Supplementary Materials for

Iron-Nickel Dual-Catalysis: A New Engine for Olefin Functionalization and the Formation of Quaternary Centers

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Contents

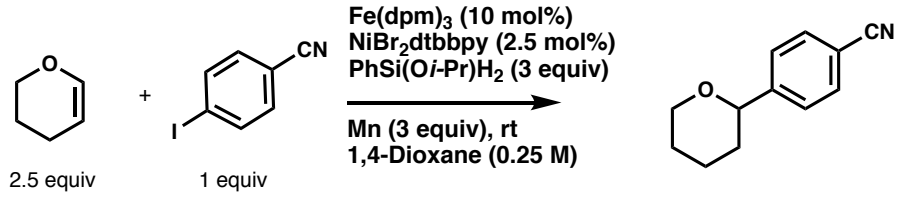
Materials and Methods

1,4-dioxane (ACS grade), hexanes (ACS grade), diethyl ether (anhydrous ACS grade), and pentanes (ACS grade) were purchased from Fisher Chemical and used without further purification. The olefins and aryl iodides listed below were purchased from the listed suppliers. Reactions were monitored via GC/MS analysis on Agilent 7820A/5975 GC/MSD system with helium as a carrier gas. Additionally, reactions were monitored by thin layer chromatography (TLC) using precoated silica gel plates from EDM Chemicals (TLC Silica gel 60 F254, 250 mm thickness). Flash column chromatography was performed over Silica gel 60 (particle size 0.04-0.063 mm) from EDM Chemicals. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DPX-400, Bruker DPX-500 or Bruker DPX-600 (equipped with cryoprobe) spectrometers using residual solvent peaks as an internal standard ($CDCl_3$ @ 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR). NMR data are denoted with apparent multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, and combinations thereof.

Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. Commercially available substrates were purchased from Sigma, Aldrich, Fluka, Oakwood, TCI Chemicals, Alfa Aesar, Fischer, Matrix Scientific, Combi-Blocks, ArK Pharm, Astatech. 1,2-Dichloroethane was obtained from Sigma, distilled from CaH_2, and stored over 4 Å molecular sieves on an argon atmosphere. *N*-Methylpyrrolidine was purchased from Aldrich, anhydrous, 99.5%. $NiBr_2$(diglyme) was obtained from Aldrich. Manganese powder was purchased from Aldrich, 325 Mesh, ≥ 99% trace metals basis. MnO_2 was obtained from Fluka, activated, ≥ 90% (RT) ≤ 1.5% loss on drying.

Optimization tables:

Table S1. Sec-alkyl conditions:[A]

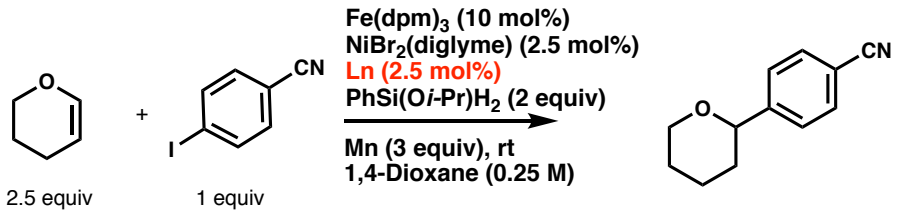


2.5 equiv 1 equiv

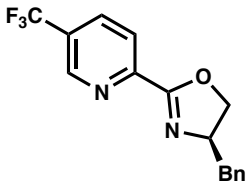
Entry	Deviations from Standard Conditions	Yield (%)[B]
1	none	81
2	no $Fe(dpm)_3$	none
3	no $NiBr_2$dtbbpy	none
4	no dtbbpy	< 5
5	no Mn	< 5
6	THF instead of 1,4-Dioxane	24
7	$Fe(acac)_3$	29
8	$Fe(dibm)_3$	61
9	$Mn(dpm)_3$	< 5
10	$Co(acac)_2$	none
11	Zn instead of Mn	< 5
12	$PhSiH_3$/EtOH	31
13	under Ar	9
14	ArBr instead of ArI	30

A: Reactions were carried out following general procedure A on a 0.10 mmol scale. B: Yields were determined by GC-FID using dodecane as internal standard.

Table S2. Ligand screen sec-alkyl conditions:[A]

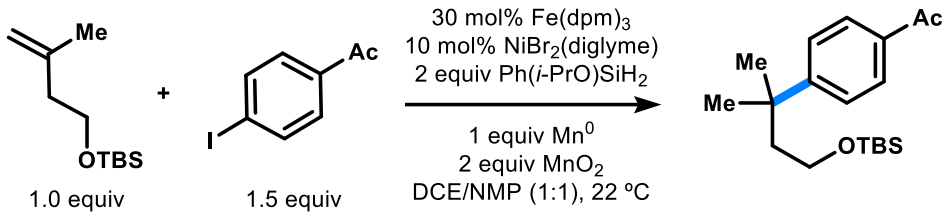


2.5 equiv 1 equiv

Entry	Ligand	Yield (%)[B]
1	none	1
2	dtbbpy	56
3	1,10-phenanthroline	9
4	bipy	8
5	4,4-OMe-2,2-bipy	13
6		7

A: Reactions were carried out following general procedure A on a 0.10 mmol scale. B: Yields were determined by GC-FID using dodecane as internal standard.

Table S3. Screening of *tert*-alkyl conditions[A]



Entry	Deviation from Standard Conditions	Yield (%)[B]
1	none	68
2	10 mol% $NiBr_2$(dtbbpy)	none
3	No NMP	none
4	No MnO_2	20
5	1 equiv H_2O	none
5	5 mol% $NiBr_2$(diglyme)	54
6	No $Fe(dpm)_3$	none
7	No $NiBr_2$(diglyme)	none
8	No Mn	none
9	1 equiv Ph(*i*-PrO)SiH_2	28
10	1 equiv MnO_2	54
11	10 mol% $Fe(dpm)_3$	20
12	2 equiv Mn	43
13	Open to air since start	23

A: Reactions were carried out following general procedure B on a 0.10 mmol scale. B: Yields were determined by GC-FID using dodecane as internal standard.

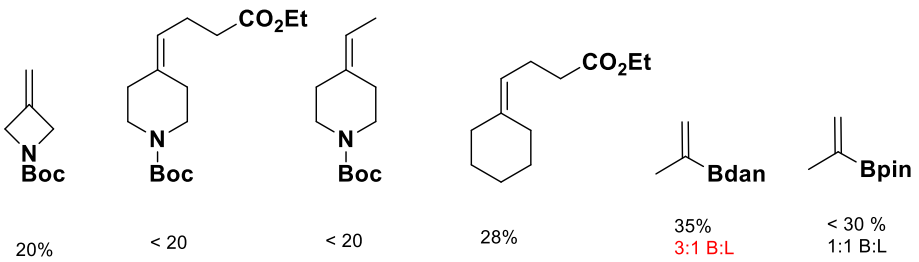
Comment on the silanes:

Other commercially available silanes, such as DEMS, triethyl silane, diphenyl silane, PMHS did not catalyze the HAT. Phenylsilane was also unsuccessful, however in the presence of alcoholic solvents, $PhSiH_3$ has been proposed to form $Ph(OR)SiH_2$ in situ. $PhSiH_3$/OEt and $PhSiH_3$/i-PrOH were both able to be used in place of $Ph(i\text{-}PrO)SiH_2$ for the *sec*-alkyl conditions with reduced yields (31% and 41% respectively). Alcoholic solvent:$PhSiH_3$ was employed in a 2:1 ratio. Overall, the alcoholic solvents contributed to a higher amount of protodehalogenation, which was observed in a larger extent at elevated temperatures (60 °C).

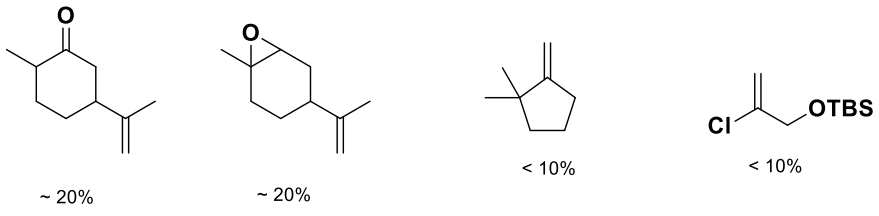
Under the *tert*-alkyl conditions, $PhSiH_3$/*i*-PrOH had a significant deterioration in yield with only 15% of the product obtained. Again, at elevated temperatures, the reaction was significantly hindered, yielded only traces of product.

Limitations of the methodology

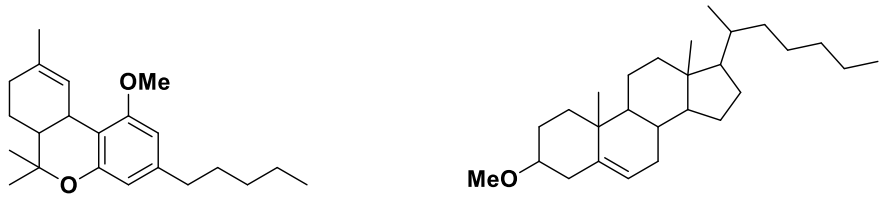
Other explored olefins



20% | < 20 | < 20 | 28% | 35% 3:1 B:L | < 30 % 1:1 B:L

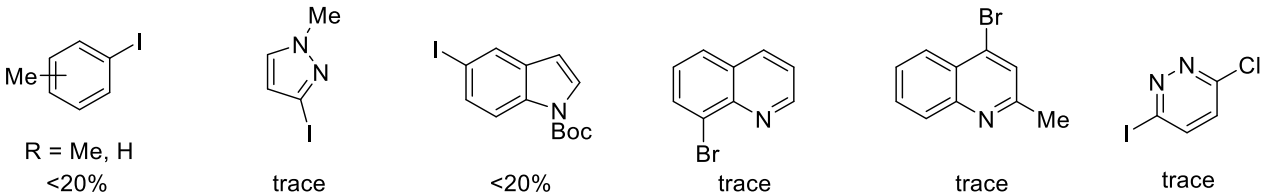


~ 20% | ~ 20% | < 10% | < 10%



sluggish HAT | sluggish HAT
Hydration > hydrogenation

Aryl halides

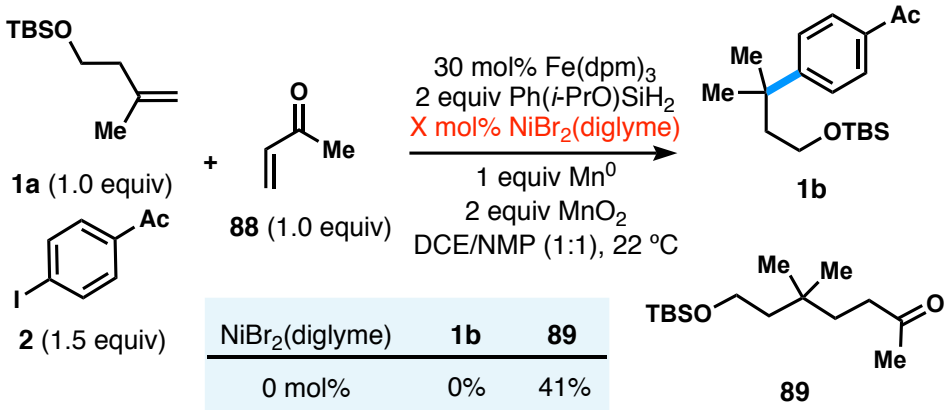


R = Me, H <20% | trace | <20% | trace | trace | trace

Further Radical experiments for tertiary conditions:

Competition Giese Reaction:

Olefins are known to engage with Fe-H in HAT reactions with the resulting carbon-centered radical subsequently participating in a Giese reaction with Michael acceptors (such as methyl vinyl ketone (MVK) **89**).[1] To probe if the olefin would participate in known Giese behavior under our reaction conditions, MVK was added to the reaction both in the presence and absence of nickel (below). In both cases, Giese product was observed. In the absence of nickel no desired arylation product was observed.

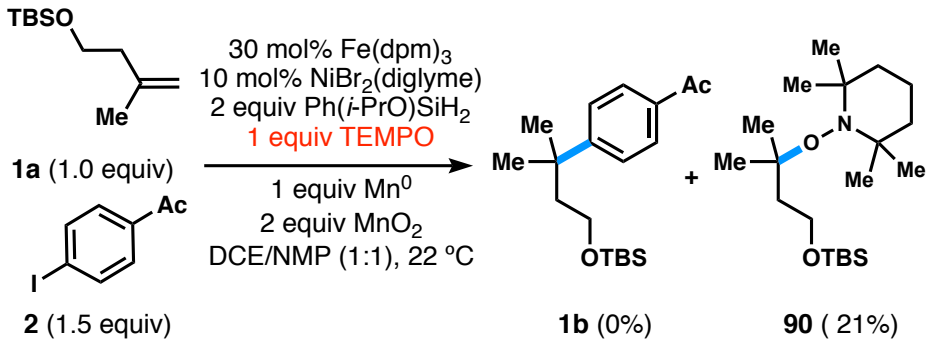


$NiBr_2$(diglyme)	1b	89
0 mol%	0%	41%
10 mol%	31%	33%

Procedure:

Adapted from general procedure B, a 1-dram vial equipped with a stir bar was charged with $Fe(dpm)_3$ (18.2 mg, 0.03 mmol, 30 mol%), Mn^0 powder (5.5 mg, 0.1 mmol, 1.0 equiv), $NiBr_2$(diglyme) (3.5 mg, 0.01 mmol, 10 mol%), and 4-iodoacetophenone (39 mg, 0.15 mmol, 1.5 equiv). The 1-dram vial was placed under an N_2 balloon and the system was vented for 10 minutes. Anhydrous 1,2-DCE (0.5 mL) was added, followed by the olefin **1a** (25 μL, 0.1 mmol, 1.0 equiv). Anhydrous NMP (0.5 mL) was added and the reaction was vigorously stirred (RPM over 1050) for 1.5 hours at room temperature during which time a color change was observed from bright red to light brown. After 1.5 h, the N_2 balloon and septum were removed and methyl vinyl ketone (10 μL, 0.1 mmol, 1 equiv) and activated MnO_2 (52.5 mg, 0.6 mmol, 2.0 equiv) was added. The septum was placed back into the neck of the round bottom and an air balloon was placed into the system (due to the volatility of MVK). The first portion of Ph(*i*-PrO)SiH_2 (18 μL, 0.1 mmol, 1 equiv) was added and the reaction was stirred vigorously for 1 h at room temperature. After 1 h, a second portion of Ph(*i*-PrO)SiH_2 (18 μL, 0.1 mmol, 1.0 equiv) was added and the reaction was stirred for an additional 15 h at room temperature. Upon completion, the reaction was filtered through a pad of silica and eluted with EtOAc (20 mL). The reaction was then washed with 10% NaCl (3 x 5 mL), and dried over $MgSO_4$. The solvent was removed *in vacuo* and the product was purified via flash column chromatography. Spectroscopic data matched with reported literature.[2]

TEMPO Trapping:



Procedure:
Adapted from general procedure B, a 1-dram vial equipped with a stir bar was charged with $Fe(dpm)_3$ (18.2 mg, 0.03 mmol, 30 mol%), Mn^0 powder (5.5 mg, 0.1 mmol, 1.0 equiv), $NiBr_2$(diglyme) (3.5 mg, 0.01 mmol, 10 mol%), and 4-iodoacetophenone (39 mg, 0.15 mmol, 1.5 equiv). The 1-dram vial was placed under an N_2 balloon and the system was vented for 10 minutes. Anhydrous 1,2-DCE (0.5 mL) was added, followed by the olefin **1a** (25 μL, 0.1 mmol, 1.0 equiv). Anhydrous NMP (0.5 mL) was added and the reaction was vigorously stirred (RPM over 1050) for 1.5 hours at room temperature during which time a color change was observed from bright red to light brown. After 1.5 h, the N_2 balloon and septum were removed and TEMPO (15.6 mg, 0.1 mmol, 1 equiv) and activated MnO_2 (52.5 mg, 0.6 mmol, 2.0 equiv) was added. The septum was placed back into the neck of the round bottom and a 20G 1x ½ needle was placed through the septum. The first portion of PhSi(*i*-PrO)H_2 (18 μL, 0.1 mmol, 1 equiv) was added and the reaction was stirred vigorously for 1 h at room temperature. After 1 h, a second portion of Ph(*i*-PrO)SiH_2 (18 μL, 0.1 mmol, 1.0 equiv) was added and the reaction was stirred for an additional 15 h at room temperature. Upon completion, the reaction was filtered through a pad of silica and eluted with EtOAc (20 mL). The reaction was then washed with 10% NaCl (3 x 5 mL), and dried over $MgSO_4$. The solvent was removed *in vacuo* and the product was purified via flash column chromatography.

Rf: 0.3 (100% hexanes), anisaldehyde

^{1}H NMR: (600 MHz, $CDCl_3$) δ 3.83 (t, *J* = 7.9 Hz, 2H), 1.88 (t, *J* = 7.7, Hz, 2H), 1.60 – 1.37 (m, 6H), 1.28 (s, 6H), 1.11 (s, 6H), 1.06 (s, 6H), 0.90 (s, 9H), 0.07 (s, 6H);

^{13}C NMR: (151 MHz, $CDCl_3$) δ 78.31, 60.21, 59.33, 46.33, 41.01, 34.91, 27.56, 26.18, 20.79, 17.29, -5.02.

LCMS: found (*M* + *H*) 358.3. $C_{20}H_{43}NO_2Si$ requires *M* + *H*, 358.31.

General Procedure A

A flame-dried large culture tube (20 x 125 mm, Fisherbrand) containing stir bar (15.9 x 6.35 mm, egg-shaped, Fisherbrand), cap and septum was charged with aryl iodide (0.3 mmol, 1.0 equiv), $Fe(dpm)_3$ (18.2 mg, 0.030 mmol, 0.1 equiv), $NiBr_2$(dtbbpy) (3.6 mg, 0.0075 mmol, 0.025 equiv), Mn^0 (49.0 mg, 0.90 mmol, 3.0 equiv) and olefin (if solid 0.75 mmol, 2.5 equiv). The reaction was attached to a high-vac manifold, evacuated and backfilled with nitrogen (3 cycles). The reaction was removed from the manifold and placed under an N_2 balloon before being charged with anhydrous 1,4-dioxane (1.0 mL), olefin (if liquid: 2.5 equiv., 0.75 mmol) and Ph(*i*-PrO)SiH_2 (166.0 μL, 0.9 mmol, 3.0 equiv). The reaction was stirred vigorously (>800 RPM) at room temperature for 2 h, after which time the reaction was exposed to air by removing the N_2 balloon and placing a 20G 1x ½ needle through the septum to equilibrate the system. (Note: since oxygen is crucial for a successful reaction, the septum can be removed for a short time ~1 min and replaced to allow for a faster equilibration, however we have found that a vent needle is generally sufficient). The reaction was stirred until complete consumption of the aryl iodide as measured by TLC or GC-MS. The reaction was filtered through a pad of silica and eluted with EtOAc (20 mL). The solvent was removed *in vacuo* and the resulting residue was purified by flash column chromatography to yield the pure desired product.

General Notes about the system:

1) When argon is used in place of nitrogen, the equilibration to an air atmosphere was often sluggish and incomplete. Nitrogen is the preferred inert gas for the 2 h induction period.

2) Due to the heterogeneity of the reaction, turbulent stirring was necessary to ensure equal distribution of the Mn^0 powder as well as oxygen consumption.

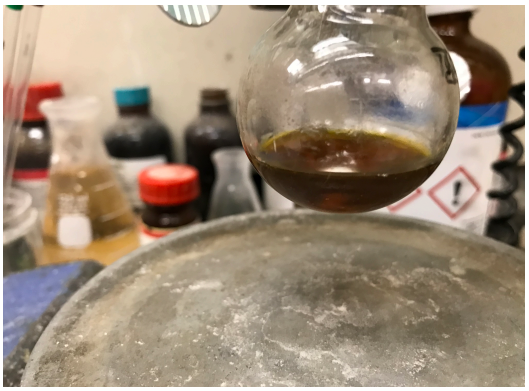
General Procedure B

A flame-dried 25 mL round bottom flask equipped with a stir bar was charged with $Fe(dpm)_3$ (54.5 mg, 0.09 mmol, 30 mol%), Mn^0 powder (16.5 mg, 0.3 mmol, 1.0 equiv), $NiBr_2$(diglyme) (10.6 mg, 0.03 mmol, 10 mol%), olefin (if solid: 0.3 mmol, 1.0 equiv), and aryl iodide (if solid: 0.45 mmol, 1.5 equiv). The flask was attached to a high-vac manifold, evacuated and backfilled with nitrogen (3 cycles). The flask was removed from the manifold, quickly equipped with septum and placed under N_2 (balloon). Anhydrous 1,2-DCE (1.5 mL) was added, followed by the olefin (0.3 mmol, 1.0 equiv) or aryl iodide (0.45 mmol, 1.5 equiv) if liquid. Anhydrous NMP (1.5 mL) was added and the reaction was vigorously stirred (RPM over 1050) for 1.5 hours at room temperature during which time a color change was observed from bright red to light brown (see pictures below). After 1.5 h, the N_2 balloon and septum were removed and activated MnO_2 (52.5 mg, 0.6 mmol, 2.0 equiv) was added. The septum was placed back into the neck of the round bottom and a 20G 1x ½ needle was placed through the septum. The first portion of PhSi(*i*-PrO)H_2 (54 μL, 0.3 mmol, 1 equiv) was added and the reaction was stirred vigorously for 1 h at room temperature. After 1 h, a second portion of Ph(*i*-PrO)SiH_2 (54 μL, 0.3 mmol, 1.0 equiv) was added and the reaction was stirred for an additional 15 h at room temperature. Upon completion, the reaction was filtered through a pad of silica and eluted with EtOAc (20 mL). The reaction was then washed with 10% NaCl (3 x 5 mL), and dried over $MgSO_4$. The solvent was removed *in vacuo* and the product was purified via flash column chromatography.

NOTE: In the case of some non-polar substrates, a silane-dpm byproduct was observed (^{1}H NMR peaks: 4.87 (s), 1.27 (s), 1.21 (s)). This impurity could be removed by dissolving the product in 1 mL THF (stabilized by BHT) and 1 mL 5 M NaOH and stirring vigorously overnight. The product could then be extracted with ethyl acetate and dried over Na_2SO_4 to yield the clean product after concentration.

Beginning of reaction:

After 1.5 hour:



Color change: All of our successful reactions had the color change observed above. When the reaction was left under air for the induction period (1.5 h), this color change was not observed and the yield was significantly worse (see optimization tables). Additionally, insufficient stirring was also observed to prevent this color change and resulted in poor yielding reactions.

Stirring and stir bars: The stirring was found to be extremely important for achieving reproducible reactions: vigorously at over 1050 RPM was necessary. To allow for an even distribution of Mn^0 powder throughout the reaction medium, we found that large stir bars (size for this scale: 15.9 x 6.35 mm, egg-shaped, Fisherbrand) were necessary. Similarly, performing the reaction in a round bottom flask allowed for a better suspension of Mn^0. Reactions done in culture tubes (20 x 125 mm, Fisherbrand) were generally poorer yielding and did not observe the above color change (~10-20% lower in yield).

Reactions on 0.1 mmol scale could be run in a 1-dram vial or a 10 mL round bottom with similar efficiency.

In the case of volatile olefins, an air balloon can be used in place of a vent needle with no deterioration in yield.

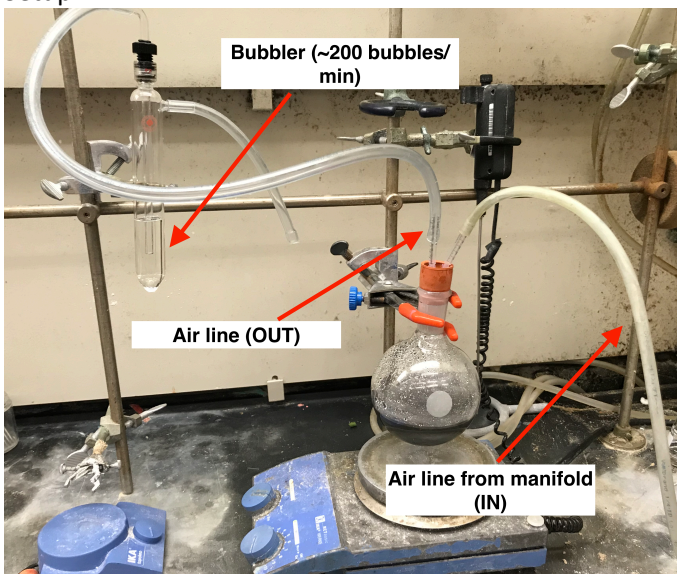
Modified procedure for gram scale reaction:

A flame-dried 500 mL round bottom flask equipped with a stir bar was charged with $Fe(dpm)_3$ (908 mg, 1.5 mmol, 30 mol%), Mn^0 powder (275 mg, 5 mmol, 1.0 equiv), $NiBr_2$(diglyme) (176.4 mg, 0.5 mmol, 10 mol%), and 4-iodoacetophenone (1.845 g, 7.5 mmol, 1.5 equiv). The flask was attached to a high-vac manifold, evacuated and backfilled with nitrogen (3 cycles). The flask was removed from the manifold, quickly equipped with septum and placed under N_2 (balloon). Anhydrous 1,2-DCE (25 mL) was added, followed by the olefin **1a** (1.0 g, 5.0 mmol, 1.0 equiv). Anhydrous NMP (25 mL) was added and the reaction was vigorously stirred (RPM over 1050) for 1.5 hours at room temperature during which time a color change was observed from bright red to light brown. After 1.5 h, the N_2 balloon and septum were removed and activated MnO_2 (869 mg, 10 mmol, 2.0 equiv) was added. The septum was placed back into the neck of the round bottom and a bubbler was attached (see pictures below) to provide a constant stream of air throughout the course of the reaction. The first portion of PhSi(*i*-PrO)H_2 (922 μL, 5 mmol, 1 equiv) was added and the reaction was stirred vigorously for 1 h at room temperature. After 1 h, a second portion of Ph(*i*-PrO)SiH_2 (922 μL, 5 mmol, 1.0 equiv) was added and the reaction was stirred for an additional 15 h at room temperature. Upon completion, the reaction was filtered through a pad of silica and eluted with EtOAc (20 mL). The reaction was then washed with 10% NaCl (3 x 50 mL), and dried over $MgSO_4$. The solvent was removed *in vacuo* and the product was purified via flash column chromatography (8% EtOAc/hex) to yield **1b** (829 mg, 52%).

NOTE: The bubbler was set to ~200 bubbles/minute, which was the slowest rate we could obtain from our air line. Using this method, a noticeable amount of hydration byproduct was observed, which was absent under our standard reaction conditions and accounts for the difference in yield from 0.3 mmol scale. We anticipate that a slower air flow rate would minimize this byproduct. Using an air balloon or a vent needle in place of the bubbler resulted in incomplete consumption of the olefin starting material and a decrease in yield.

Turbulent stirring is necessary for air uptake in the solvent.

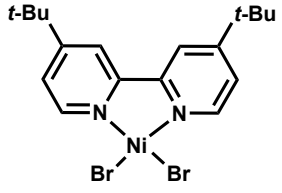
Setup:



Synthesis of $Fe(dpm)_3$

Iron(III) diipivaloylmethane. Adapted from the literature procedure,[3] 2,2,6,6-tetramethylheptane-3,5-dione (9.9 g, 53.8 mmol, 3.0 equiv), and $NaOAc•3H_2O$ (7.3 g, 53.8 mmol, 3.0 equiv) was dissolved in an aqueous solution of EtOH (1:1 EtOH:H_2O, 100 mL). $FeCl_3$ (2.9 g, 18.0 mmol, 1.0 equiv) was added and the resulting slurry was heated at 60 °C with stirring for 1 h. The slurry was cooled at room temperature over 10 min, cooled at 0 °C for 15 min, and then filtered, washing with 10 mL (9:1 EtOH/H_2O) to give an orange powder. The orange powder was dissolved in 600 mL EtOH, filtered over a cotton plug and the volatiles removed to give a red powder that was dried under high vacuum overnight and could then be used without further purification.

Synthesis of $NiBr_2$(dtbbpy)



Following the literature procedure,[4] a flame-dried 25 mL round bottom equipped with a stir bar and septum was charged with $NiBr_2$(glyme) (462.93 mg, 1.5 mmol, 1.0 equiv), and 4,4'-di-*tert*-butyl-2,2'-bipyridyl (417 mg, 1.5 mmol, 1.0 equiv) and placed under argon. Anhydrous THF (8.4 mL) was added and the reaction was stirred at room temp for 24 h. The solid was filtered off and washed with diethyl ether to afford the desired compound that was used without further purification.

Synthesis of Ph(i-PrO)SiH_2[5]

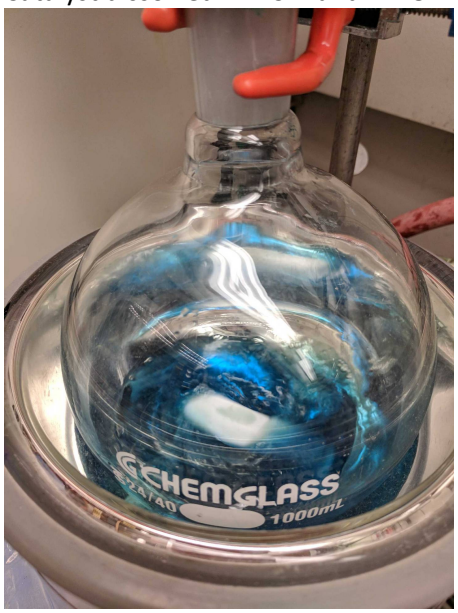
$Cu(hfac)_2 \bullet xH_2O$ was dried by heating to 80 ℃ under vacuum until dehydrated (usually 12 h) (noticeable via a color change from clover green to dark blue). A flame-dried 1 L round bottom flask equipped with stir bar and septum was charged with the $Cu(hfac)_2$ (1.43 g, 3.0 mmol, 1.5 mol%) and set under argon. Anhydrous DCM (70 mL) and anhydrous *i*-PrOH (23.11 mL, 300.0 mmol, 1.5 equiv) were added and the resulting blue solution was cooled to 0 ℃ using an ice-water bath. Phenylsilane (24.65 mL, 200.0 mmol, 1.0 equiv) was introduced in a single portion (CAUTION: gas evolution at the beginning) and the reaction was kept at 0 ℃ with stirring until 95% consumption of phenylsilane as monitored by GC-FID (usually 1.5 h). If the reaction is left stirring for a prolonged time, a larger distribution of byproducts is observed. After completion, a 150 mL of hexanes were added, the suspension was filtered through celite, and the volatiles were removed *in vacuo*. The product was isolated via distillation under reduced pressure (41–43 ℃ at 2.4 Torr, 60–62 ℃ for $Ph(i\text{-}PrO)_2SiH$ as the major byproduct). Using a 46 cm mirrored vacuum jacketed column, the distillation consistently yielded >95% pure product (see below for pictures of the reaction setup). For prolonged storage, the product was stored in a schlenk flask, under argon at -20 ℃.

Notes:

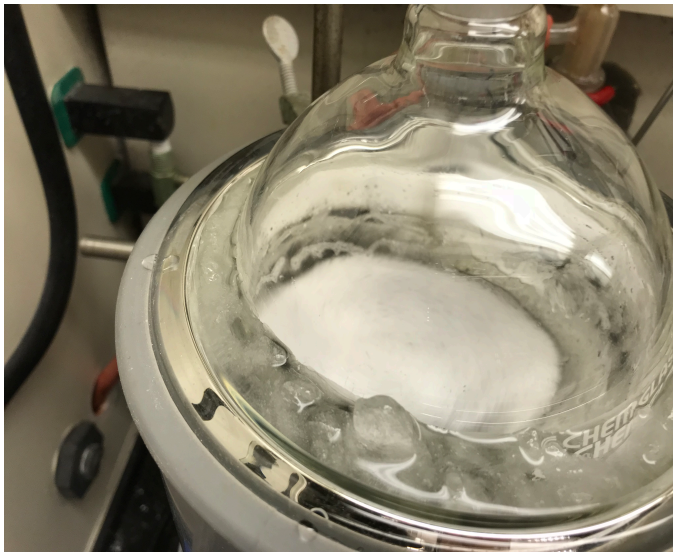
1) After approximately 3 months under **regular atmosphere**, the silane was found to have developed ~15% of impurities, therefore it is highly recommended that the silane is stored under **inert atmosphere**.

2) Acetone and alcoholic solvents have been found to accelerate degradation of $PhSi(Oi\text{-}Pr)H_2$. As a precaution, microsyringes used for small-scale reactions with the silane are rinsed with DCM (instead of acetone) for cleaning.

Catalyst dissolved in DCM and *i*-PrOH

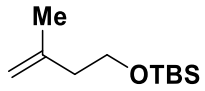


After addition of phenylsilane



Distillation setup:

Synthesis of Starting Materials

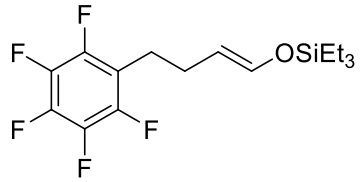


***tert*-Butyldimethyl((3-methylbut-3-en-1-yl)oxy)silane (3a)**

In a 250 mL round botton flask with a magnetic stirring bar, 3-methylbut-3-en-1-ol (4 mL, 39.4 mmol, 1.0 equiv) and 40 mL of dichloromethane were added. t*ert*-Butyldimethylsilyl chloride (7.4 g, 49.2 mmol, 1.25 equiv) and imidazole (5.4 g, 78.8 mmol, 2 equiv) were added and the reaction mixture stirred at room temperature overnight. The reaction was quenched with water (50 mL) and extracted with dichloromethane (3 x 30 mL). The organic phase was washed with brine (50 mL) and dried over $MgSO_4$. The product was obtained by distillation with a Kugelrohr apparatus (5 mbar, 110 – 115 °C) as a colorless liquid (6.5 g, 82% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.73 (ddq, *J* = 35.4, 2.1, 1.3 Hz, 2H), 3.71 (t, *J* = 7.1 Hz, 2H), 2.24 (td, *J* = 7.1, 1.1 Hz, 2H), 1.74 (t, *J* = 1.2 Hz, 3H), 0.89 (s, 9H), 0.05 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.25, 111.60, 62.30, 41.30, 26.10, 23.05, 18.50, -5.13.



(*E*)-Triethyl((3-(perfluorophenyl)prop-1-en-1-yl)oxy)silane (15a)

Step 1. Olefin cross metathesis. Following a procedure from Grubbs and coworkers,[6] a mixture of 1-allyl-2,3,4,5,6-pentafluorobenzene (1.15 mL, 7.5 mmol, 1.5 equiv), acrylaldehyde (334 µL, 5.0 mmol, 1.0 equiv) and Grubbs-Hoveyda II (156.6 mg, 5 mol%) in dichloromethane (25 mL) were heated under reflux (40 °C) overnight. The solvent was evaporated and the crude mixture isolated by flash column chromatography using 20% ethyl acetate in hexane. 4-(Perfluorophenyl)but-2-enal was obtained as a colorless liquid (563.8 mg, 48% yield)

Step 2. Isomerization. Following a modified procedure from Hashimoto and coworkers,[7] in a 25 mL round bottom flask with a magnetic stirring bar were added 4-(perfluorophenyl)but-2-enal (490 mg, 2.07 mmol, 1.0 equiv), triethylsilane (1 mL) and $Rh_2(OAc)_4$ (914 mg, 1.0 equiv) and 6 mL of dichloromethane. The reaction was heated under reflux for 24 h. The solvent was evaporated and the pure product was isolated by flash column chromatography using 100% hexanes and obtained as a colorless liquid (374.1 mg, 51% yield).

R_f: 0.90 (5% EtOAc in hexanes), $KMnO_4$;

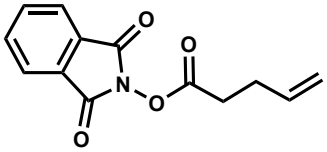
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.21 (dt, *J* = 5.8, 1.3 Hz, 1H), 4.42 (td, *J* = 7.4, 5.6 Hz, 1H), 2.74 (tt, *J* =

7.5, 1.7 Hz, 2H), 2.38 (qd, *J* = 7.4, 1.3 Hz, 2H), 0.93 (t, *J* = 7.9 Hz, 9H), 0.60 (q, *J* = 7.9 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.28, 107.50, 23.41, 22.56, 6.50, 4.49;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 6.174 min;

MS: (EI, 70 eV): *m/z* (%) $C_{16}H_{21}F_5OSi$ calc. 352.13: 352.1 (1), 181 (32), 171.1 (100), 115.1 (93), 87 (51), 77 (23), 59 (31).



1,3-dioxoisoindolin-2-yl pent-4-enoate (16a).

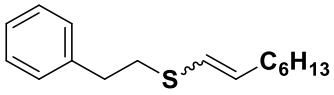
Adapted from the literature preparation,[8] a 50 mL flame-dried round bottom flask containing a Teflon-coated stir bar and septum was placed under argon and charged with 4-pentenoic acid (510 μL, 5.0 mmol, 1.0 equiv), and DCM (25.0 mL). The flask was then charged with *N*-hydroxyphthalimide (816 mg, 5.0 mmol, 1.0 equiv), and 4-dimethylaminopyridine (61.0 mg, 0.5 mmol, 0.1 equiv). *N*, *N'*-Dicyclohexylcarbodiimide (1.03 g, 5.0 mmol, 1.0 equiv) was dissolved in 25.0 mL DCM and added as a solution. The reaction was stirred overnight at room temperature. The reaction was filtered and the solvent removed *in vacuo*. The redox active ester was purified using flash chromatography (SiO_2, 4:1 hexanes: EtOAc) to yield the title compound as a thick oil (1.04 g, 84%).

R_f: 0.30 (20% EtOAc in Hexanes) UV and $KMnO_4$;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H), 5.89 (ddt, *J* = 16.8, 10.2, 6.4 Hz, 1H), 5.17 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.11 (dd, *J* = 10.4, 0.9 Hz, 1H), 2.78 (t, *J* = 7.4 Hz, 2H), 2.54 (q, *J* = 7.2 Hz, 2H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.14, 162.08, 135.38, 134.91, 129.09, 124.13, 116.79, 30.54, 28.59;

HRMS: *m/z* (ESI): found (*M* + *H*) 246.0770. $C_{13}H_{11}NO_4$ requires *M* + *H*, 246.0766.



oct-1-en-1-yl(phenethyl)sulfane (18a)
Following a literature procedure,[3] to a mixture of 2-phenylethanethiol (1.61 mL, 12.0 mmol, 1.0 equiv) in 1,4-dioxane (12 mL) was added 1-octyne (2.66 mL, 18.0 mmol, 1.5 equiv) and AIBN (98.4 mg, 5 mol%). The reaction mixture was stirred under reflux for 12 h. The reaction was diluted with ethyl acetate (50 mL), washed with water (3 x 20 mL) and the organic phase dried over $MgSO_4$. The product was isolated by flash column chromatography (100:1 hexanes: EtOAc) and obtained as a colorless liquid (1.64 g, 57% yield) as an inseparable mixture of E/Z isomers.

Data for the mixture of isomers:
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dddd, *J* = 8.2, 6.7, 2.5, 1.1 Hz, 2H), 7.25 – 7.17 (m, 3H), 5.97 – 5.86 (m, 1H), 5.74 – 5.54 (m, 1H), 2.99 – 2.82 (m, 4H), 2.10 (dqd, *J* = 16.0, 7.1, 1.4 Hz, 2H), 1.44 – 1.20 (m, 7H), 0.93 – 0.84 (m, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.38, 132.06, 130.64, 128.70, 128.67, 128.61, 124.50, 122.23, 36.15, 35.44, 33.36, 31.86, 29.44, 29.35, 29.11, 28.90, 22.78, 14.25.

Data is in accordance with the literature (*2*).

3-methyleneoxetane (20a) was prepared using a Peterson Olefination.

Step 1: To a flame-dried 100 mL round bottom, equipped with stir bar and septum was charged with 40 mL diethyl ether and set under argon. The flask was brought to 0 ℃ using an ice water bath before being charged with a 1.0 M solution of (Trimethylsilyl)methylmagnesium chloride in diethyl ether (24.0 mL, 24.0 mmol, 1.2 equiv). 3-Oxetanone (1.3 mL, 20.0 mmol, 1.0 equiv) was added and white precipitate formed immediately. The flask was removed from the ice-water bath and allowed to stir at room temperature for 5 h during which time the solution turned into a thick slurry. The reaction was quenched with water and extract with diethyl ether (3 x 50 mL). The combined organics were washed with $NaHCO_3$ and brine before being dried over Na_2SO_4. The solvent was removed *in vacuo* to deliver 3-((trimethylsilyl)methyl)oxetan-3-ol as a yellow oil (3.2 g, 20 mmol, quant) which was carried onto step 2 without further purification.

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.56 (d, *J* = 8.2 Hz, 4H), 2.52 (s, 1H), 1.28 (s, 2H), 0.05 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 87.13, 75.75, 27.54, -0.17.

Step 2: To a flame dried 3-neck 100 mL round bottom equipped with stir bar and septa was added KH (25–35% dispersion in mineral oil) (9.6 g, 60.0 mmol, 4.0 equiv) and placed under

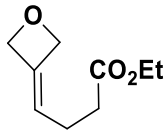
argon. The KH was washed with dry hexanes (3 x 5 mL). The hexane wash was added dropwise at 0 ℃ to a flask containing isopropanol. **Warning: KH can ignite when exposed to air. Precaution should be taken in dealing with the washing and quenching of KH**. The flask was then charged with dry THF (15 mL, 1 M) and brought to 0 ℃. 3-((Trimethylsilyl)methyl)oxetan-3-ol (2.41 g, 15.0 mmol, 1.0 equiv) was added dropwise over 15 min and the reaction was allowed to stir at 0 ℃ for an addition 30 min before being warmed to room temperature and stirred for an addition 28 h. A noticeable amount of hydrogen evolution was observed over the first 3 h. The olefin was not visible by TLC and as a result the reaction was monitored by NMR (10 μL aliquots quenched in 1 mL MeOD). Upon completion, one of the septum was removed and a short path distillation head equipped with a flame-dried 25 mL recover flask was attached. The 3-neck reaction flask was placed in an ambient temperature water bath and the recovery flask was placed in a -75 ℃ acetone/dry ice bath. The setup was placed under vacuum and gradually lowered to 20 torr and distilled to near dryness. The anticipated boiling point of the olefin is approximately 70 ℃. The recovery flask was removed and immediately placed under argon (Note: prior literature has proposed that this olefin forms a peroxide during heated distillation.[9] As a precaution, we used only a vacuum distillation and the olefin was stored under argon at -20 ℃.) The distillation head was removed and the 3-neck flask was cooled to 0 ℃ with an ice water bath before being diluted with 20 mL of hexanes. The residual KH was quenched with drop-wise addition of isopropanol at 0 ℃. The molarity of the olefin in THF was calculated via ^{1}H NMR: to 1 mL of $CDCl_3$ was added 10 μL of DCM and 10 μL of the olefin/THF solution. Typical olefin concentration was between 0.68–0.73 M (10.2 mmol, 14 mL, 68%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.21 (t, *J* = 2.5 Hz, 4H), 4.82 (p, *J* = 2.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.13, 104.19, 80.07.

General information for Wittig olefination reactions

The reactions were carried out under an atmosphere of argon using dry solvents. The corresponding Wittig reagents (when not commercially available) were obtained by refluxing the alkyl halide with triphenylphosphine (0.95 equiv) in toluene (1 M solution) for 18–24 h. After cooling to room temperature, the corresponding Wittig reagent is obtained by filtration and employed without further purification.



