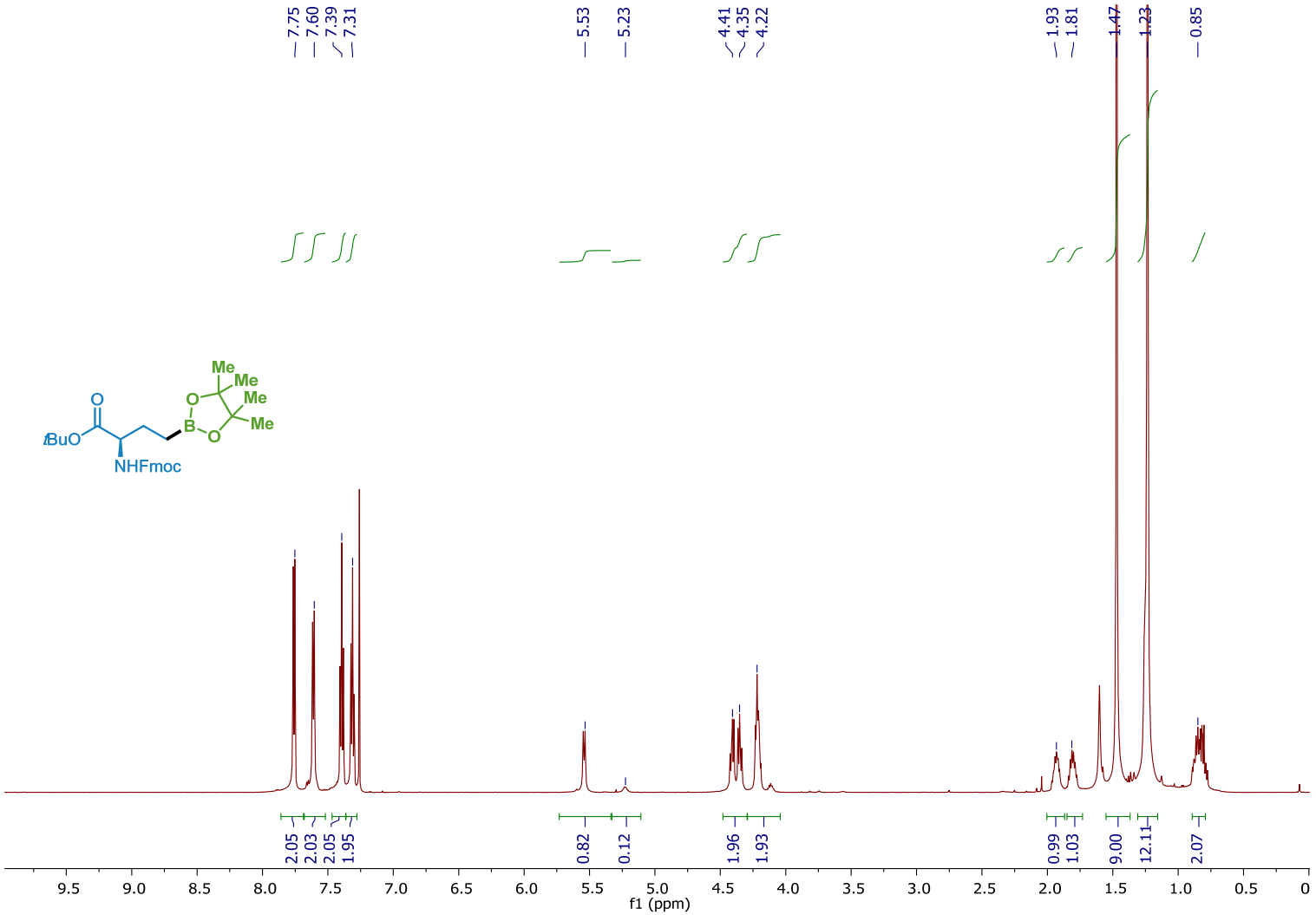
**Compound 40 $^{1}$H NMR**