Ethyl 4-(oxetan-3-ylidene)butanoate (21a)

In a 100 mL round bottom flask with a magnetic stirring bar were added (4-ethoxy-4-oxobutyl)triphenylphosphonium bromide (3.44 g, 7.5 mmol, 1.5 equiv) and THF (26 mL). The suspension was cooled to 0 °C with an ice/water bath and potassium *tert*-butoxide (7.5 mL, 1.0 M in THF, 1.5 equiv) was added. The reaction turned yellow-orange and was left to stir at 0 °C for 30 min. A solution of 3-oxetanone (300 μL, 5.0 mmol, 1.0 equiv) in 3 mL of THF was added to the reaction mixture at 0 °C and then stirred at room temperature overnight. The crude reaction

mixture was quenched with sat. NH_4Cl (20 mL) and extracted with EtOAc (3 x 30 mL). The organic phase was washed with brine (50 mL) and dried over $MgSO_4$. The product was isolated by flash column chromatography and obtained as a colorless liquid (582 mg, 68% yield).

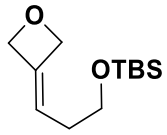
R_f: 0.60 (30% EtOAc in hexanes), anisaldehylde, $KMnO_4$;

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.27 – 5.08 (m, 5H), 4.14 (q, *J* = 7.2 Hz, 2H), 2.35 (t, *J* = 7.3 Hz, 2H), 2.17 (q, *J* = 7.5 Hz, 2H), 1.26 (t, *J* = 7.3, 6.8 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.97, 117.72, 79.47, 78.86, 60.62, 33.83, 23.85, 14.38;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 4.933 min;

MS: (EI, 70 eV): *m/z* (%) $C_9H_{14}O_3$ calc. 170.09: 113 (39), 95 (69), 82 (26), 81 (32), 69 (42), 67 (100), 59.9 (52), 53 (35).



***tert*-Butyldimethyl(3-(oxetan-3-ylidene)propoxy)silane (22a)**

In a 100 mL round bottom flask with a magnetic stirring bar were added (3-((*tert*-butyldimethylsilyl)oxy)propyl)triphenylphosphonium bromide (1.61 g, 3.13 mmol, 1.25 equiv) and THF (15 mL). The suspension was cooled to 0 °C with an ice/water bath and potassium *tert*-butoxide (3.13 mL, 1.0 M in THF, 1.25 equiv) were added. The reaction turned yellow-orange and was left to stir at 0 °C for 30 min. A solution of 3-oxetanone (150 µL, 2.5 mmol, 1 equiv) in 2 mL of THF was added to the reaction mixture at 0 °C and then stirred at room temperature overnight. The crude reaction mixture was quenched with sat. NH_4Cl (20 mL) and extracted with EtOAc (3 x 30 mL). The organic phase was washed with brine (50 mL) and dried over $MgSO_4$. The product was isolated by flash column chromatography and obtained as a colorless liquid (446 mg, 78% yield).

R_f: 0.27 (10% EtOAc in hexanes), anisaldehylde, $KMnO_4$;

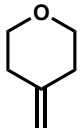
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.26 – 5.12 (m, 5H), 3.61 (t, *J* = 6.6 Hz, 2H), 2.10 – 2.01 (m, 2H), 0.90 (s, 9H), 0.05 (s, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.06, 116.29, 79.52, 78.99, 62.36, 31.89, 25.84, 18.34, -5.28;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 5.728

min;

MS: (EI, 70 eV): *m/z* (%) $C_{12}H_{24}O_2Si$ calc. 228.15: 131 (20), 127 (35), 101 (48), 75 (100), 73 (46), 59 (30), 57 (13).



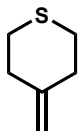
4-methylenetetrahydro-2*H*-pyran (24a).

Following the literature preparation,[10] a 100 mL flame-dried round bottom equipped with stir bar and septum was placed under argon. To a suspension of methyl triphenylphosphonium bromide (5.37 g, 15.0 mmol, 1.5 equiv) in diethyl ether (50 mL), was added solid potassium *tert*-butoxide (1.68 g, 15.0 mmol, 1.5 equiv) at 0 ℃. The mixture was warmed to room temperature and stirred for 1 h. Tetrahydro-4*H*-pyran-4-one (911 μL, 10.0 mmol, 1.0 equiv) was added and the reaction was stirred at room temperature overnight. Upon complete consumption of the ketone as monitored by TLC, the reaction was quenched with H_2O and extracted with Et_2O (3 x 50 mL). The combined organics were washed with brine and dried over $MgSO_4$. The solvent was removed *in vacuo* (CATION: olefin is volatile). The olefin was purified with flash column chromatography (9:1 pentane: Et_2O) to yield the title compound as a volatile clear, colorless oil (156 mg, 16%). Data matched reported spectra.[9]

R_f: 0.8 (9:1 pentane in Et_2O) $KMnO_4$;

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.71 (s, 2H), 3.68 (t, *J* = 5.4 Hz, 4H), 2.24 (t, *J* = 5.8, 5.4 Hz, 4H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.72, 108.43, 69.48, 35.76.



4-methylenetetrahydro-2*H*-pyran (25a).

Adapted from literature procedure,[10] a 100 mL flame dried round bottom equipped with stir bar and septum, was placed under argon. To a suspension of methyl triphenylphosphonium bromide (3.68 g, 10.3 mmol, 1.2 equiv) in THF (25 mL), was added potassium *tert*-butoxide (1.0 M in THF, 10.3 mL, 10.3 mmol, 1.2 equiv) at 0 ℃. The mixture was warmed to room temperature and stirred for 1 h. Tetrahydro-4*H*-thiopyran-4-one (1.0 g, 8.6 mmol, 1.0 equiv) was

added and the reaction was stirred at room temperature overnight. Upon complete consumption of the ketone as monitored by TLC, the reaction was quenched with H_2O and extracted with Et_2O (3 x 50 mL). The combined organics were washed with brine and dried over $MgSO_4$. The solvent was removed *in vacuo*. The olefin was purified with flash column chromatography (9:1 hexanes: Et_2O) to yield the title compound as a pungent, clear, colorless oil (438 mg, 45%).

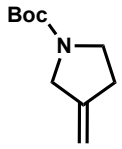
R_f: 0.5 (100% hexanes) $KMnO_4$;

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.70 (s, 2H), 2.68 – 2.63 (m, 4H), 2.49 – 2.43 (m, 4H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.81, 110.11, 37.02, 30.97;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 2.621;

MS: (EI, 70 eV): *m/z* (%) $C_6H_{10}S$ calc. 114.05: 114 (100), 99 (85), 86 (85), 79.1 (27), 67 (48), 53 (24).



***N*-Boc-3-methylenepyrrolidine (26a).**

Adapted from literature procedure,[10] a 50 mL flame dried round bottom equipped with stir bar and septum, was placed under argon. To a suspension of methyl triphenylphosphonium bromide (2.1 g, 6.0 mmol, 1.2 equiv) in THF (6 mL), was added potassium *tert*-butoxide (1.0 M in THF, 6.0 mL, 6.0 mmol, 1.2 equiv) at 0 ℃. The mixture was warmed to room temperature and stirred for 1 h. *N*-Boc-3-pyrrolidinone (926.1 g, 5.0 mmol, 1.0 equiv) was added as a solution in THF (6 mL) and the reaction was stirred at room temperature overnight. Upon complete consumption of the ketone as monitored by TLC, the reaction was quenched with H_2O and extracted with Et_2O (3 x 50 mL). The combined organics were washed with brine and dried over $MgSO_4$. The solvent was removed *in vacuo*. The olefin was purified with flash column chromatography (4:1 hexanes: EtOAc) to yield the title compound as a clear, colorless oil (636 mg, 69%).

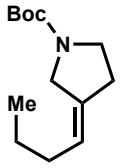
R_f: 0.5 (20% EtOAc in hexanes) $KMnO_4$;

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.99 – 4.91 (m, 2H), 3.90 (d, *J* = 23.3 Hz, 2H), 3.45 (d, *J* = 20.5 Hz,

2H), 2.54 (t, *J* = 7.4 Hz, 2H), 1.46 (s, 9H);

^{13}C NMR (126 MHz, $CDCl_3$, sum of 2 rotamers) δ 154.50, 146.18, 145.29, 106.76, 106.59, 79.30, 50.44, 50.15, 45.95, 45.54, 32.25, 31.57, 28.56;

HRMS: *m/z* (ESI): found (*M* + *H*) 184.1333. $C_{10}H_{17}NO_2$ requires *M + H*, 184.1338.



***N*-Boc-3-butylidenepyrrolidine (27a).**

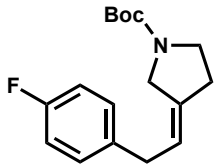
Adapted from literature procedure,[10] a 50 mL flame dried round bottom equipped with stir bar and septum, was placed under argon. To a suspension of butyl triphenylphosphonium bromide (2.4 g, 6.0 mmol, 1.2 equiv) in THF (6 mL), was added potassium *tert*-butoxide (1.0 M in THF, 6.0 mL, 6.0 mmol, 1.2 equiv) at 0 ℃. The mixture was warmed to room temperature and stirred for 1 h. *N*-Boc-3-pyrrolidinone (926.1 g, 5.0 mmol, 1.0 equiv) was added as a solution in THF (6 mL) and the reaction was stirred at room temperature overnight. Upon complete consumption of the ketone as monitored by TLC, the reaction was quenched with H_2O and extracted with Et_2O (3 x 50 mL). The combined organics were washed with brine and dried over $MgSO_4$. The solvent was removed *in vacuo*. The olefin was purified with flash column chromatography (4:1 hexanes: EtOAc) to yield the title compound as a clear, colorless oil (736 mg, 65%).

Rf: 0.5 (20% EtOAc in hexanes) $KMnO_4$;

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.38 – 5.26 (m, 1H), 3.95 – 3.81 (m, 2H), 3.43 (t, *J* = 26.6 Hz, 2H), 2.49 (q, *J* = 8.6, 7.7 Hz, 2H), 1.98 (qt, *J* = 7.4, 1.4 Hz, 1H), 1.93 (qt, *J* = 7.4, 1.4 Hz, 1H), 1.47 (d, *J* = 6.9 Hz, 9H), 1.38 (q, *J* = 7.3 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$, sum of 2 rotamers) δ 154.81, 154.67, 136.07 (broad), 122.38, 121.93, 79.32, 79.25, 50.60 (broad), 47.52 (broad), 45.64 (broad), 45.42 (broad), 31.53, 31.27, 28.66, 28.65, 22.72, 22.69, 13.88, 13.86;

HRMS: *m/z* (ESI): found (*M* + *H*) 226.1807. $C_{13}H_{23}NO_2$ requires *M + H*, 226.1810.



_N_-Boc-3-(2-(4-fluorophenyl)ethylidene)pyrrolidine (28a).

Step 1: (4-fluorophenethyl)triphenylphosphonium bromide. Adapted from literature procedure,[11] a 250 mL flame dried round bottom equipped with a stir bar was charged with triphenylphosphine (11.8 g, 42.8 mmol, 0.95 equiv) and placed under argon. 2-(4-Fluorophenyl)ethyl bromide (6.3 mL, 45.0, 1.0 equiv) was added followed by dry toluene (50 mL). A reflux condenser was attached and the solution was refluxed at 110 ℃ for 18 h. Upon cooling, the solution was filtered and washed with cold hexanes (3 x 50 mL) to give the title compound in quantitative yield, which was carried on without further purification.

Step 2: *N*-Boc-3-(2-(4-fluorophenyl)ethylidene)pyrrolidine (28a). Adapted from literature procedure,[10] a 50 mL flame dried round bottom equipped with stir bar and septum, was placed under argon. To a suspension of (4-fluorophenethyl)triphenylphosphonium bromide (2.8 g, 6.0 mmol, 1.2 equiv) in THF (6 mL), was added potassium *tert*-butoxide (1.0 M in THF, 6.0 mL, 6.0 mmol, 1.2 equiv) at 0 ℃. The mixture was warmed to room temperature and stirred for 1 h. *N*-Boc-3-pyrrolidinone (926.1 g, 5.0 mmol, 1.0 equiv) was added as a solution in THF (6 mL) and the reaction was stirred at room temperature overnight. Upon complete consumption of the ketone as monitored by TLC, the reaction was quenched with H_2O and extracted with Et_2O (3 x 50 mL). The combined organics were washed with brine and dried over $MgSO_4$. The solvent was removed *in vacuo*. The olefin was purified with flash column chromatography (4:1 hexanes: EtOAc) to yield the title compound as a clear, colorless oil (357 mg, 25%).

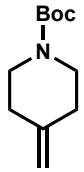
R_f: 0.5 (20% EtOAc in hexanes) $KMnO_4$;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 – 7.09 (m, 2H), 6.97 (tt, *J* = 9.9, 9.5, 5.2, 2.8 Hz, 2H), 5.56 – 5.43 (m, 1H), 3.96 (s, 2H), 3.48 (d, *J* = 38.0 Hz, 2H), 3.31 (dd, *J* = 34.6, 7.5 Hz, 2H), 2.58 (m, 2H),1.47 (d, *J* = 7.7 Hz, 9H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.52 (d, *J* = 243.9 Hz), 154.71 (d, *J* = 16.1 Hz), 136.25 (d, *J* = 3.2 Hz), 129.66, 120.95, 120.66, 120.36, 120.29, 115.36 (d, *J* = 21.3 Hz)., 79.58, 79.49, 50.79, 50.51, 47.75, 47.61, 45.86, 45.60, 45.43, 45.14, 34.92, 34.62, 28.67, 28.66, 28.65. (vinyl peak at C3 too broad for characterization);

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.63;

HRMS: *m/z* (ESI): found (*M* + *H*) 292.1711. $C_{17}H_{22}FNO_2$ requires *M* + *H*, 292.1713.



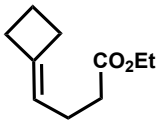
***N*-Boc-4-methylenepiperidine (29a).**

Adapted from literature procedure,[10] a 100 mL flame dried round bottom equipped with stir bar and septum, was placed under argon. To a suspension of methyl triphenylphosphonium bromide (8.6 g, 24.0 mmol, 1.2 equiv) in THF (24 mL), was added potassium *tert*-butoxide (1.0 M in THF, 24.0 mL, 24.0 mmol, 1.2 equiv) at 0 ℃. The mixture was warmed to room temperature and stirred for 1 h. *N*-Boc-4-piperidone (4.0 g, 20.0 mmol, 1.0 equiv) was added as a solution in THF (12 mL) and the reaction was stirred at room temperature overnight. Upon complete consumption of the ketone as monitored by TLC, the reaction was quenched with H_2O and extracted with Et_2O (3 x 50 mL). The combined organics were washed with brine and dried over $MgSO_4$. The solvent was removed *in vacuo*. The olefin was purified with flash column chromatography (4:1 hexanes: EtOAc) to yield the title compound as a clear, colorless oil (3.48 g, 88%).

R_f: 0.5 (20% EtOAc in hexanes) $KMnO_4$;

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.71 (s, 2H), 3.39 (t, *J* = 5.9 Hz, 4H), 2.15 (t, *J* = 5.9 Hz, 4H), 1.44 (d, *J* = 1.1 Hz, 9H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.47, 109.13, 79.57, 45.37 (broad), 34.62, 28.53.



ethyl 4-cyclobutylidenebutanoate (30a).

Step 1: (4-ethoxy-4-oxobutyl)triphenylphosphonium bromide. Adapted from literature procedure,[11] a 250 mL flame dried round bottom equipped with a stir bar was charged with triphenylphosphine (11.2 g, 42.8 mmol, 0.95 equiv) and placed under argon. Ethyl-4-bromobutyrate (6.4 mL, 45.0, 1.0 equiv) was added followed by dry toluene (50 mL). A reflux condenser was attached and the solution was refluxed at 110 ℃ for 18 h. Upon cooling, the solution was filtered and washed with cold hexanes (3 x 50 mL) to give the title compound in

quantitative yield, which was carried on without further purification.

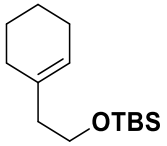
Step 2: ethyl 4-cyclobutylidenebutanoate (30a). Adapted from literature procedure,[10] a 100 mL flame dried round bottom equipped with stir bar and septum, was placed under argon. To a suspension of (4-ethoxy-4-oxobutyl)triphenylphosphonium bromide (2.74 g, 6.0 mmol, 1.2 equiv) in THF (6 mL), was added potassium *tert*-butoxide (1.0 M in THF, 6.0 mL, 6.0 mmol, 1.2 equiv) at 0 ℃. The mixture was warmed to room temperature and stirred for 1 h. Cyclobutanone (374 μL, 5.0 mmol, 1.0 equiv) was added as a solution in THF (6 mL) and the reaction was stirred at room temperature overnight. Upon complete consumption of the ketone as monitored by TLC, the reaction was quenched with H_2O and extracted with Et_2O (3 x 50 mL). The combined organics were washed with brine and dried over $MgSO_4$. The solvent was removed *in vacuo*. The olefin was purified with flash column chromatography (9:1 hexanes: EtOAc) to yield the title compound as a clear, colorless oil (639 mg, 76%).

R_f: 0.4 (10% EtOAc in hexanes) $KMnO_4$;

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.05 – 5.00 (m, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.68 – 2.60 (m, 4H), 2.31 (td, *J* = 7.4, 0.8 Hz, 2H), 2.19 (q, *J* = 8.0, 7.4, 6.9 Hz, 2H), 1.92 (p, *J* = 8.2 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.59, 141.76, 118.31, 60.37, 34.64, 31.01, 29.35, 23.77, 17.12, 14.41;
GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 4.429;

MS: (EI, 70 eV): *m/z* (%) $C_{10}H_{16}O_2$ calc. 168.12: 168.1 (10), 140.1 (23), 122.1 (10), 111 (15), 95.1 (100), 81.1 (56), 79.1 (96), 67.1 (56), 53.1, (26).



tert-Butyl(2-(cyclohex-1-en-1-yl)ethoxy)dimethylsilane (32a)

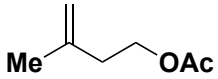
Step 1. Hydrolysis. Following a literature procedure,[12] to a 100 mL round bottom flask with a magnetic stirring bar was added 2-(cyclohex-1-en-1-yl)acetonitrile (1 equiv., 5.0 g, 41.26 mmol), methanol (24 mL) and concentrated sulfuric acid (4.0 mL). The mixture was refluxed for 72 h. After that time, the crude reaction mixture was diluted with water (30 mL) and extracted with diethyl ether (3 x 25 mL). The organic phase was washed with NaHCO3 (2 x 20 mL) and dried over MgSO4. Purification by flash column chromatography (9:1 hexanes: EtOAc) produced methyl 2-(cyclohex-1-en-1-yl)acetate (5.3 g, 84% yield).

Step 2 and 3. Reduction and protection. To a 100 mL round bottom flask with a magnetic stirring bar was added methyl 2-(cyclohex-1-en-1-yl)acetate (1 equiv., 2.0 g, 13 mmol) and diethyl ether (20 mL). The flask was cooled down to 0 °C in a ice/water bath and then LiAlH4 (1.5 equiv., 20 mmol, 4 M solution in diethyl ether) was added to the mixture and stirred at room temperature for 3 h. After that time, the crude reaction mixture was diluted with diethyl ether (20 mL) and 5 mL of water were slowly added at 0 °C, followed by 15 mL of NaOH 15% m/v, followed by 15 mL of water. The mixture was left to stir for 15 min at room temperature. After that time, MgSO4 was added and the mixture stirred another 15 min at room temperature. Filtration and evaporation of volatiles gave 2-(cyclohex-1-en-1-yl)ethan-1-ol that was used for the next step without further purification. To a 100 mL round bottom flask with a magnetic stirring bar was added 2-(cyclohex-1-en-1-yl)ethan-1-ol (1 equiv., 13 mmol), dichloromethane (40 mL), TBDMS (1.25 equiv., 2.4 g, 16.3 mmol) and imidazole (2 equiv., 1.7 g, 26 mmol) and the mixture stirred at room temperature overnight. Evaporation of the volatiles and purification by flash column chromatography gave tert-butyl(2-(cyclohex-1-en-1-yl)ethoxy)dimethylsilane (1.35 g, 43% yield) as a colorless liquid.

R_f: 0.30 (100% hexanes), $KMnO_4$;

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.42 (tq, *J* = 3.7, 1.3 Hz, 1H), 3.65 (t, *J* = 7.3 Hz, 2H), 2.18 – 2.12 (m, 2H), 2.01 – 1.89 (m, 4H), 1.65 – 1.57 (m, 2H), 1.54 (qd, *J* = 6.0, 2.3 Hz, 2H), 0.89 (s, 9H), 0.05 (s, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.01, 122.93, 62.64, 41.65, 28.91, 26.12, 25.43, 23.14, 22.57, 18.52, -5.09.



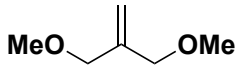
3-methylbut-3-en-1-yl acetate (35a).

Following the literature preparation,[13] a flame dried 100 mL round bottom equipped with a stir bar and septum was set under argon and charged with 3-methyl-3-buten-1-ol (2.0 mL, 20 mmol, 1.0 equiv), 4-dimethylaminopyridine (100 mg, 0.8 mmol, 0.04 equiv), pyridine (30 mL), and acetic anhydride (4.0 mL, 42.0 mmol, 2.1 equiv). The reaction was stirred at room temperature overnight. Upon complete consumption of the alcohol as monitored by TLC, the reaction was poured into H_2O and extracted with Et_2O (3 x 50 mL). The combined organics were washed with $NaHCO_3$, dried over Na_2SO_4, and the solvent was removed *in vacuo*. The olefin was purified by flash column chromatography (SiO_2, 9:1 hexanes: Et_2O) to yield the title compound as a volatile, pungent, clear colorless oil (1.05 g, 41%). Data is in accordance with literature (11).

R_f: 0.3 (10% EtOAc in hexanes) $KMnO_4$;

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.79 (s, 1H), 4.72 (s, 1H), 4.17 (t, *J* = 6.9, 0.8 Hz, 2H), 2.32 (t, *J* = 6.8, 1.2 Hz, 2H), 2.03 (s, 3H), 1.74 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.18, 141.80, 112.31, 62.76, 36.78, 22.59, 21.07.

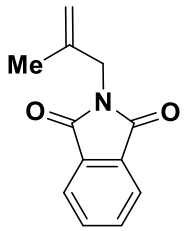


3-methoxy-2-(methoxymethyl)prop-1-ene (37a).

Following the literature procedure,[14] a flame dried 25 mL round bottom equipped with a stir bar and septum was set under argon and charged with a solution of 3-chloro-2-chloromethyl-1-propene (1.06 mL, 10.0 mmol, 1.0 equiv) in THF (2.5 mL) at 0 ℃. A solution of NaOMe (25 wt. % in MeOH, 6.25 mL, 28.0 mmol, 2.8 equiv) was added and the ice-bath was removed. The reaction was stirred at room temperature for 20 h and at 35 ℃ for 20 h. Upon complete consumption of the starting material as monitored by TLC, the reaction was quenched with sat. NH_4Cl and diluted with Et_2O. The combined organics were dried over Na_2SO_4. The solution was then distilled using a short path to remove the Et_2O, THF, and MeOH to yield the pure title compound as a volatile, light yellow oil (800 mg, 69%) with a reported boiling point of 120–130 ℃. Data is in accordance with reported literature (12).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.17 (s, 2H), 3.91 (s, 4H), 3.32 (s, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.62, 114.10, 73.35, 58.17.

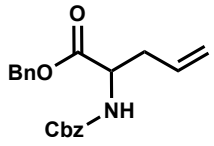


2-(2-methylallyl)isoindoline-1,3-dione (38a)

Following a procedure from Fürstner and coworkers,[15] to a 50 mL round bottom flask with a magnetic stirring bar was added phthalimide (1.41 g, 9.6 mmol, 1 equiv), DMF (10 mL), K_2CO_3 (2.6 g, 2 equiv) and 3-chloro-2-methylpropene (1.0 mL, 1.5 equiv). The mixture was stirred at 80 °C for 12 h. After cooling down, the crude reaction mixture was filtered through a plug of silica gel and the volatiles evaporated to form 2-(2-methylallyl)isoindoline-1,3-dione (775 mg, 41% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H), 7.76 – 7.70 (m, 2H), 4.89 (h, *J* = 1.3 Hz, 1H), 4.82 (dq, *J* = 2.4, 1.0 Hz, 1H), 4.23 (dd, *J* = 1.7, 0.9 Hz, 2H), 1.78 (dt, *J* = 1.5, 0.7 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.22, 139.45, 134.15, 132.19, 123.50, 112.13, 43.42, 20.56.



Benzyl 2-(((benzyloxy)carbonyl)amino)pent-4-enoate (40a)

Step 1: *N*-CBz-allyl glycine. Allyl glycine (1.15 g, 10.0 mmol, 1.0 equiv) and sodium bicarbonate (2.35 g, 28.0 mmol, 2.8 equiv) were dissolved in H_2O (30 mL) at room temperature. Benzyl chloroformate was added dropwise to this solution. After 3.5 h, an additional 10 mL H_2O was added and the mixture was diluted with Et_2O (40 mL) and separated. The aqueous layer was extracted with Et_2O (40 mL) and the organic layers were discarded. The aqueous layer was acidified with 10% citric acid (30 mL) and extracted with Et_2O (3 x 60 mL). The combined organics were dried over Na_2SO_4 and concentrated. The resulting viscous oil was used without further purification (2.27 g, 91%).

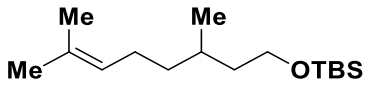
Step 2: benzyl 2-(((benzyloxy)carbonyl)amino)pent-4-enoate (40a). Following literature procedure,[16] a flame dried 10 mL round bottom flask equipped with stir bar and septum was placed under argon and charged with *N*-CBz-allyl glycine (1.0 g, 4.0 mmol, 1.0 equiv) and potassium carbonate (835 mg, 6.0 mmol, 1.5 equiv). DMF (4 mL) was added and the reaction was stirred at room temperature for 10 mins. Benzyl bromide (705 μL, 6.0 mmol, 1.5 equiv) was added dropwise and the reaction was heated to 50 ℃ for 8 h. Upon complete consumption of starting material as monitored by TLC, H_2O (10 mL) and ethyl acetate (10 mL) were added and separated. The aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organics were washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude was purified by flash column chromatography (5:1 hexanes: EtOAc) to yield a white solid (998 mg, 74%).

R_f: 0.3 (20% EtOAc in hexanes) UV and $KMnO_4$;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.28 (m, 10H), 5.63 (ddt, *J* = 17.3, 10.4, 7.2 Hz, 1H), 5.29 (d, *J* = 8.2 Hz, 1H), 5.25 – 5.01 (m, 6H), 4.51 (q, *J* = 6.4 Hz, 1H), 2.55 (ddt, *J* = 27.8, 14.1, 7.2 Hz, 2H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.70, 155.85, 136.36, 135.38, 131.99, 128.77, 128.68, 128.65, 128.51, 128.34, 128.26, 119.66, 67.37, 67.16, 53.47, 36.85;

HRMS: *m/z* (ESI): found (*M* + *H*) 340.1549. $C_{20}H_{21}NO_4$ requires *M* + *H*, 340.1549.



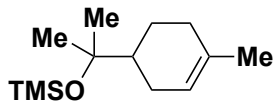
***tert*-Butyl((3,7-dimethyloct-6-en-1-yl)oxy)dimethylsilane (41a)**

To a 100 mL round bottom flask with a magnetic stirring bar was added citronellol (1.83 mL, 10 mmol, 1.0 equiv), dichloromethane (20 mL), TBDMS (1.88g, 12.5 mmol, 1.25 equiv) and imidazole (1.36 g, 20 mmol, 2 equiv) and the mixture stirred at room temperature overnight. Evaporation of the volatiles and purification by flash column chromatography gave tert-butyl(2-(cyclohex-1-en-1-yl)ethoxy)dimethylsilane (1.68 g, 62% yield) as a colorless liquid.

R_f: 0.50 (100% hexanes), $KMnO_4$;

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.10 (tdt, *J* = 7.1, 2.8, 1.4 Hz, 1H), 3.69 – 3.58 (m, 2H), 2.04 – 1.90 (m, 2H), 1.70 – 1.66 (m, 3H), 1.60 (d, *J* = 1.3 Hz, 3H), 1.58 – 1.52 (m, 2H), 1.36 – 1.29 (m, 2H), 1.15 (dddd, *J* = 13.4, 9.6, 7.5, 5.9 Hz, 1H), 0.89 (s, 9H), 0.05 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 131.22, 125.05, 61.62, 40.10, 37.37, 29.27, 26.14, 25.88, 25.65, 19.79, 18.51, 17.79, -5.10, -5.12;



trimethyl((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)oxy)silane (45a).

A flame dried 100 mL round bottom flask equipped with stir bar and septum was placed under argon. The flask was charged with DCM (50 mL), α-terpineol (829 μL, 5.0 mmol, 1.0 equiv), and triethyl amine (6.9 mL, 50.0 mmol, 10.0 equiv). The reaction was cooled to 0 ℃ with an ice-water bath and TMSOTf (1.84 mL, 10.0 mmol, 2.0 equiv) was added dropwise over 30 s. The reaction was stirred at 0 ℃ for 1 h, which upon complete consumption of the starting material as monitored by TLC, the reaction was quenched with $NaHCO_3$ and extracted with DCM (3 x 50 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*. The title compound was isolated by flash column chromatography (SiO_2, 95:1 hexanes: Et_2O) to yield the product as a viscous clear, colorless oil (956 mg, 84%).

R_f: 0.8 (5% Et_2O in hexanes) anisaldehyde;

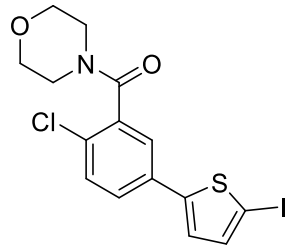
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.38 (s, 1H), 2.06 – 1.90 (m, 3H), 1.85 (ddd, *J* = 12.6, 5.3, 2.4 Hz, 1H), 1.77 (dd, *J* = 4.3, 2.1 Hz, 1H), 1.64 (s, 3H), 1.45 (ddq, *J* = 14.1, 7.5, 2.4 Hz, 1H), 1.27 – 1.13 (m, 7H), 0.10 (s, 9H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 134.03, 121.21, 75.87, 45.91, 31.33, 27.86, 27.08, 24.14, 23.54, 2.77;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 70 °C/min to 250 °C, then 5 °C/min to 280 °C): t_R = 4.349;

MS: (EI, 70 eV): *m/z* (%) $C_{13}H_{26}OSi$ calc. 226.18: 225.2 (1), 211.1 (4), 143.1 (5), 136.1 (36), 131.1 (100), 121.1 (29), 107.1 (4), 93.1 (24), 73.1 (64).

Aryl halide synthesis



(2-chloro-5-(5-iodothiophen-2-yl)phenyl)(morpholino)methanone

Step 1. **Suzuki coupling**. Following a procedure from Glorius and coworkers,[18] to a 100 mL round bottom flask with a magnetic stirring bar was added 2-iodothiophene (166 µL, 1.5 mmol, 1.0 equiv), (4-chloro-3-(morpholine-4-carbonyl)phenyl)boronic acid (445 mg, 1.65 mmol, 1.1 equiv), DMF (25 mL) and Na_2CO_3 (7.5 mmol, 1 M solution, 5.0 equiv). The mixture was degassed with argon for 10 min and then $Pd(PPh_3)_4$ (174 mg, 10 mol%) was added and the mixture further degassed with argon for 2 min. The reaction was heated at 85 °C overnight. After cooling at room temperature, ethyl acetate (50 mL) and water (20 mL) were added. The phases were separated and the organic phase was washed with brine (3 x 15 mL). The organic phase was dried over $MgSO_4$ and the volatiles removed under vacuum. Purification by flash column chromatography (3:2 hexanes: EtOAc) gave (2-chloro-5-(thiophen-2-yl)phenyl)(morpholino)methanone (423 mg, 92% yield) as a white solid.

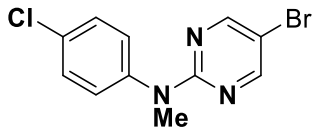
Step 2. **Iodination**. To a 25 mL round bottom flask with a magnetic stirring bar was added (2-chloro-5-(thiophen-2-yl)phenyl)(morpholino)methanone (307 mg, 1.0 mmol, 1.0 equiv), chloroform (6 mL) and glacial acetic acid (2 mL). N-iodosuccinimide (390 mg, 1.88 mmol, 1.88 equiv) was added and the reaction stirred at room temperature overnight. Volatiles were removed under reduced pressure and the crude mixture purified by flash column chromatography (3:2 hexanes: EtOAc) to afford (2-chloro-5-(5-iodothiophen-2-

yl)phenyl)(morpholino)methanone (356 mg, 82% yield) as a white solid.

R_f: 0.43 (40% EtOAc in hexanes), anisaldehyde, UV;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 1H), 7.43 (d, *J* = 2.2 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.23 (dt, *J* = 3.8, 0.7 Hz, 1H), 6.97 (d, *J* = 3.8 Hz, 1H), 3.94 – 3.86 (m, 1H), 3.83 – 3.75 (m, 3H), 3.71 (ddd, *J* = 11.5, 6.8, 3.2 Hz, 1H), 3.61 (ddd, *J* = 11.5, 6.2, 3.2 Hz, 1H), 3.33 (ddd, *J* = 13.5, 6.2, 3.2 Hz, 1H), 3.25 (ddd, *J* = 13.4, 6.8, 3.2 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.53, 147.97, 138.28, 136.15, 133.15, 130.43, 129.65, 127.52, 125.68, 124.97, 76.95, 66.94, 66.83, 47.30, 42.27;



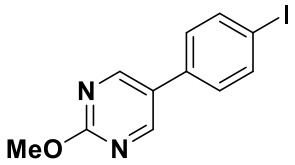
5-bromo-*N*-(4-chlorophenyl)-*N*-methylpyrimidin-2-amine

To a 100 mL round bottom flask with a magnetic stirring bar was added 5-bromo-2-chloropyrimidine (2.0 g, 10.34 mmol, 1.0 equiv), 1-propanol (20 mL), DIPEA (2.16 mL, 12.4 mmol, 1.2 equiv) and 4-chloro-*N*-methylaniline (1.45 mL, 12.4 mmol, 1.2 equiv). The mixture was heated under reflux for 24 h. After cooling to room temperature, volatiles were removed and the product purified by flash column chromatography (9:1 hexanes: EtOAc) to give 5-bromo-*N*-(4-chlorophenyl)-*N*-methylpyrimidin-2-amine (1.59 g, 52% yield) as a white solid.

R_f: 0.54 (10% EtOAc in hexanes), UV;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (s, 2H), 7.38 – 7.35 (m, 2H), 7.25 – 7.22 (m, 2H), 3.48 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.15, 158.03, 143.68, 131.64, 129.51, 127.83, 107.65, 39.01.



5-(4-iodophenyl)-2-methoxypyrimidine

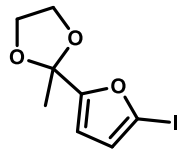
Following a literature procedure,[19] to a 25 mL round bottom flask was added 1,4-diiodobenzene (442 mg, 1.5 mmol, 1.5 equiv), (2-methoxypyrimidin-5-yl)boronic acid (153.9 mg, 1.0 mmol, 1.0

equiv), 1,4-dioxane (3 mL) and a 2 M solution of Na_2CO_3 (1.9 mL). The mixture was degassed with argon for 10 min. To the mixture, [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) ($Pd(dppf)Cl_2$,) (41 mg, 5 mol%) was added and the reaction mixture further degassed with argon for 2 min. The crude reaction mixture was heated under reflux for 15 h. After cooling at room temperature, ethyl acetate (20 mL) and water (10 mL) were added. The phases were separated and the organic phase was washed with brine (3 x 5 mL). The organic phase was dried over $MgSO_4$ and the volatiles removed under vacuum. Purification by flash column chromatography (4:1 hexanes: EtOAc) gave 5-(4-iodophenyl)-2-methoxypyrimidine (100 mg, 32% yield) as a white solid.

R_f: 0.43 (20% EtOAc in hexanes), UV;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 2H), 7.84 – 7.79 (m, 2H), 7.28 – 7.24 (m, 5H), 4.07 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.44, 157.29, 138.59, 134.13, 128.40, 127.48, 94.17, 55.30;



2-(5-iodofuran-2-yl)-2-methyl-1,3-dioxolane

Step 1. Acetal formation. Following a literature procedure,[19] to a 25 mL round bottom flask was added 2-acetylfuran (1.0 mL, 10.0 mmol, 1.0 equiv), ethylene glycol (2.5 mL, 44 mmol, 4.4 equiv), trimethyl orthoformate anhydrous (2.2 mL, 20 mmol, 2 equiv), and $LiBF_4$ (150 mg, 1.6 mmol, 16 mol%). The mixture stirred at 95 °C overnight. The reaction crude was diluted with EtOAc (30 mL) and washed with H_2O (3x10 mL), the organic phase was dried over $MgSO_4$ and the volatiles removed under vacuum. Purification by flash column chromatography (4:1 hexanes: EtOAc) gave 2-(furan-2-yl)-2-methyl-1,3-dioxolane as a colorless oil (54% yield).

Step 2. Iodination. To a 25 mL round bottom flask was added 2-(furan-2-yl)-2-methyl-1,3-dioxolane (462.5 mg, 3.0 mmol, 1.0 equiv) and THF (11 mL) and the reaction cooled down to -78 °C. *n*-BuLi (1.8 mL, 3.9 mmol, 1.3 equiv) was slowly added and the reaction warmed to 0 °C and stirred at that temperature for 10 min. The reaction was cooled down to -78 °C and I_2 (990 mg, 3.9 mmol, 1.3 equiv) dissolved on THF (2.2 mL) was added slowly. The mixture was left to warm slowly to 0 °C and stirred at that temperature for 2 h. Water was added (10 mL) and EtOAc (20 mL). The organic phase was washed with brine and dried over $MgSO_4$. Purification by column chromatography (4:1 hexanes: EtOAc) gave the expected product as a pale yellow oil (640 mg, 74% yield, 10:1 mixture of C2:C3 isomers). Data is for the major isomer.

R_f: 0.40 (20% EtOAc in hexanes), UV, anisaldehyde;

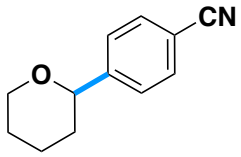
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.45 (d, *J* = 3.2 Hz, 1H), 6.23 (d, *J* = 3.2 Hz, 1H), 4.07 – 3.96 (m, 4H), 1.71 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.87, 120.49, 109.48, 104.31, 87.74, 65.16, 24.29;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 5.265 min;

MS: (EI, 70 eV): *m/z* (%) $C_8H_9IO_3$ calc. 279.96: 279.9 (16), 264.9 (100), 220.8 (75), 126.8 (19), 93 (48), 87 (52), 65 (17).

Substrate Characterization



4-(tetrahydro-2*H*-pyran-2-yl)-benzonitrile (1b).

Following General Procedure A, a mixture of 4-iodobenzonitrile (68.7 mg, 0.3 mmol, 1.0 equiv), 3,4-dihydro-2*H*-pyran (**1a**) (64 μL, 0.75 mmol, 2.5 equiv) was stirred for 48 h. Purification by flash column chromatography (SiO_2, 9:1 hexanes: Et_2O) furnished the title compound as a clear, colorless oil (45.4 mg, 81%).

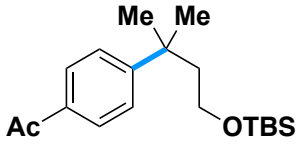
R_f: 0.2 (10% EtOAc in hexanes), UV and $KMnO_4$ stain;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 7.48 – 7.43 (m, 2H), 4.37 (dd, *J* = 11.2, 2.5 Hz, 1H), 4.18 – 4.12 (m, 1H), 3.61 (td, *J* = 11.6, 2.9 Hz, 1H), 2.00 – 1.91 (m, 1H), 1.87 – 1.82 (m, 1H), 1.74 – 1.57 (m, 3H), 1.55 – 1.43 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.85, 132.30, 126.49, 119.12, 111.05, 79.22, 69.04, 34.25, 25.78, 23.93;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 6.512;

MS: (EI, 70 eV): *m/z* (%) $C_{12}H_{13}NO$ calc. 187.10: 186.1 (37), 158.1 (12), 144.1 (8), 130 (100), 116 (27), 102 (32), 84 (18), 76 (12), 63 (6), 56 (38), 51 (8).



1-(4-(4-((*tert*-butyldimethylsilyl)oxy)-2-methylbutan-2-yl)phenyl)ethan-1-one (3b).

Following General Procedure B, a mixture of 4-iodoacetophenone (110.7 mg, 0.45 mmol, 1.5 equiv), and *tert*-butyldimethyl((3-methylbut-3-en-1-yl)oxy)silane (**3a**) (60.1 mg, 0.3 mmol, 1.0 equiv) [or from *tert*-butyldimethyl((3-methylbut-2-en-1-yl)oxy)silane (**3a'**)] was stirred for 16 h. Purification by flash column chromatography (SiO_2, 9:1 hexanes: EtOAc) furnished the title compound as clear, pale yellow oil (62.3 mg, 65% from **3a** and 48.3 mg, 50% from **3a'**).

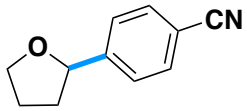
R_f: 0.4 (10% EtOAc in hexanes), UV and anisaldehyde;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 – 7.88 (m, 2H), 7.45 – 7.41 (m, 2H), 3.42 (t, *J* = 7.3 Hz, 2H), 2.59 (s, 3H), 1.93 (t, *J* = 7.3 Hz, 2H), 1.35 (s, 6H), 0.83 (s, 9H), -0.05 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.03, 155.09, 134.86, 128.44, 126.10, 60.28, 46.68, 37.31, 29.35, 26.71, 26.04, 18.36, -5.21;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 70 °C/min to 250 °C, then 5 °C/min to 280 °C): t_R = 6.993;

MS: (EI, 70 eV): *m/z* (%) $C_{19}H_{32}O_2Si$ calc. 320.22: 321.3 (1), 319.2 (1), 263.2 (100), 191.1 (78), 177.1 (45), 161.1 (10), 124.1 (9), 75.1 (38).



4-(tetrahydrofuran-2-yl)benzonitrile (5b).

Following General Procedure A, a mixture of 4-iodobenzonitrile (68.7 mg, 0.3 mmol, 1.0 equiv), 2,3-dihydrofuran (**5a**) (56.7 μL, 0.75 mmol, 2.5 equiv) was stirred for 36 h. Purification by flash column chromatography (SiO_2, 7:3 hexanes: EtOAc) furnished the title compound as a clear,

colorless oil (34.0 mg, 65%).

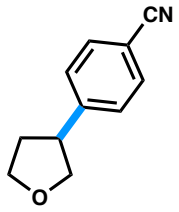
R_f: 0.3 (20% EtOAc in hexanes), UV and $KMnO_4$;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 2H), 7.45 – 7.41 (m, 2H), 4.93 (t, *J* = 7.2 Hz, 1H), 4.09 (dt, *J* = 8.4, 6.8 Hz, 1H), 3.96 (ddd, *J* = 8.3, 7.3, 6.4 Hz, 1H), 2.37 (dtd, *J* = 12.8, 7.2, 5.8 Hz, 1H), 2.04 – 1.96 (m, 2H), 1.73 (dq, *J* = 12.3, 7.9 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.36, 132.29, 126.28, 119.09, 110.92, 79.94, 69.07, 34.82, 26.04;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 6.163;

MS: (EI, 70 eV): *m/z* (%) $C_{11}H_{11}NO$ calc. 173.08: 173.1 (12) 172.1 (48), 145.1 (28), 142.1 130 (100), 116 (18), 102 (24), 76 (8), 71 (5), 63 (5), 51 (6).



4-(tetrahydrofuran-3-yl)benzonitrile (6b).

Following General Procedure A, a mixture of 4-iodobenzonitrile (68.7 mg, 0.3 mmol, 1.0 equiv), 2,5-dihydrofuran (**6a**) (56.7 μL, 0.75 mmol, 2.5 equiv) was stirred for 12 h. Purification by flash column chromatography (SiO_2, 7:3 hexanes: EtOAc) furnished the title compound as a clear, colorless oil (38.0 mg, 73%).