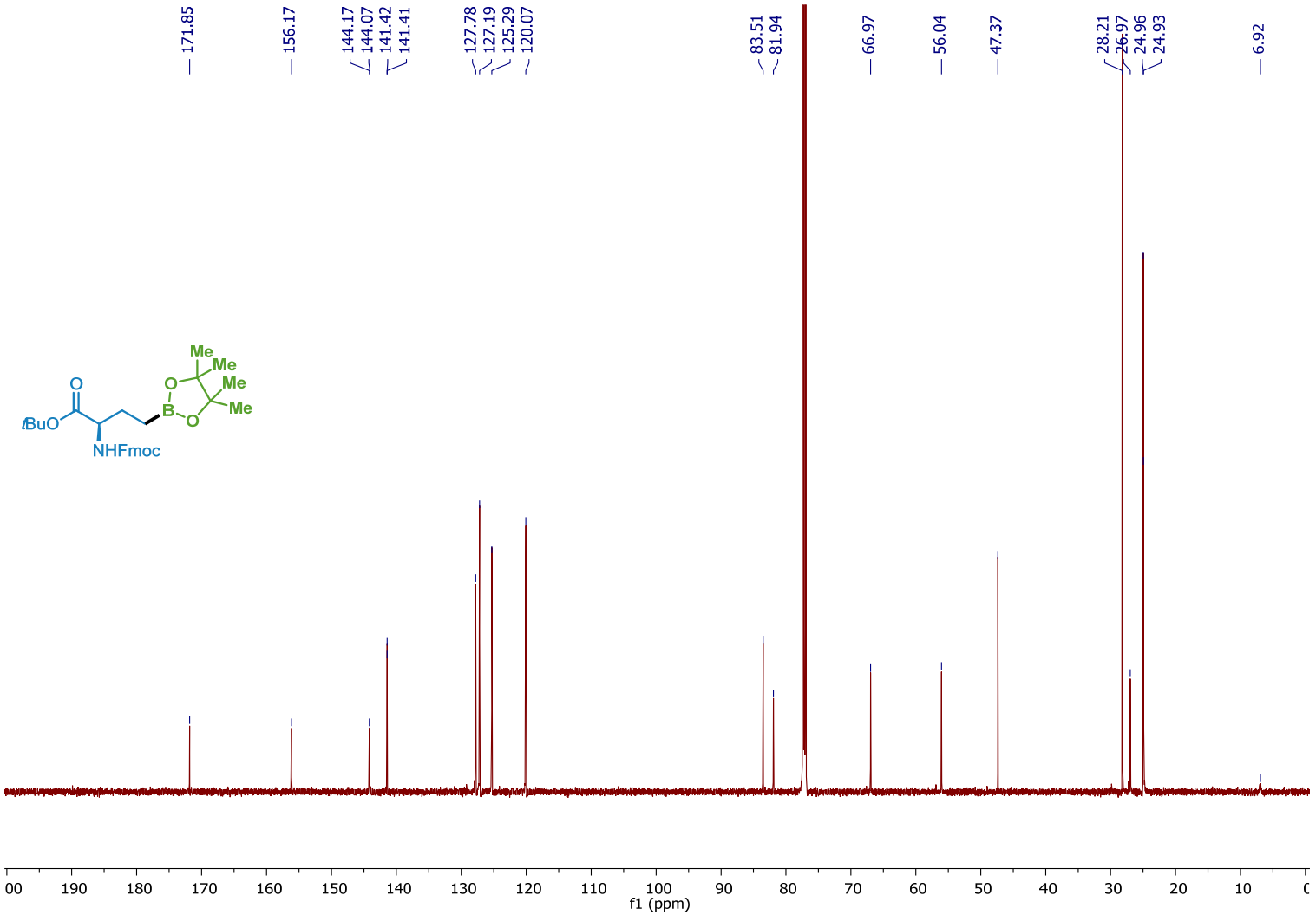
**Compound 40 $^{13}$C NMR**



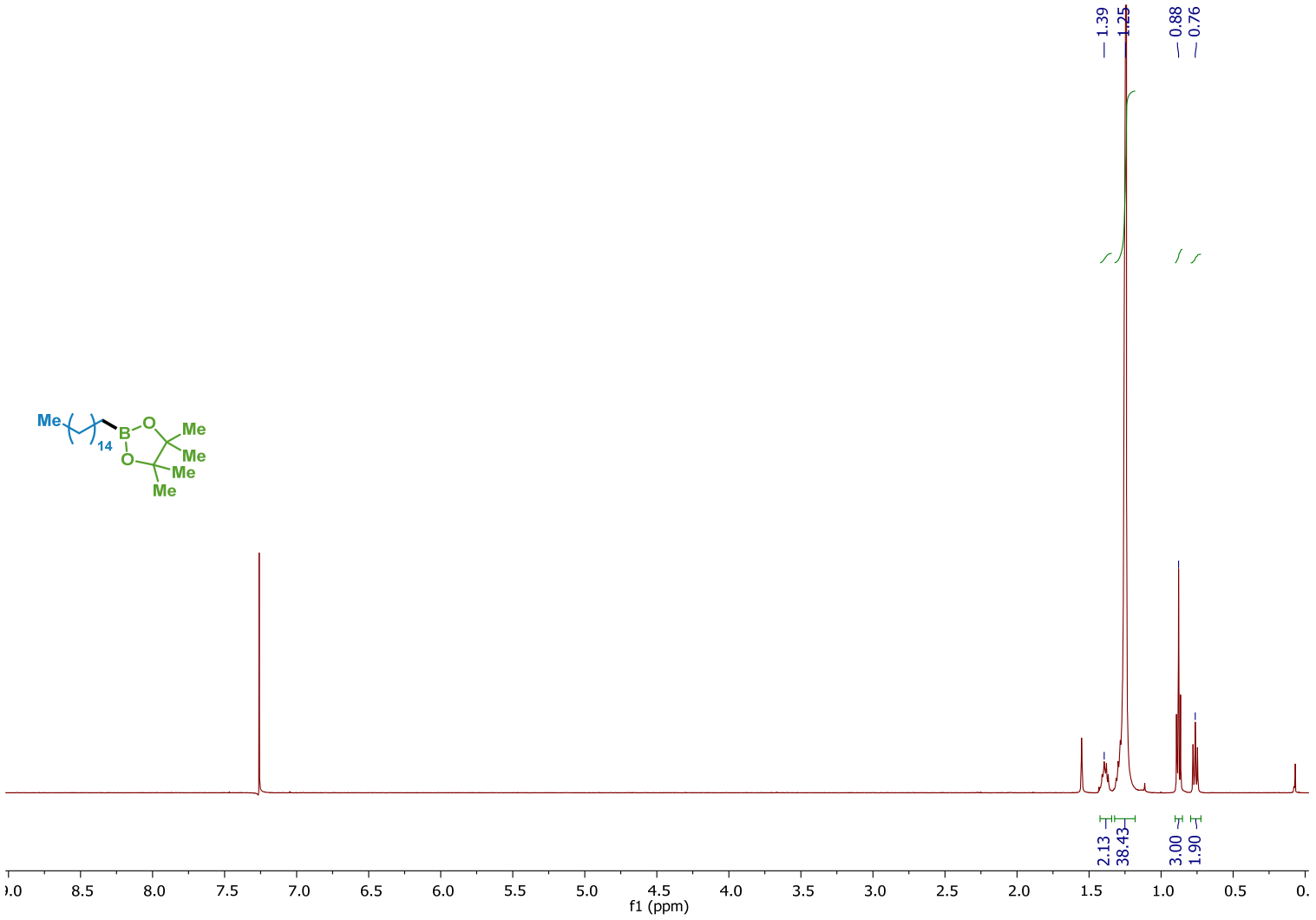