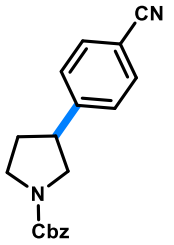
R_f: 0.3 (30% EtOAc in hexanes), UV and $KMnO_4$ stain;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.38 – 7.34 (m, 2H), 4.12 (dd, *J* = 8.7, 7.3 Hz, 1H), 4.08 (td, *J* = 8.4, 4.7 Hz, 1H), 3.92 (dt, *J* = 8.6, 7.6 Hz, 1H), 3.76 (dd, *J* = 8.7, 6.5 Hz, 1H), 3.46 (p, 1H), 2.45 – 2.38 (m, 1H), 1.98 (dq, *J* = 12.5, 7.7 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.04, 132.58, 128.18, 119.00, 110.54, 74.44, 68.53, 45.16, 34.73;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 6.352;

MS: (EI, 70 eV): *m/z* (%) $C_{11}H_{11}NO$ calc. 173.08: 173.1 (9), 143.1 (100), 128 (6), 116.1 (39), 103 (5), 77 (4), 63 (4).



Benzyl 3-(4-cyanophenyl)pyrrolidine-1-carboxylate (7b)

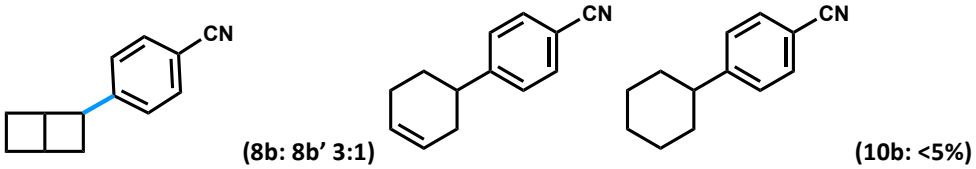
Following the general procedure A, the reaction was carried out with 4-iodobenzonitrile (68.7 mg, 0.3 mmol, 1.0 equiv) and benzyl 2,5-dihydro-1H-pyrrole-1-carboxylate (**7a**) (135 µL, 0.75 mmol, 2.5 equiv) for 48 h. Purification by flash column chromatography (4:1 hexanes: EtOAc) afforded benzyl 3-(4-cyanophenyl)pyrrolidine-1-carboxylate as a colorless oil (50.1 mg, 55%).

R_f: (20% EtOAc in hexanes), UV;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 – 7.54 (m, 2H), 7.41 – 7.29 (m, 7H), 5.20 – 5.14 (m, 2H), 3.97 – 3.80 (m, 2H), 3.69 (dddd, *J* = 28.5, 11.2, 8.2, 3.2 Hz, 1H), 3.56 – 3.33 (m, 2H), 2.38 – 2.26 (m, 1H), 2.05 – 1.93 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) (mixture of two rotamers) δ 154.73, 146.83, 136.73, 132.49, 128.57, 128.51, 128.25, 128.14, 128.06, 128.04, 128.01, 127.94, 127.87, 118.69, 110.85, 67.34, 66.97, 66.92, 51.91, 51.76, 45.99, 45.54, 44.19, 43.26, 42.66, 33.03, 32.17;

HRMS *m/z* (ESI): found (*M* + *H*) 307.1443. $C_{19}H_{18}N_2O_2H$ requires *M* + *H*, 307.1447.



(8b: 8b' 3:1) **(10b: <5%)**

4-((2*S*)-bicyclo[2.2.0]hexan-2-yl)benzonitrile (8b).

Following General Procedure A, a mixture of 4-iodobenzonitrile (68.7 mg, 0.3 mmol, 1.0 equiv), and bicyclo[2.2.0]hex-2-ene (**8a**) (60.1 mg, 0.75 mmol, 2.5 equiv) was stirred for 48 h. Purification by flash column chromatography (SiO_2, 95:5 hexanes: Et_2O) furnished the title compound as a clear, colorless oil as a mixture between xx and ring-opened **8b'** in a 3:1 ratio

with <5% of **10b** which results as hydrogenation of the ring opened product (38.5 mg, ^{1}H NMR yield: 70%).

R_f: 0.4 (5% Et_2O in hexanes), UV and $KMnO_4$ stain;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 2H), 7.34 – 7.31 (m, 2H), 3.66 (td, *J* = 7.5, 2.6 Hz, 1H), 2.93 – 2.77 (m, 2H), 2.62 – 2.43 (m, 4H), 2.21 – 2.14 (m, 2H);

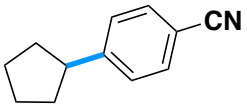
^{13}C NMR (151 MHz, $CDCl_3$) δ 153.04, 132.36, 127.34, 119.38, 109.47, 46.75, 43.75, 36.30, 33.19, 27.53, 27.51.

8b'
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 2H), 7.34 – 7.31 (m, 2H), 5.77 (d, *J* = 2.7 Hz, 2H), 2.91 – 2.81 (m, 1H), 2.33 – 2.25 (m, 1H), 2.22 – 2.09 (m, 3H), 1.96 – 1.89 (m, 1H), 1.75 (dddd, *J* = 12.7, 11.7, 10.4, 5.8 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.92, 132.41, 127.91, 127.27, 126.21, 119.29, 109.97, 40.45, 32.96, 29.37, 25.58;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 6.547 (major product);

MS: (EI, 70 eV): *m/z* (%) $C_{13}H_{13}N$ calc. 183.10 (major product): 183.1 (12), 168.1 (8), 154.1 (11), 142.1 (100), 129.1 (49), 115.1 (34), 102 (6), 89 (7), 77 (5), 67.1 (5).



4-cyclopentylbenzonitrile (9b).

Following General Procedure A, a mixture of 4-iodobenzonitrile (68.7 mg, 0.3 mmol, 1.0 equiv), and cyclopentene (**9a**) (66 μL, 0.75 mmol, 2.5 equiv) was stirred for 24 h. Purification by flash column chromatography (SiO_2, 95:5 hexanes: Et_2O) furnished the title compound as a clear, yellow oil (43.0 mg, 84%).

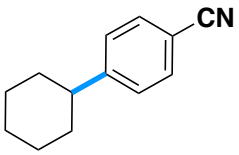
R_f: 0.3 (5% Et_2O in hexanes), UV and $KMnO_4$ stain;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 2H), 7.34 – 7.31 (m, 2H), 3.04 (tt, *J* = 9.7, 7.6 Hz, 1H), 2.14 – 2.05 (m, 2H), 1.87 – 1.78 (m, 2H), 1.77 – 1.67 (m, 2H), 1.62 – 1.52 (m, 2H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.48, 132.23, 128.05, 119.37, 109.57, 46.16, 34.57, 25.67;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 6.117;

MS: (EI, 70 eV): *m/z* (%) $C_{12}H_{13}N$ calc. 171.10: 171.1 (34), 156.1 (4), 142.1 (32), 129.1 (100), 116 (18), 102 (8), 89 (7), 77 (4), 68 (4), 55 (3).



4-cyclohexylbenzonitrile (10b).

Following General Procedure A, a mixture of 4-iodobenzonitrile (68.7 mg, 0.3 mmol, 1.0 equiv), cyclohexene (**10a**) (66 μL, 0.75 mmol, 2.5 equiv) was stirred for 28 h. Purification by flash column chromatography (SiO_2, 95:5 hexanes: Et_2O) furnished the title compound as a clear, colorless oil (39.5 mg, 71%).

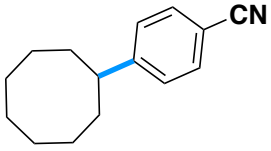
R_f: 0.3 (5% Et_2O in hexanes), UV and $KMnO_4$ stain;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 2H), 7.31 – 7.28 (m, 2H), 2.56 (t, *J* = 2.8 Hz, 1H), 1.92 – 1.82 (m, 4H), 1.80 – 1.73 (m, 1H), 1.45 – 1.35 (m, 4H), 1.30 – 1.22 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.63, 132.34, 127.81, 119.37, 109.71, 44.91, 34.13, 26.75, 26.07.

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 6.512;

MS: (EI, 70 eV): *m/z* (%) $C_{13}H_{15}N$ calc. 185.12: 185.1 (32), 156.1 (7), 142.1 (23), 129 (100), 116 (28), 102 (7), 89 (7) 82.1 (5), 77 (4), 67 (6).



4-cyclooctylbenzonitrile (11b).

Following General Procedure A, a mixture of 4-iodobenzonitrile (68.7 mg, 0.3 mmol, 1.0 equiv), cyclooctene (**11a**) (98 μL, 0.75 mmol, 2.5 equiv) was stirred for 16 h. Purification by flash column chromatography (SiO_2, 95:5 hexanes: Et_2O) furnished the title compound as a clear, colorless oil (43.3 mg, 68%).

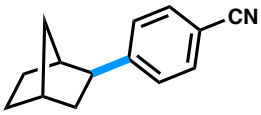
R_f: 0.3 (5% Et_2O in hexanes), UV and $KMnO_4$ stain;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 2H), 7.29 – 7.26 (m, 2H), 2.81 (tt, *J* = 9.7, 3.4 Hz, 1H), 1.87 – 1.48 (m, 14H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.99, 132.36, 127.93, 119.39, 109.43, 45.05, 34.38, 26.91, 26.37, 25.99;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 7.513;

MS: (EI, 70 eV): *m/z* (%) $C_{15}H_{19}N$ calc. 213.15: 213.2 (10), 156.1 (2), 142.1 (11), 129.1 (100), 116.1 (19), 103.1 (4), 89 (4) 55.1 (7).



4-bicyclo[2.2.1]heptan-2-yl)benzonitrile (12b).

Following General Procedure A, a mixture of 4-iodobenzonitrile (68.7 mg, 0.3 mmol, 1.0 equiv), norbornene (**12a**) (70.6 mg, 0.75 mmol, 2.5 equiv) was stirred for 16 h. Purification by flash column chromatography (SiO_2, 95:5 hexanes: Et_2O) furnished the title compound as a pale yellow oil (40.6 mg, 69%).

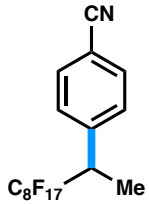
R_f: 0.3 (5% Et_2O in hexanes), UV and $KMnO_4$ stain;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 – 7.54 (m, 2H), 7.33 – 7.28 (m, 2H), 2.78 (dd, *J* = 8.7, 5.6 Hz, 1H), 2.40 – 2.36 (m, 2H), 1.82 (ddd, *J* = 11.7, 9.1, 2.4 Hz, 1H), 1.67 – 1.55 (m, 3H), 1.47 (dq, *J* = 9.9, 1.9 Hz, 1H), 1.39 – 1.34 (m, 1H), 1.31 – 1.26 (m, 1H), 1.23 (dtd, *J* = 9.9, 2.9, 1.5 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.32, 132.20, 127.95, 119.36, 109.26, 47.63, 42.68, 39.26, 36.97, 36.31, 30.59, 28.84;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 6.953;

MS: (EI, 70 eV): *m/z* (%) $C_{14}H_{15}N$ calc. 197.12: 197.1 (23), 168.1 (7), 154 (11), 140.1 (13), 130.1 (100), 116.1 (17), 102 (7), 89.1 (8), 81.1 (24), 67.1 (33).



4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecan-2-yl)benzonitrile (13b).

Following General Procedure A, a mixture of 4-iodobenzonitrile (68.7 mg, 0.3 mmol, 1.0 equiv), 1*H*, 1*H*, 2*H*-perfluoro-1-decene (**13a**) (200 μL, 0.75 mmol, 2.5 equiv), and **$NiBr_2$(dtbbpy) (7.6 mg, 0.015 mmol, 5 mol%)** was stirred for 48 h **in 800 μL of 1,4-dioxane**. Purification by flash column chromatography (SiO_2, 95:5 hexanes: Et_2O) furnished the title compound as a white solid (53.0 mg, 32%).

R_f: 0.5 (5% Et_2O in hexanes), faint $KMnO_4$;

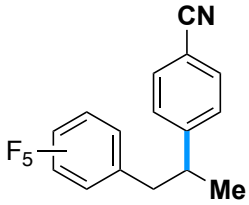
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 – 7.64 (m, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 3.61 (td, *J* = 15.6, 7.7 Hz, 1H), 1.55 (d, *J* = 7.1 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.85, 132.57, 129.85, 118.50, 112.46, 42.73 (t, *J* = 22.0 Hz), 29.86, 14.71;

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.96 (m), -115.66 (m), -119.83 (m), -120.08 (m), -121.94 (m), -122.11 (m), -122.96 (m), -126.35 (m);

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 5.665;

MS: (EI, 70 eV): *m/z* (%) $C_{17}H_8F_{17}N$ calc. 549.04: 549.2 (6.7), 130 (100), 103 (9), 69 (7).



4-(1-(perfluorophenyl)propan-2-yl)benzonitrile (14b).

Following General Procedure A, a mixture of 4-iodobenzonitrile (68.7 mg, 0.3 mmol, 1.0 equiv),

and allylpentafluorobenzene (**14a**) (115 μL, 0.75 mmol, 2.5 equiv) was stirred for 11 h. Purification by flash column chromatography (SiO_2, 95:5 hexanes:Et_2O) furnished the title compound as an off-white solid (76.9 mg, 82% in an 13:1 branched:linear ratio).

R_f: 0.3 (5% Et_2O in hexanes), UV and KMnO4;

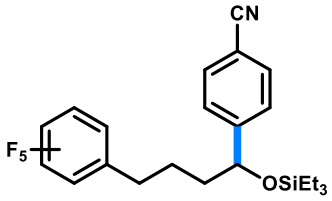
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 2H), 7.30 – 7.27 (m, 2H), 3.12 (h, *J* = 7.2 Hz, 1H), 2.94 (dd, *J* = 7.2, 1.8 Hz, 2H), 1.33 (d, *J* = 6.9 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.60, 132.57, 127.79, 118.93, 110.87, 40.08, 31.00, 20.80;

^{19}F NMR (376 MHz, $CDCl_3$) δ -143.26 (m), -156.50 (t, *J*= 20.6 Hz), -162.46 (m);

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 6.941;

MS: (EI, 70 eV): *m/z* (%) $C_{16}H_{10}F_5N$ calc. 311.07: 311.1 (8), 181 (9), 103 (18), 77 (7).



4-(4-(Perfluorophenyl)-1-((triethylsilyl)oxy)butyl)benzonitrile (15b)

Following the general procedure A, the reaction was carried out with 4-iodobenzonitrile (68.7 mg, 0.3 mmol, 1.0 equiv) and triethyl((4-(perfluorophenyl)but-1-en-1-yl)oxy)silane (**15a**) (264.3 mg, 0.75 mmol, 2.5 equiv) for 46 h. Purification by flash column chromatography (95:5 hexanes: ethyl acetate) afforded 4-(4-(perfluorophenyl)-1-((triethylsilyl)oxy)butyl)benzonitrile (15b) as a colorless solid (64.8 mg, 48%).

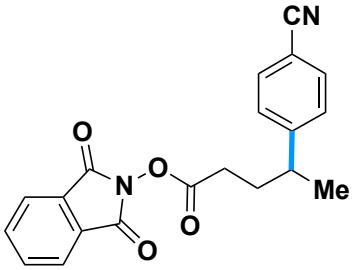
R_f: 0.25 (5% ethyl acetate in hexanes), UV;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 2H), 7.41 – 7.38 (m, 2H), 4.75 (dd, *J* = 7.1, 4.0 Hz, 1H), 2.75 – 2.66 (m, 2H), 1.81 – 1.54 (m, 4H), 0.89 (t, *J* = 8.0 Hz, 9H), 0.54 (qd, *J* = 7.9, 3.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.77, 132.28, 126.58, 119.06, 111.12, 73.76, 39.83, 24.91, 22.31, 6.84, 4.89;

^{19}F NMR (376 MHz, $CDCl_3$) δ -144.47 (dd, *J* = 23.0, 8.5 Hz), -157.95 (t, *J* = 20.8 Hz), -162.98 (td, *J* = 21.9, 8.2 Hz);

HRMS: *m/z* (ESI): found (*M* + *H*) 456.1773. $C_{23}H_{26}F_5NOSi$ requires *M* + *H*, 456.1782.



1,3-dioxoisoindolin-2-yl-4-(4-cyanophenyl)pentanoate (16b).

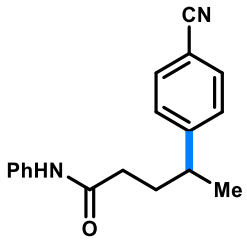
Following General Procedure A, a mixture of 4-iodobenzonitrile (68.7 mg, 0.3 mmol, 1.0 equiv), and 1,3-dioxoisoindolin-2-yl pent-4-enoate (**16a**) (184 mg, 0.75 mmol, 2.5 equiv), and **$NiBr_2$(dtbbpy) (7.2 mg, 0.015 mmol, 5 mol%)** was stirred for 48 h. Purification by flash column chromatography (SiO_2, 4:1 hexanes: EtOAc) furnished the title compound as a clear gel (72.8 mg, 70%, 8:1 B:L).

R_f: 0.2 (20% EtOAc in hexanes), UV and anisaldehyde;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.65 – 7.62 (m, 2H), 7.38 – 7.34 (m, 2H), 2.99 – 2.92 (m, 1H), 2.60 – 2.47 (m, 2H), 2.16 – 2.08 (m, 1H), 2.06 – 1.98 (m, 1H), 1.34 (d, *J* = 6.9 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.28, 162.04, 151.31, 134.97, 132.70, 128.98, 128.06, 124.13, 119.04, 110.58, 39.15, 32.65, 29.21, 21.69;

HRMS: *m/z* (ESI): found (*M* + *H*) 349.1188. $C_{20}H_{16}N_2O_4$ requires *M* + *H*, 349.1188.



4-(4-Cyanophenyl)-*N*-phenylpentanamide (17b)

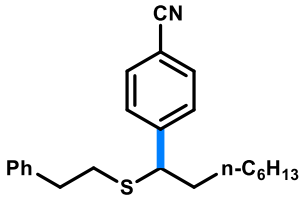
Following the general procedure A, the reaction was carried out with 4-iodobenzonitrile (68.7 mg, 0.3 mmol, 1.0 equiv) and *N*-phenylpent-4-enamide (131.4 mg, 0.75 mmol, 2.5 equiv) for 48 h. Purification by flash column chromatography (7:3 hexanes: EtOAc) afforded 4-(4-cyanophenyl)-*N*-phenylpentanamide (17a) as a pale yellow solid (56.0 mg, 68%).

R_f: 0.30 (30% ethyl acetate in hexanes), UV;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.56 – 7.51 (m, 2H), 7.51 – 7.46 (m, 2H), 7.31 – 7.26 (m, 4H), 7.09 (t, *J* = 7.5 Hz, 1H), 2.88 – 2.78 (m, 1H), 2.19 (t, *J* = 7.6 Hz, 2H), 2.11 – 2.04 (m, 1H), 1.94 (ddt, *J* = 14.0, 9.0, 7.3 Hz, 1H), 1.27 (d, *J* = 6.9 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.82, 152.24, 137.95, 132.39, 128.97, 128.01, 124.27, 119.81, 118.99, 109.90, 39.64, 35.26, 33.15, 22.01;

HRMS: *m/z* (ESI): found (*M* + *H*) 279.1502. $C_{18}H_{18}N_2O$ requires *M* + *H*, 279.1497.



4-(1-(Phenethylthio)octyl)benzonitrile (18b)

Following the general procedure A, the reaction was carried out with 4-iodobenzonitrile (68.7 mg, 0.3 mmol, 1.0 equiv) and oct-1-en-1-yl(phenethyl)sulfane (**18a**) (165.1 mg, 0.75 mmol, 2.5 equiv) for 48 h. Purification by flash column chromatography (3:2 hexanes: toluene) afforded 4-(1-(phenethylthio)octyl)benzonitrile as a colorless solid (71.6 mg, 52%).

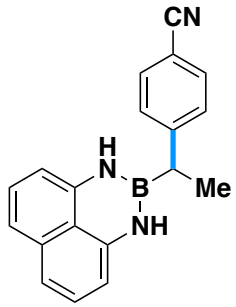
R_f: 0.21 (40% toluene in hexanes), UV;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 2H), 7.43 – 7.38 (m, 2H), 7.32 – 7.27 (m, 2H), 7.25 – 7.21 (m, 1H), 7.12 – 7.08 (m, 1H), 3.74 (dd, *J* = 8.6, 6.4 Hz, 1H), 2.78 (qdd, *J* = 13.8, 8.8, 6.7 Hz, 2H), 2.58 – 2.45 (m, 2H), 1.87 (dddd, *J* = 13.6, 9.9, 6.4, 5.3 Hz, 1H), 1.77 (dddd, *J* = 13.7, 9.9, 8.6, 5.1 Hz, 1H), 1.39 – 1.22 (m, 11H), 0.89 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.07, 140.36, 132.44, 128.77, 128.58, 126.57, 118.96, 110.91, 49.90, 36.43, 36.21, 32.70, 31.86, 29.34, 29.15, 27.69, 22.73, 14.21;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 70 °C/min to 250 °C, then 5 °C/min to 280 °C): t_R = 10.329 min.

MS: (EI, 70 eV): *m/z* (%) $C_{23}H_{29}NS$ calc. 351.20: 351.2 (32), 252.1 (34), 218.1 (22), 214.2 (45), 144.1 (30), 130 (85), 116.1 (100), 105.1 (61), 91.1 (57).



4-(1-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)ethyl)benzonitrile (19b).

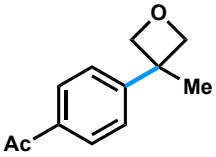
Following General Procedure A, a mixture of 4-iodobenzonitrile (68.7 mg, 0.3 mmol, 1.0 equiv), and 2-vinyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (**19a**) (146 mg, 0.75 mmol, 2.5 equiv) was stirred for 24 h. Purification by flash column chromatography (SiO_2, 7:1 hexanes: EtOAc) furnished the title compound as a pale yellow foam (65.6 mg, 74%).

R_f: 0.25 (15% EtOAc in hexanes), UV and KMnO4;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 2H), 7.33 – 7.30 (m, 2H), 7.12 – 7.05 (m, 2H), 7.02 (dd, *J* = 7.2, 1.2 Hz, 2H), 6.27 (dd, *J* = 7.3, 1.0 Hz, 2H), 5.40 (s, 2H), 2.62 (q, *J* = 7.5 Hz, 1H), 1.45 (d, *J* = 7.5 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.74, 140.61, 136.34, 132.72, 128.47, 127.67, 119.61, 119.22, 118.17, 109.50, 106.13, 16.53;

^{11}B NMR (160 MHz, $CDCl_3$) δ 31.62;



1-(4-(3-methyloxetan-3-yl)phenyl)ethan-1-one (20b).

Following General Procedure B on a 0.1 mmol scale, a mixture of 4-iodoacetophenone (36.9 mg, 0.15 mmol, 1.5 equiv), and 3-methyleneoxetane (**20a**) (0.44 M solution in THF) (227 μL, 0.1 mmol, 1.0 equiv) was stirred for 16 h. Purification by preparative TLC (SiO_2, 7:3 hexanes: EtOAc) furnished the title compound as a white solid (10.0 mg, 53%).

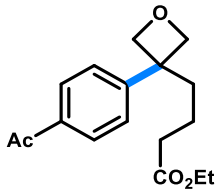
R_f: 0.3 (30% EtOAc in hexanes), UV and anisaldehyde;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 7.31 – 7.27 (m, 2H), 4.97 (d, *J* = 5.6 Hz, 2H), 4.67 (d, *J* = 5.6 Hz, 2H), 2.60 (s, 3H), 1.74 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.71, 152.02, 135.54, 128.93, 125.46, 83.45, 43.81, 27.77, 26.74.

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 5.717;

MS: (EI, 70 eV): *m/z* (%) $C_{12}H_{14}O_2$ calc. 190.10: 190 (1), 160.1 (37) 145.1 (100), 115 (24), 91.1 (11).



Ethyl 4-(3-(4-acetylphenyl)oxetan-3-yl)butanoate (21b)
Following the general procedure B, the reaction was carried out with 1-(4-iodophenyl)ethan-1-one (110.7 mg, 0.45 mmol, 1.5 equiv) and ethyl 4-(oxetan-3-ylidene)butanoate (**21a**) (51.1 mg, 0.3 mmol, 1.0 equiv). Purification by flash column chromatography (3:2 hexanes: EtOAc) afforded ethyl 4-(3-(4-acetylphenyl)oxetan-3-yl)butanoate (21b) as a clear, colorless oil (51.0 mg, 59%).

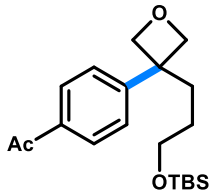
R_f: 0.32 (40% EtOAc in hexanes), anisaldehyde, UV;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.88 (m, 2H), 7.17 – 7.05 (m, 2H), 4.96 (d, *J* = 5.7 Hz, 2H), 4.68 (d, *J* = 5.8 Hz, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.59 (s, 3H), 2.25 (t, *J* = 7.3 Hz, 2H), 2.16 – 2.06 (m, 2H), 1.47 – 1.36 (m, 2H), 1.22 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.66, 173.17, 150.14, 128.79, 126.11, 81.51, 60.52, 47.67, 40.37, 34.21, 29.82, 26.71, 20.03, 14.34;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 6.014 min;

MS: (EI, 70 eV): *m/z* (%) $C_{17}H_{22}O_4$ calc. 290.15: 290.1 (100), 218.9 (10), 187.1 (17), 168.1 (20), 143 (29), 115.9 (20).



1-(4-(3-(3-((*tert*-Butyldimethylsilyl)oxy)propyl)oxetan-3-yl)phenyl)ethan-1-one (22b)
Following the general procedure B, the reaction was carried out with 1-(4-iodophenyl)ethan-1-one (10.7 mg, 0.45 mmol, 1.5 equiv) and *tert*-butyldimethyl(3-(oxetan-3-ylidene)propoxy)silane (**22a**) (68.5 mg, 0.3 mmol, 1.0 equiv). Purification by flash column chromatography afforded 1-(4-(3-(3-((t*ert*-Butyldimethylsilyl)oxy)propyl)oxetan-3-yl)phenyl)ethan-1-one (22b) as a clear, colorless oil (42.4 mg, 41%).

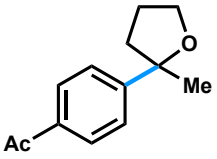
R_f: 0.58 (20% EtOAc in hexanes), UV, anisaldehyde;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.90 (m, 2H), 7.17 – 7.10 (m, 2H), 4.96 (d, *J* = 5.7 Hz, 2H), 4.68

(d, *J* = 5.7 Hz, 2H), 3.54 (t, *J* = 6.3 Hz, 2H), 2.59 (s, 3H), 2.21 – 2.08 (m, 2H), 1.37 – 1.27 (m, 2H), 0.85 (s, 9H), -0.01 (s, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.69, 150.60, 135.47, 128.72, 126.16, 81.72, 62.93, 47.54, 37.36, 27.92, 26.71, 26.04, 18.42, -5.21;

HRMS: *m/z* (ESI): found (*M* + *H*) 349.2202. $C_{20}H_{32}O_3Si$ requires *M* + *H*, 349.2199.



1-(4-(2-methyltetrahydrofuran-2-yl)phenyl)ethan-1-one (23b).

Following General Procedure B, a mixture of 4-iodoacetophenone (110.7 mg, 0.45 mmol, 1.5 equiv), and 2,3-dihydro-5-methylfuran (**23a**) (25.2 mg, 0.3 mmol, 1.0 equiv) was stirred for 16 h **under an air balloon**. Purification by flash column chromatography (SiO_2, 4:1 hexanes: EtOAc) furnished the title compound as a clear, pale yellow oil (18.3 mg, 30%).

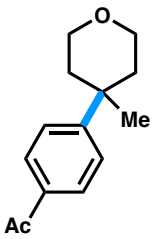
R_f: 0.3 (20% EtOAc in hexanes), UV and anisaldehyde;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 – 7.90 (m, 2H), 7.51 – 7.47 (m, 2H), 4.07 – 4.00 (m, 1H), 3.92 (td, *J* = 8.0, 5.6 Hz, 1H), 2.59 (s, 3H), 2.22 – 2.15 (m, 1H), 2.10 – 1.96 (m, 2H), 1.84 – 1.74 (m, 1H), 1.53 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.99, 153.94, 135.64, 128.51, 125.11, 84.36, 67.87, 39.64, 29.55, 26.75, 25.91;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 70 °C/min to 250 °C, then 5 °C/min to 280 °C): t_R = 5.671;

MS: (EI, 70 eV): *m/z* (%) $C_{13}H_{16}O_2$ calc. 204.12: 206.9 (1), 202.1 (1), 189.1 (100), 159.1 (4), 147 (66), 115.1 (6), 104 (6), 91 (9), 77 (5).



1-(4-(4-methyltetrahydro-2*H*-pyran-4-yl)phenyl)ethan-1-one (24b).

Following General Procedure B, a mixture of 4-iodoacetophenone (110.7 mg, 0.45 mmol, 1.5 equiv), and 4-methylenetetrahydro-2*H*-pyran (**24a**) (29.4 mg, 0.3 mmol, 1.0 equiv) was stirred for 16 h. Purification by flash column chromatography (SiO_2, 4:1 hexanes: EtOAc) furnished the title compound as a clear, colorless oil (35.2 mg, 54%).

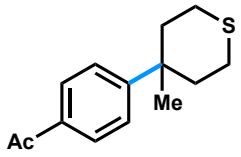
R_f: 0.2 (20% EtOAc in hexanes), UV and anisaldehyde;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 – 7.91 (m, 2H), 7.44 – 7.40 (m, 2H), 3.78 (ddd, *J* = 11.3, 7.9, 3.2 Hz, 2H), 3.66 (ddd, *J* = 11.7, 6.8, 3.6 Hz, 2H), 2.59 (s, 3H), 2.15 – 2.09 (m, 2H), 1.78 (dddd, *J* = 13.7, 6.5, 3.2, 1.0 Hz, 2H), 1.30 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.86, 154.76, 135.09, 128.76, 125.99, 64.47, 37.55, 36.28, 33.03, 26.69;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 70 °C/min to 250 °C, then 5 °C/min to 280 °C): t_R = 6.312;

MS: (EI, 70 eV): *m/z* (%) $C_{14}H_{18}O_2$ calc. 218.13: 218 (19), 203.1 (30), 174.1 (82), 159.1 (82), 145.1 (100), 131.1 (52), 115.1 (44), 91.1 (27), 83 (14), 77 (11).



1-(4-(4-methyltetrahydro-2*H*-thiopyran-4-yl)phenyl)ethan-1-one (25b).

Following General Procedure B, a mixture of 4-iodoacetophenone (110.7 mg, 0.45 mmol, 1.5 equiv), and 4-methylenetetrahydro-2*H*-thiopyran (**25a**) (34.0 mg, 0.3 mmol, 1.0 equiv) was stirred for 16 h. Purification by flash column chromatography (SiO_2, 9:1 hexanes: EtOAc) furnished the title compound as a stenchless, clear, colorless oil (29.7 mg, 42%, 6:1 B:L).

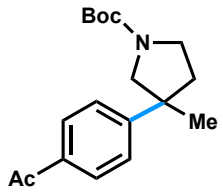
R_f: 0.2 (10% EtOAc in hexanes), UV and anisaldehyde;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 – 7.92 (m, 2H), 7.45 – 7.41 (m, 2H), 2.73 – 2.61 (m, 4H), 2.61 (s, 3H), 2.40 (ddd, *J* = 14.0, 8.0, 3.1 Hz, 2H), 1.94 (ddd, *J* = 14.0, 8.7, 3.1 Hz, 2H), 1.24 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.85, 154.00, 135.07, 128.85, 126.25, 38.57, 37.83, 34.04, 26.70, 24.49;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 70 °C/min to 250 °C, then 5 °C/min to 280 °C): t_R = 7.027;

MS: (EI, 70 eV): *m/z* (%) $C_{14}H_{18}OS$ calc. 234.11: 234.1 (100), 219.1 (12), 206.1 (11), 191.1 (14), 174.1 (10), 163.1 (31), 159.1 (23), 145.1 (35), 131.1 (17), 115.1 (34), 91.1 (17), 77 (9).



***N*-Boc-3-(4-acetylphenyl)-3-methylpyrrolidine (26b).**

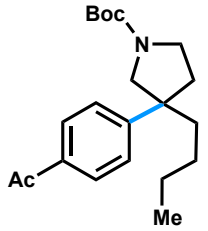
Following General Procedure B, a mixture of 4-iodoacetophenone (110.7 mg, 0.45 mmol, 1.5 equiv), and *N*-Boc-3-methylenepyrrolidine (**26a**) (55.0 mg, 0.3 mmol, 1.0 equiv) was stirred for 16 h. Purification by flash column chromatography (SiO_2, 4:1 hexanes: EtOAc) furnished the title compound as a clear, colorless oil (65.8 mg, 72% as a sum of 2 rotamers).

R_f: 0.2 (20% EtOAc in hexanes), UV and anisaldehyde;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 – 7.90 (m, 2H), 7.36 – 7.32 (m, 2H), 3.62 (dd, *J* = 28.7, 10.8 Hz, 1H), 3.57 – 3.40 (m, 3H), 2.59 (s, 3H), 2.20 – 2.12 (m, 1H), 2.11 – 2.05 (m, 1H), 1.48 (d, *J* = 7.0 Hz, 9H), 1.37 (d, *J* = 4.9 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) (2 rotamers) δ 197.76, 197.72, 154.83, 152.73, 135.46, 128.75, 126.06, 126.02, 79.59, 79.48, 57.34, 56.65, 46.19, 45.37, 44.84, 44.54, 37.85, 37.01, 28.63, 27.59, 26.68;

HRMS: *m/z* (ESI): found (*M* + *Na*) 326.1739. $C_{18}H_{25}NO_3$ requires *M* + *Na*, 326.1732.



***N*-Boc-3-(4-acetylphenyl)-3-butylpyrrolidine (27b).**

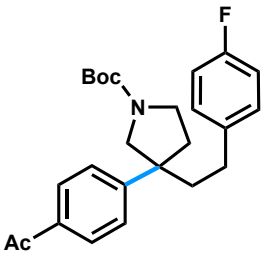
Following General Procedure B, a mixture of 4-iodoacetophenone (110.7 mg, 0.45 mmol, 1.5 equiv), and *N*-Boc- 3-butylidenepyrrolidine (**27a**) (67.6 mg, 0.3 mmol, 1.0 equiv) was stirred for 16 h. Purification by flash column chromatography (SiO_2, 4:1 hexanes: EtOAc) furnished the title compound as a clear, colorless oil (67.5 mg, 65% as a sum of 2 rotamers).

R_f: 0.2 (20% EtOAc in hexanes), UV and anisaldehyde;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 2H), 7.33 – 7.29 (m, 2H), 3.73 – 3.55 (m, 2H), 3.52 – 3.27 (m, 2H), 2.61 (s, 3H), 2.22 – 2.07 (m, 2H), 1.82 – 1.73 (m, 1H), 1.70 – 1.59 (m, 1H), 1.50 (d, *J* = 14.6 Hz, 9H), 1.24 – 1.13 (m, 2H), 1.03 – 0.90 (m, 2H), 0.80 (q, *J* = 7.0 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) (2 rotamers) δ 197.89, 197.84, 154.86, 154.83, 151.03, 135.42, 128.55, 126.86, 126.80, 79.60, 79.47, 55.88, 55.14, 50.11, 49.32, 44.58, 44.24, 39.76, 39.62, 36.57, 35.34, 28.72, 28.66, 27.27, 27.23, 26.70, 23.15, 14.01, 14.00;

HRMS: *m/z* (ESI): found (*M* + *Na*) 368.2200. $C_{21}H_{31}NO_3$ requires *M* + *Na*, 368.2202.



***N*-Boc-3-(4-acetylphenyl)-3-(4-fluorophenethyl)pyrrolidine (28b).**

Following General Procedure B, a mixture of 4-iodoacetophenone (110.7 mg, 0.45 mmol, 1.5 equiv), and *N*-Boc-3-(2-(4-fluorophenyl)ethylidene)pyrrolidine (87.3 mg, 0.3 mmol, 1.0 equiv) was stirred for 16 h. Purification by flash column chromatography (SiO_2, 9:1 PhMe: EtOAc) furnished the title compound as a clear, pale yellow oil (84.1 mg, 68%, as a sum of 2 rotamers).

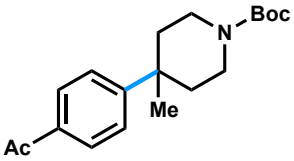
R_f: 0.4 (10% EtOAc in toluene), UV and anisaldehyde;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 – 7.91 (m, 2H), 7.37 – 7.29 (m, 2H), 6.97 – 6.84 (m, 4H), 3.80 – 3.53 (m, 2H), 3.52 – 3.24 (m, 2H), 2.62 (s, 3H), 2.34 – 2.11 (m, 4H), 2.12 – 2.00 (m, 1H), 1.93 (ddd, *J* = 13.7, 11.5, 5.6 Hz, 1H), 1.52 – 1.33 (m, 9H);

^{13}C NMR (151 MHz, $CDCl_3$, 2 rotamers) δ 197.83, 197.79, 161.39 (d, *J* = 243.8 Hz) 154.83, 154.74, 150.22, 150.19, 137.29 (d, *J* = 11.3 Hz), 135.72, 135.70, 129.60 (d, *J* = 7.8, 2.7 Hz), 128.77, 126.86, 126.81, 115.27 (d, *J* = 21.2 Hz), 79.77, 79.65, 55.77, 54.92, 50.17, 49.38, 44.49, 44.14, 42.13, 41.91, 36.82, 35.38, 30.84, 30.77, 28.70, 28.63, 26.72;

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.62, -117.68;

HRMS: *m/z* (ESI): found (*M* + *H*) 412.2268. $C_{25}H_{30}FNO_3$ requires *M* + *H*, 412.2288.



***N*-Boc-4-(4-acetylphenyl)-4-methylpiperidine (29b).**

Following General Procedure B, a mixture of 4-iodoacetophenone (110.7 mg, 0.45 mmol, 1.5 equiv), and *N*-Boc-4-methylenepiperidine (**29a**) (59.2 mg, 0.3 mmol, 1.0 equiv) was stirred for 16 h. Purification by flash column chromatography (SiO_2, 4:1 hexanes: EtOAc) furnished the title compound as a clear, colorless oil (54.1 mg, 57%).

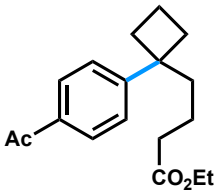
R_f: 0.2 (20% EtOAc in hexanes), UV and anisaldehyde;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 – 7.91 (m, 2H), 7.45 – 7.41 (m, 2H), 3.54 – 3.45 (m, 2H), 3.43 –

3.34 (m, 2H), 2.59 (s, 3H), 2.12 – 2.03 (m, 2H), 1.76 – 1.66 (m, 2H), 1.45 (s, 9H), 1.27 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.82, 155.02, 154.00, 135.10, 128.76, 126.09, 79.55, 37.06, 28.78, 28.56, 26.67 (piperidine ring carbons too broad to identify);

HRMS: *m/z* (ESI): found (*M* + *Na*) 340.1882. $C_{19}H_{27}NO_3$ requires *M* + *Na*, 340.1889.



Ethyl 4-(1-(4-acetylphenyl)cyclobutyl)butanoate (30b).

Following General Procedure B, a mixture of 4-iodoacetophenone (110.7 mg, 0.45 mmol, 1.5 equiv), and ethyl 4-cyclobutylidenebutanoate (**30a**) (50.5 mg, 0.3 mmol, 1.0 equiv) was stirred for 16 h. Purification by flash column chromatography (SiO_2, 9:1 hexanes: EtOAc) followed by washing with 5 M NaOH/THF yielded the title compound as a clear, pale yellow oil (54.0 mg, 62%, 10:1 B:L).

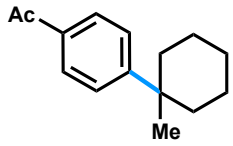
R_f: 0.2 (10% EtOAc in hexanes), UV and anisaldehyde;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 – 7.87 (m, 2H), 7.21 – 7.15 (m, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.58 (d, *J* = 3.2 Hz, 3H), 2.39 – 2.32 (m, 2H), 2.21 – 2.13 (m, 4H), 2.12 – 2.00 (m, 2H), 1.88 – 1.78 (m, 2H), 1.36 – 1.28 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.99, 173.60, 155.94, 134.70, 128.38, 126.08, 60.36, 46.80, 41.78, 34.56, 32.84, 26.71, 20.32, 16.12, 14.36;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 70 °C/min to 250 °C, then 5 °C/min to 280 °C): t_R = 7.410;

MS: (EI, 70 eV): *m/z* (%) $C_{18}H_{24}O_3$ calc. 288.17: 288.2 (67), 260.2 (65), 245.1 (21), 214.1 (8), 199.1 (17), 187.1 (36), 172.1 (100), 157.1 (53), 143.1 (64), 129.1 (80), 115.1 (62), 102.1 (16), 91.1 (17), 77.1 (12).



1-(4-(1-methylcyclohexyl)phenyl)ethan-1-one (31b).

Following General Procedure B, a mixture of 4-iodoacetophenone (110.7 mg, 0.45 mmol, 1.5 equiv), and 1-methylcyclohexene (**31a**) (29.0 mg, 0.3 mmol, 1.0 equiv) was stirred for 16 h. Purification by flash column chromatography (SiO_2, 9:1 hexanes: EtOAc) followed by washing with 5 M NaOH/THF yielded the title compound as a clear, pale yellow oil (38.3 mg, 60%).

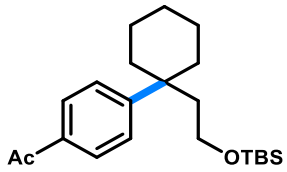
R_f: 0.3 (10% EtOAc in hexanes), UV and anisaldehyde;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 – 7.89 (m, 2H), 7.49 – 7.45 (m, 2H), 2.59 (s, 3H), 2.08 – 1.97 (m, 2H), 1.65 – 1.52 (m, 4H), 1.49 – 1.35 (m, 4H), 1.19 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.04, 156.00, 134.61, 128.57, 126.31, 38.65, 37.87, 26.68, 26.38, 22.75;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 70 °C/min to 250 °C, then 5 °C/min to 280 °C): t_R = 6.335;

MS: (EI, 70 eV): *m/z* (%) $C_{15}H_{20}O$ calc. 216.15: 216.2 (44), 201.1 (100), 173.1 (8), 160.1 (18), 145.1 (47), 131.1 (19), 115.1 (24), 105.1 (11), 91.1 (14), 77 (6).



1-(4-(1-(2-((*tert*-Butyldimethylsilyl)oxy)ethyl)cyclohexyl)phenyl)ethan-1-one (32b)

Following the general procedure B, the reaction was carried out with 1-(4-iodophenyl)ethan-1-one (110.7 mg, 0.45 mmol, 1.5 equiv) and tert-butyl(2-(cyclohex-1-en-1-yl)ethoxy)dimethylsilane (**32a**) (72.1 mg, 0.3 mmol, 1.0 equiv). Purification by flash column chromatography (95:5 hexane: EtOAc) and wash with NaOH 5 M in THF overnight afforded 1-(4-(1-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)cyclohexyl)phenyl)ethan-1-one as a clear, colorless oil (38.8 mg, 36%).