**Compound 41 $^{1}$H NMR**



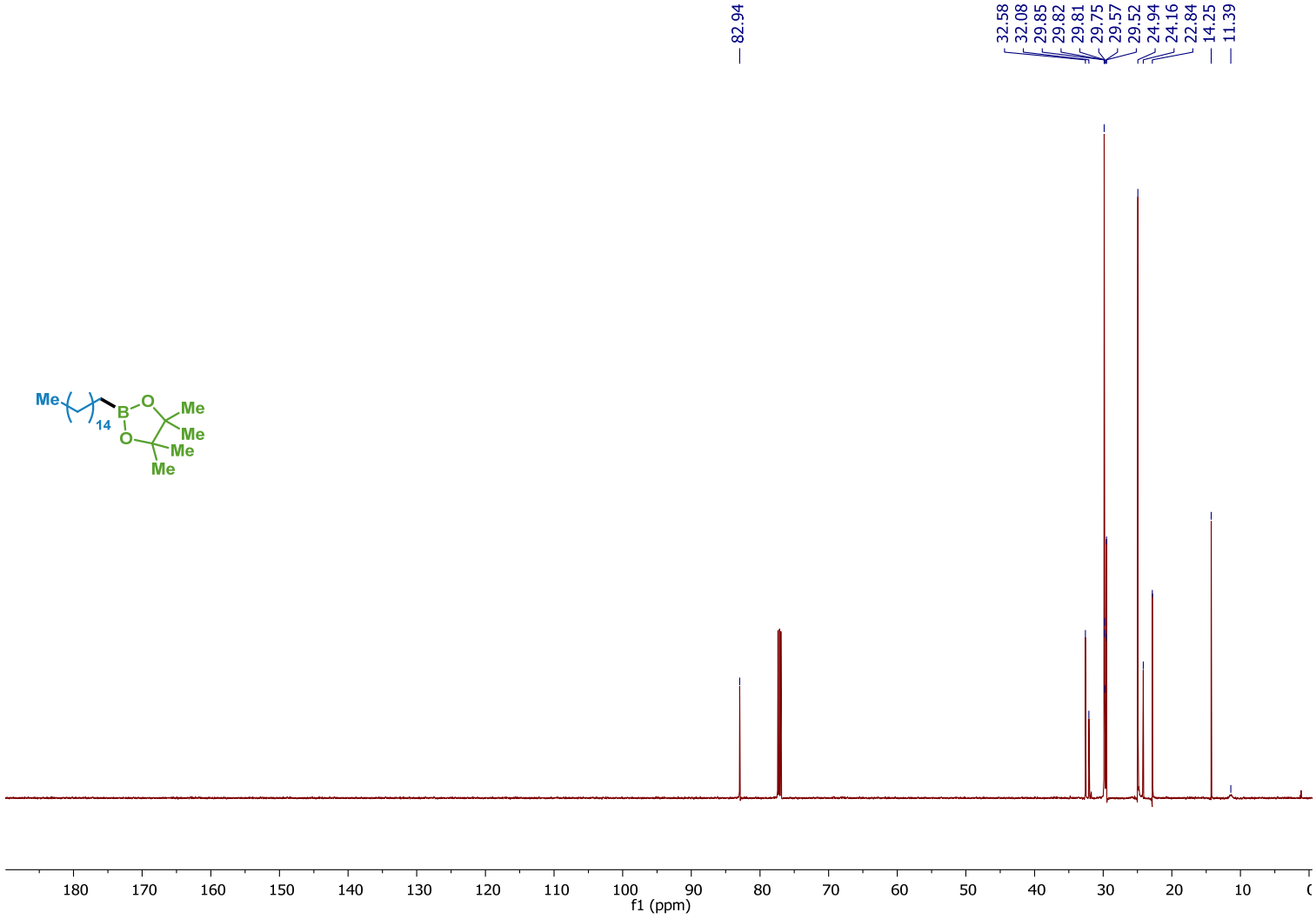