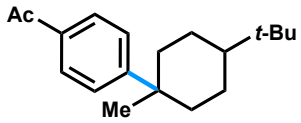
R_f: 0.54 (5% EtOAc in hexanes), anisaldehyde, UV;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 2H), 7.47 – 7.42 (m, 2H), 3.31 (dd, *J* = 8.0, 7.0 Hz, 2H), 2.62 (s, 3H), 2.10 (t, *J* = 10.1 Hz, 2H), 1.84 (t, *J* = 7.5 Hz, 2H), 1.69 (ddd, *J* = 13.4, 9.8, 3.4 Hz, 2H), 1.63 – 1.55 (m, 2H), 1.49 – 1.43 (m, 2H), 1.38 (ddq, *J* = 14.4, 8.0, 4.2, 3.6 Hz, 2H), 0.83 (d, *J* =

0.7 Hz, 9H), -0.07 (d, *J* = 0.8 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.06, 153.05, 134.67, 128.44, 127.11, 59.57, 41.02, 36.61, 30.46, 26.70, 26.51, 26.02, 22.44, 18.33, -5.24;

HRMS: *m/z* (ESI): found (*M* + *H*) 361.2568. $C_{22}H_{36}O_2Si$ requires *M* + *H*, 361.2563.



1-(4-(4-(*tert*-butyl)-1-methylcyclohexyl)phenyl)ethan-1-one (33b).

Following General Procedure B, a mixture of 4-iodoacetophenone (110.7 mg, 0.45 mmol, 1.5 equiv), and 1-(*tert*-butyl)-4-methylenecyclohexane (**33a**) (45.7 mg, 0.3 mmol, 1.0 equiv) was stirred for 16 h. Purification by prep TLC (SiO_2, 4:1 hexanes: EtOAc) followed by washing with 5 M NaOH/THF yielded the title compound as a white solid (43.1 mg, 50%, 2:1 d.r., 7:1 B:L).

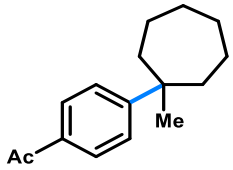
R_f: 0.7 (20% EtOAc in hexanes), UV and anisaldehyde

^{1}H NMR (600 MHz, $CDCl_3$, sum of diastereomers) δ 7.94 – 7.83 (m, 3H), 7.52 – 7.38 (m, 3H), 2.59 (s, 4.5H), 2.44 – 2.38 (m, 1H), 1.94 – 1.88 (m, 2H), 1.76 – 1.69 (m, 2H), 1.65 – 1.51 (m, 4H), 1.49 – 1.31 (m, 4H), 1.25 (s, 5H), 0.89 (s, 12.5H).

^{13}C NMR (151 MHz, $CDCl_3$, sum of diastereomers) δ 198.10, 198.04, 158.60, 153.85, 135.05, 134.71, 128.66, 128.40, 126.84, 125.53, 48.59, 48.57, 38.29, 38.17, 32.56, 32.44, 30.46, 30.16, 27.70, 27.62, 26.68, 26.66, 24.08, 23.86, 23.19, 21.78.

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 70 °C/min to 250 °C, then 5 °C/min to 280 °C): t_R = 7.313

MS: (EI, 70 eV): *m/z* (%) $C_{19}H_{28}O$ calc. 272.21: 272.2 (32), 257.2 (64), 216.2 (36), 201.1 (52), 174.1 (19), 160.1 (37), 145.1 (63), 134.1 (68), 115.1 (34), 105.1 (23), 91 (26), 77.1 (11), 57.1 (100).



1-(4-(1-Methylcycloheptyl)phenyl)ethan-1-one (34b)

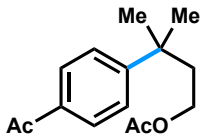
Following the general procedure B, the reaction was carried out with 4-iodoacetophenone (110.7 mg, 0.45 mmol, 1.5 equiv) and methylenecycloheptane (**34a**) (33.1 mg, 0.3 mmol, 1.0 equiv). Purification by flash column chromatography and wash with NaOH 5 M in THF overnight afforded 1-(4-(1-methylcycloheptyl)phenyl)ethan-1-one (34b) as a clear, colorless oil (42.1 mg, 62%, 4:1 B:L). Data corresponds to the major isomer.

R_f: 0.46 (95:5 EtOAc in hexanes), anisaldehyde, UV;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 – 7.89 (m, 2H), 7.47 – 7.43 (m, 2H), 2.58 (s, 3H), 1.72 – 1.44 (m, 12H), 1.23 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.02, 134.50, 129.48, 128.42, 126.36, 41.90, 40.78, 32.37, 30.01, 26.67, 23.80;

HRMS *m/z* (ESI): found (*M* + *H*) 231.1756. $C_{16}H_{22}OH$ requires *M* + *H*, 231.1749.



3-(4-acetylphenyl)-3-methylbutyl acetate (35b).

Following General Procedure B, a mixture of 4-iodoacetophenone (110.7 mg, 0.45 mmol, 1.5 equiv), and 3-methylbut-3-en-1-yl acetate (**35a**) (38.5 mg, 0.3 mmol, 1.0 equiv) was stirred for 16 h. Purification by flash column chromatography (SiO_2, 7:3 hexanes:EtOAc) furnished the title compound as clear, pale yellow oil (42.5 mg, 57%).

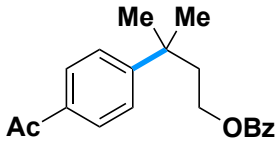
R_f: 0.5 (30% EtOAc in hexanes), UV and anisaldehyde;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.89 (m, 2H), 7.46 – 7.42 (m, 2H), 3.90 (t, *J* = 7.3 Hz, 2H), 2.59 (s, 3H), 2.03 (t, *J* = 7.4 Hz, 2H), 1.90 (s, 3H), 1.38 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.89, 171.10, 154.16, 135.08, 128.55, 126.05, 61.80, 42.17, 37.20, 29.13, 26.70, 21.00;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 70 °C/min to 250 °C, then 5 °C/min to 280 °C): t_R = 6.323;

MS: (EI, 70 eV): *m/z* (%) $C_{15}H_{20}O_3$ calc. 248.14: 248.1 (2), 233.1 (8), 188.1 (5), 161.1 (100), 145.1 (7), 133.1 (8), 115.1 (7), 105.1 (4), 91.1 (5).



3-(4-acetylphenyl)-3-methylbutyl benzoate (36b).

Following General Procedure B, a mixture of 4-iodoacetophenone (110.7 mg, 0.45 mmol, 1.5 equiv), and 3-methylbut-2-en-1-yl benzoate (**36a**) (57.0 mg, 0.3 mmol, 1.0 equiv) was stirred for 16 h. Purification by flash column chromatography (SiO_2, 9:1 hexanes: EtOAc) furnished the title compound as clear, pale yellow oil (54.9 mg, 59%).

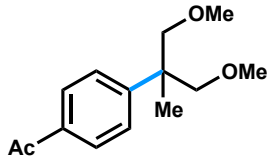
R_f: 0.4 (10% EtOAc in hexanes), UV and anisaldehyde;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 2H), 7.82 (dt, *J* = 8.3, 1.3 Hz, 2H), 7.53 – 7.45 (m, 3H), 7.36 (t, *J* = 7.4 Hz, 2H), 4.19 (t, *J* = 7.0 Hz, 2H), 2.55 (s, 3H), 2.18 (t, *J* = 7.0 Hz, 2H), 1.44 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.85, 166.58, 154.32, 135.01, 132.99, 130.24, 129.59, 128.61, 128.34, 126.08, 62.28, 42.40, 37.30, 29.23, 26.68;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 70 °C/min to 250 °C, then 5 °C/min to 280 °C): t_R = 8.704;

MS: (EI, 70 eV): *m/z* (%) $C_{20}H_{22}O_3$ calc. 310.16: 310.2 (3), 295.2 (6), 188.1 (15), 161,1 (100), 145.1 (10), 133.1 (6), 115.1 (6), 105 (27), 77.1 (21).



1-(4-(1,3-dimethoxy-2-methylpropan-2-yl)phenyl)ethan-1-one (37b).

Following General Procedure B, a mixture of 4-iodoacetophenone (110.7 mg, 0.45 mmol, 1.5 equiv), and 3-methoxy-2-(methoxymethyl)prop-1-ene (**37a**) (34.8 mg, 0.3 mmol, 1.0 equiv) was stirred for 16 h. Purification by flash column chromatography (SiO_2, 4:1 hexanes: EtOAc) furnished the title compound as clear, pale yellow oil (27.4 mg, 39%).

R_f: 0.3 (20% EtOAc in hexanes), UV and anisaldehyde ;

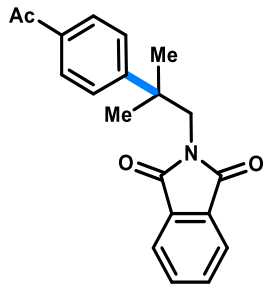
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.89 (m, 2H), 7.49 – 7.46 (m, 2H), 3.57 (dd, *J* = 30.2, 9.2 Hz, 4H), 3.33 (s, 6H), 2.58 (s, 3H), 1.35 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.03, 150.50, 135.31, 128.36, 126.97, 78.23, 59.54, 44.14, 26.71,

21.35;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 70 °C/min to 250 °C, then 5 °C/min to 280 °C): t_R = 5.877;

MS: (EI, 70 eV): *m/z* (%) $C_{14}H_{20}O_3$ calc. 236.14: 236.2 (3), 191.1 (25), 160.1 (70), 145.1 (100), 115.1 (19), 105.1 (6), 91.1 (10), 77 (6).



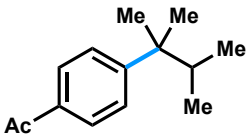
2-(2-(4-Acetylphenyl)-2-methylpropyl)isoindoline-1,3-dione (38b)
Following the general procedure B, the reaction was carried out with 1-(4-iodophenyl)ethan-1-one (110.7 mg, 0.45 mmol, 1.5 equiv) and 2-(2-methylallyl)isoindoline-1,3-dione (**38a**) (60.4 mg, 0.3 mmol, 1.0 equiv). Purification by flash column chromatography (4:1 hexane: EtOAc) afforded 2-(2-(4-acetylphenyl)-2-methylpropyl)isoindoline-1,3-dione as a colorless solid (0.192 mmol, 61.4 mg, 64%, 12:1 branched:linear). Data corresponds to the major isomer.

R_f: 0.22 (20% EtOAc in hexanes), anisaldehyde, UV;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.89 (m, 2H), 7.80 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.70 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.56 – 7.53 (m, 2H), 3.81 (s, 2H), 2.58 (s, 3H), 1.42 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.89, 168.69, 152.26, 135.41, 134.13, 131.95, 128.40, 126.57, 123.43, 49.39, 40.84, 26.89, 26.72;

HRMS *m/z* (ESI): found (*M* + *H*) 322.1447. $C_{20}H_{19}NO_3H$ requires *M* + *H*, 322.1443.



1-(4-(2,3-dimethylbutan-2-yl)phenyl)ethan-1-one (39b).

Following General Procedure B, a mixture of 4-iodoacetophenone (110.7 mg, 0.45 mmol, 1.5 equiv), and tetramethylethylene (**39a**) (25.2 mg, 0.3 mmol, 1.0 equiv) was stirred for 16 h **under an air balloon**. Purification by flash column chromatography (SiO_2, 9:1 hexanes: EtOAc) followed by washing with 5 M NaOH/THF yielded the title compound as clear, pale yellow oil (12.7 mg, 21%).

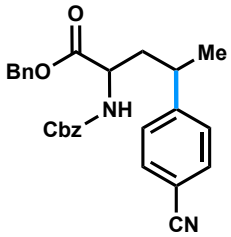
R_f: 0.3 (10% EtOAc in hexanes), UV and anisaldehyde;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.87 (m, 2H), 7.43 – 7.40 (m, 2H), 2.59 (s, 3H), 1.94 (m, 1H), 1.43 (s, 6H), 0.76 (d, *J* = 6.9 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.13, 156.43, 134.62, 128.16, 126.50, 41.17, 38.29, 26.69, 24.70, 18.01;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 70 °C/min to 250 °C, then 5 °C/min to 280 °C): t_R = 5.414;

MS: (EI, 70 eV): *m/z* (%) $C_{14}H_{20}O$ calc. 204.15: 204.1 (2), 161.1 (100), 145.1 (5), 133.1 (10), 115.1 (7), 105.1 (6), 91.1 (7).



benzyl-2-(((benzyloxy)carbonyl)amino)-4-(4-cyanophenyl)pentanoate (40b).

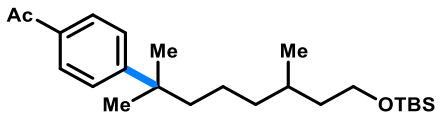
Following General Procedure A, a mixture of 4-iodobenzonitrile (68.7 mg, 0.3 mmol, 1.0 equiv), and benzyl 2-(((benzyloxy)carbonyl)amino)pent-4-enoate (**40a**) (184 mg, 0.75 mmol, 2.5 equiv), and **$NiBr_2$(dtbbpy) (7.2 mg, 0.015 mmol, 5 mol%)** was stirred for 26 h. Purification by flash column chromatography (SiO_2, 7:3 hexanes: EtOAc) furnished the title compound as a clear, colorless thick oil (94.3 mg, 71%, 2:1 d.r.).

R_f: 0.3 (30% EtOAc in hexanes), UV and anisaldehyde;

^{1}H NMR (600 MHz, MeOD, sum of 2 diastereomers (2:1 ratio)) δ 7.64 – 7.53 (m, 3H), 7.41 – 7.18 (m, 18H), 5.16 – 4.99 (m, 7.5H), 3.84 – 3.71 (m, 1.5H), 2.99 – 2.89 (m, 1.5H), 2.17 – 2.05 (m, 1.5H), 1.97 (ddd, *J* = 14.1, 11.0, 4.7 Hz, 1.5H), 1.27 (d, *J* = 7.0 Hz, 4.5H).

^{13}C NMR (151 MHz, MeOD, major diastereomer) δ 173.83, 158.52, 152.49, 138.25, 137.23, 133.55, 129.58, 129.50, 129.42, 129.31, 129.17, 129.07, 128.89, 119.80, 111.30, 67.87, 67.67, 53.90, 39.97, 38.07, 22.52.

HRMS: *m/z* (ESI): found (*M* + *H*) 443.1971. $C_{27}H_{26}N_2O_4H$ requires *M + H*, 443.1971.



1-(4-(8-((*tert*-Butyldimethylsilyl)oxy)-2,6-dimethyloctan-2-yl)phenyl)ethan-1-one (41b)

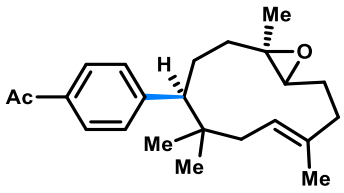
Following the general procedure B, the reaction was carried out with 1-(4-iodophenyl)ethan-1-one (110.7 mg, 0.45 mmol, 1.5 equiv) and *tert*-butyl((3,7-dimethyloct-6-en-1-yl)oxy)dimethylsilane (**41a**) (81.2 mg, 0.3 mmol, 1.0 equiv). Purification by flash column chromatography (9:1 hexanes: EtOAc) and wash with NaOH 5 M in THF overnight afforded 1-(4-(8-((*tert*-Butyldimethylsilyl)oxy)-2,6-dimethyloctan-2-yl)phenyl)ethan-1-one as a clear, colorless oil (61.0 mg, 53%).

R_f: 0.90 (10% EtOAc in hexanes), anisaldehyde;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.86 (m, 2H), 7.44 – 7.39 (m, 2H), 3.66 – 3.52 (m, 2H), 2.59 (s, 3H), 1.65 – 1.53 (m, 3H), 1.51 – 1.44 (m, 2H), 1.31 (s, 6H), 1.28 – 1.17 (m, 4H), 1.11 – 0.97 (m, 3H), 0.87 (s, 9H), 0.77 (d, *J* = 6.5 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.07, 155.78, 134.66, 128.37, 126.18, 61.55, 44.70, 40.02, 38.37, 37.81, 30.47, 29.38, 29.00, 28.90, 26.70, 26.13, 22.16, 19.82, 18.49, -5.13;

HRMS *m/z* (ESI): found (*M* + *H*) 391.3037. $C_{24}H_{42}O_2SiH$ requires *M* + *H*, 391.3032.



1-(4-((E)-1,5,5,8-Tetramethyl-12-oxabicyclo[9.1.0]dodec-7-en-4-yl)phenyl)ethan-1-one (42b)

Following the general procedure B, the reaction was carried out with 1-(4-iodophenyl)ethan-1-one (110.7 mg, 0.45 mmol, 1.5 equiv) and (–)-caryophyllene oxide (**42a**) (66.1 mg, 0.3 mmol, 1.0 equiv). Purification by flash column chromatography (4:1 hexanes: EtOAc) and washed with NaOH 5 M in THF overnight afforded 1-(4-((E)-1,5,5,8-Tetramethyl-12-oxabicyclo[9.1.0]dodec-7-en-4-yl)phenyl)ethan-1-one as a clear, colorless oil (34.4 mg, 34%, 10:1 dr).

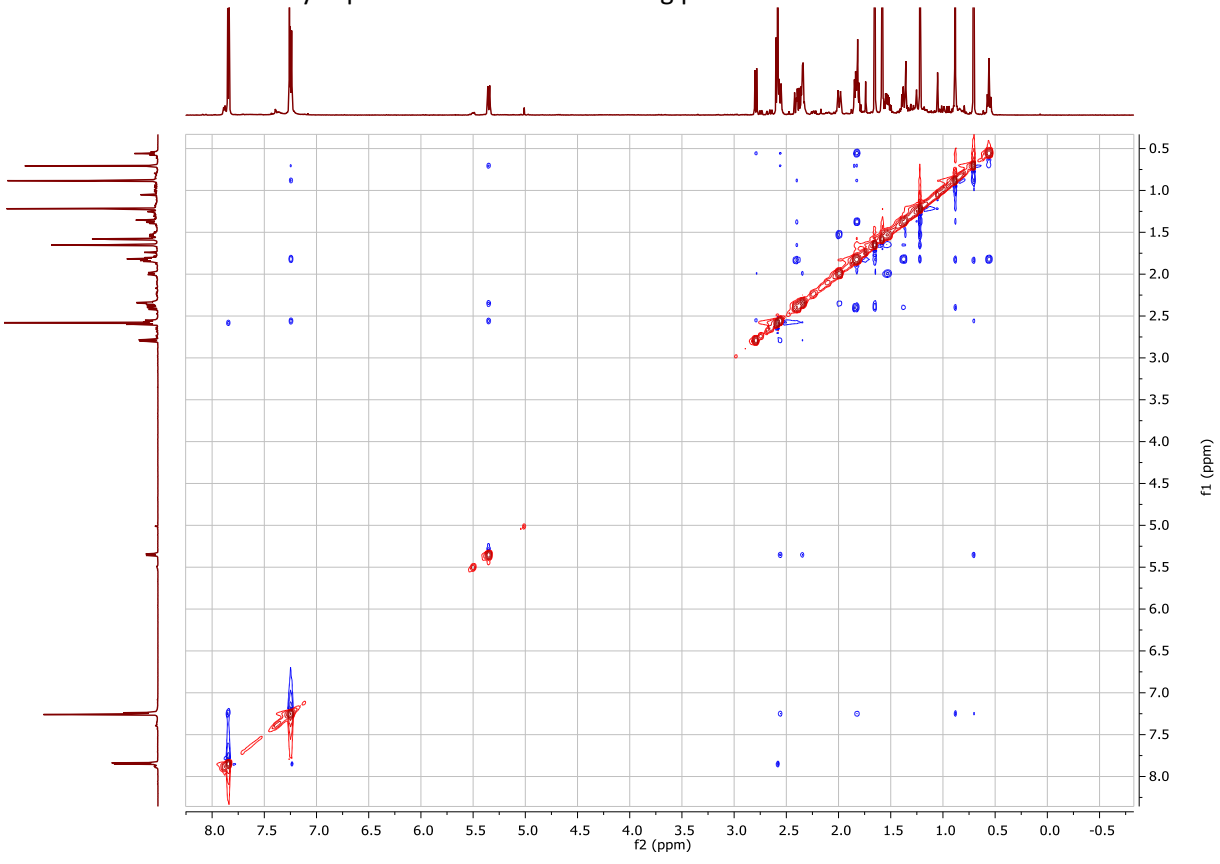
R_f: 0.41 (20% EtOAc in hexanes), anisaldehyde, UV;

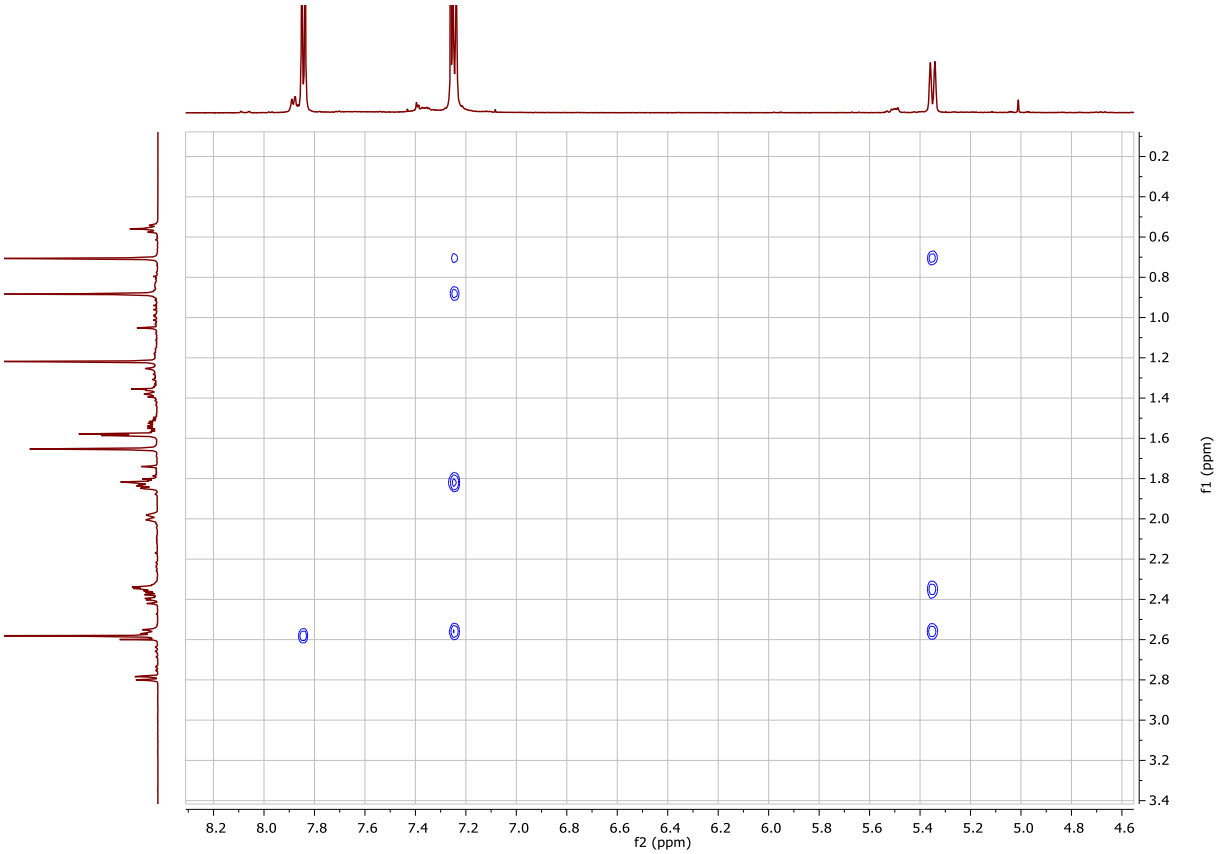
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 5.35 (d, *J* = 11.0 Hz, 1H), 2.79 (dd, *J* = 11.0, 1.7 Hz, 1H), 2.62 – 2.53 (m, 4H), 2.43 – 2.33 (m, 2H), 2.03 – 1.95 (m, 1H), 1.86 – 1.78 (m, 3H), 1.65 (t, *J* = 1.5 Hz, 3H), 1.58 – 1.47 (m, 2H), 1.42 – 1.34 (m, 1H), 1.22 (d, *J* = 0.9 Hz, 3H), 0.88 (s, 3H), 0.71 (s, 3H), 0.59 – 0.51 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.05, 148.57, 135.60, 134.32, 127.88, 122.66, 63.39, 62.82, 54.36, 40.04, 37.68, 36.84, 36.61, 28.17, 26.71, 24.13, 24.11, 23.62, 17.96, 15.72;

HRMS *m/z* (ESI): found (*M* + *H*) 341.2490. $C_{23}H_{32}O_2H$ requires *M* + *H*, 341.2481.

NOESY study allowed for the characterization of the assigned molecule conformation following the interaction of the vinylic proton with its surrounding protons.





1-(4-(2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)phenyl)ethan-1-one (43b).

Following General Procedure B, a mixture of 4-iodoacetophenone (110.7 mg, 0.45 mmol, 1.5 equiv), and β-pinene (**43a**) (40.9 mg, 0.3 mmol, 1.0 equiv) was stirred for 16 h. Purification by flash column chromatography (SiO_2, 9:1 hexanes: EtOAc) followed by washing with 5 M NaOH/THF yielded the title compound as clear, pale yellow oil (25.9 mg, 34%, 10:1 B:L).

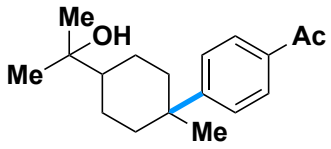
R_f: 0.6 (20% EtOAc in hexanes), UV and anisaldehyde;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 – 7.87 (m, 2H), 7.44 – 7.41 (m, 2H), 5.30 (s, 1H), 2.59 (s, 3H), 1.99 – 1.85 (m, 2H), 1.81 – 1.67 (m, 4H), 1.66 – 1.55 (m, 4H), 1.31 (s, 3H), 1.27 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.09, 156.07, 134.71, 134.06, 128.19, 126.55, 121.01, 44.87, 40.65, 31.56, 27.21, 26.70, 25.08, 24.97, 24.62, 23.41;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 70 °C/min to 250 °C, then 5 °C/min to 280 °C): t_R = 7.038;

MS: (EI, 70 eV): *m/z* (%) $C_{18}H_{24}O$ calc. 256.18: 256.1 (38), 162 (61), 147 (8), 133 (6), 115 (10), 105 (7), 95 (100), 77 (16), 67 (34).



1-(4-(4-(2-hydroxypropan-2-yl)-1-methylcyclohexyl)phenyl)ethan-1-one (44b).

Following General Procedure B, a mixture of 4-iodoacetophenone (110.7 mg, 0.45 mmol, 1.5 equiv), and α-terpineol (**44a**) (46.3 mg, 0.3 mmol, 1.0 equiv) was stirred for 16 h. Purification by flash column chromatography (SiO_2, 3:2 hexanes: EtOAc) furnished the title compound as white solid (20.7 mg, 25%, 2:1 d.r).

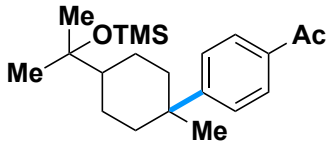
R_f: 0.3 (40% EtOAc in hexanes), UV and anisaldehyde;

^{1}H NMR (600 MHz, $CDCl_3$, sum of diastereomers) δ 7.94 – 7.87 (m, 3H), 7.50 – 7.44 (m, 3H), 2.59 (d, *J* = 3.2 Hz, 4H), 2.44 – 2.39 (m, 1H), 1.98 – 1.92 (m, 2H), 1.84 – 1.78 (m, 2H), 1.70 – 1.59 (m, 4H), 1.52 – 1.29 (m, 5H), 1.29 – 1.21 (m, 13H);

^{13}C NMR (151 MHz, $CDCl_3$, sum of diastereomers) δ 198.10, 198.06, 158.22, 153.45, 134.81, 134.66, 128.77, 128.46, 126.80, 125.51, 72.91, 72.81, 49.36, 48.86, 37.82, 37.71, 37.24, 35.05, 27.30, 27.18, 26.70, 26.69, 24.12, 23.89, 23.23;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 70 °C/min to 250 °C, then 5 °C/min to 280 °C): t_R = 7.742;

MS: (EI, 70 eV): *m/z* (%) $C_{18}H_{26}O_2$ calc. 274.19: 256.1 (11), 241 (6), 216.1 (8), 201 (7), 185 (5), 160 (34), 145 (100), 131 (16), 121 (35), 115 (47), 91 (36), 81 (28), 67 (24), 55 (29).



1-(4-(1-methyl-4-(2-((trimethylsilyl)oxy)propan-2-yl)cyclohexyl)phenyl)ethan-1-one (45b).

Following General Procedure B, a mixture of 4-iodoacetophenone (110.7 mg, 0.45 mmol, 1.5 equiv), and trimethyl((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)oxy)silane (**45a**) (67.9 mg, 0.3 mmol, 1.0 equiv) was stirred for 16 h. Purification by flash column chromatography (SiO_2, 9:1 hexanes: EtOAc) followed by washing with 5 M NaOH/THF yielded the title compound as a clear, colorless oil (41.7 mg, 40%, 2:1 d.r, 13:1 B:L).

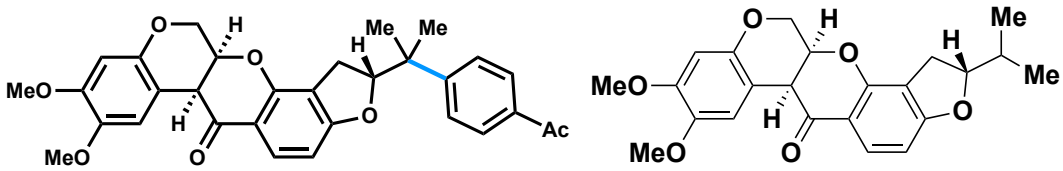
R_f: 0.3 (10% EtOAc in hexanes), UV and anisaldehyde;

^{1}H NMR (600 MHz, $CDCl_3$, sum of diastereomers) δ 7.93 – 7.89 (m, 3H), 7.51 – 7.43 (m, 3H), 2.59 (s, 5H), 2.44 – 2.39 (m, 1H), 1.95 – 1.88 (m, 2H), 1.79 – 1.73 (m, 2H), 1.66 – 1.58 (m, 4H), 1.48 – 1.30 (m, 5H), 1.28 – 1.19 (m, 13H), 0.12 (s, 9H), 0.02 (s, 4H);

^{13}C NMR (151 MHz, $CDCl_3$, sum of diastereomers) δ 198.13, 198.07, 158.55, 153.77, 134.73, 134.54, 128.65, 128.42, 126.87, 125.55, 75.91, 75.89, 50.09, 49.57, 37.95, 37.84, 37.34, 35.03, 27.71, 27.46, 26.70, 26.68, 24.05, 23.85, 23.14, 2.77, 2.67;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 70 °C/min to 250 °C, then 5 °C/min to 280 °C): t_R = 8.103 (major diastereomer);

MS: (EI, 70 eV): *m/z* (%) $C_{21}H_{34}O_2Si$ calc. 346.23: 346.3 (1), 331.2 (8), 288.2 (14), 256.2 (8), 160.1 (8), 145.1 (22), 131.1 (100), 115.1 (10), 73.1 (30) (major diastereomer);



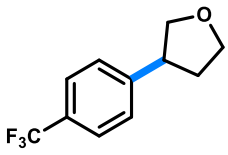
2-(2-(4-acetylphenyl)propan-2-yl)-8,9-dimethoxy-1,2,12,12a-tetrahydrochromeno[3,4-*b*]furo[2,3-*h*]chromen-6(6a*H*)-one (46b).

Following General Procedure B **on 0.1 mmol scale** with **modifications below**, a mixture of 4-iodoacetophenone (36.9 mg, 0.15 mmol, 1.5 equiv), rotenone (**46a**) (39.4 mg, 0.1 mmol, 1.0 equiv), **$Fe(dibm)_3$ (26.1 mg, 0.05 mmol, 50 mol%), and $NiBr_2$(diglyme) (10.6 mg, 0.03 mmol, 30 mol%) was stirred for 2.5 h.** *Prolonged reaction times resulted in oxidation of the hydrofuran core to the benzofuran in both the starting material and the arylated product*. Due to product instability on silica, the compound was purified by prep HPLC to yield a 2:1 mixture of the desired product with hydrogenation of rotenone as a light brown solid (total isolated: 11.5 mg, ^{1}H NMR yield of desired product: 16%).

^{1}H NMR (600 MHz, CD_3CN) δ 7.92 – 7.87 (m, 2H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.60 – 7.55 (m, 2H), 6.49 – 6.42 (m, 3H), 5.13 (dd, *J* = 9.7, 8.5 Hz, 1H), 4.93 (ddd, *J* = 4.1, 2.9, 1.2 Hz, 1H), 4.46 (dd, *J* = 12.3, 3.0 Hz, 1H), 4.15 (d, *J* = 12.5 Hz, 1H), 3.79 (d, *J* = 3.7 Hz, 1H), 3.73 (s, 3H), 3.62 (s, 3H), 2.93 (dd, *J* = 16.1, 9.7 Hz, 1H), 2.73 (dd, *J* = 16.1, 8.5 Hz, 1H), 2.54 (s, 3H), 1.40 (d, *J* = 15.4 Hz, 6H);

^{13}C NMR (151 MHz, CD_3CN) δ 198.57, 189.75, 168.11, 158.64, 151.77, 150.84, 148.69, 144.73, 136.40, 130.30, 128.96, 128.16, 114.19, 114.15, 111.76, 106.04, 105.19, 102.10, 93.00, 73.08, 66.98, 56.76, 56.31, 45.04, 42.94, 28.65, 26.94, 23.88;

HRMS: *m/z* (ESI): found (*M* + *H*) 515.2065. $C_{31}H_{30}O_7$ requires *M* + *H*, 515.2070.



3-(4-(Trifluoromethyl)phenyl)tetrahydrofuran (49)

Following the general procedure A, the reaction was carried out with 1-iodo-4-(trifluoromethyl)benzene (44.1 µL, 0.3 mmol, 1.0 equiv) and 2,5-dihydrofuran (**6a**) (56.7 µL, 0.75 mmol, 2.5 equiv) for 48 h. Purification by flash column chromatography (9:1 hexanes: EtOAc) afforded 3-(4-(trifluoromethyl)phenyl)tetrahydrofuran (49) as a clear, colorless oil (35.3 mg, 55%).

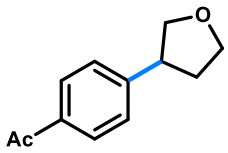
R_f: 0.25 (10% EtOAc in hexanes), anisaldehyde;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 4.14 (dd, *J* = 8.6, 7.4 Hz, 1H), 4.08 (td, *J* = 8.4, 4.7 Hz, 1H), 3.93 (dt, *J* = 8.6, 7.6 Hz, 1H), 3.76 (dd, *J* = 8.6, 6.9 Hz, 1H), 3.46 (p, *J* = 7.5 Hz, 1H), 2.47 – 2.36 (m, 1H), 2.00 (dq, *J* = 12.5, 7.8 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.34, 128.96 (q, *J* = 32.6 Hz), 127.70, 125.63 (q, *J* = 3.9 Hz), 125.24 (q, J = 271.73 Hz), 74.58, 68.56, 44.94, 34.77;

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.68;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 4.778 min;
MS: (EI, 70 eV): *m/z* (%) $C_{11}H_{11}F_3O$ calc. 216.08: 216.1 (9), 186 (70), 127 (5), 117.1 (100), 115 (28).



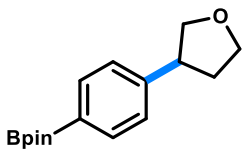
1-(4-(tetrahydrofuran-3-yl)phenyl)ethan-1-one (50)
Following the general procedure A, the reaction was carried out with 4-iodoacetophenone (73.8 mg, 0.3 mmol, 1.0 equiv) and 2,5-dihydrofuran (**6a**) (56.7 µL, 0.75 mmol, 2.5 equiv) for 48 h. Purification by flash column chromatography (9:1 hexanes: EtOAc) afforded 1-(4-(tetrahydrofuran-3-yl)phenyl)ethan-1-one (50) as a clear, colorless oil (0.198 mmol, 37.2 mg, 66%).

R_f: 0.34 (10% EtOAc in hexanes), anisaldehyde, UV;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 2H), 7.35 – 7.30 (m, 2H), 4.12 (dd, *J* = 8.7, 7.5 Hz, 1H), 4.07 (td, *J* = 8.4, 4.7 Hz, 1H), 3.91 (dt, *J* = 8.6, 7.6 Hz, 1H), 3.75 (dd, *J* = 8.6, 6.9 Hz, 1H), 3.45 (p, *J* = 7.6 Hz, 1H), 2.57 (s, 3H), 2.43 – 2.34 (m, 1H), 2.02 – 1.96 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.77, 148.80, 135.67, 128.82, 127.53, 74.48, 68.56, 45.05, 34.69, 26.67;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 5.731 min;
MS: (EI, 70 eV): *m/z* (%) $C_{12}H_{14}O_2$ calc. 190.10: 190.1 (17), 175.1 (34), 145.1 (100), 115.1 (31), 91.1 (16), 65 (4).



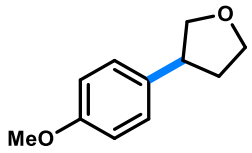
4,4,5,5-Tetramethyl-2-(4-(tetrahydrofuran-3-yl)phenyl)-1,3,2-dioxaborolane (51)

Following the general procedure A, the reaction was carried out with 2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (99.0 mg, 0.3 mmol, 1.0 equiv) and 2,5-dihydrofuran (**6a**) (56.7 µL, 0.75 mmol, 2.5 equiv) for 48 h. Purification by flash column chromatography afforded 4,4,5,5-Tetramethyl-2-(4-(tetrahydrofuran-3-yl)phenyl)-1,3,2-dioxaborolane as a clear, colorless oil as a mixture with 4,4,5,5-tetramethyl-2-(4-(tetrahydrofuran-2-yl)phenyl)-1,3,2-dioxaborolane (2:1 ratio of isomers, 46.1 mg, 57%). Data is for the major regioisomer.

R_f: 0.30 (10 % EtOAc in hexanes), anisaldehyde;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 2H), 7.34 (dt, *J* = 7.2, 0.7 Hz, 2H), 4.92 (t, *J* = 7.2 Hz, 1H), 4.10 (dt, *J* = 8.2, 6.8 Hz, 1H), 3.98 – 3.88 (m, 1H), 2.33 (dtd, *J* = 12.7, 7.2, 5.8 Hz, 1H), 2.03 – 1.96 (m, 2H), 1.82 – 1.74 (m, 1H), 1.34 (s, 12H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.99, 134.96, 124.96, 83.85, 80.73, 68.88, 34.85, 26.10, 25.00. One C is not visible (C–B bond).



3-(4-Methoxyphenyl)tetrahydrofuran (52)
Following the general procedure A, the reaction was carried out with 1-iodo-4-methoxybenzene (70.2 mg, 0.3 mmol, 1.0 equiv) and 2,5-dihydrofuran (**6a**) (56.7 µL, 0.75 mmol, 2.5 equiv) for 48 h. Purification by flash column chromatography afforded 3-(4-methoxyphenyl)tetrahydrofuran (52) as a clear, colorless oil (24.5 mg, 46%).

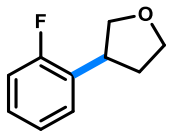
R_f: 0.28 (10% EtOAc in hexanes), anisaldehyde;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 – 7.15 (m, 2H), 6.87 – 6.84 (m, 2H), 4.14 – 4.11 (m, 1H), 4.06 (td, *J* = 8.3, 4.4 Hz, 1H), 3.94 – 3.88 (m, 1H), 3.80 (s, 3H), 3.67 (t, *J* = 8.0 Hz, 1H), 3.36 (p, *J* = 7.9 Hz, 1H), 2.37 – 2.30 (m, 1H), 1.97 (dq, *J* = 12.4, 8.2 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.36, 134.65, 128.31, 114.11, 74.88, 68.64, 55.43, 44.36, 34.87.

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 5.293 min;

MS: (EI, 70 eV): *m/z* (%) $C_{11}H_{14}O_2$ calc. 178.10: 178.1 (80), 148.1 (100), 147.1 (93), 133 (29), 117.1 (35), 91.1 (24), 77 (31).



3-(2-Fluorophenyl)tetrahydrofuran (53)
Following the general procedure A, the reaction was carried out with 1-fluoro-2-iodobenzene (35.0 µL , 0.3 mmol, 1.0 equiv) and 2,5-dihydrofuran (**6a**) (56.7 µL, 0.75 mmol, 2.5 equiv) for 48 h. Purification by flash column chromatography afforded 3-(2-Fluorophenyl)tetrahydrofuran (53) as a clear, colorless oil (34.6 mg, 70%).

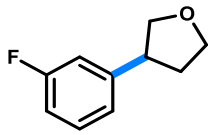
R_f: 0.34 (10% EtOAc in hexanes), UV;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (td, *J* = 7.7, 1.8 Hz, 1H), 7.20 (dddd, *J* = 8.1, 7.1, 5.2, 1.8 Hz, 1H), 7.10 (td, *J* = 7.5, 1.3 Hz, 1H), 7.03 (ddd, *J* = 10.6, 8.2, 1.3 Hz, 1H), 4.14 (ddd, *J* = 8.2, 7.2, 0.8 Hz, 1H), 4.05 (td, *J* = 8.3, 5.0 Hz, 1H), 3.93 (dt, *J* = 8.4, 7.4 Hz, 1H), 3.76 (ddd, *J* = 8.2, 7.2, 0.6 Hz, 1H), 3.68 (p, *J* = 7.6 Hz, 1H), 2.36 (dtd, *J* = 12.4, 7.8, 5.0 Hz, 1H), 2.04 (dq, *J* = 12.3, 7.7 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.02 (d, *J* = 245.4 Hz), 129.54 (d, *J* = 14.4 Hz), 128.23 (d, *J* = 4.8 Hz), 128.09 (d, *J* = 8.3 Hz), 124.39 (d, *J* = 3.5 Hz), 115.51 (d, *J* = 22.4 Hz), 73.35, 68.37, 37.96, 33.23;

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.80;

HRMS *m/z* (ESI): found (*M* + *Na*) 189.0691. $C_{10}H_{11}FONa$ requires *M* + *Na*, 189.0692.



3-(3-Fluorophenyl)tetrahydrofuran (54)
Following the general procedure A, the reaction was carried out with 1-fluoro-3-iodobenzene (35.2 µL, 0.3 mmol, 1.0 equiv) and 2,5-dihydrofuran (**6a**) (56.7 µL, 0.75 mmol, 2.5 equiv) for 48 h. Purification by flash column chromatography afforded 3-(3-fluorophenyl)tetrahydrofuran (54) as a clear, colorless oil (20.5 mg, 42%).

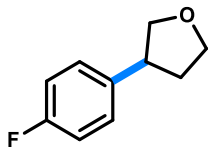
R_f: 0.30 (10% EtOAc in hexanes), UV;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 1H), 7.03 (ddt, *J* = 7.7, 1.6, 0.7 Hz, 1H), 6.96 (dt, *J* = 10.2, 2.1 Hz, 1H), 6.91 (tdd, *J* = 8.5, 2.6, 1.0 Hz, 1H), 4.12 (dd, *J* = 8.5, 7.5 Hz, 1H), 4.06 (td, *J* = 8.4, 4.6 Hz, 1H), 3.91 (dt, *J* = 8.5, 7.6 Hz, 1H), 3.72 (dd, *J* = 8.5, 7.2 Hz, 1H), 3.40 (p, *J* = 7.7 Hz, 1H), 2.41 – 2.32 (m, 1H), 1.99 (dq, *J* = 12.4, 7.9 Hz, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.12, 163.14 (d, *J* = 245.8 Hz), 130.15, 123.05, 114.24 (d, *J* = 21.6 Hz), 113.49 (d, *J* = 21.0 Hz), 74.57, 68.55, 44.87, 34.66;

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.40.

HRMS *m/z* (ESI): found (*M* + *Na*) 189.0694. $C_{10}H_{11}FONa$ requires *M* + *Na*, 189.0692.



3-(4-Fluorophenyl)tetrahydrofuran (55)

Following the general procedure A, the reaction was carried out with 1-fluoro-4-iodobenzene (34.6 µL, 0.3 mmol, 1.0 equiv) and 2,5-dihydrofuran (**6a**) (56.7 µL, 0.75 mmol, 2.5 equiv) for 48 h. Purification by flash column chromatography afforded 3-(4-fluorophenyl)tetrahydrofuran (55) as a clear, colorless oil (19.5 mg, 39%).

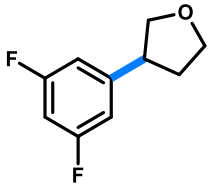
R_f: 0.39 (10 % EtOAc in hexanes), UV;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 – 7.18 (m, 2H), 7.03 – 6.97 (m, 2H), 4.12 (dd, *J* = 8.5, 7.4 Hz, 1H), 4.06 (td, *J* = 8.4, 4.5 Hz, 1H), 3.91 (dt, *J* = 8.4, 7.5 Hz, 1H), 3.69 (dd, *J* = 8.5, 7.3 Hz, 1H), 3.39 (p, *J* = 7.7 Hz, 1H), 2.41 – 2.31 (m, 1H), 1.96 (dq, *J* = 12.4, 8.0 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.68 (d, *J* = 244.5 Hz), 138.54 (d, *J* = 2.8 Hz), 128.75 (d, *J* = 7.9 Hz), 115.47 (d, *J* = 21.1 Hz), 74.81, 68.57, 44.40, 34.89;

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.96;

HRMS *m/z* (ESI): found (*M* + *Na*) 189.0689. $C_{10}H_{11}FONa$ requires *M* + *Na*, 189.0692.



3-(3,5-Difluorophenyl)tetrahydrofuran (56)

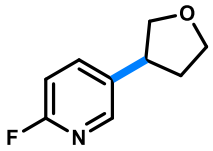
Following the general procedure A, the reaction was carried out with 1,3-difluoro-5-iodobenzene (36.2 µL, 0.3 mmol, 1.0 equiv) and 2,5-dihydrofuran (**6a**) (56.7 µL, 0.75 mmol, 2.5 equiv) for 48 h. Purification by flash column chromatography afforded 3-(4-fluorophenyl)tetrahydrofuran (56) as a clear, colorless oil (31.0 mg, 57% yield).

R_f: 0.35 (10% EtOAc in hexanes), UV;

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.82 – 6.74 (m, 2H), 6.66 (tt, *J* = 8.9, 2.3 Hz, 1H), 4.11 – 4.07 (m, 1H), 4.05 (dt, *J* = 8.4, 4.2 Hz, 1H), 3.90 (dt, *J* = 8.6, 7.5 Hz, 1H), 3.72 (dd, *J* = 8.6, 6.7 Hz, 1H), 3.43 – 3.33 (m, 1H), 2.44 – 2.31 (m, 1H), 1.96 (dq, *J* = 12.5, 7.7 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.07 (d, *J* = 12.9 Hz), 162.42 (d, *J* = 13.1 Hz), 147.29 (t, *J* = 8.8 Hz), 110.26 (d, *J* = 5.0 Hz), 110.12 (d, *J* = 5.0 Hz), 102.02 (t, *J* = 25.4 Hz), 74.30, 68.41, 44.85, 34.49;

^{19}F NMR (376 MHz, $CDCl_3$) δ -110.19.



2-Fluoro-5-(tetrahydrofuran-3-yl)pyridine (57)

Following the general procedure A, the reaction was carried out with 2-fluoro-5-iodopyridine (66.9 mg, 0.3 mmol, 1.0 equiv) and 2,5-dihydrofuran (**6a**) (56.7 µL, 0.75 mmol, 2.5 equiv) for 48 h. Purification by flash column chromatography afforded 2-Fluoro-5-(tetrahydrofuran-3-yl)pyridine (57) as a clear, colorless oil (30.9 mg, 62%).

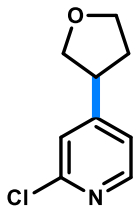
R_f: 0.23 (20% EtOAc in hexanes), UV;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (ddd, *J* = 2.7, 1.3, 0.7 Hz, 1H), 7.67 (dddd, *J* = 8.3, 7.7, 2.6, 0.5 Hz, 1H), 6.91 – 6.84 (m, 1H), 4.09 (dd, *J* = 8.7, 7.3 Hz, 1H), 4.06 (td, *J* = 8.4, 4.7 Hz, 1H), 3.90 (dt, *J* = 8.6, 7.6 Hz, 1H), 3.70 (dd, *J* = 8.7, 6.6 Hz, 1H), 3.45 – 3.37 (m, 1H), 2.46 – 2.32 (m, 1H), 1.93 (ddt, *J* = 12.5, 8.3, 7.5 Hz, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.68 (d, *J* = 237.5 Hz), 146.36 (d, *J* = 14.5 Hz), 139.74 (d, *J* = 8.0 Hz), 136.33, 109.60 (d, *J* = 37.3 Hz), 74.42, 68.36, 41.66, 34.65;

^{19}F NMR (376 MHz, $CDCl_3$) δ -71.45;

HRMS *m/z* (ESI): found (*M* + *H*) 168.0829. $C_9H_{10}FNOH$ requires *M* + *H*, 168.0825.



2-Chloro-4-(tetrahydrofuran-3-yl)pyridine (58)

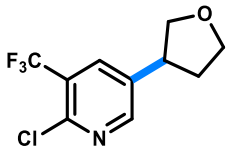
Following the general procedure A, the reaction was carried out with 2-chloro-4-iodopyridine (71.8 mg, 0.3 mmol, 1.0 equiv) and 2,5-dihydrofuran (**6a**) (56.7 µL, 0.75 mmol, 2.5 equiv) for 48 h. Purification by flash column chromatography afforded 2-Chloro-4-(tetrahydrofuran-3-yl)pyridine (58) as a clear, colorless oil (31.7 mg, 58%).

R_f: 0.21 (30% EtOAc in hexanes), UV;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 5.1 Hz, 1H), 7.21 (s, 1H), 7.09 (dd, *J* = 5.2, 1.5 Hz, 1H), 4.11 – 4.01 (m, 2H), 3.89 (dt, *J* = 8.7, 7.5 Hz, 1H), 3.75 (dd, *J* = 8.8, 6.0 Hz, 1H), 3.36 (dq, *J* = 8.4, 6.9 Hz, 1H), 2.47 – 2.35 (m, 1H), 2.01 – 1.90 (m, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.02, 152.00, 149.92, 123.09, 121.43, 73.85, 68.35, 44.15, 34.16;

HRMS *m/z* (ESI): found (*M* + *H*) 184.0532. $C_9H_{10}ClNOH$ requires *M* + *H*, 184.0529.



2-Chloro-5-(tetrahydrofuran-3-yl)-3-(trifluoromethyl)pyridine (59)

Following the general procedure A, the reaction was carried out with 2-chloro-5-iodo-3-(trifluoromethyl)pyridine (92.2 mg, 0.3 mmol, 1.0 equiv) and 2,5-dihydrofuran (**6a**) (56.7 µL, 0.75 mmol, 2.5 equiv) for 48 h. Purification by flash column chromatography afforded 2-chloro-5-(tetrahydrofuran-3-yl)-3-(trifluoromethyl)pyridine (59) as a clear, colorless oil (36.0 mg, 48%).

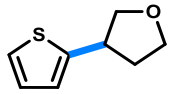
R_f: 0.27 (20% EtOAc in hexanes), UV;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 2.4 Hz, 1H), 7.88 (d, *J* = 2.4 Hz, 1H), 4.20 – 4.04 (m, 2H), 3.93 (dt, *J* = 8.5, 7.6 Hz, 1H), 3.77 (dd, *J* = 8.9, 5.8 Hz, 1H), 3.55 – 3.43 (m, 1H), 2.47 (dtd, *J* = 12.8, 8.0, 4.8 Hz, 1H), 1.96 (dq, *J* = 12.5, 7.5 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.33 (q, *J* = 1.2 Hz), 147.13 (q, *J* = 1.4 Hz), 138.44, 135.31 (q, *J* = 4.8 Hz), 125.39 (q, *J* = 33.1 Hz), 122.26 (q, *J* = 273.0 Hz), 74.19, 68.31, 41.72, 34.63;

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.87;

HRMS *m/z* (ESI): found (*M* + *H*) 252.0403. $C_{10}H_9ClF_3NOH$ requires *M* + *H*, 252.0406.



3-(Thiophen-2-yl)tetrahydrofuran (60)

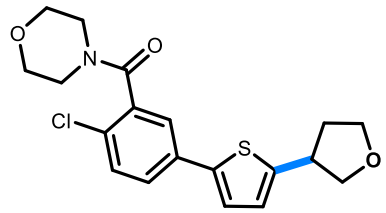
Following the general procedure A, the reaction was carried out with 2-iodothiophene (33.1 µL , 0.3 mmol, 1.0 equiv) and 2,5-dihydrofuran (**6a**) (56.7 µL, 0.75 mmol, 2.5 equiv) for 48 h. Purification by flash column chromatography afforded 3-(thiophen-2-yl)tetrahydrofuran (60) as a clear, colorless oil (23.7 mg, 52%).

R_f: 0.30 (10% EtOAc in hexanes), UV;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.94 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.87 (dt, *J* = 3.5, 1.0 Hz, 1H), 4.14 (dd, *J* = 8.0, 6.9 Hz, 1H), 4.04 (td, *J* = 8.4, 5.1 Hz, 1H), 3.93 (dt, *J* = 8.5, 7.4 Hz, 1H), 3.77 – 3.64 (m, 2H), 2.40 (dtd, *J* = 12.8, 7.7, 5.1 Hz, 1H), 2.12 – 2.01 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.94, 126.90, 123.76, 123.47, 74.91, 68.28, 40.50, 35.35;

HRMS *m/z* (ESI): found (*M* + *H*) 155.0530. $C_8H_{10}OSH$ requires *M* + *H*, 155.0531.



(2-Chloro-5-(5-(tetrahydrofuran-3-yl)thiophen-2-yl)phenyl)(morpholino)methanone (66)

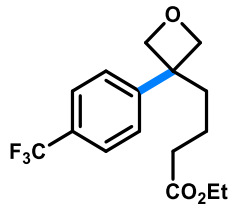
Following the general procedure A, the reaction was carried out with 2-iodothiophene (33.1 µL, 0.3 mmol, 1.0 equiv) and 2,5-dihydrofuran (**6a**) (56.7 µL, 0.75 mmol, 2.5 equiv) for 48 h. Purification by flash column chromatography afforded 3-(thiophen-2-yl)tetrahydrofuran (66) as a clear, colorless oil (60.8 mg, 54%).

R_f: 0.28 (1:1 hexane: ethyl acetate), anisaldehyde, UV;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (ddd, *J* = 8.5, 2.3, 1.0 Hz, 1H), 7.46 (d, *J* = 2.2 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.13 (d, *J* = 3.6 Hz, 1H), 6.84 (dd, *J* = 3.7, 0.8 Hz, 1H), 4.12 (ddd, *J* = 8.7, 7.0, 1.9 Hz, 1H), 4.05 (tdd, *J* = 8.3, 5.3, 1.0 Hz, 1H), 3.96 – 3.85 (m, 2H), 3.83 – 3.73 (m, 4H), 3.72 – 3.63 (m, 2H), 3.60 (ddd, *J* = 11.5, 6.2, 3.2 Hz, 1H), 3.33 (ddd, *J* = 13.5, 6.2, 3.1 Hz, 1H), 3.25 (ddd, *J* = 13.5, 6.8, 3.2 Hz, 1H), 2.41 (dtd, *J* = 12.5, 7.6, 5.0 Hz, 1H), 2.11 – 2.00 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.74, 147.18, 147.13, 139.93, 135.92, 134.09, 130.23, 128.85, 127.30, 127.27, 125.09, 124.71, 123.93, 123.90, 74.73, 68.20, 66.94, 66.82, 47.28, 42.23, 40.78, 35.19;

HRMS *m/z* (ESI): found (*M* + *H*) 378.0932. $C_{19}H_{20}ClNO_3SH$ requires *M* + *H*, 378.0931.



Ethyl 4-(3-(4-(trifluoromethyl)phenyl)oxetan-3-yl)butanoate (62)

Following the general procedure B, the reaction was carried out with 4-(trifluoromethyl)phenyliodide (67.5 µL, 0.45 mmol, 1.5 equiv) or 4-(trifluoromethyl)phenylbromide (63.0 µL, 0.45 mmol, 1.5 equiv) and ethyl 4-(oxetan-3-ylidene)butanoate (**21a**) (51.1 mg, 0.3 mmol, 1.0 equiv). Purification by flash column chromatography (7:3 hexanes: EtOAc) afforded ethyl 4-(3-(4-(trifluoromethyl)phenyl)oxetan-3-yl)butanoate (62) as a clear colorless oil (50.3 mg, 53% from aryl iodide) (38.0 mg, 41% from aryl bromide).

R_f: 0.34 (30% EtOAc in hexanes), anisaldehyde;

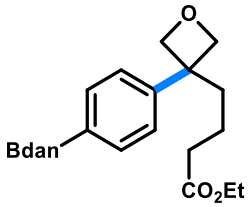
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 2H), 7.19 – 7.12 (m, 2H), 4.95 (d, *J* = 5.7 Hz, 2H), 4.69 (d, *J* = 5.8 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 2.26 (t, *J* = 7.3 Hz, 2H), 2.15 – 2.08 (m, 2H), 1.47 – 1.38 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.18, 148.77, 128.95 (q, *J* = 32.6 Hz), 126.28, 125.66 (q, *J* = 3.8 Hz), 124.22 (q, *J* = 271.9 Hz), 81.48, 60.56, 47.54, 40.36, 34.20, 19.98, 14.34;

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.73;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 6.661 min;

MS: (EI, 70 eV): *m/z* (%) $C_{16}H_{19}F_3O_3$ calc. 316.13: 317.1 (5), 287.1 (10), 223.1 (8), 167.1 (100), 75 (26).



Ethyl 4-(3-(4-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)phenyl)oxetan-3-yl)butanoate (63)

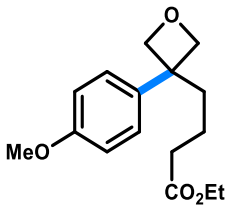
Following the general procedure B, the reaction was carried out with 2-(4-iodophenyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (166.5 mg, 0.45 mmol, 1.5 equiv) and ethyl 4-(oxetan-3-ylidene)butanoate (**21a**) (51.1 mg, 0.3 mmol, 1.0 equiv). Purification by flash column chromatography afforded ethyl 4-(3-(4-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)phenyl)oxetan-3-yl)butanoate (63) as a clear, colorless oil (47.3 mg, 38% 7:3 B:L). Data corresponds to the major isomer.

Note: Compound was unstable to silica isolation and slowly decomposed.

R_f: 0.44 (40% EtOAc in hexanes), anisaldehyde, UV;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.58 (m, 2H), 7.21 – 7.04 (m, 6H), 6.42 (dd, *J* = 7.3, 1.0 Hz, 2H), 6.04 (s, 2H), 5.00 (d, *J* = 5.7 Hz, 2H), 4.70 (d, *J* = 5.7 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.27 (t, *J* = 7.4 Hz, 2H), 2.16 – 2.08 (m, 2H), 1.53 – 1.39 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.33, 146.92, 141.16, 136.48, 131.83, 129.17, 127.75, 125.76, 119.97, 118.00, 106.17, 81.77, 60.51, 47.53, 40.56, 34.33, 20.12, 14.38.



Ethyl 4-(3-(4-methoxyphenyl)oxetan-3-yl)butanoate (64)

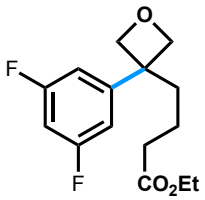
Following the general procedure B, the reaction was carried out with 4-(methoxy)iodobenzene (105.3 mg, 0.45 mmol, 1.5 equiv) and ethyl 4-(oxetan-3-ylidene)butanoate (**21a**) (51.1 mg, 0.3 mmol, 1.0 equiv). Purification by flash column chromatography (4:1 hexane: EtOAc) afforded ethyl 4-(3-(4-methoxyphenyl)oxetan-3-yl)butanoate (64) as a clear, colorless oil (0.135 mmol, 37.0 mg, 45%).

R_f: 0.34 (20% EtOAc in hexanes), anisaldehyde;

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.98 – 6.94 (m, 2H), 6.89 – 6.86 (m, 2H), 4.93 (d, *J* = 5.6 Hz, 2H), 4.64 (d, *J* = 5.6 Hz, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 2.25 (t, *J* = 7.4 Hz, 2H), 2.09 – 2.04 (m, 2H), 1.47 – 1.40 (m, 2H), 1.22 (d, *J* = 7.2 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.40, 158.13, 136.78, 126.89, 114.02, 82.05, 60.46, 55.43, 46.81, 40.67, 34.41, 20.16, 14.37;

HRMS *m/z* (ESI): found (*M* + *H*) 279.1632. $C_{16}H_{22}O_4H$ requires *M* + *H*, 279.1636.



ethyl 4-(3-(3,5-difluorophenyl)oxetan-3-yl)butanoate (65).

Following General Procedure B, a mixture of 3,5-difluoroiodobenzene (108 mL, 0.45 mmol, 1.5 equiv), and ethyl 4-(oxetan-3-ylidene)butanoate (**21a**) (51.1 mg, 0.3 mmol, 1.0 equiv) was

stirred for 16 h. Purification by flash column chromatography (SiO_2, 4:1 hexanes: EtOAc) furnished the title compound as a clear, pale yellow oil (43.7 mg, 51%).

R_f: 0.3 (20% EtOAc in hexanes), UV and anisaldehyde;

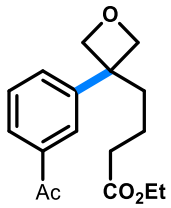
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.69 (tt, *J* = 9.0, 8.2, 2.4, 2.1 Hz, 1H), 6.58 (dt, *J* = 6.8, 2.1 Hz, 2H), 4.88 (d, *J* = 5.8 Hz, 2H), 4.64 (d, *J* = 5.8 Hz, 2H), 4.11 (q, 2H), 2.28 (t, *J* = 7.3 Hz, 2H), 2.10 – 2.06 (m, 2H), 1.47 – 1.40 (m, 2H), 1.24 (t, *J* = 7.2, 0.7 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.11, 163.31 (dd, *J* = 249.2, 13.0 Hz), 148.72 (t, *J* = 8.6, 8.0 Hz), 109.13 – 108.91 (m), 102.18 (t, *J* = 25.3 Hz), 81.28, 60.56, 47.52, 40.08, 34.16, 19.96, 14.33;

^{19}F NMR (376 MHz, $CDCl_3$) δ -109.36;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 70 °C/min to 250 °C, then 5 °C/min to 280 °C): t_R = 6.226;

MS: (EI, 70 eV): *m/z* (%) $C_{15}H_{18}F_2O_3$ calc. 284.12: 254.1 (27), 193.1 (10), 180.1 (94), 165 (100), 151 (29), 133 (18), 127 (58), 119 (13), 88.1 (18), 60 (20).



Ethyl 4-(3-(3-acetylphenyl)oxetan-3-yl)butanoate (66)

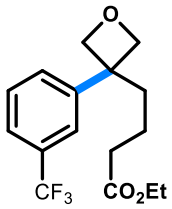
Following the general procedure B, the reaction was carried out with 3-iodoacetophenone (62.7 µL, 0.45 mmol, 1.5 equiv) and ethyl 4-(oxetan-3-ylidene)butanoate (**21a**) (51.1 mg, 0.3 mmol, 1.0 equiv). Purification by flash column chromatography afforded ethyl 4-(3-(3-acetylphenyl)oxetan-3-yl)butanoate (66) as a clear, colorless oil (0.165 mmol, 47.9 mg, 55%).

R_f: 0.31 (40% EtOAc in hexanes), anisaldehyde, UV;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (ddd, *J* = 7.7, 1.7, 1.0 Hz, 1H), 7.63 (t, *J* = 1.7 Hz, 1H), 7.44 (td, *J* = 7.7, 0.5 Hz, 1H), 7.24 (ddd, *J* = 7.7, 2.0, 1.1 Hz, 1H), 4.96 (d, *J* = 5.8 Hz, 2H), 4.68 (d, *J* = 5.8 Hz, 2H), 4.08 (q, *J* = 7.2 Hz, 2H), 2.60 (s, 3H), 2.24 (t, *J* = 7.3 Hz, 2H), 2.14 – 2.07 (m, 2H), 1.45 – 1.38 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.17, 145.43, 130.60, 126.89, 125.25, 81.57, 60.47, 47.45, 40.44, 34.21, 26.81, 20.01, 14.31;

HRMS *m/z* (ESI): found (*M* + *H*) 291.1600. $C_{17}H_{22}O_4H$ requires *M* + *H*, 291.1596.



Ethyl 4-(3-(3-(trifluoromethyl)phenyl)oxetan-3-yl)butanoate (67)

Following the general procedure B, the reaction was carried out with 3-(trifluoromethyl)iodobenzene (64.9 µL, 0.45 mmol, 1.5 equiv) and ethyl 4-(oxetan-3-ylidene)butanoate (**21a**) (51.1 mg, 0.3 mmol, 1.0 equiv). Purification by flash column chromatography afforded ethyl 4-(3-(3-(trifluoromethyl)phenyl)oxetan-3-yl)butanoate (67) as a clear, colorless oil (0.135 mmol, 38.8 mg, 41%).

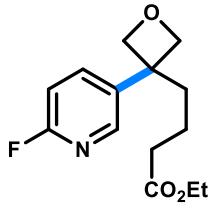
R_f: 0.31 (40 % EtOAc in hexanes), anisaldehyde, UV;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 1H), 7.48 (tt, *J* = 7.8, 0.7 Hz, 1H), 7.28 (tt, *J* = 1.7, 0.8 Hz, 1H), 7.25 – 7.21 (m, 1H), 4.95 (d, *J* = 5.8 Hz, 2H), 4.70 (d, *J* = 5.8 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 2.27 (t, *J* = 7.3 Hz, 2H), 2.14 – 2.08 (m, 2H), 1.50 – 1.38 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.16, 145.77, 131.10 (q, *J* = 32.1 Hz), 129.34 (q, *J* = 1.3 Hz), 129.19, 124.18 (q, *J* = 272 Hz), 123.54 (q, *J* = 3.8 Hz), 122.55 (q, *J* = 3.8 Hz), 81.48, 60.55, 47.49, 40.38, 34.22, 19.99, 14.34;

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.82;

HRMS *m/z* (ESI): found (*M* + *H*) 317.1366. $C_{16}H_{19}FO_3H$ requires *M* + *H*, 317.1365.



Ethyl 4-(3-(6-fluoropyridin-3-yl)oxetan-3-yl)butanoate (68)

Following the general procedure B, the reaction was carried out with 2-fluoro-5-iodopyridine (100.3 mg, 0.45 mmol, 1.5 equiv) and ethyl 4-(oxetan-3-ylidene)butanoate (**21a**) (51.1 mg, 0.3 mmol, 1.0 equiv). Purification by flash column chromatography afforded ethyl 4-(3-(6-fluoropyridin-3-yl)oxetan-3-yl)butanoate (68) as a clear, colorless oil (46.3 mg, 58%).

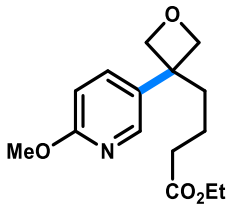
R_f: 0.33 (40% EtOAc in hexanes), UV;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (dt, *J* = 2.8, 0.9 Hz, 1H), 7.50 (ddd, *J* = 8.5, 7.5, 2.7 Hz, 1H), 6.91 (ddd, *J* = 8.5, 3.1, 0.7 Hz, 1H), 4.90 (d, *J* = 5.9 Hz, 2H), 4.68 (d, *J* = 5.9 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.27 (t, *J* = 7.2 Hz, 2H), 2.13 – 2.06 (m, 2H), 1.46 – 1.38 (m, 2H), 1.21 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.96, 162.43 (d, *J* = 238.7 Hz), 145.19 (d, *J* = 14.9 Hz), 138.81 (d, *J* = 7.8 Hz), 137.64 (d, *J* = 5.2 Hz), 109.66, 81.34, 60.53, 45.35, 39.90, 34.01, 19.84, 14.29;

^{19}F NMR (376 MHz, $CDCl_3$) δ -70.82;

HRMS *m/z* (ESI): found (*M* + *H*) 268.1353. $C_{14}H_{18}FNO_3H$ requires *M* + *H*, 268.1349.



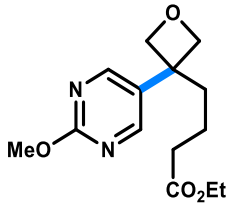
Ethyl 4-(3-(6-methoxypyridin-3-yl)oxetan-3-yl)butanoate (69)
Following the general procedure B, the reaction was carried out with 5-iodo-2-methoxypyridine (106.0 mg, 0.45 mmol, 1.5 equiv) and ethyl 4-(oxetan-3-ylidene)butanoate (**21a**) (51.1 mg, 0.3 mmol, 1.0 equiv). Purification by flash column chromatography afforded ethyl 4-(3-(6-methoxypyridin-3-yl)oxetan-3-yl)butanoate (69) as a clear, colorless oil (32.5 mg, 40%, 9:1 branched:linear mixture). Data corresponds to the major isomer.

R_f: 0.40 (100% EtOAc), phosphomolybdic acid;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 2.6, 0.7 Hz, 1H), 7.32 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.77 (dd, *J* = 8.5, 0.7 Hz, 1H), 4.95 (d, *J* = 5.6 Hz, 2H), 4.70 (d, *J* = 5.6 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.95 (s, 3H), 2.30 (t, *J* = 7.3 Hz, 2H), 2.16 – 2.06 (m, 2H), 1.52 – 1.42 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.18, 162.97, 144.19, 136.50, 132.50, 110.97, 81.67, 60.52, 53.54, 45.21, 40.11, 34.23, 20.01, 14.34;

HRMS *m/z* (ESI): found (*M* + *H*) 280.1551. $C_{15}H_{21}NO_4H$ requires *M* + *H*, 280.1549.



Ethyl 4-(3-(2-methoxypyrimidin-5-yl)oxetan-3-yl)butanoate (70)

Following the general procedure B, the reaction was carried out with 5-bromo-2-

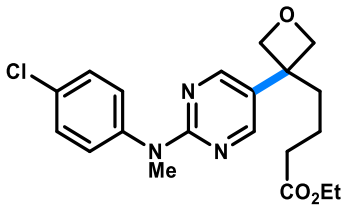
methoxypyrimidine (85.1 mg, 0.45 mmol, 1.5 equiv) and ethyl 4-(oxetan-3-ylidene)butanoate (**21a**) (51.1 mg, 0.3 mmol, 1.0 equiv). Purification by flash column chromatography afforded ethyl 4-(3-(2-methoxypyrimidin-5-yl)oxetan-3-yl)butanoate (70) as a clear, colorless oil (44.2 mg, 53%).

R_f: 0.20 (50% EtOAc in hexanes), UV;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (s, 2H), 4.87 (d, *J* = 5.9 Hz, 2H), 4.68 (d, *J* = 6.0 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 3H), 2.28 (t, *J* = 7.2 Hz, 2H), 2.12 – 2.05 (m, 2H), 1.47 – 1.39 (m, 2H), 1.20 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.86, 164.63, 157.03, 130.54, 81.24, 60.54, 55.02, 43.71, 39.39, 33.96, 19.81, 14.27;

HRMS *m/z* (ESI): found (*M* + *H*) 281.1506. $C_{14}H_{20}N_2O_4H$ requires *M* + *H*, 281.1501.



Ethyl 4-(3-(2-((4-chlorophenyl)(methyl)amino)pyrimidin-5-yl)oxetan-3-yl)butanoate (71)

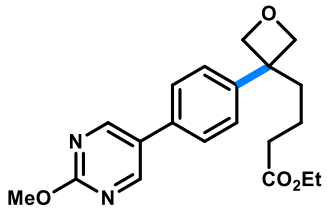
Following the general procedure B, the reaction was carried out with 5-bromo-*N*-(4-chlorophenyl)-*N*-methylpyrimidin-2-amine (134.4 mg, 0.45 mmol, 1.5 equiv) and ethyl 4-(oxetan-3-ylidene)butanoate (**21a**) (51.1 mg, 0.3 mmol, 1.0 equiv). Purification by flash column chromatography afforded ethyl 4-(3-(2-((4-chlorophenyl)(methyl)amino)pyrimidin-5-yl)oxetan-3-yl)butanoate (71) as a clear, colorless oil (35.5 mg, 31%).

R_f: 0.45 (50% EtOAc in hexanes), UV;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (s, 2H), 7.38 – 7.35 (m, 2H), 7.29 – 7.26 (m, 2H), 4.87 (d, *J* = 5.9 Hz, 2H), 4.67 (d, *J* = 5.9 Hz, 2H), 4.12 (qd, *J* = 7.1, 2.4 Hz, 2H), 3.52 (s, 3H), 2.30 (t, *J* = 7.3 Hz, 2H), 2.11 – 2.06 (m, 2H), 1.52 – 1.43 (m, 2H), 1.27 – 1.21 (m, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.10, 160.73, 155.63, 143.96, 131.32, 127.91, 126.36, 81.54, 60.63, 39.60, 38.71, 34.21, 20.02, 14.38;

HRMS *m/z* (ESI): found (*M* + *H*) 390.1580. $C_{20}H_{24}ClN_3O_3H$ requires *M* + *H*, 390.1584.



Ethyl 4-(3-(4-(2-methoxypyrimidin-5-yl)phenyl)oxetan-3-yl)butanoate (72)

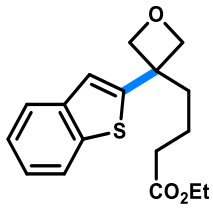
Following the general procedure B, the reaction was carried out with 5-(4-iodophenyl)-2-methoxypyrimidine (140.4 mg, 0.45 mmol, 1.5 equiv) and ethyl 4-(oxetan-3-ylidene)butanoate (**21a**) (51.1 mg, 0.3 mmol, 1.0 equiv). Purification by flash column chromatography afforded ethyl 4-(3-(4-(2-methoxypyrimidin-5-yl)phenyl)oxetan-3-yl)butanoate (72) as a clear, colorless oil (25.5 mg, 24%, 13:1 B:L).

R_f: 0.50 (50% EtOAc in hexanes), UV;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.72 (s, 2H), 7.53 – 7.47 (m, 2H), 7.20 – 7.14 (m, 2H), 4.99 (d, *J* = 5.7 Hz, 2H), 4.70 (d, *J* = 5.7 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 4.07 (s, 3H), 2.28 (t, *J* = 7.3 Hz, 2H), 2.17 – 2.11 (m, 2H), 1.52 – 1.44 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.31, 165.24, 157.40, 144.90, 132.77, 128.02, 126.88, 126.84, 81.78, 60.54, 55.22, 47.35, 40.53, 34.32, 20.13, 14.38;

HRMS *m/z* (ESI): found (*M* + *H*) 357.1816. $C_{20}H_{24}N_2O_4H$ requires *M* + *H*, 357.1814.



Ethyl 4-(3-(benzo[*b*]thiophen-2-yl)oxetan-3-yl)butanoate (73)

Following the general procedure B, the reaction was carried out with 2-iodobenzo[*b*]thiophene (117.0 mg, 0.45 mmol, 1.5 equiv) and ethyl 4-(oxetan-3-ylidene)butanoate (**21a**) (51.1 mg, 0.3 mmol, 1.0 equiv). Purification by flash column chromatography afforded ethyl 4-(3-(benzo[*b*]thiophen-2-yl)oxetan-3-yl)butanoate (73) as a clear, colorless oil (29.8 mg, 33%).

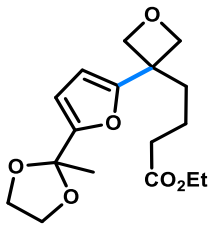
R_f: 0.50 (10% EtOAc in Toluene), UV, anisaldehyde;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.35 (ddd, *J* = 7.9, 7.2, 1.3 Hz, 1H), 7.30 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.12 (d, *J* = 0.7 Hz, 1H), 4.96 (d, *J* = 5.8 Hz, 2H), 4.70 (d, *J* = 5.9 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.33 (t, *J* = 7.3 Hz, 2H), 2.25 – 2.19 (m, 2H), 1.57 (ddt, *J* = 12.0, 8.8, 5.9 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.21, 148.72, 139.92, 139.27, 124.57, 124.24, 123.41, 122.41,

120.39, 82.20, 60.54, 45.72, 39.30, 34.23, 20.29, 14.36;

HRMS *m/z* (ESI): found (*M* + *H*) 305.1207. $C_{17}H_{20}N_2O_3SH$ requires *M* + *H*, 305.1211.



Ethyl 4-(3-(5-(2-methyl-1,3-dioxolan-2-yl)furan-2-yl)oxetan-3-yl)butanoate (74)

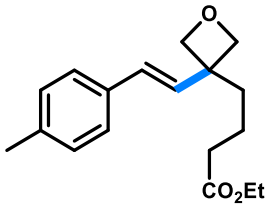
Following the general procedure B, the reaction was carried out with 2-(5-iodofuran-2-yl)-2-methyl-1,3-dioxolane (70.4 µL, 0.45 mmol, 1.5 equiv) and ethyl 4-(oxetan-3-ylidene)butanoate (**21a**) (51.1 mg, 0.3 mmol, 1.0 equiv). Purification by flash column chromatography afforded ethyl 4-(3-(5-(2-methyl-1,3-dioxolan-2-yl)furan-2-yl)oxetan-3-yl)butanoate (74) as a clear, colorless oil (51.2 mg, 53%).

R_f: 0.35 (30% EtOAc in hexanes), UV;

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.26 (d, *J* = 3.2 Hz, 1H), 6.11 (d, *J* = 3.2 Hz, 1H), 4.87 (d, *J* = 5.8 Hz, 2H), 4.56 (d, *J* = 5.8 Hz, 2H), 4.13 (qd, *J* = 7.2, 2.8 Hz, 2H), 4.08 – 3.98 (m, 4H), 2.30 (t, *J* = 7.3 Hz, 2H), 2.14 – 2.09 (m, 2H), 1.73 (s, 3H), 1.58 – 1.51 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.32, 156.27, 153.86, 107.32, 106.07, 104.75, 80.43, 65.27, 60.52, 43.36, 36.19, 34.29, 24.37, 20.26, 14.40;

HRMS *m/z* (ESI): found (*M* + *H*) 325.1656. $C_{17}H_{24}O_6H$ requires *M* + *H*, 325.1651.



Ethyl (*E*)-4-(3-(4-methylstyryl)oxetan-3-yl)butanoate (75)

Following the general procedure B, the reaction was carried out with (*E*)-1-(2-bromovinyl)-4-methylbenzene (88.7 mg, 0.45 mmol, 1.5 equiv) and ethyl 4-(oxetan-3-ylidene)butanoate (**21a**) (51.1 mg, 0.3 mmol, 1.0 equiv). Purification by flash column chromatography afforded ethyl (*E*)-4-(3-(4-methylstyryl)oxetan-3-yl)butanoate (75) as a clear, colorless oil (19.7 mg, 23%).

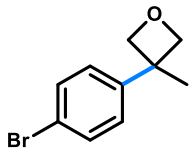
R_f: 0.35 (30% EtOAc in hexanes), UV;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.45 (d, *J* = 16.3 Hz, 1H), 6.25 (d, *J* = 16.3 Hz, 1H), 4.71 (d, *J* = 5.7 Hz, 2H), 4.51 (d, *J* = 5.7 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.40 – 2.28 (m, 5H), 1.99 – 1.89 (m, 2H), 1.68 – 1.58 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.42, 137.50, 134.25, 131.35, 129.54, 129.44, 126.24, 81.28, 60.53, 44.99, 37.91, 34.53, 21.32, 20.26, 14.41;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 7.937 min;

MS: (EI, 70 eV): *m/z* (%) $C_{18}H_{24}O_3$ calc. 288.17: 289.1 (13), 259.1 (18), 158.1 (25), 143.1 (38), 131.1 (100).



3-(4-bromophenyl)-3-methyloxetane (79)

Following the general procedure B, the reaction was carried out with 1,4-dibromobenzene **(141.6 mg, 0.6 mmol, 2.0 equiv**) and 3-methyleneoxetane (**20a**) (410 µL from 0.73 M solution in THF, 0.3 mmol, 1.0 equiv). Purification by flash column chromatography afforded 3-(4-bromophenyl)-3-methyloxetane (79) as a clear, colorless oil (26.3 mg, 39%).

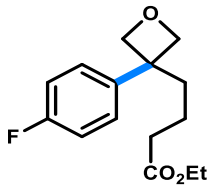
R_f: 0.30 (10% EtOAc in hexanes), anisaldehyde;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.10 – 7.07 (m, 2H), 4.91 (d, *J* = 5.6 Hz, 2H), 4.63 (d, *J* = 5.6 Hz, 2H), 1.71 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.63, 131.82, 127.06, 120.33, 83.65, 43.29, 27.71;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 5.808 min;

MS: (EI, 70 eV): *m/z* (%) $C_{10}H_{11}BrO$ calc. 226.00: 227. 9(1), 225.9 (1), 197.9 (96), 195.9 (100), 182.9 (18), 180.9 (19), 117 (52), 115 (73), 102 (46), 91 (26), 76 (15), 63 (15), 57.6 (15), 51 (20).



Ethyl 4-(3-(4-fluorophenyl)oxetan-3-yl)butanoate

Following the general procedure B, the reaction was carried out with 4-(fluoro)iodobenzene (51.9 μL, 0.45 mmol, 1.5 equiv) and ethyl 4-(oxetan-3-ylidene)butanoate (**21a**) (51.1 mg, 0.3 mmol, 1.0 equiv). Purification by flash column chromatography afforded ethyl 4-(3-(4-fluorophenyl)oxetan-3-yl)butanoate as a clear, colorless oil (40.2 mg, 51%).

R_f: 0.50 (30% EtOAc in hexanes), anisaldehyde;

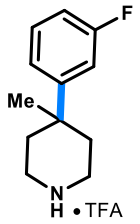
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 – 6.96 (m, 4H), 4.92 (d, *J* = 5.7 Hz, 2H), 4.65 (d, *J* = 5.7 Hz, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.25 (t, *J* = 7.3 Hz, 2H), 2.10 – 2.04 (m, 2H), 1.46 – 1.38 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.27, 161.45 (d, *J* = 245.0 Hz), 140.44 (d, *J* = 3.4 Hz), 127.39 (d, *J* = 7.8 Hz), 115.48 (d, *J* = 21.5 Hz), 81.81, 60.50, 46.98, 40.58, 34.28, 20.05, 14.35;

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.67.

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = min;

MS: (EI, 70 eV): *m/z* (%) $C_{15}H_{19}FO_3$ calc. 266.31: 266 (3), 236 (24), 191 (12), 162 (45), 147 (69), 135 (26), 133 (28), 109 (100), 101 (13), 83 (13).



2,2,2-Trifluoro-1-(4-(3-fluorophenyl)-4-methylpiperidin-1-yl)ethan-1-one (87).

Step 1: *N*-Boc-4-methylenepiperidine (29a). Preparation listed in starting material preparation.

Step 2: *N*-Boc-4-(3-fluorophenyl)-4-methylpiperidine. Following General Procedure B, a mixture of 3-fluoroiodobenzene (52.9 μL, 0.45 mmol, 1.5 equiv), and *N*-Boc-4-methylenepiperidine (29a) (59.2 mg, 0.3 mmol, 1.0 equiv) was stirred for 16 h. Purification by flash column chromatography

(SiO_2, 9:1 hexanes:EtOAc, R_f=0.2 (UV, Ninhydrin) furnished the title compound as a clear, colorless oil (52.7 mg, 60%, 7:1 B:L).

Step 3: To a 5 mL round bottom flask containing a stir bar was added *N*-Boc-4-(3-fluorophenyl)-4-methylpiperidine (52.6 mg, 0.18 mmol, 1.0 equiv), DCM (1.25 mL) and TFA (550 μL). The reaction was stirred at room temperature for 2 h until complete deprotection was observed by LC-MS after which the solvent was removed *in vacuo*. The residue was dissolved in DCM and concentrated (3 cycles) to remove residual TFA to yield the pure TFA salt as a white solid (52.0 mg, 0.18 mmol, quant).

^{1}H NMR (600 MHz, MeOD) δ 7.40 (td, *J* = 8.1, 6.3 Hz, 1H), 7.23 (ddd, *J* = 7.9, 1.9, 0.9 Hz, 1H), 7.17 (dt, *J* = 11.3, 2.2 Hz, 1H), 6.99 (tdd, *J* = 8.4, 2.6, 0.9 Hz, 1H), 3.31 – 3.26 (m, 2H), 3.04 (ddd, *J* = 12.9, 9.2, 3.3 Hz, 2H), 2.37 (dddd, *J* = 14.8, 7.0, 3.5, 1.6 Hz, 2H), 1.97 (ddd, *J* = 14.8, 9.3, 3.6 Hz, 2H), 1.32 (s, 3H).

^{13}C NMR (151 MHz, MeOD) δ 164.76 (d, *J* = 244.3 Hz), 131.78, 131.72, 126.07, 126.06, 122.46, 122.44, 114.28 (d, *J* = 21.1 Hz), 113.77 (d, *J* = 22.4 Hz), 42.13, 36.99, 34.46, 29.66.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.17, -110.50.

HRMS: *m/z* (ESI): found (*M* + *H*) 194.1351. $C_{12}H_{16}FN$ requires *M* + *H*, 194.1345.