**Compound 41 $^{13}$C NMR**



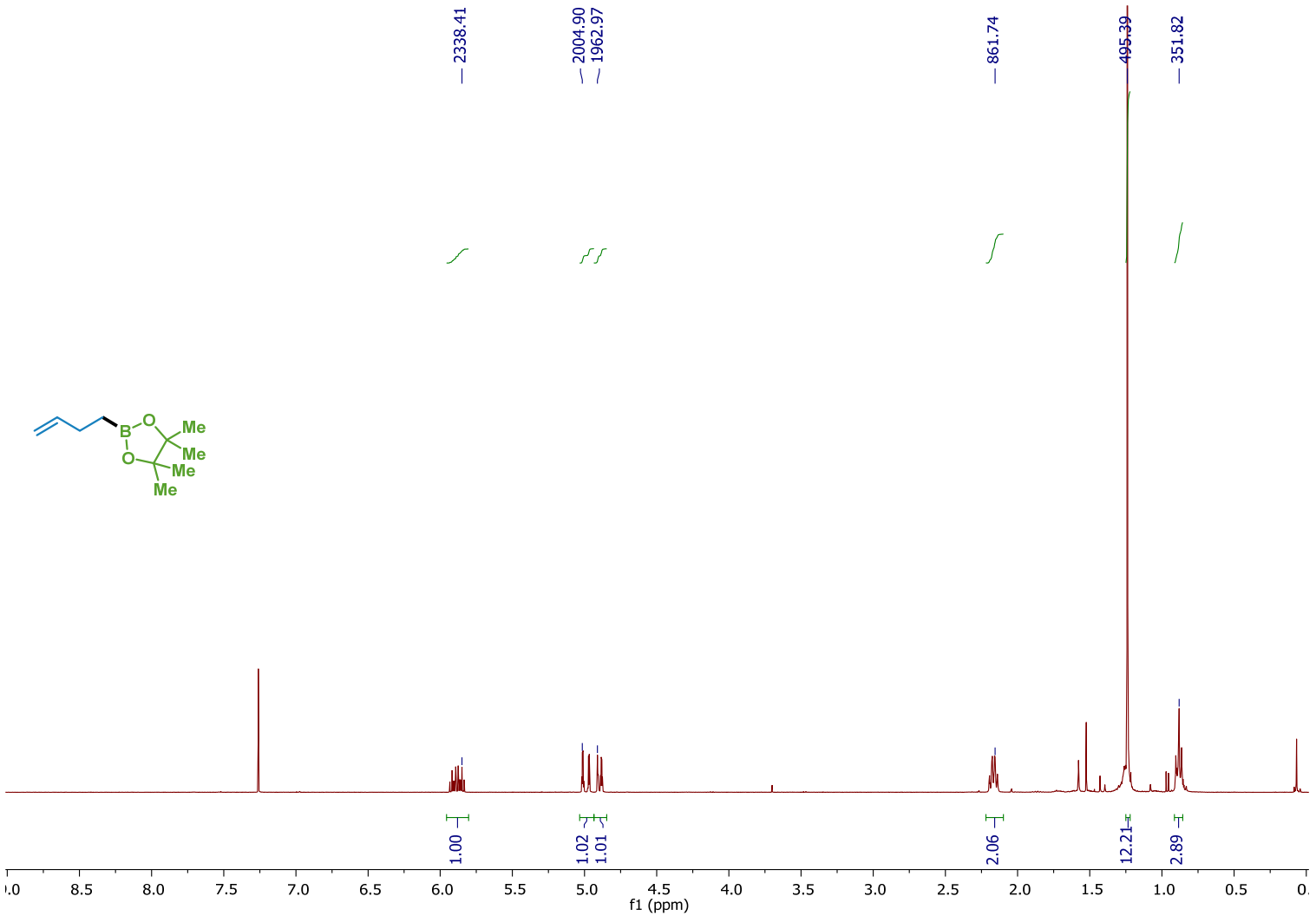