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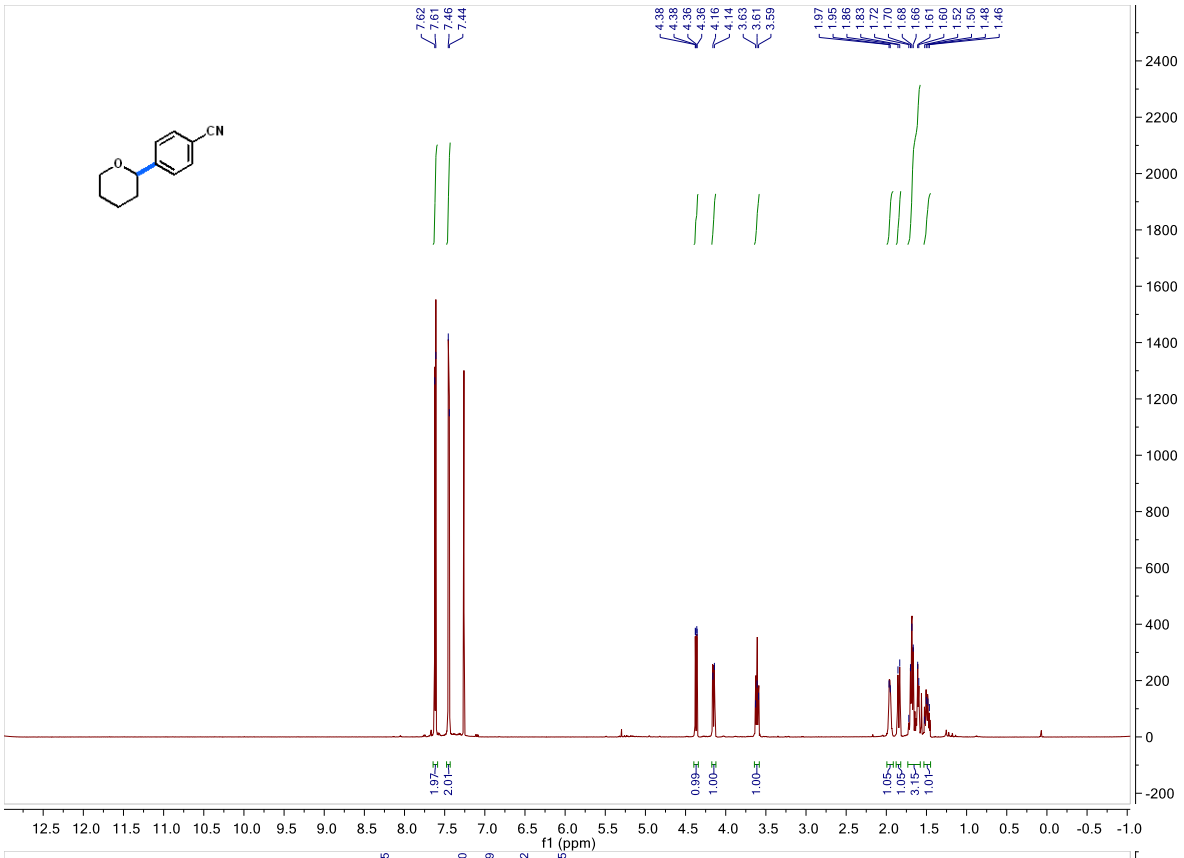
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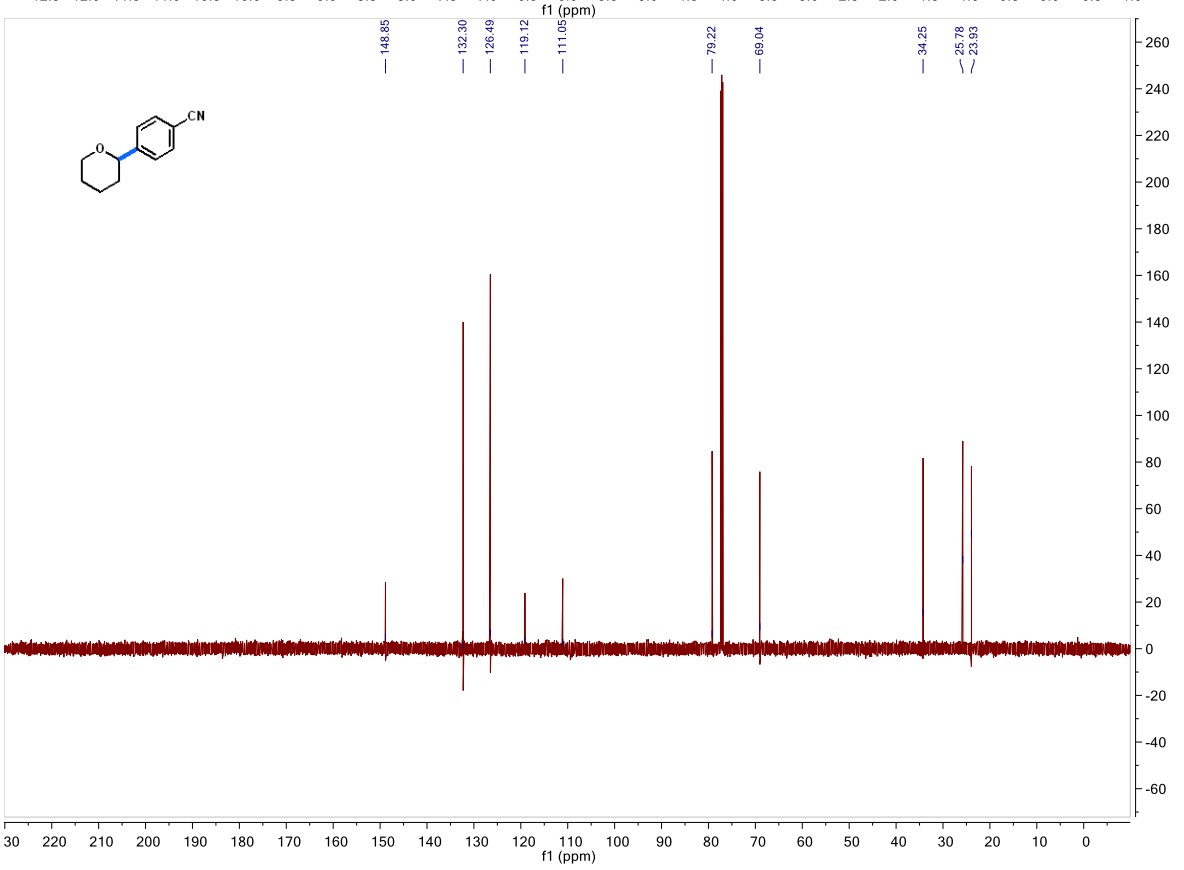
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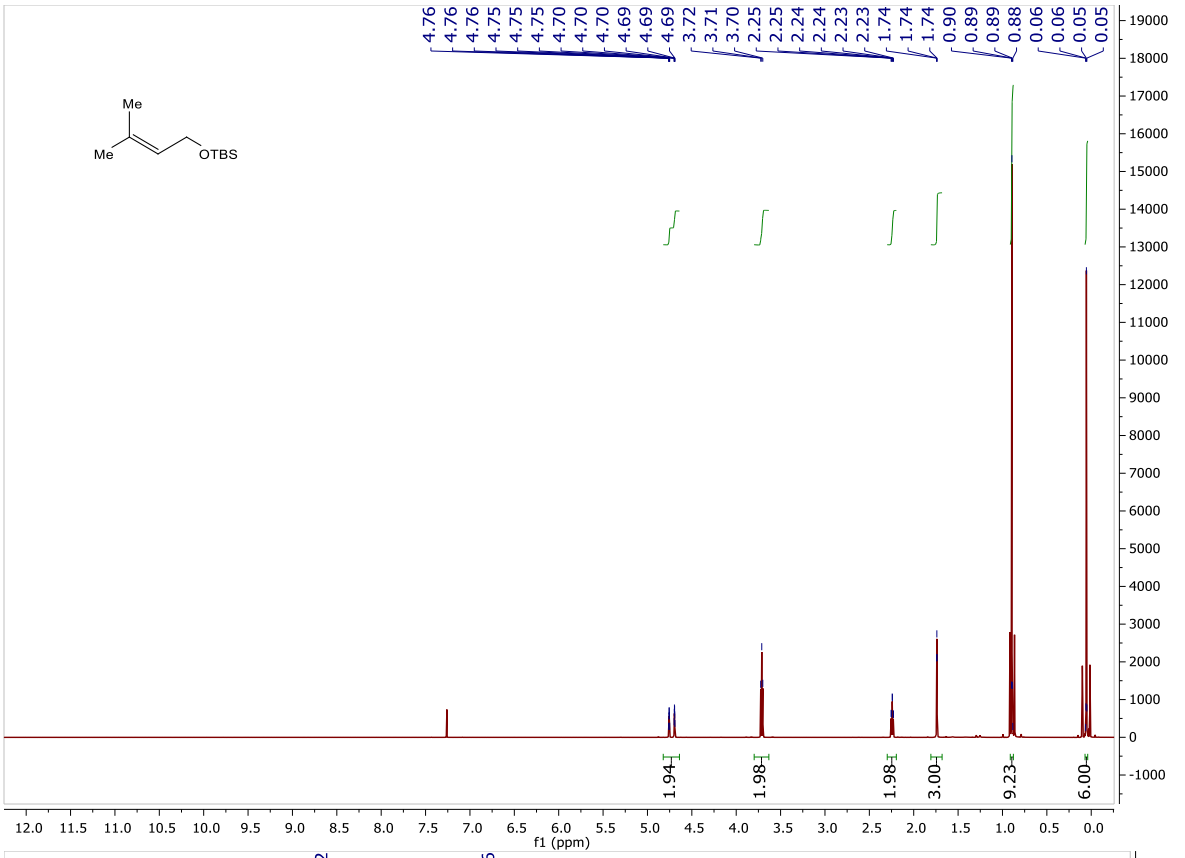
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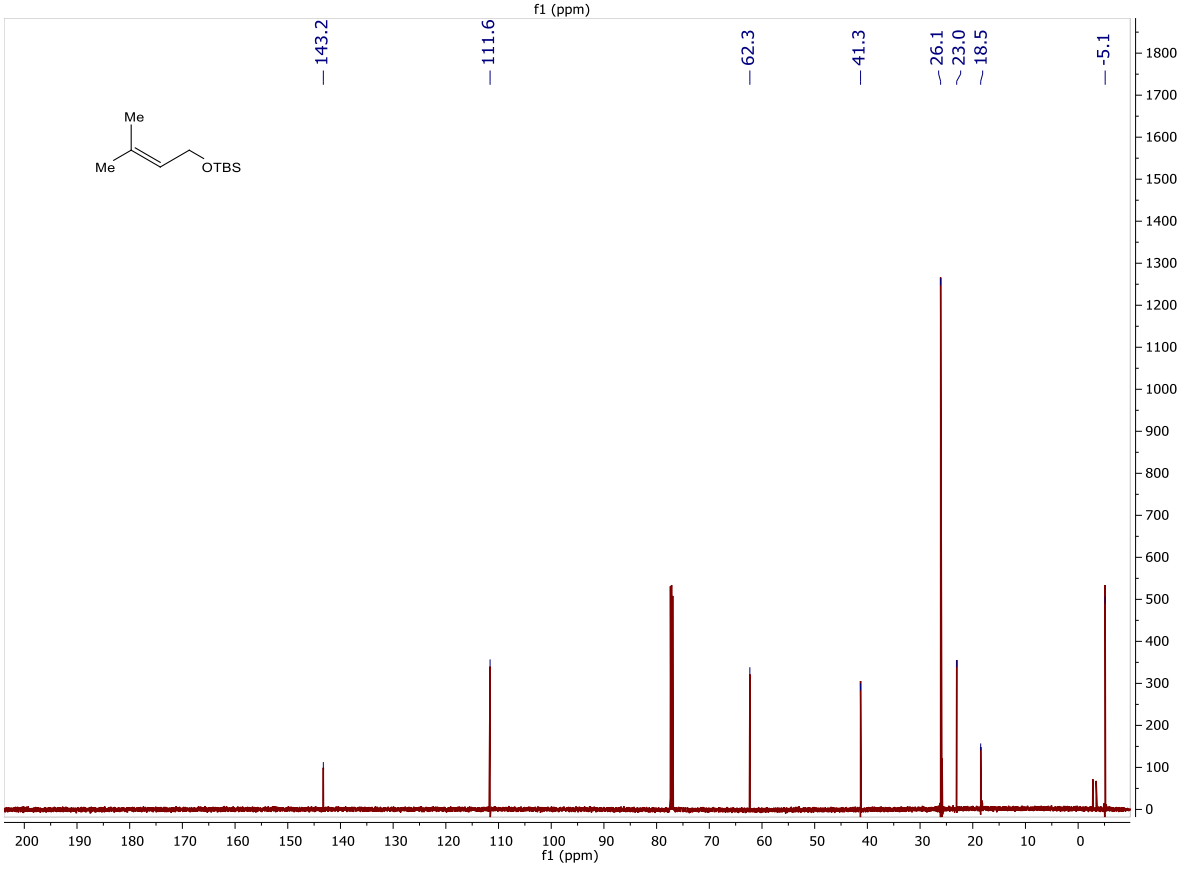
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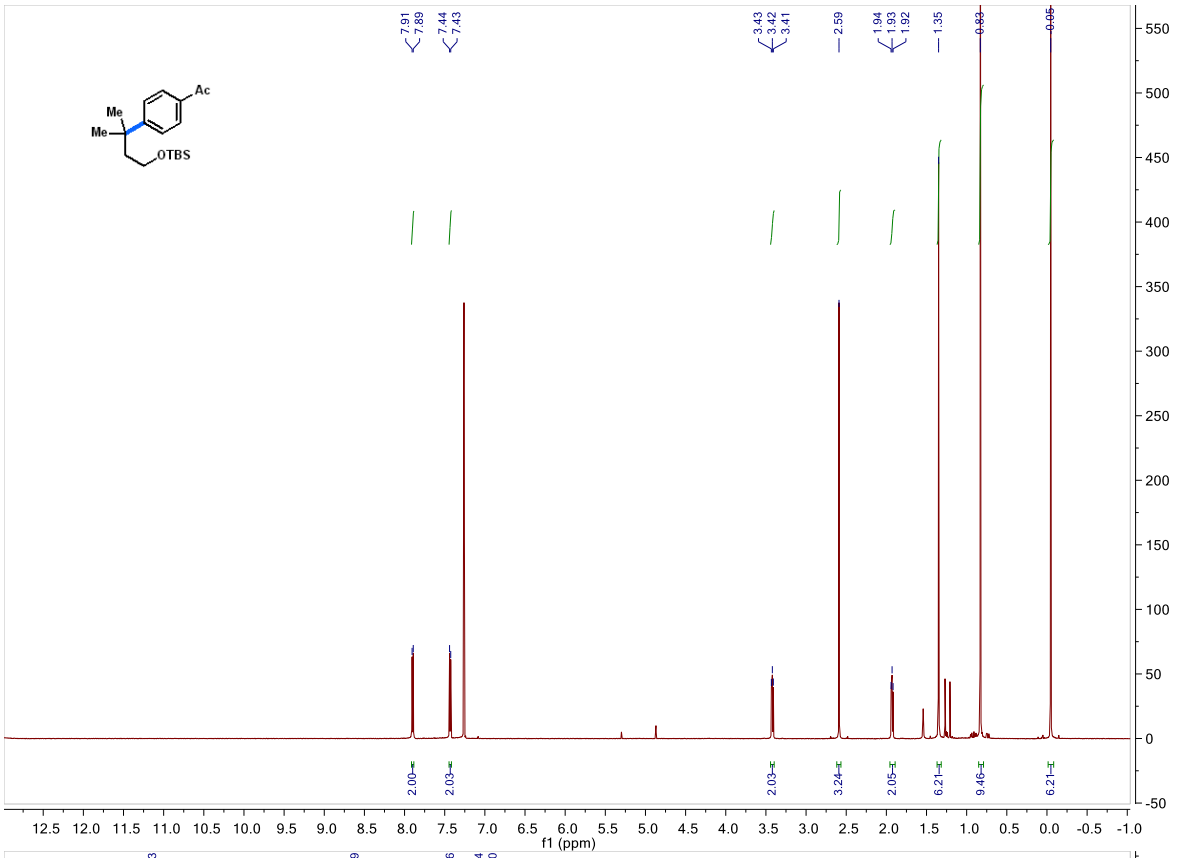
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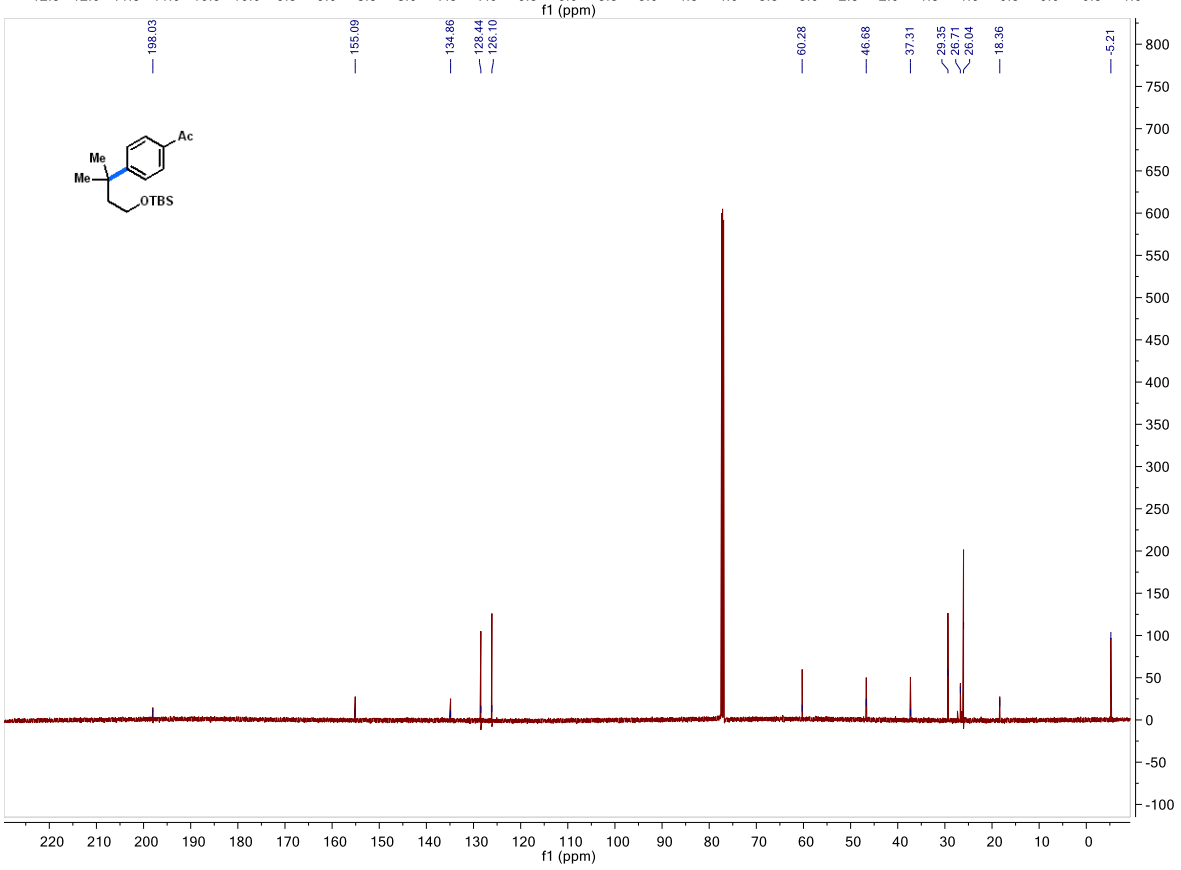
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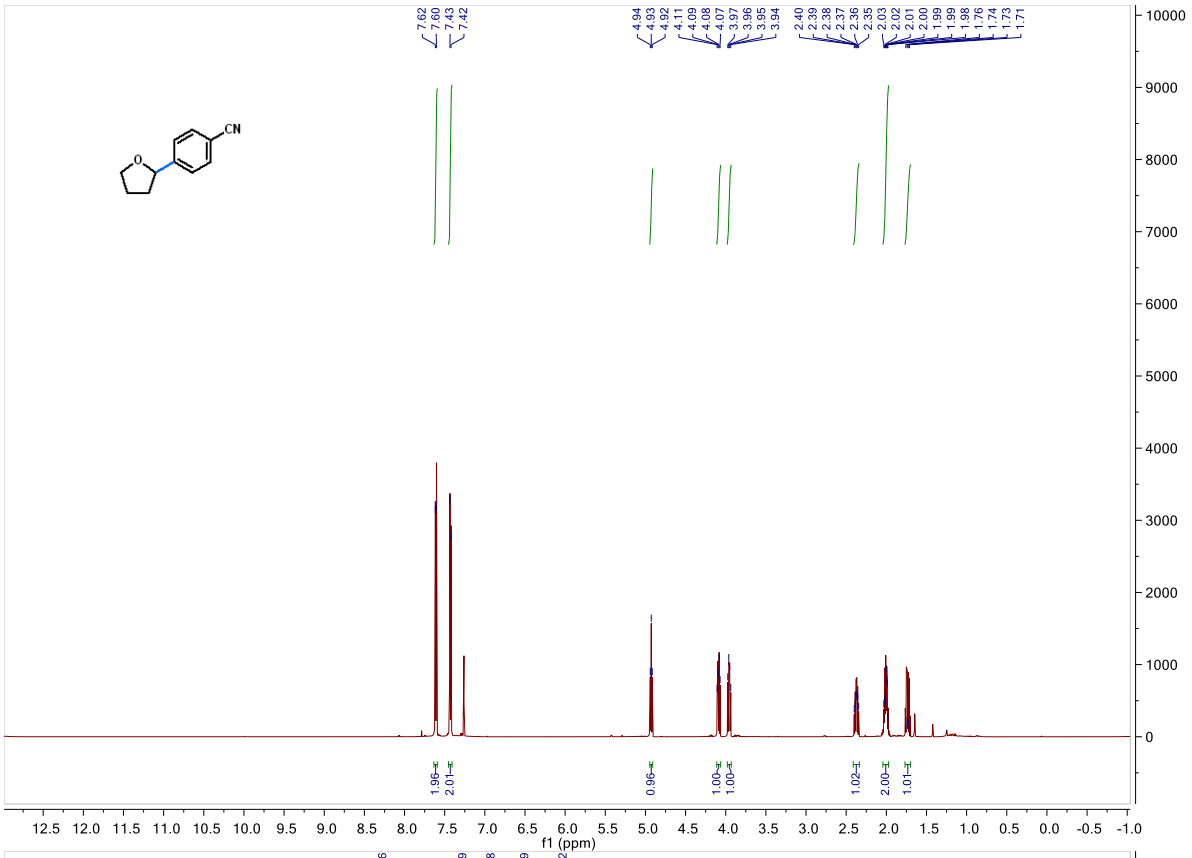
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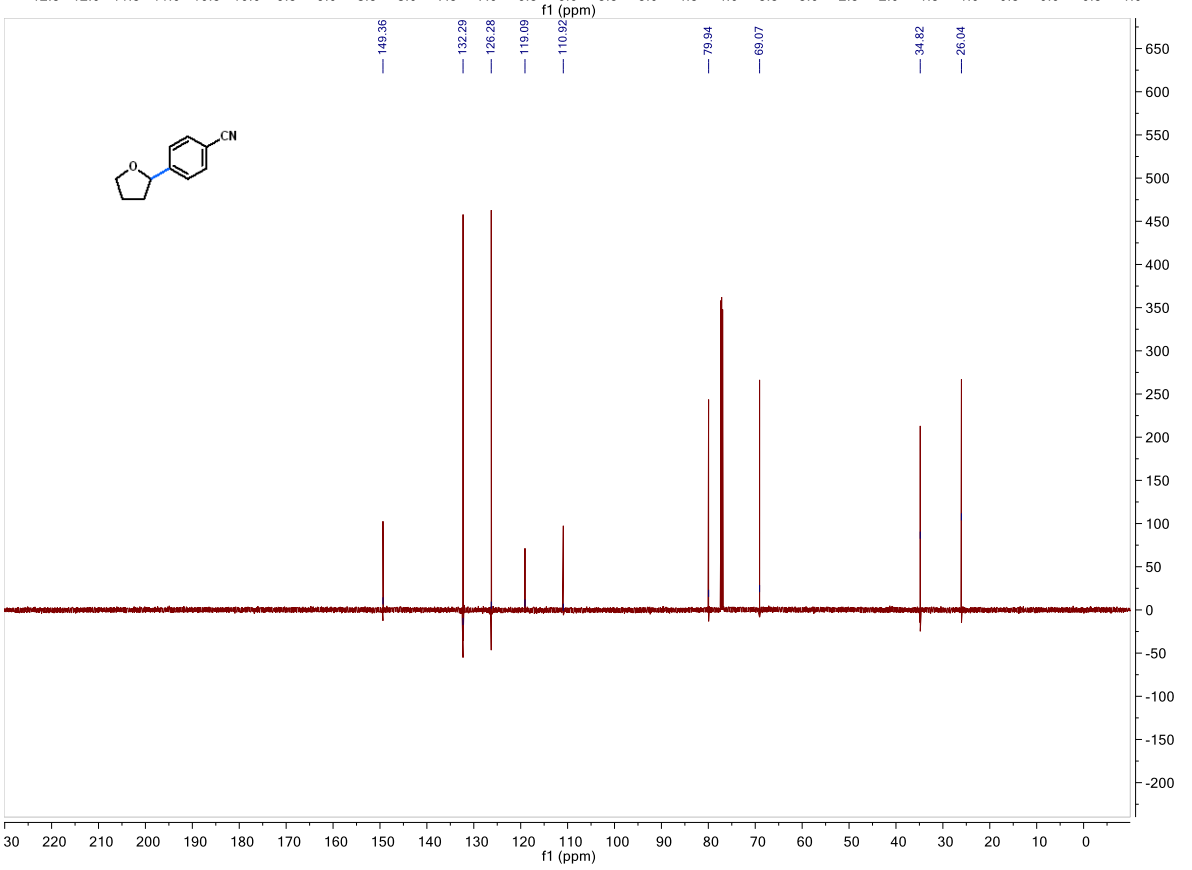
2.37
2.36
2.35
2.03
2.02
2.01
2.00
1.99
1.98
1.76
1.74
1.73
1.71
CN
O
1.96
2.01
0.96
1.00
1.00
1.02
2.00
1.01
f1 (ppm)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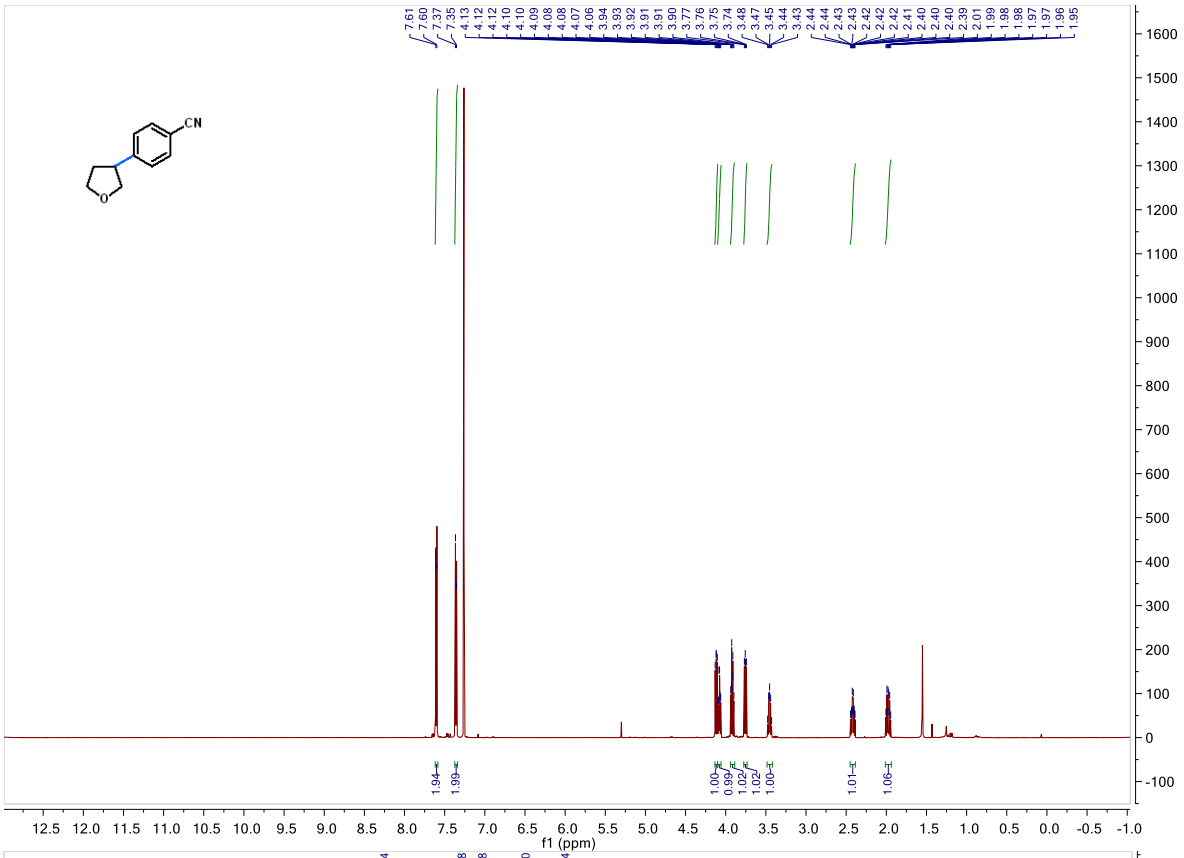
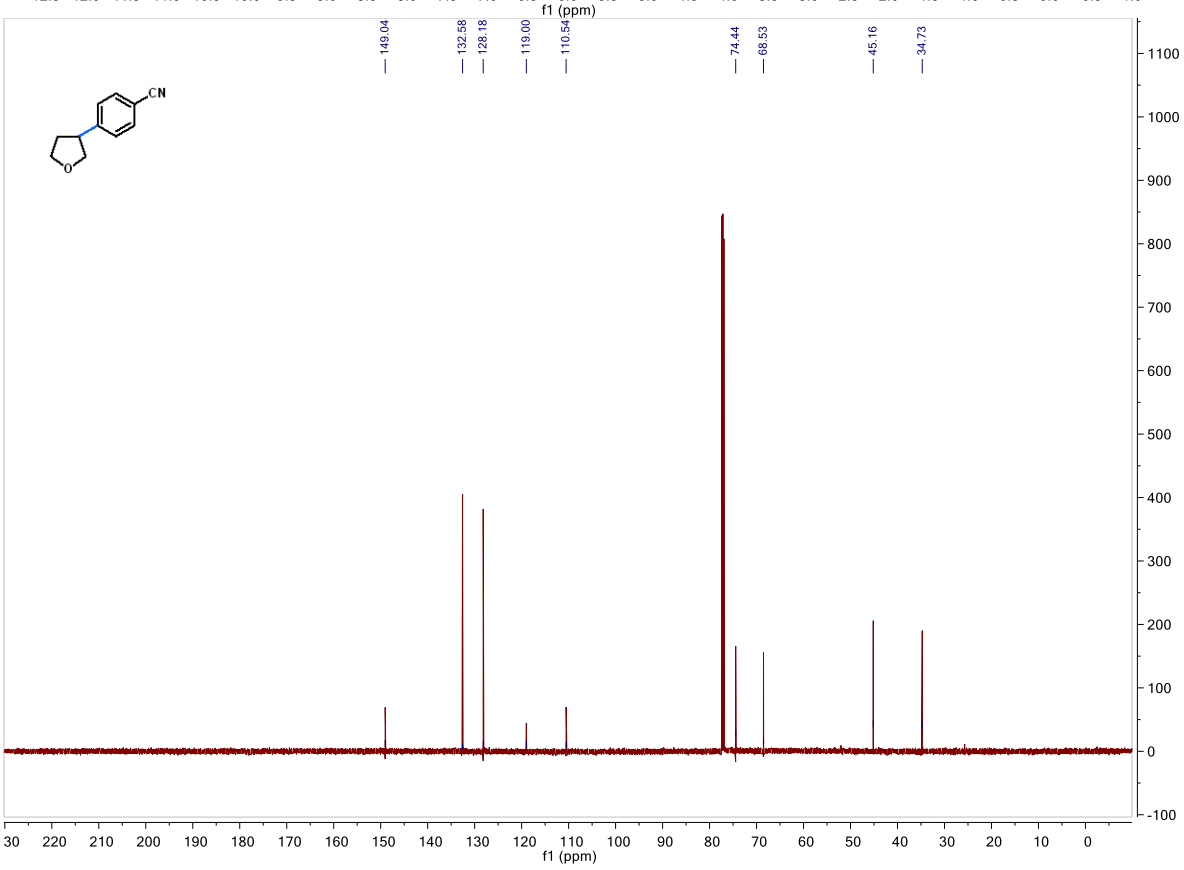
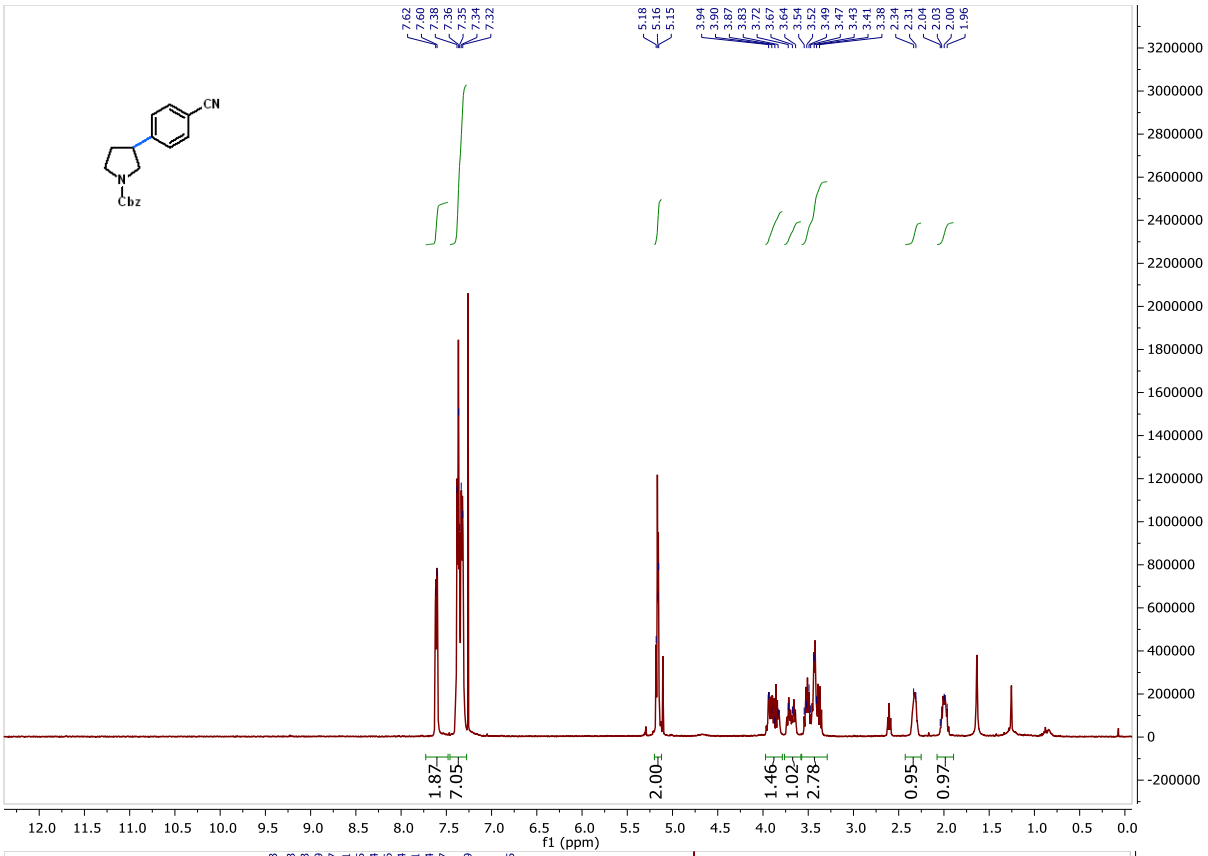
119.09
110.92
79.94
69.07
34.82
26.04
CN
O
f1 (ppm)


CN
O
7.61 7.60 7.37 7.35 4.13 4.12 4.12 4.10 4.10 4.09 4.08 4.08 4.07 4.06 3.94 3.93 3.92 3.91 3.91 3.90 3.77 3.76 3.75 3.74 3.48 3.47 3.45 3.44 3.43 2.44 2.44 2.43 2.43 2.42 2.42 2.42 2.41 2.40 2.40 2.40 2.39 2.01 1.99 1.98 1.98 1.97 1.97 1.96 1.95
1.94 1.99 1.00 0.99 1.02 1.02 1.00 1.01 1.06
f1 (ppm)


CN
O
149.04 132.58 128.18 119.00 110.54 74.44 68.53 45.16 34.73
f1 (ppm)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7.32
5.18
5.16
5.15
3.94
3.90
3.87
3.83
3.72
3.67
3.64
3.54
3.52
3.49
3.47
3.43
3.41
3.38
2.34
2.31
2.04
2.03
2.00
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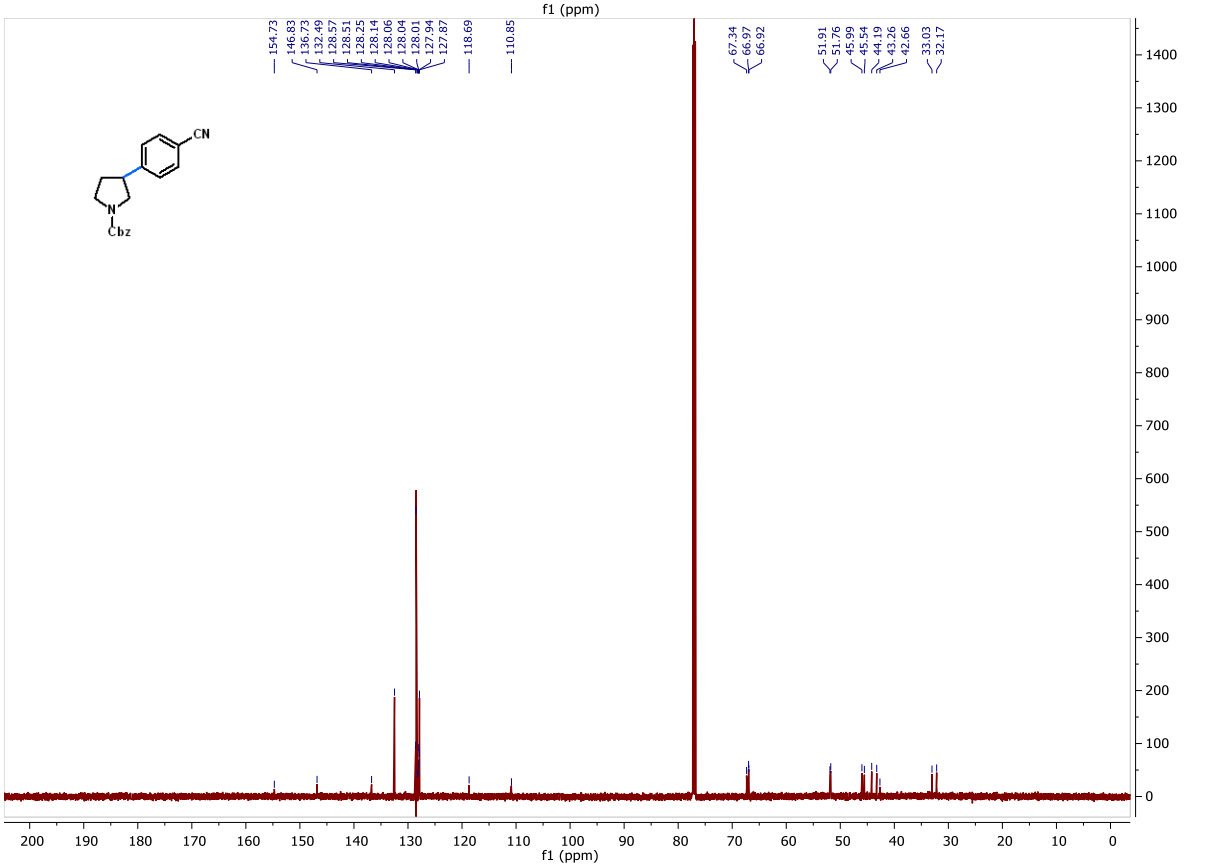
CN
N
Cbz
1.87
7.05
2.00
1.46
1.02
2.78
0.95
0.97
f1 (ppm)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128.51
128.25
128.14
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128.04
128.01
127.94
127.87
118.69
110.85
67.34
66.97
66.92
51.91
51.76
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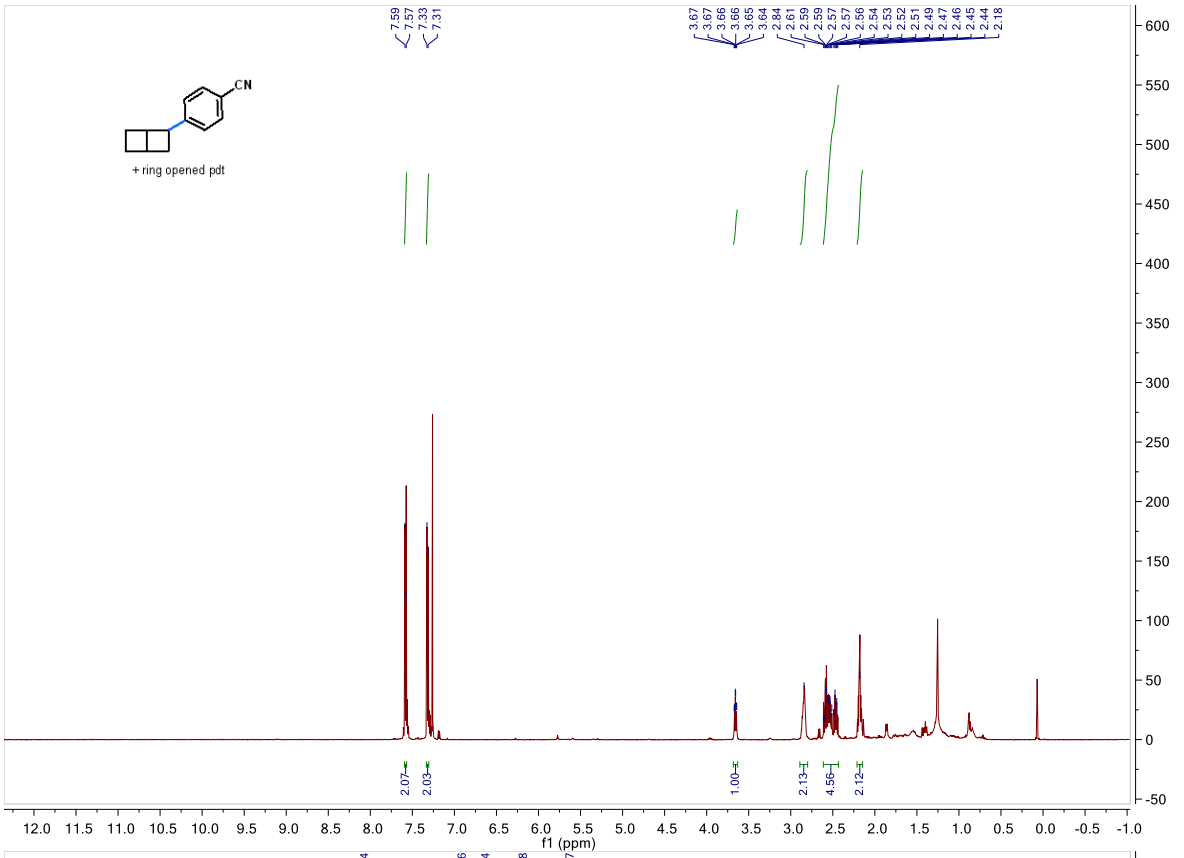
45.54
44.19
43.26
42.66
33.03
32.17
CN
N
Cbz
f1 (ppm)


7.59
7.57
7.33
7.31
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3.67
3.66
3.66
3.65
3.64
2.84
2.61
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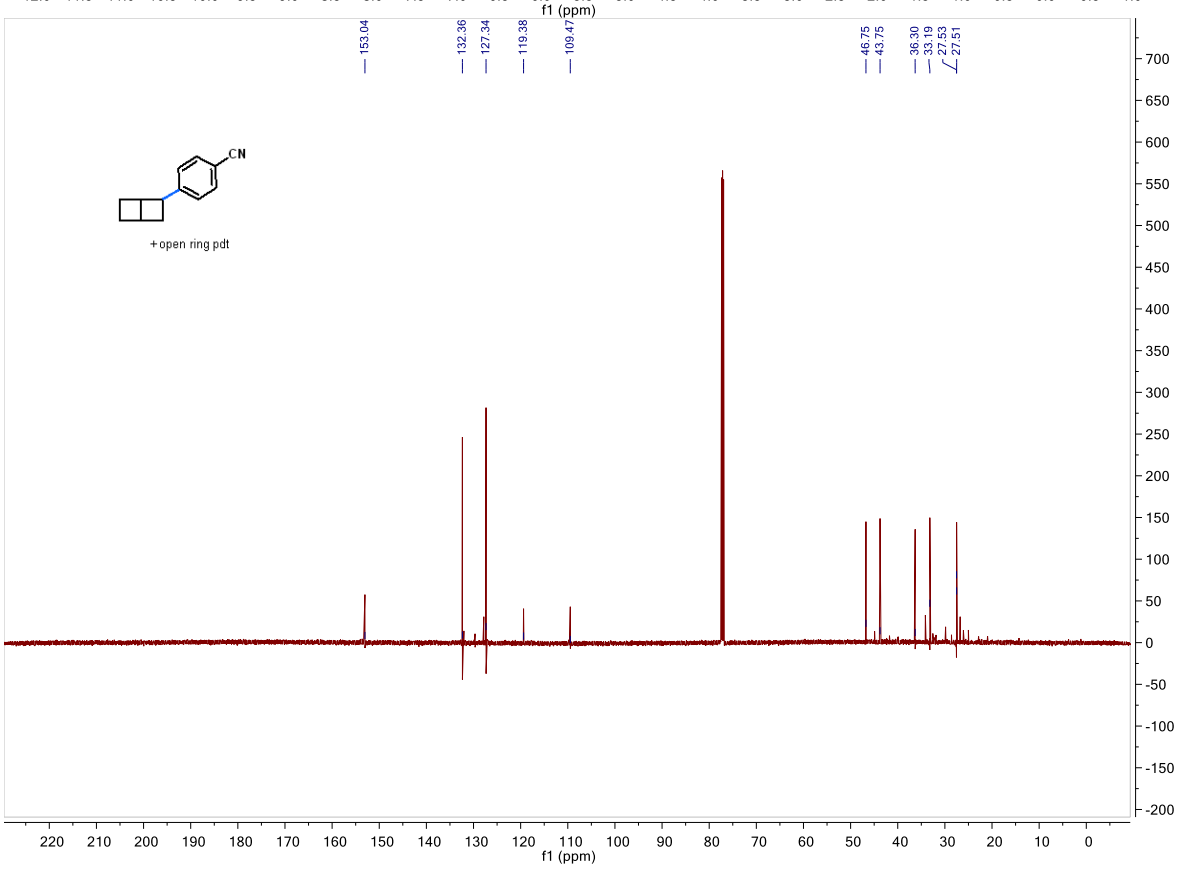
2.59
2.57
2.57
2.56
2.54
2.53
2.52
2.51
2.49
2.47
2.46
2.45
2.44
2.18
CN
+ ring opened pdt
2.07
2.03
1.00
2.13
4.56
2.12
f1 (ppm)