**Compound 42 $^{1}$H NMR**



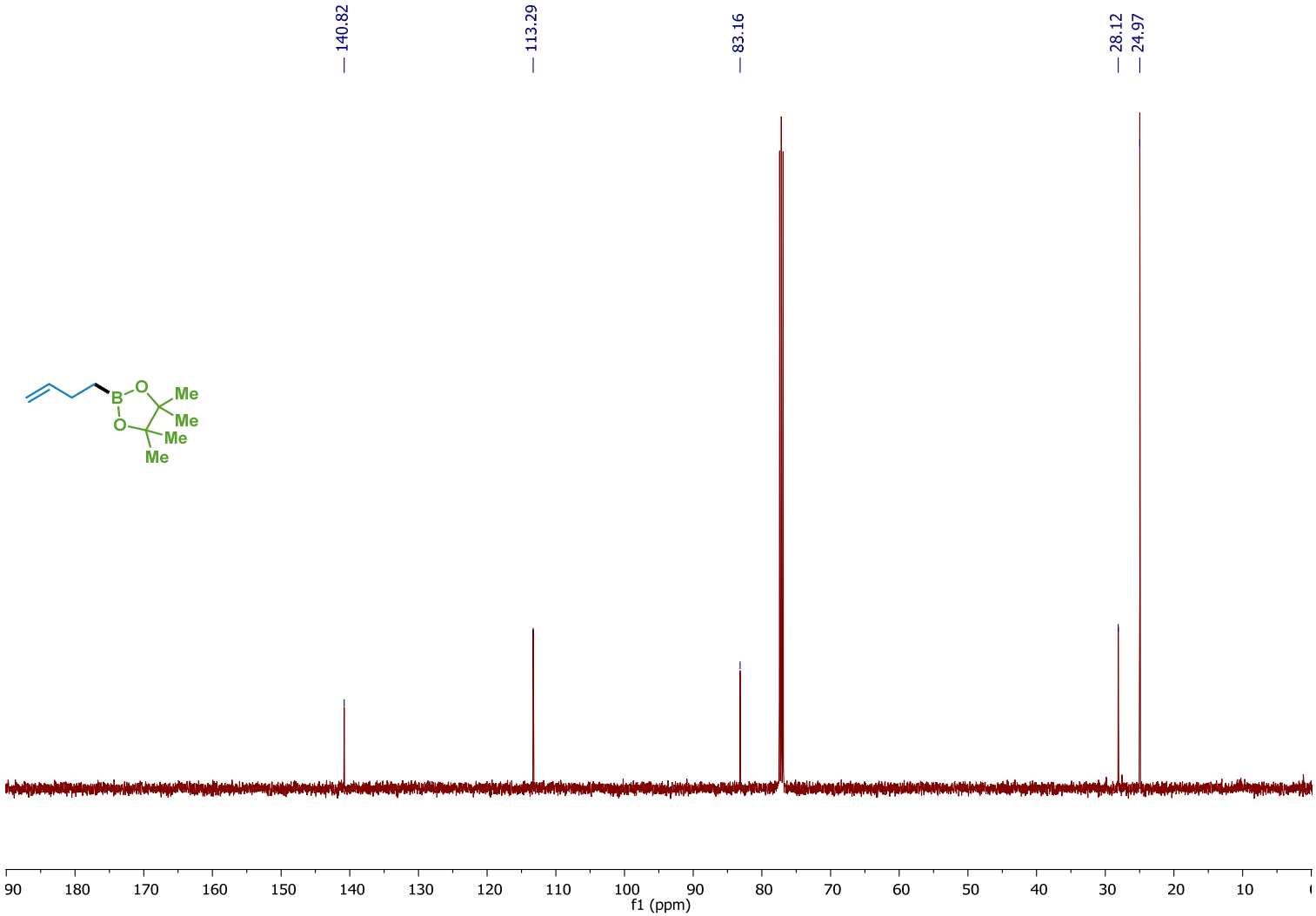
**Compound 42 $^{13}$C