153.04
132.36
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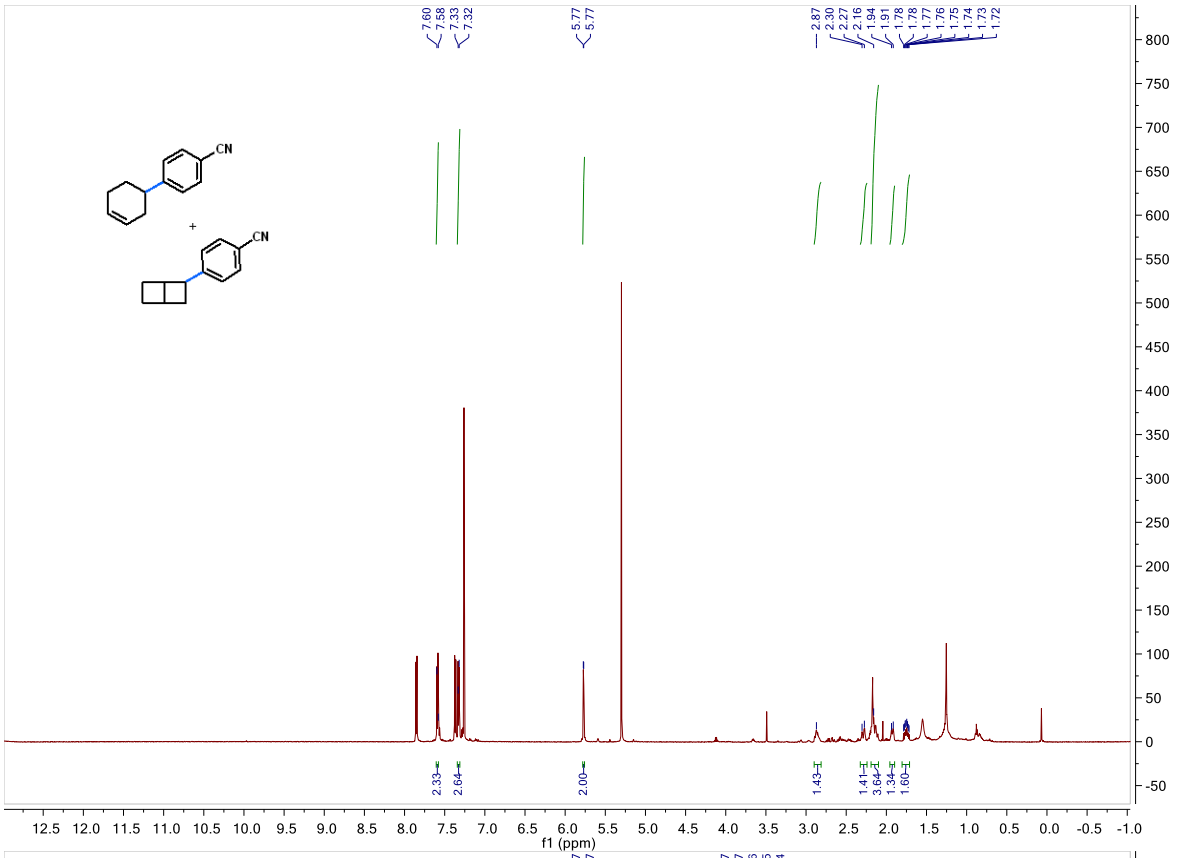
119.38
109.47
46.75
43.75
36.30
33.19
27.53
27.51
CN
+ open ring pdt
f1 (ppm)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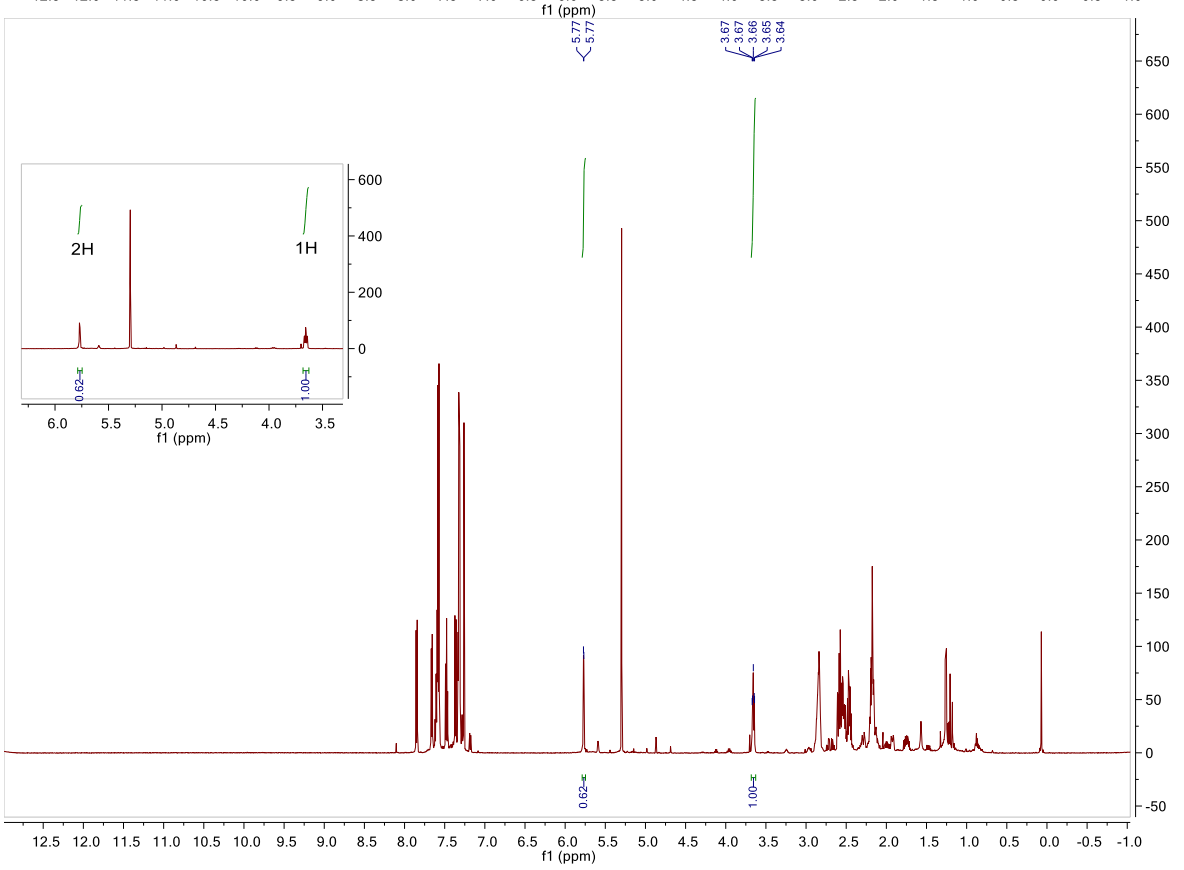
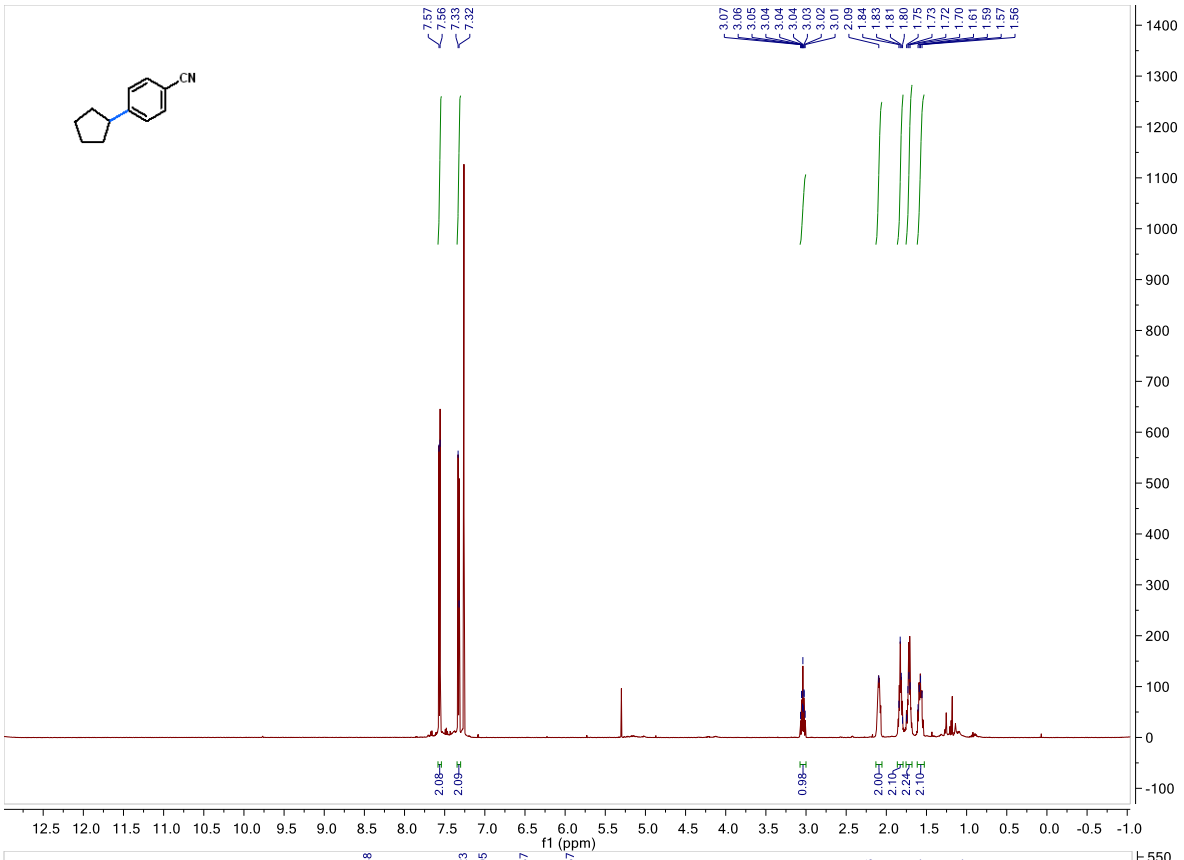
7.58
7.33
7.32
5.77
5.77
2.87
2.30
2.27
2.16
1.94
1.91
1.78
1.78
1.77
1.76
1.75
1.74
1.73
1.72
CN
CN
2.33
2.64
2.00
1.43
1.41
3.64
1.34
1.60
f1 (ppm)


5.77
5.77
3.67
3.67
3.66
3.65
3.64
2H
1H
0.62
1.00
f1 (ppm)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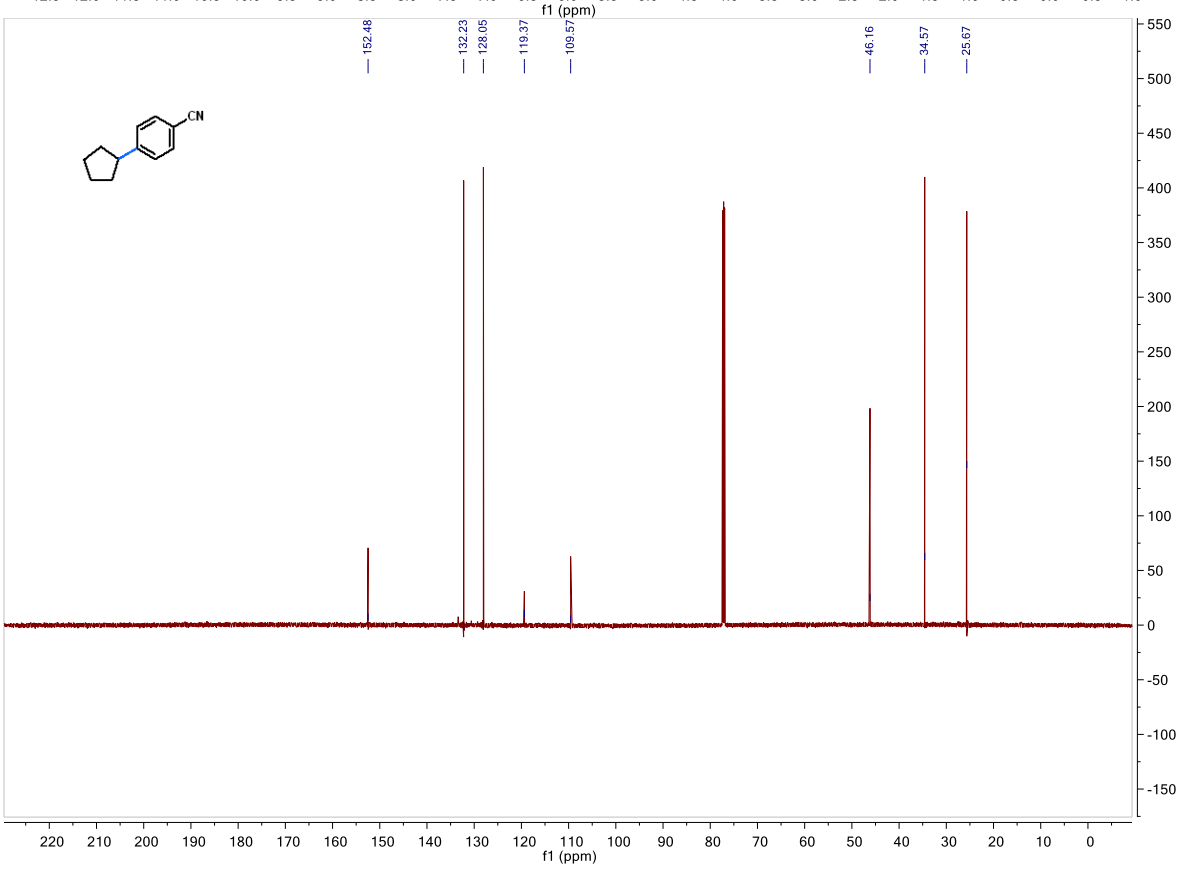
7.56
7.33
7.32
3.07
3.06
3.05
3.04
3.04
3.04
3.03
3.02
3.01
2.09
1.84
1.83
1.81
1.80
1.75
1.73
1.72
1.70
1.61
1.59
1.57
1.56
CN
2.08
2.09
0.98
2.00
2.10
2.24
2.10
f1 (ppm)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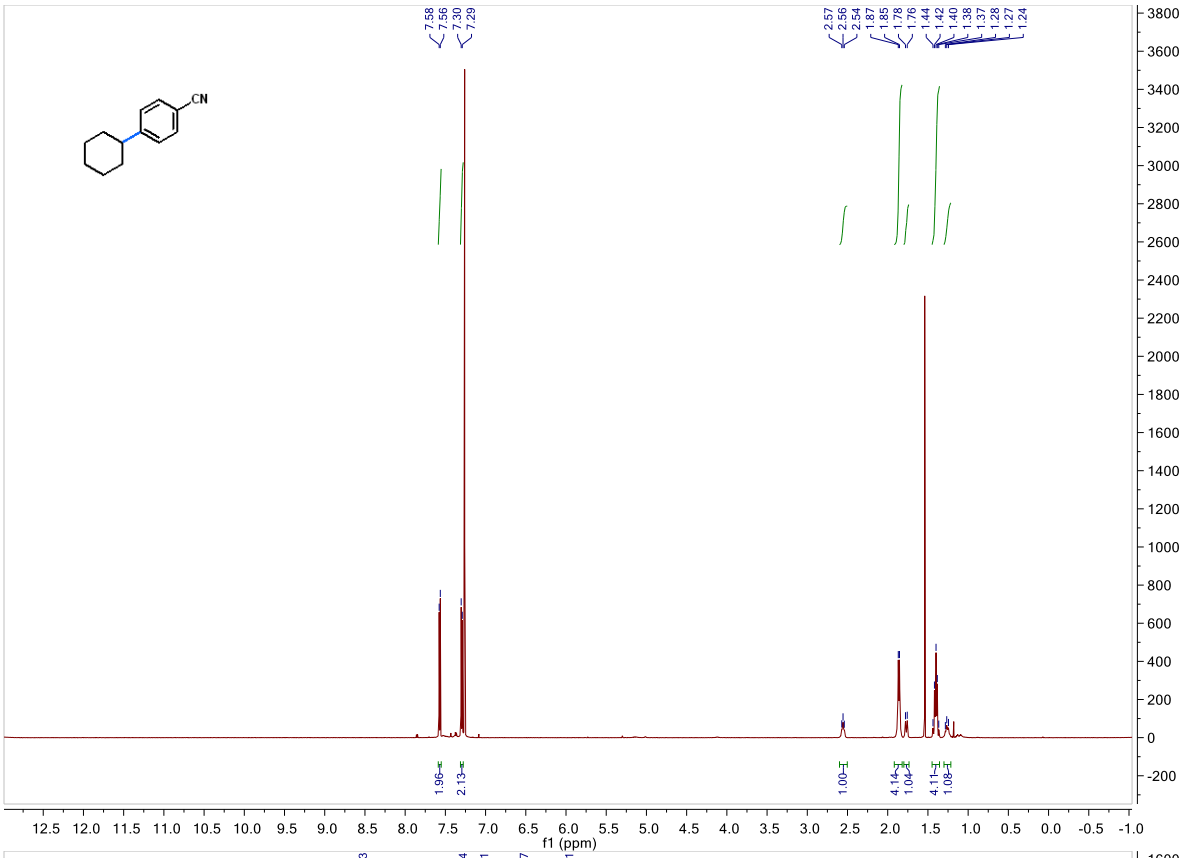
109.57
46.16
34.57
25.67
CN
f1 (ppm)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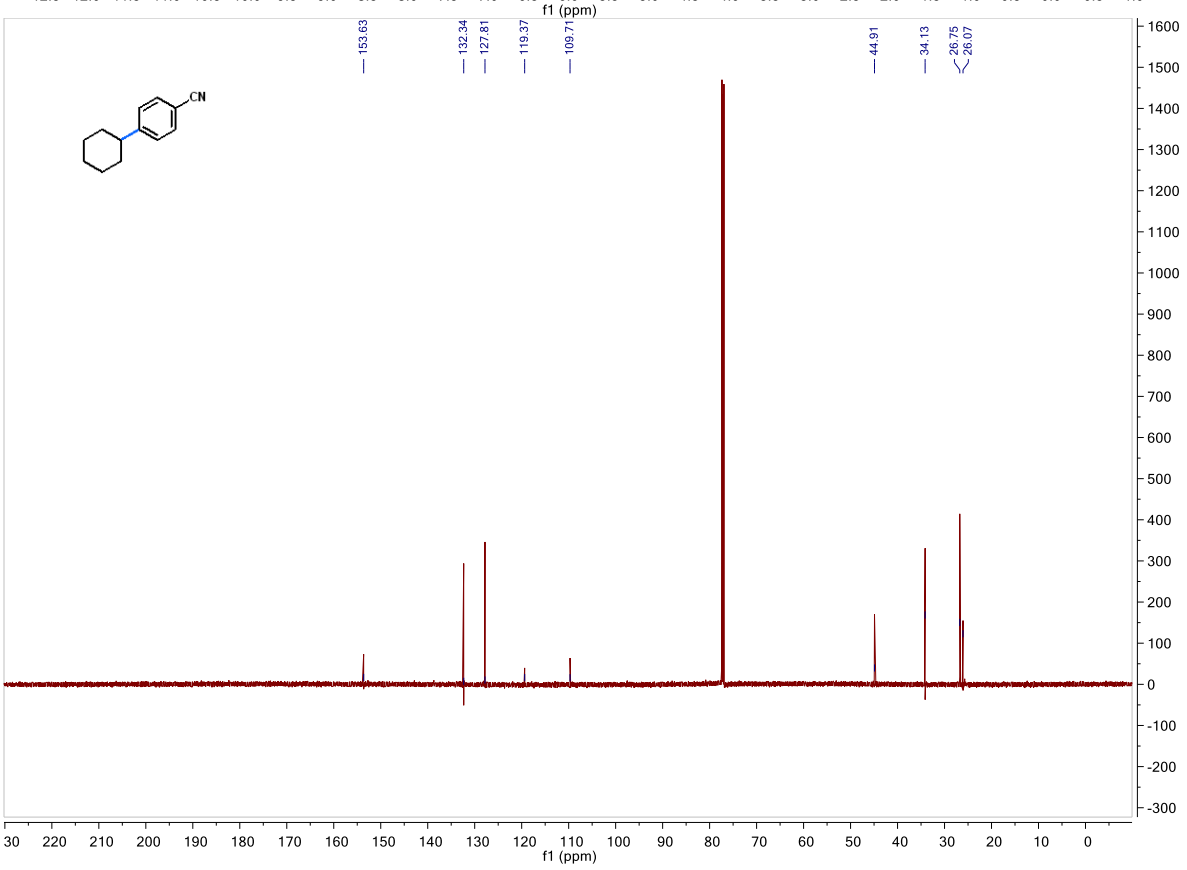
7.56
7.30
7.29
2.57
2.56
2.54
1.87
1.85
1.78
1.76
1.44
1.42
1.40
1.38
1.37
1.28
1.27
1.24
CN
1.96
2.13
1.00
4.14
1.04
4.11
1.08
f1 (ppm)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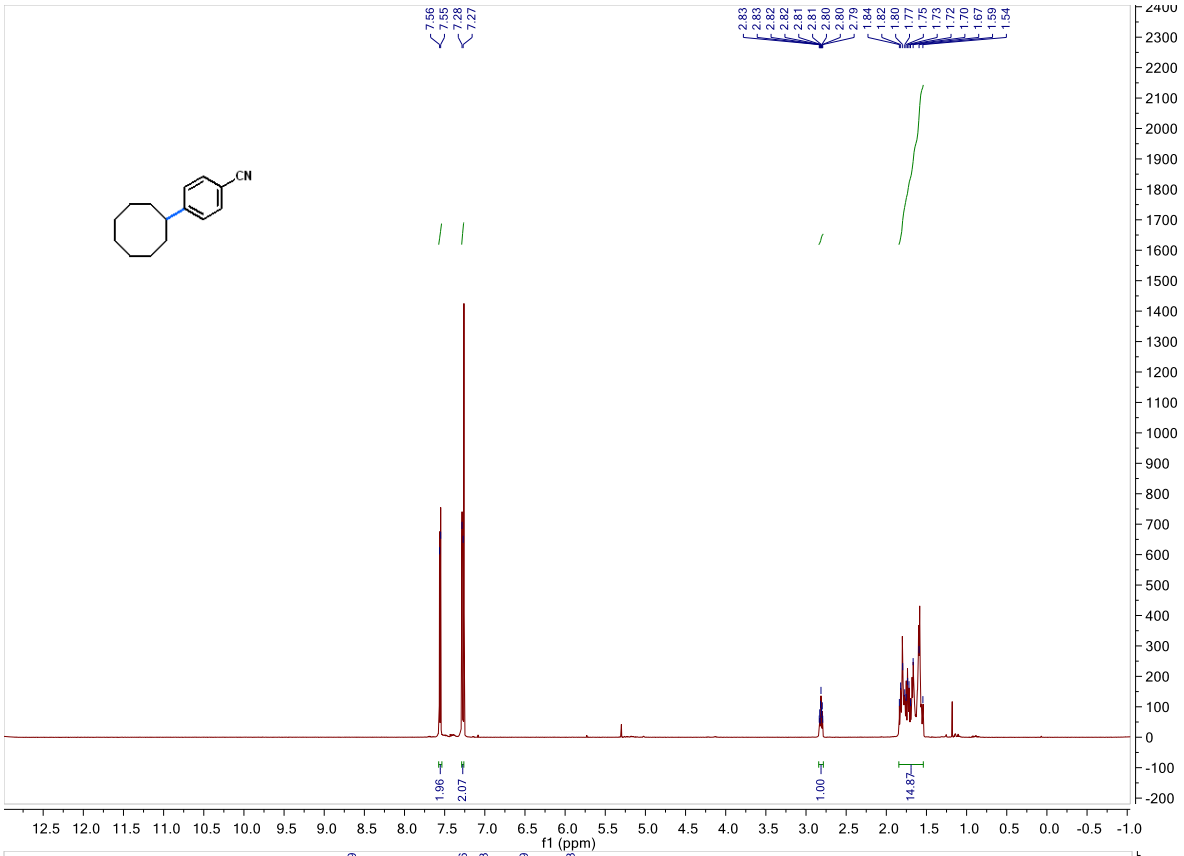
119.37
109.71
44.91
34.13
26.75
26.07
CN
f1 (ppm)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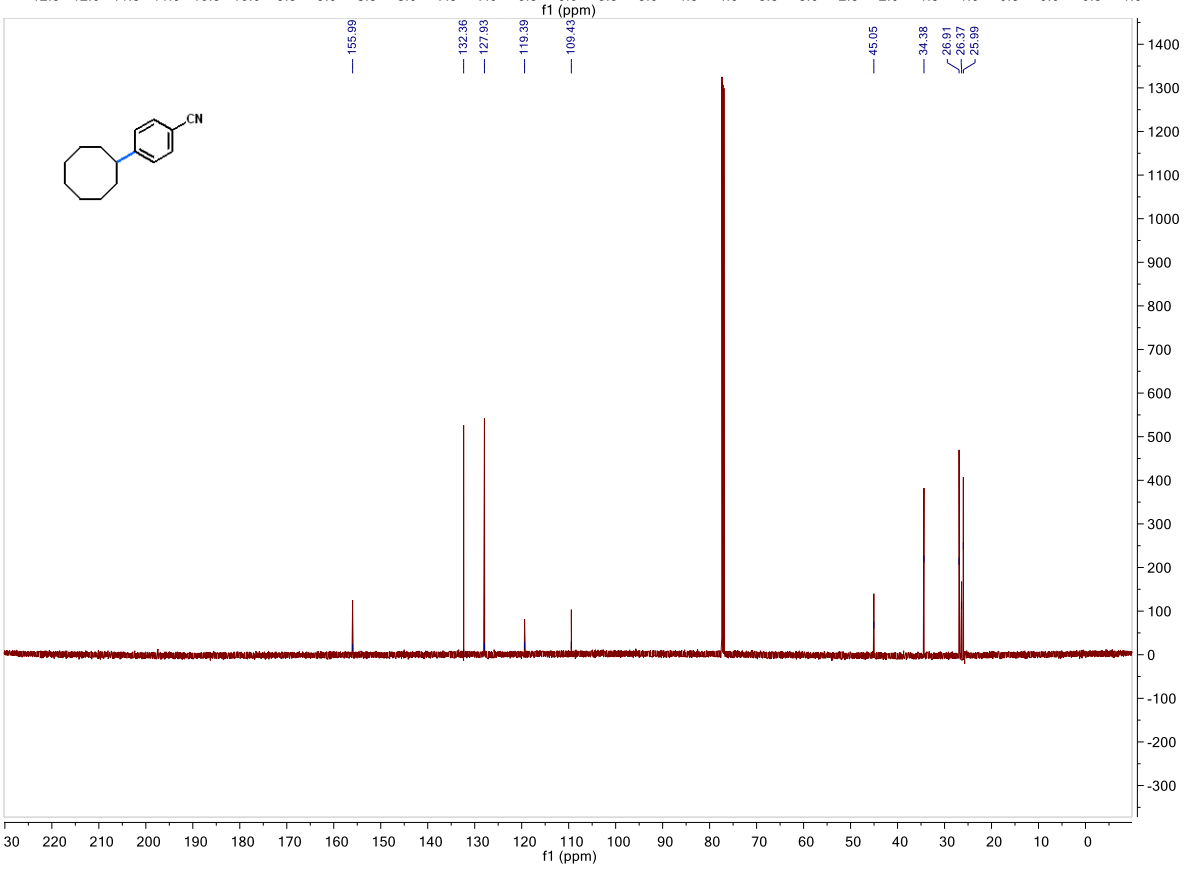
7.55
7.28
7.27
2.83
2.83
2.82
2.82
2.81
2.81
2.80
2.80
2.79
1.84
1.82
1.80
1.77
1.75
1.73
1.72
1.70
1.67
1.59
1.54
CN
1.96
2.07
1.00
14.87
f1 (ppm)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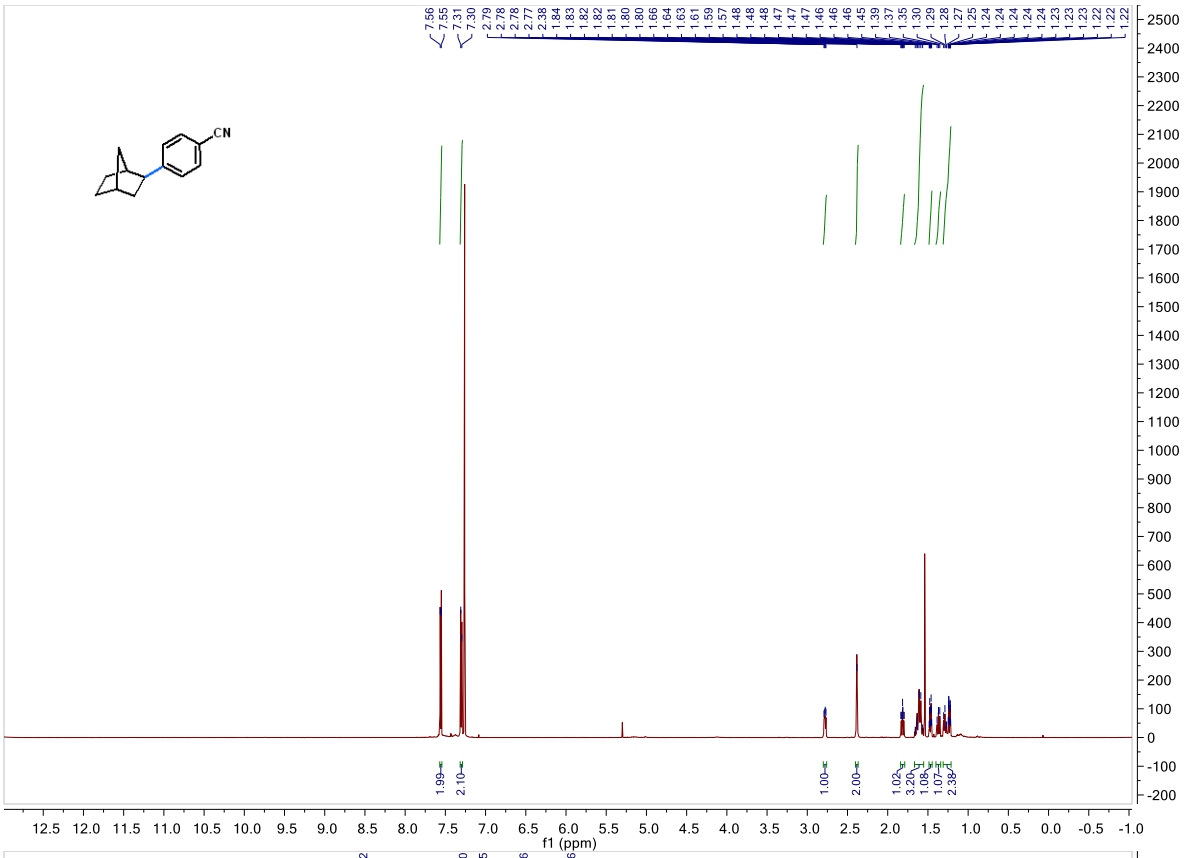
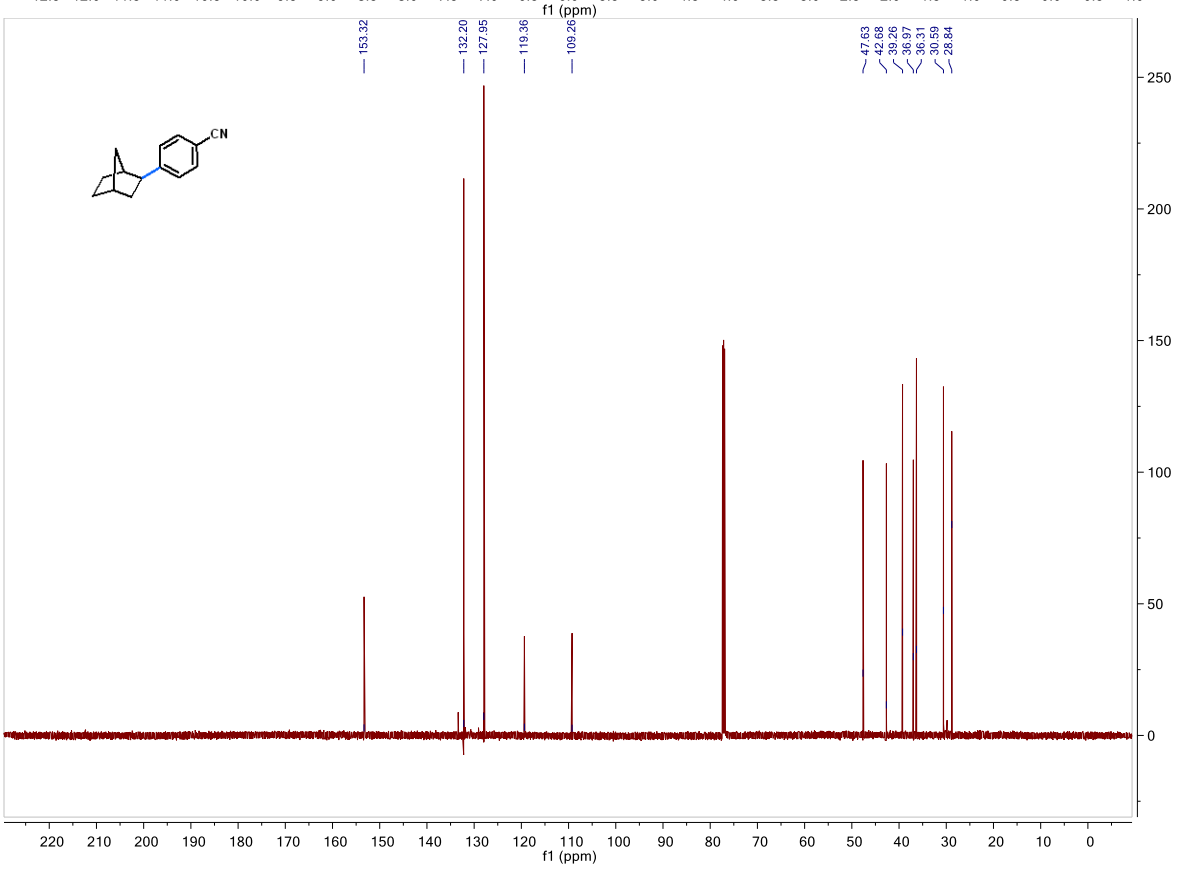
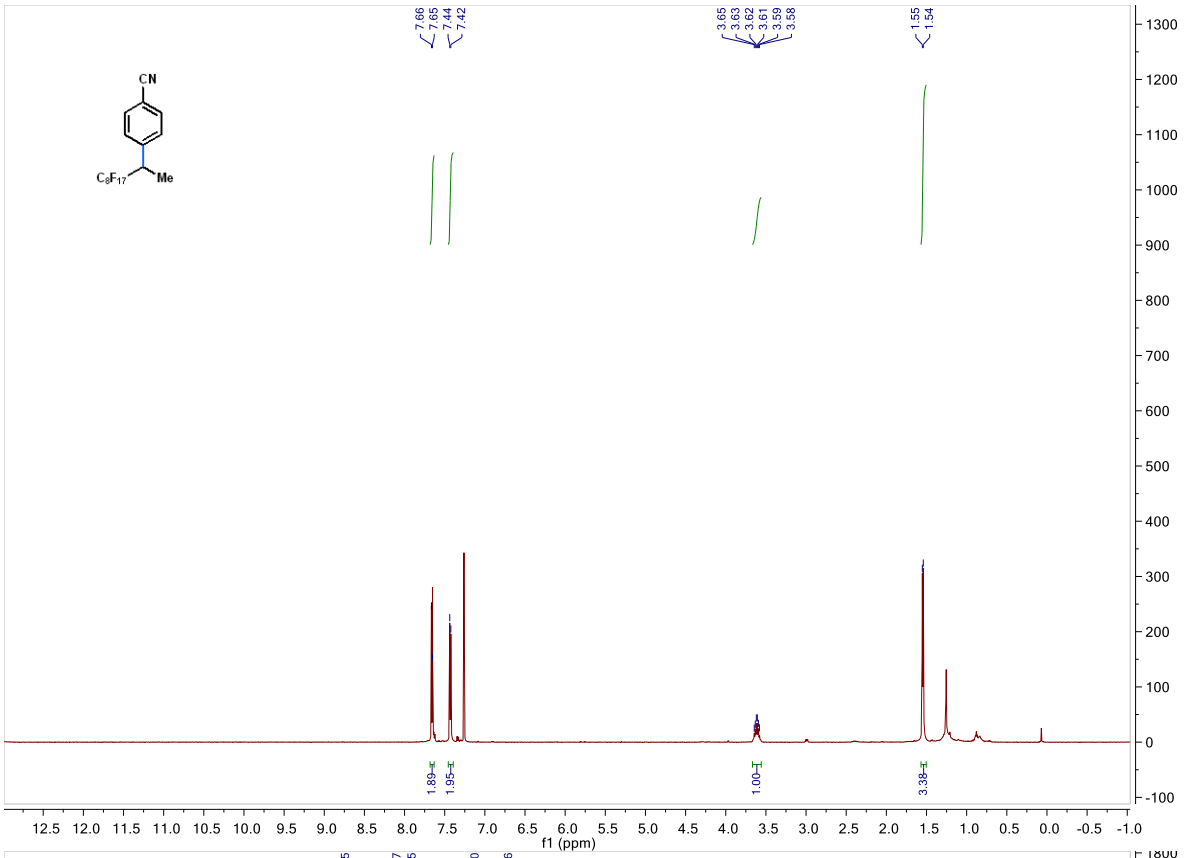
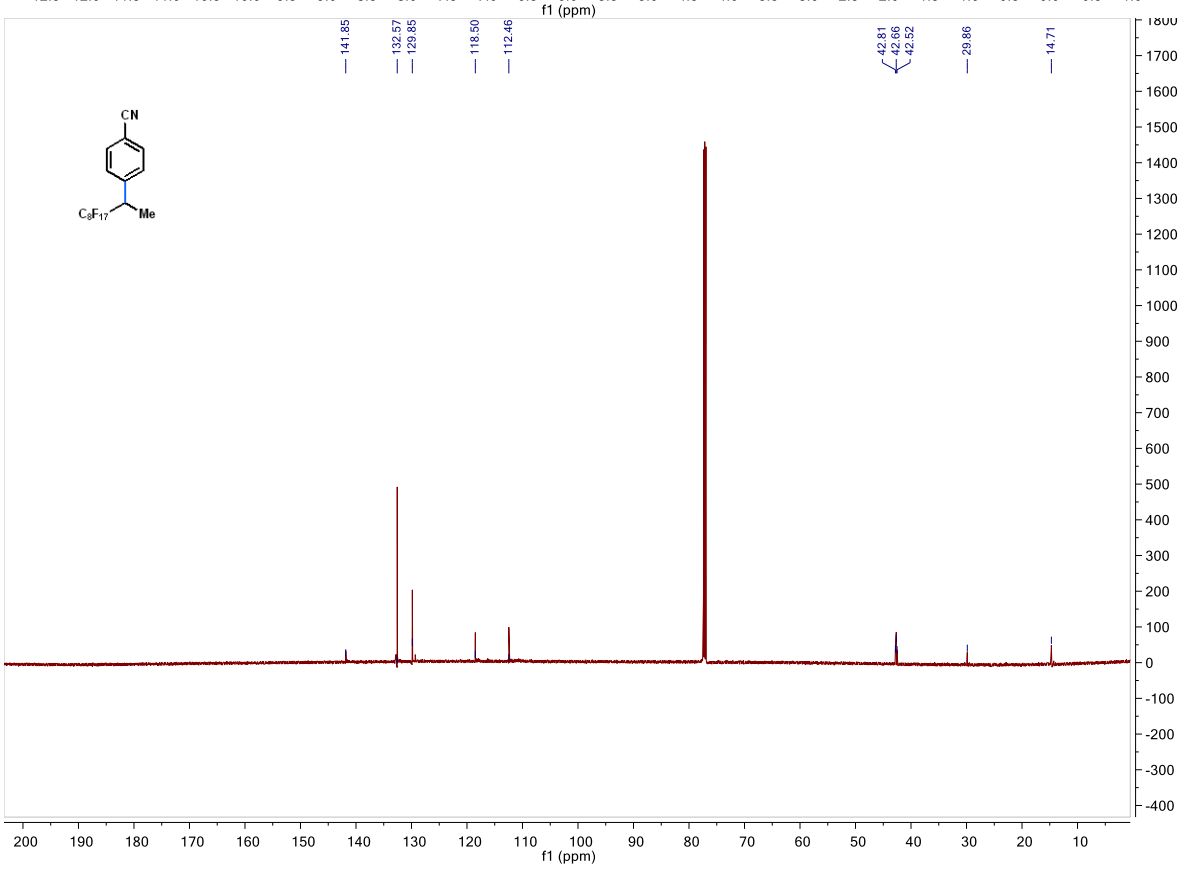
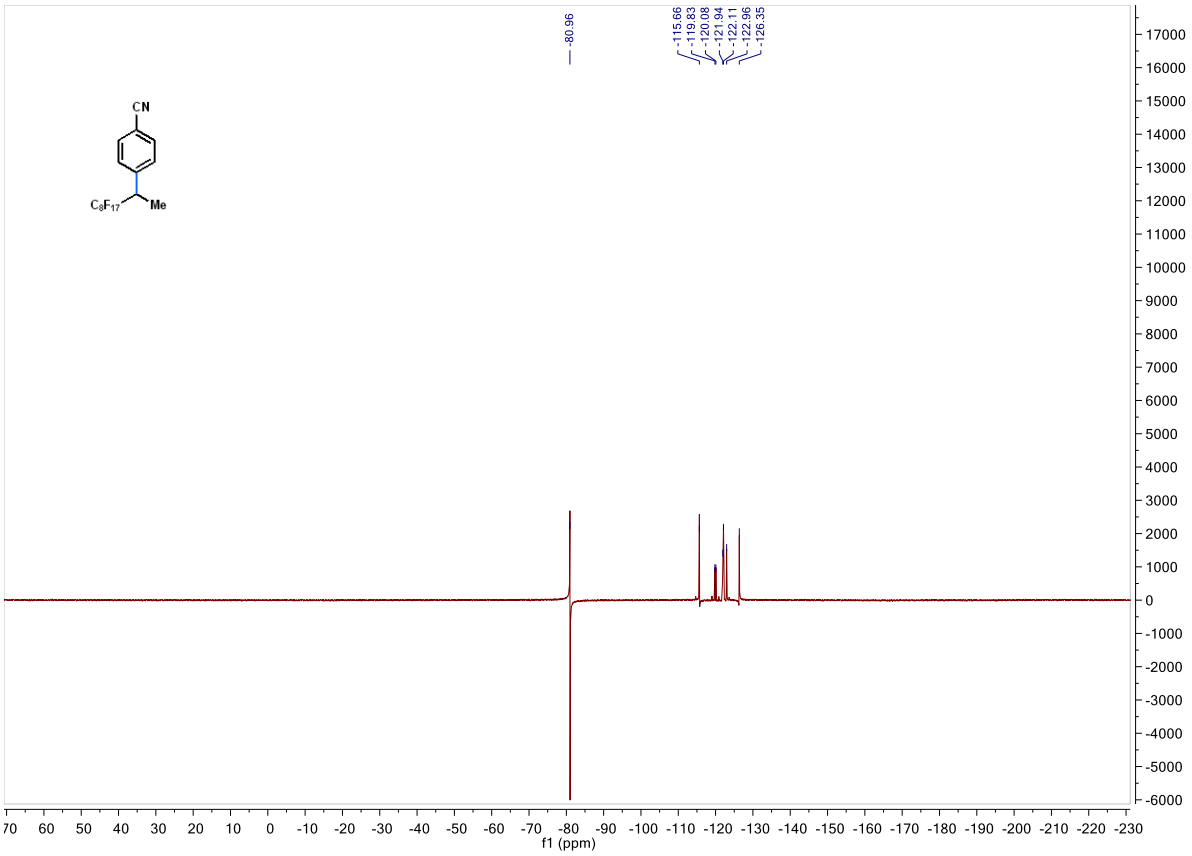
132.36
127.93
119.39
109.43
45.05
34.38
26.91
26.37
25.99
CN
f1 (ppm)