NMR**



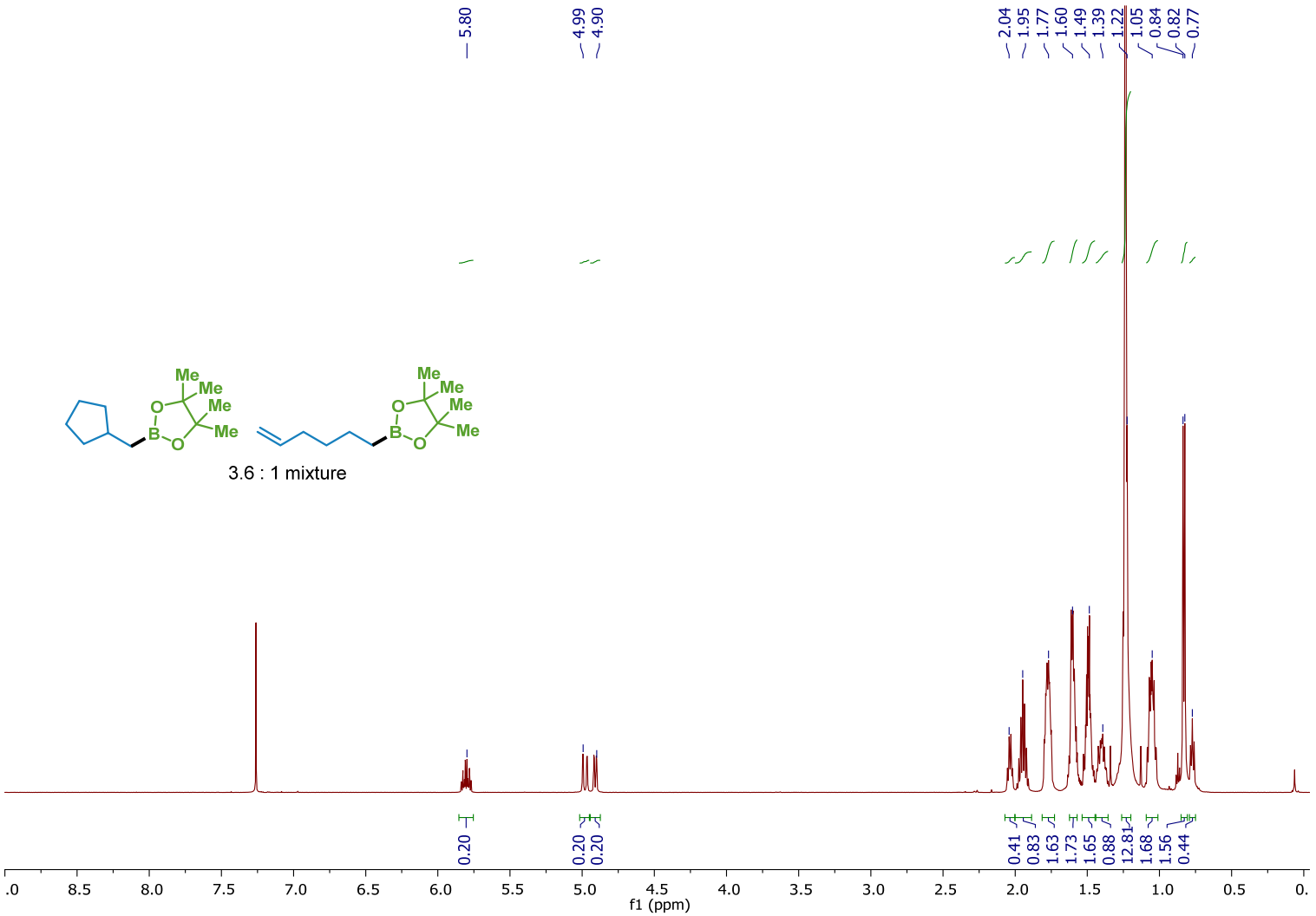
**Compound 48 $^{1}$H NMR**



**Compound 48 $^{13}$C NMR**



**Mixture 49 $^{1}$H NMR**



**Mixture 49 $^{13}$C NMR**