CN
f1 (ppm)


CN
153.32
132.20
127.95
119.36
109.26
47.63
42.68
39.26
36.97
36.31
30.59
28.84
f1 (ppm)


7.66
7.65
7.44
7.42
3.65
3.63
3.62
3.61
3.59
3.58
1.55
1.54
CN
C8F17
Me
1.89
1.95
1.00
3.38
f1 (ppm)


141.85
132.57
129.85
118.50
112.46
42.81
42.66
42.52
29.86
14.71
CN
C8F17
Me
f1 (ppm)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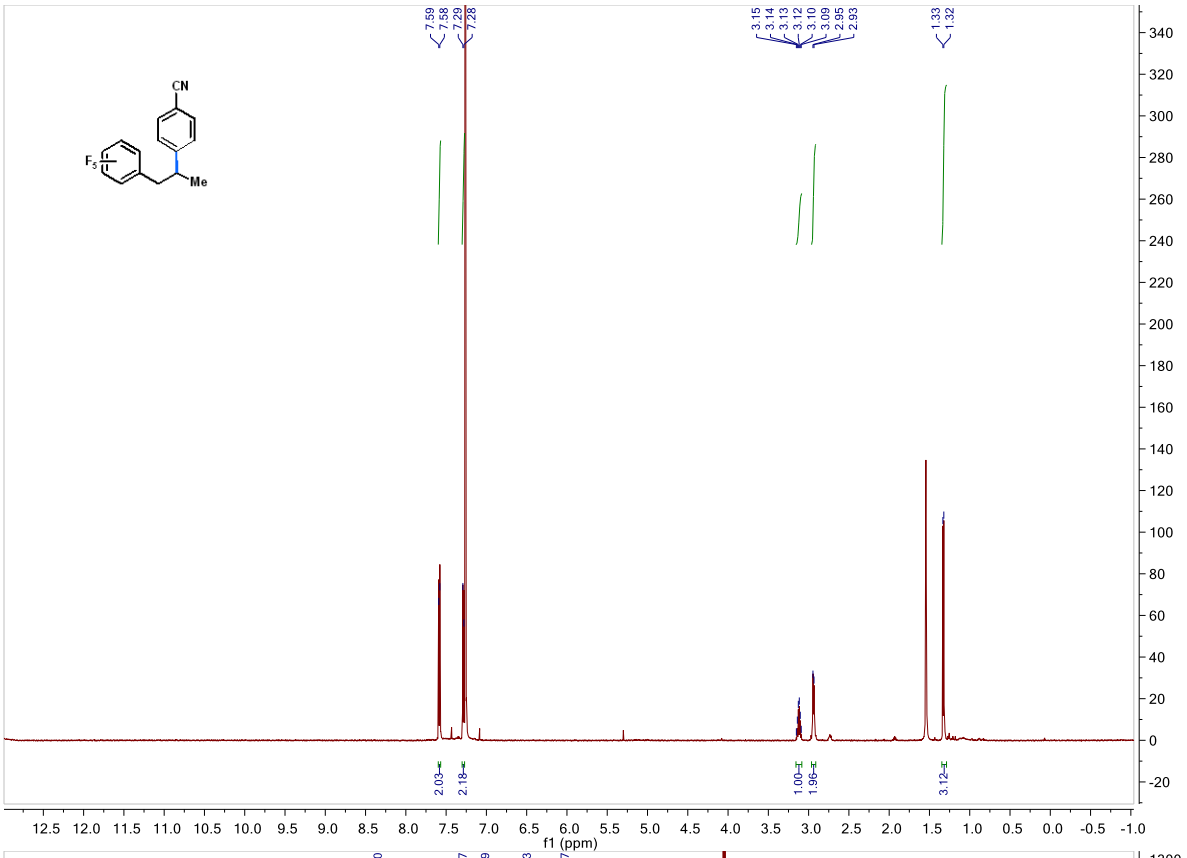
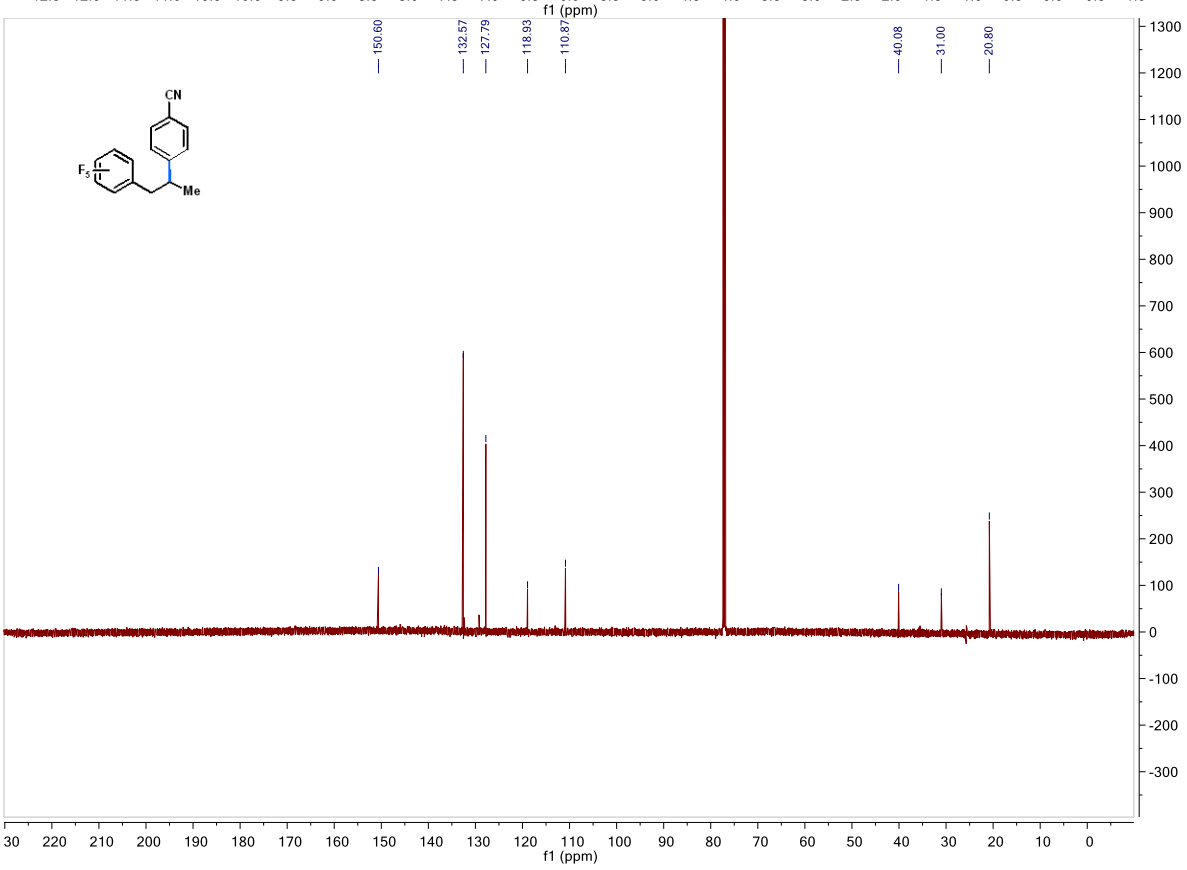
-122.11
-122.96
-126.35
CN
C8F17
Me
f1 (ppm)


7.59
7.58
7.29
7.28
3.15
3.14
3.13
3.12
3.10
3.09
2.95
2.93
1.33
1.32
CN
F5
Me
2.03
2.18
1.00
1.96
3.12
f1 (ppm)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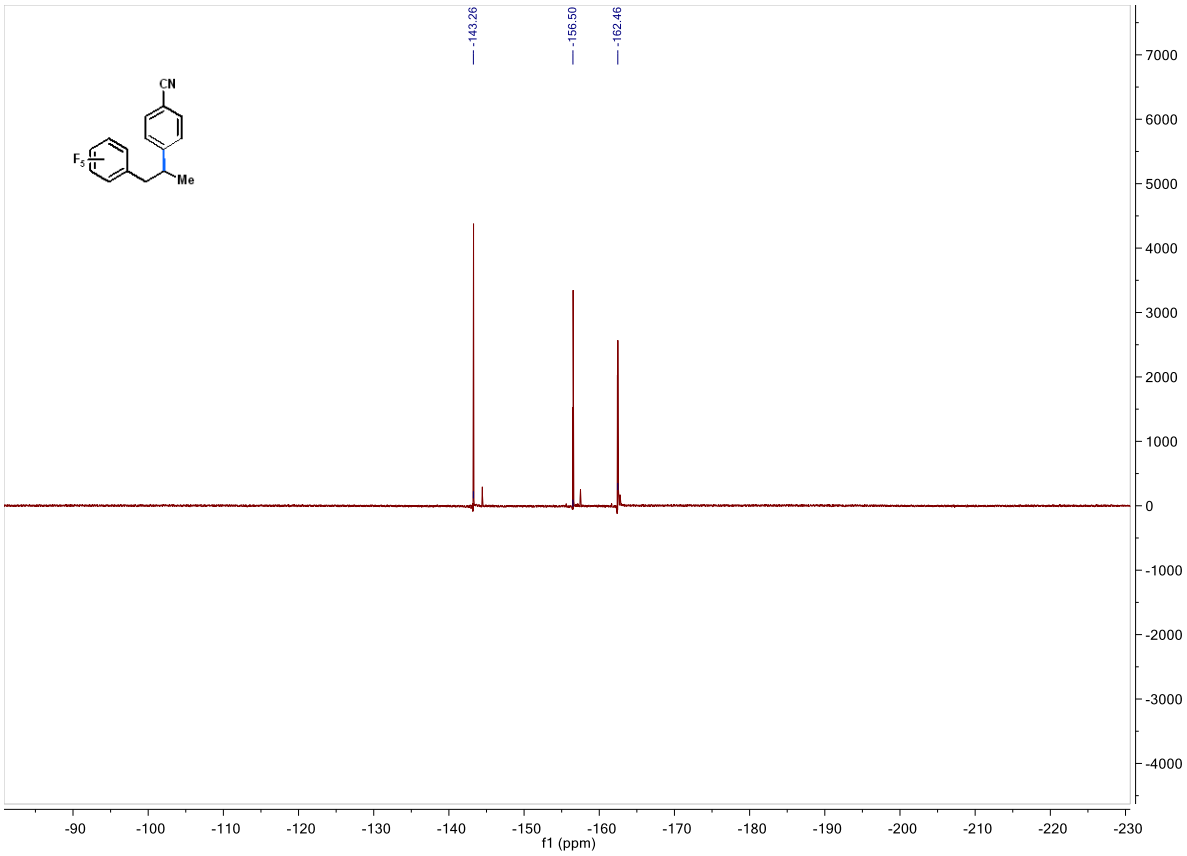
110.87
40.08
31.00
20.80
CN
F5
Me
f1 (ppm)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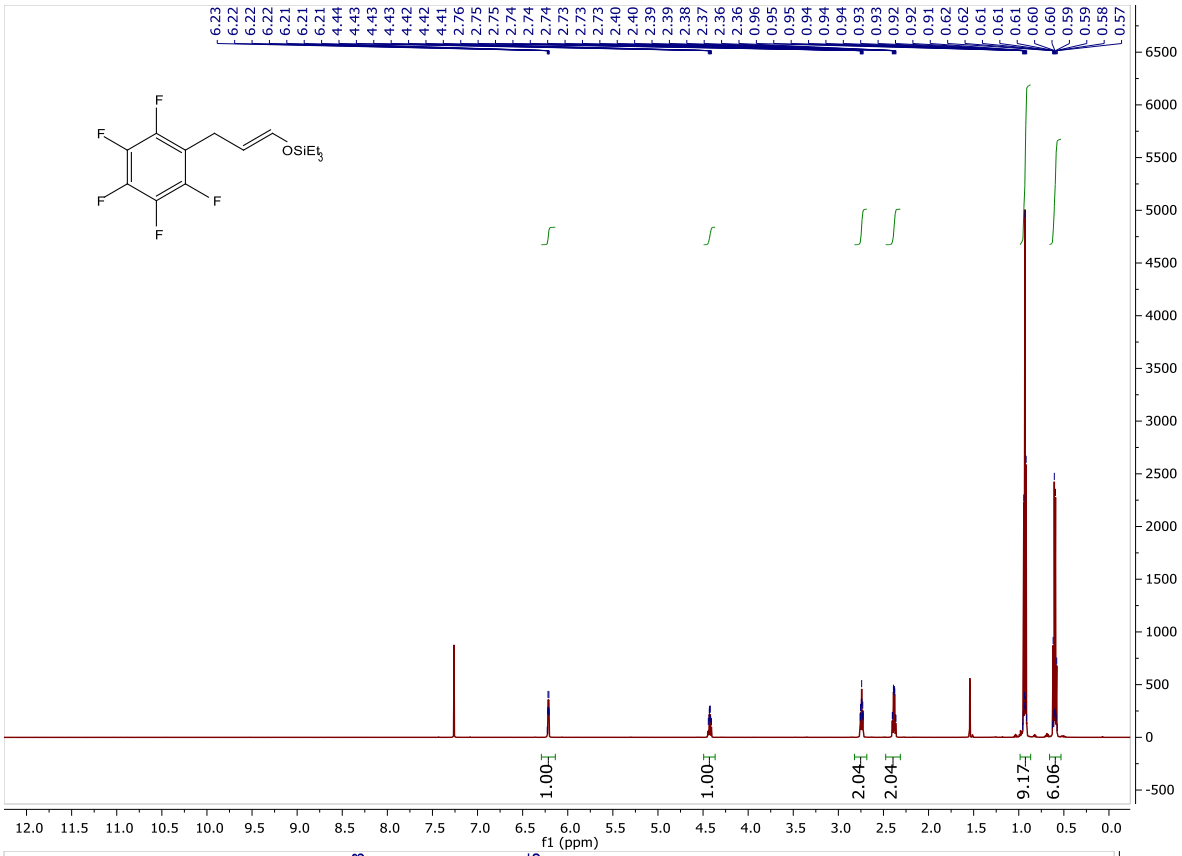
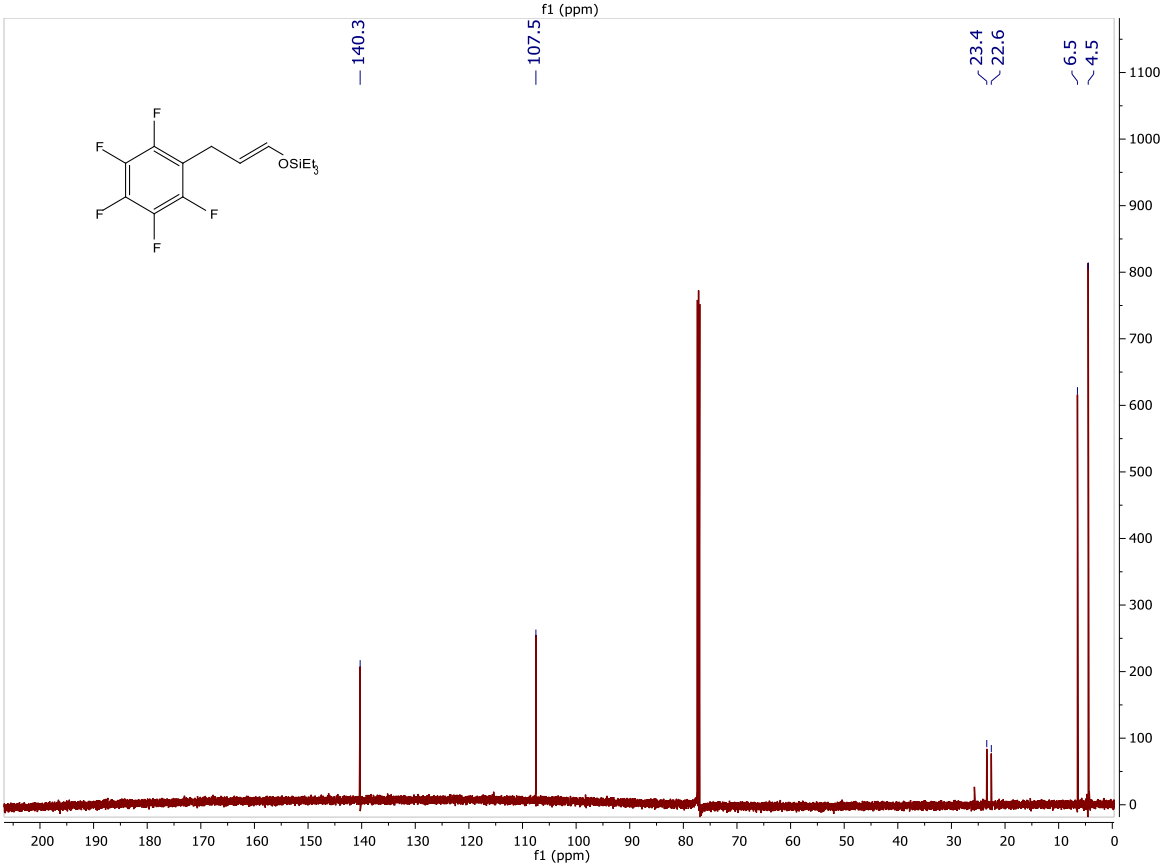
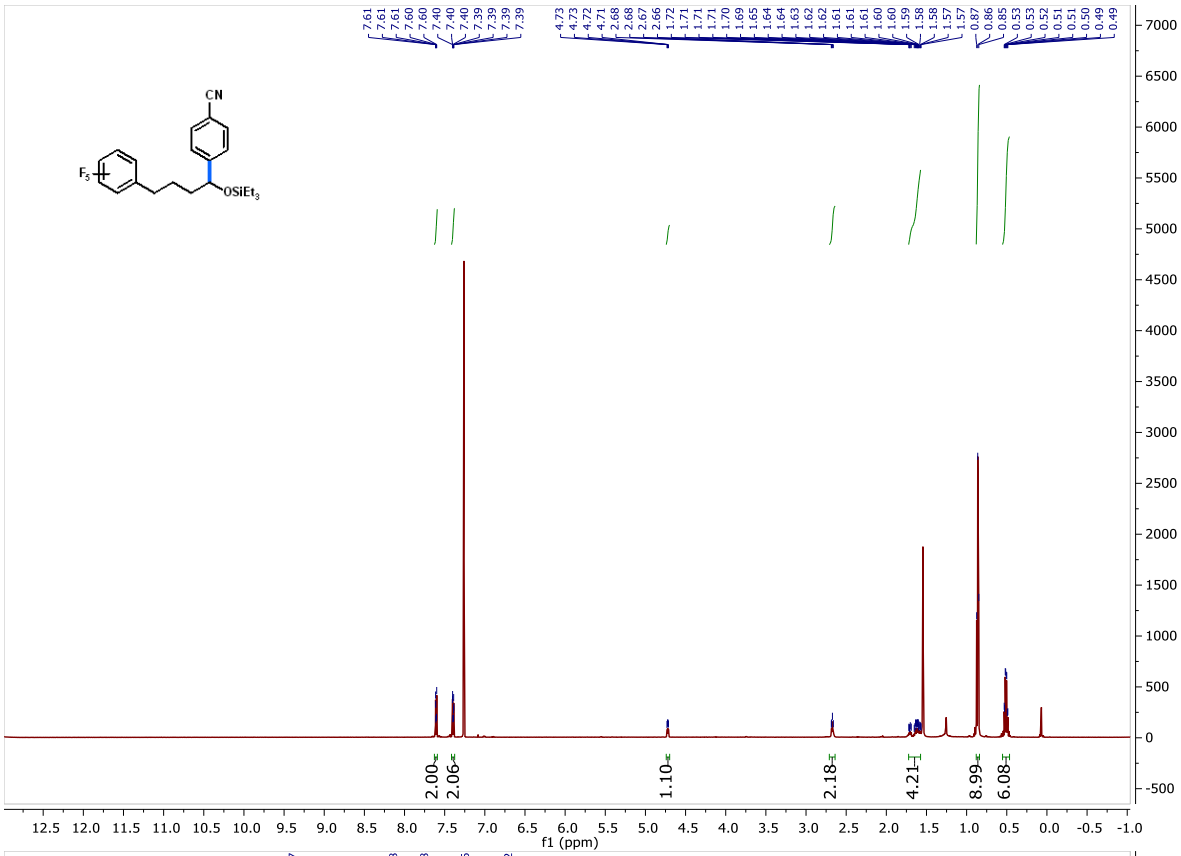
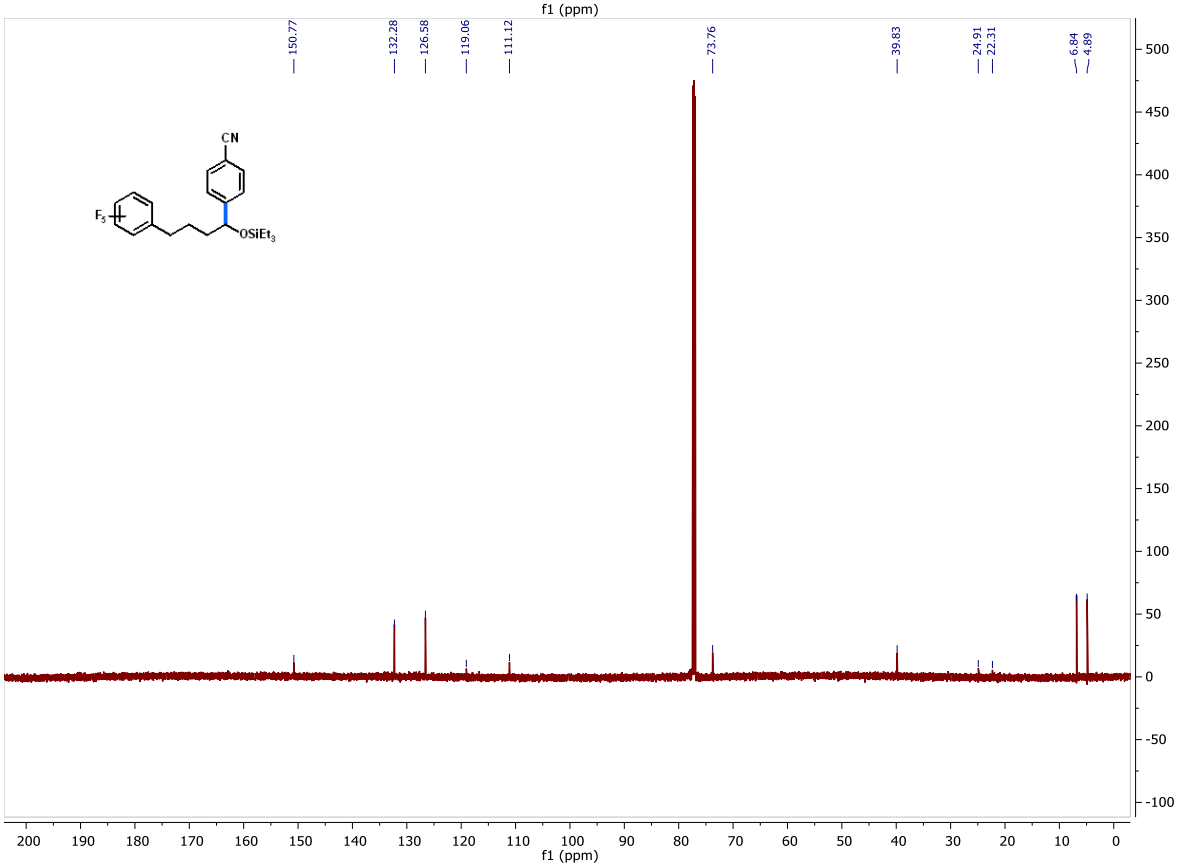
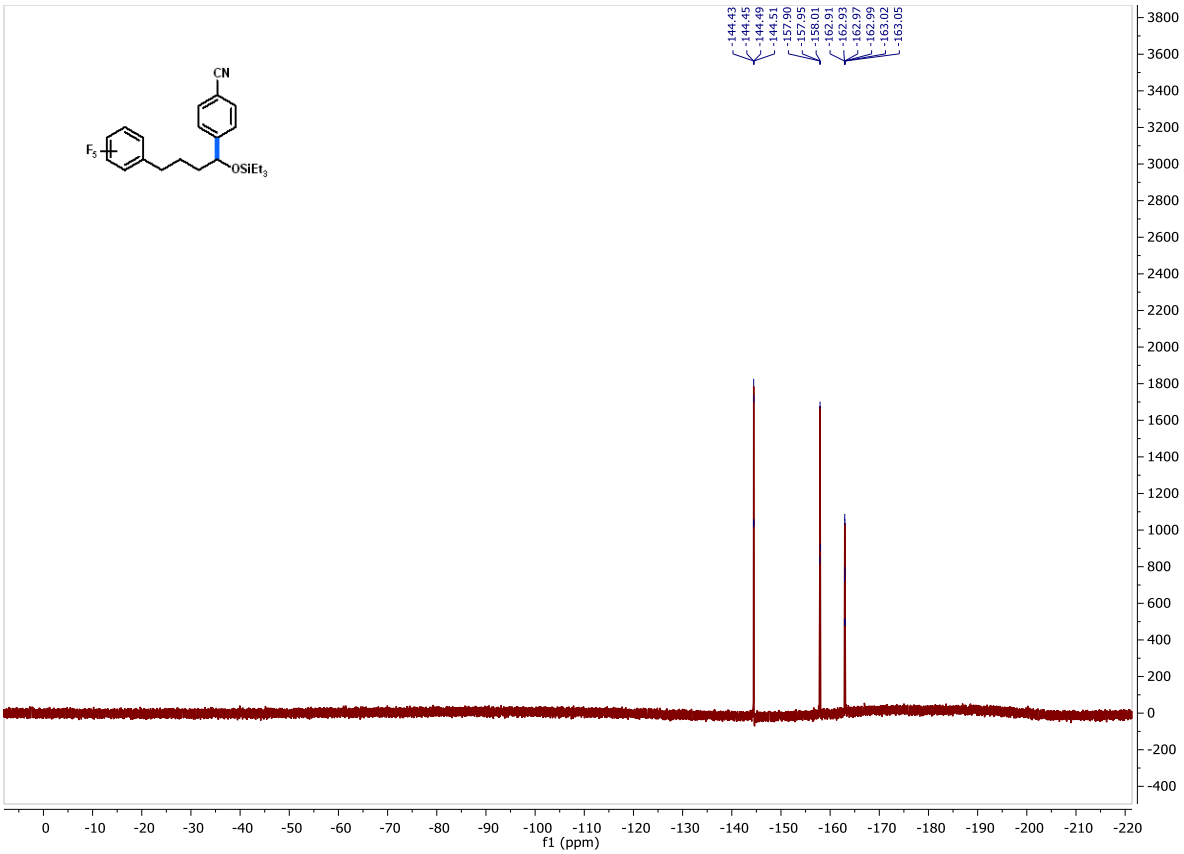
-156.50
-162.46
CN
F
Me
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)


F
F
F
F
F
OSiEt3
6.23 6.22 6.22 6.22 6.21 6.21 6.21 4.44 4.43 4.43 4.43 4.42 4.42 4.41 2.76 2.75 2.75 2.74 2.74 2.74 2.73 2.73 2.73 2.40 2.40 2.39 2.39 2.38 2.37 2.36 2.36 0.96 0.95 0.95 0.94 0.94 0.94 0.93 0.93 0.92 0.92 0.91 0.62 0.62 0.61 0.61 0.61 0.60 0.60 0.59 0.59 0.58 0.57
1.00
1.00
2.04
2.04
9.17
6.06
f1 (ppm)


F
F
F
F
F
OSiEt3
140.3
107.5
23.4
22.6
6.5
4.5
f1 (ppm)


CN
F5
OSiEt3
7.61 7.61 7.61 7.60 7.60 7.40 7.40 7.40 7.39 7.39 7.39 7.39
4.73 4.73 4.72 4.71 2.68 2.68 2.67 2.66 1.72 1.71 1.71 1.71 1.70 1.69 1.65 1.64 1.64 1.63 1.62 1.62 1.61 1.61 1.61 1.60 1.60 1.59 1.58 1.58 1.57 1.57
0.87 0.86 0.85 0.53 0.53 0.52 0.51 0.51 0.50 0.49 0.49
2.00 2.06 1.10 2.18 4.21 8.99 6.08
f1 (ppm)


CN
F5
OSiEt3
150.77 132.28 126.58 119.06 111.12 73.76 39.83 24.91 22.31 6.84 4.89
f1 (ppm)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-144.45
-144.49
-144.51
-157.90
-157.95
-158.01
-162.91
-162.93
-162.97
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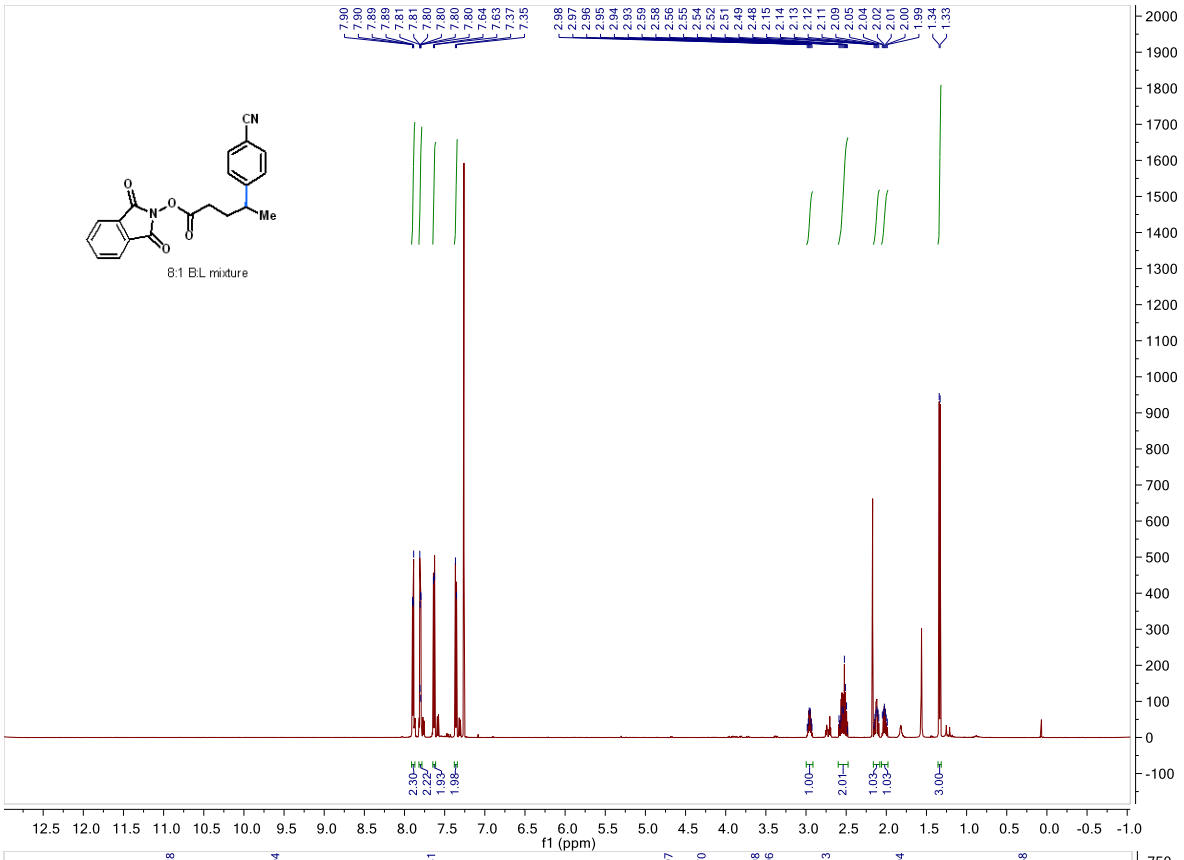
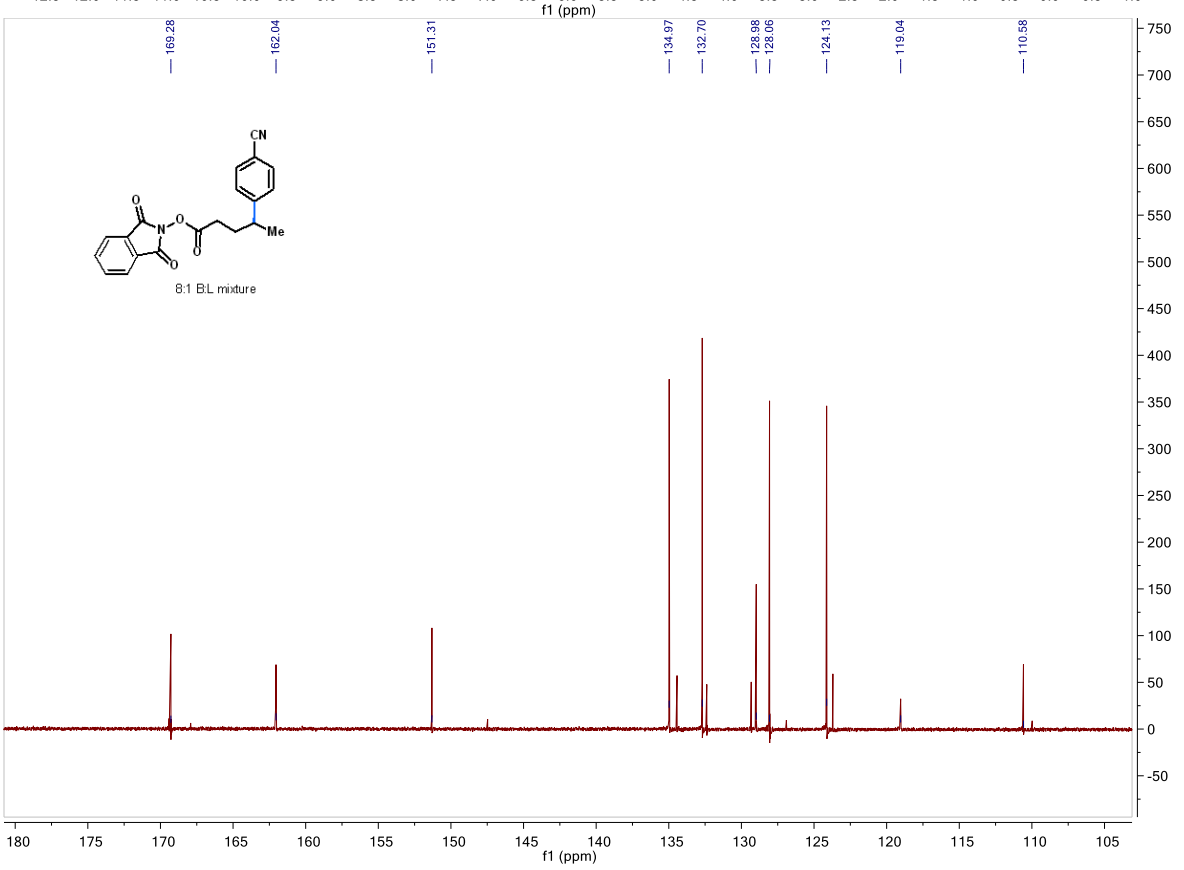
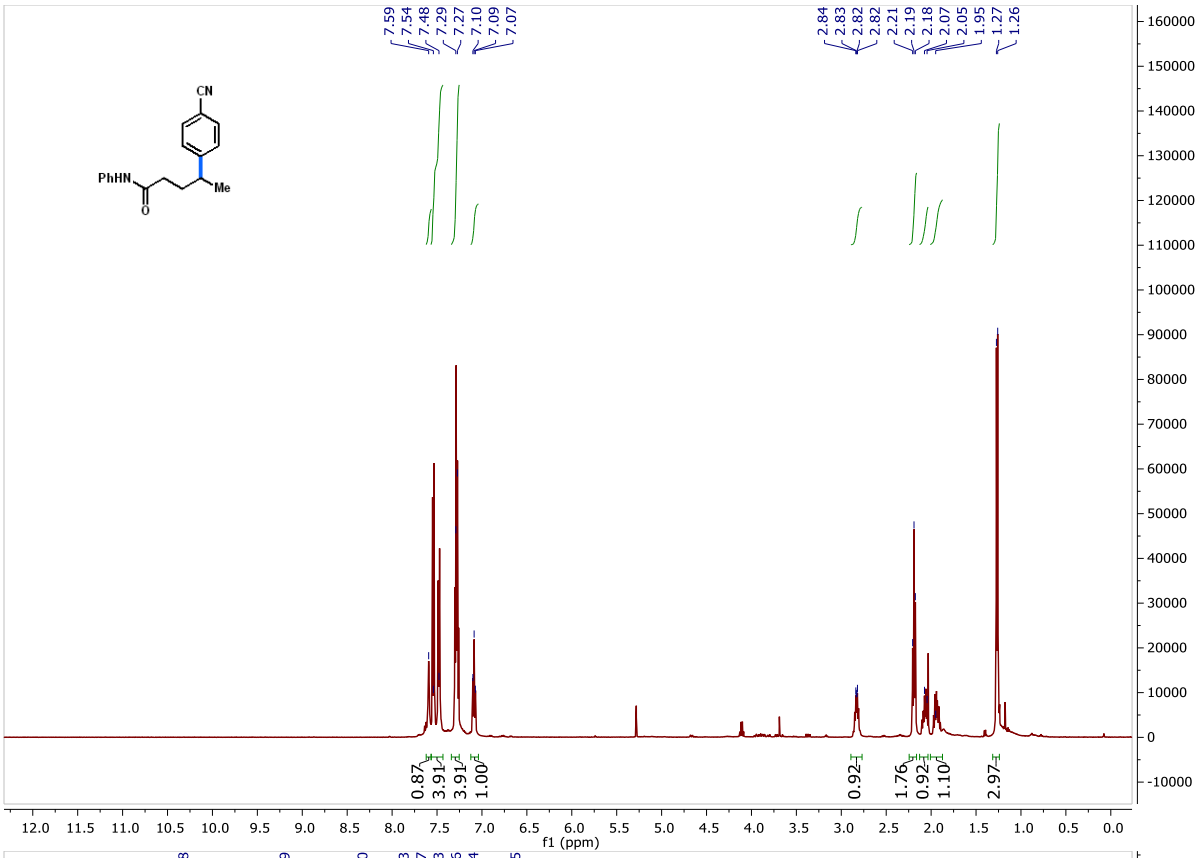
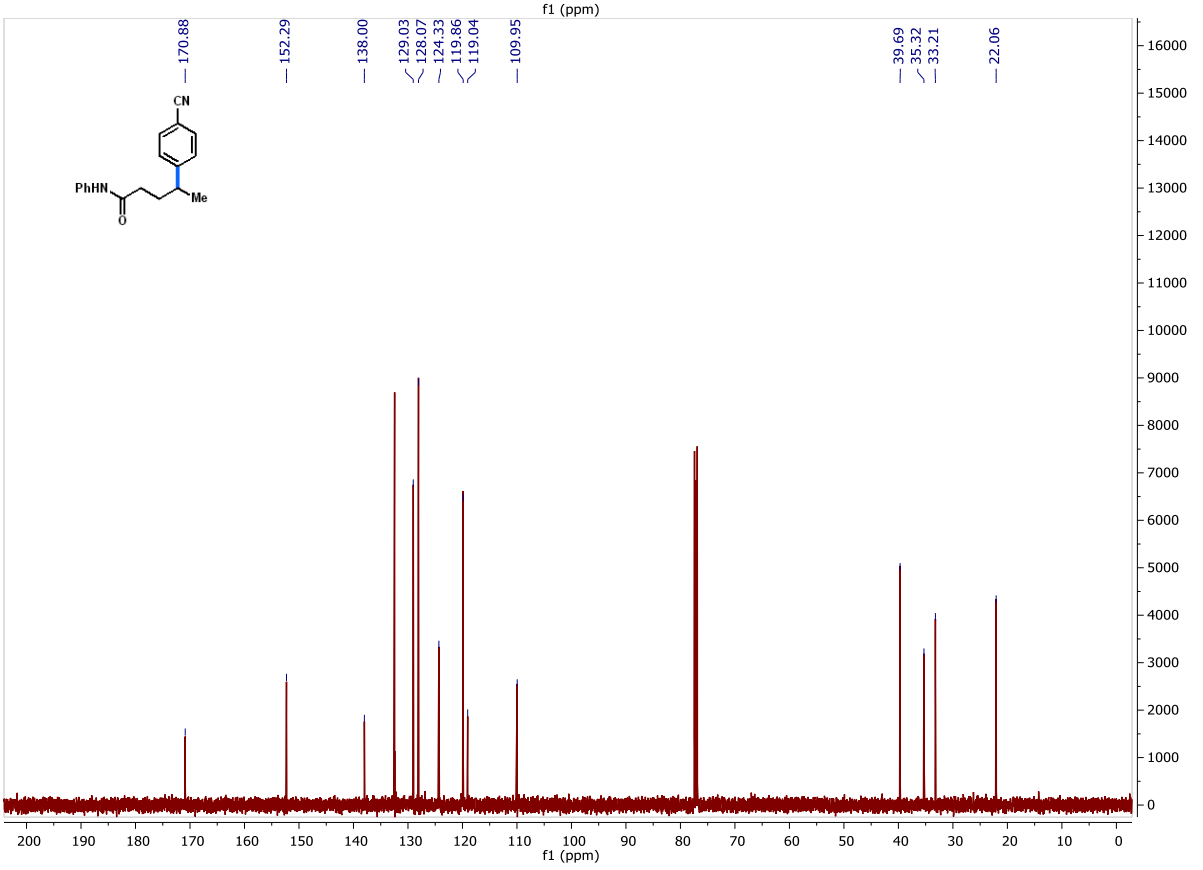
-163.05
CN
F5
OSiEt3
f1 (ppm)


CN
Me
8:1 B:L mixture
f1 (ppm)


169.28
162.04
151.31
134.97
132.70
128.98
128.06
124.13
119.04
110.58
CN
Me
8:1 B:L mixture
f1 (ppm)


7.59
7.54
7.48
7.29
7.27
7.10
7.09
7.07
2.84
2.83
2.82
2.82
2.21
2.19
2.18
2.07
2.05
1.95
1.27
1.26
CN
PhHN
O
Me
0.87
3.91
3.91
1.00
0.92
1.76
0.92
1.10
2.97
f1 (ppm)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138.00
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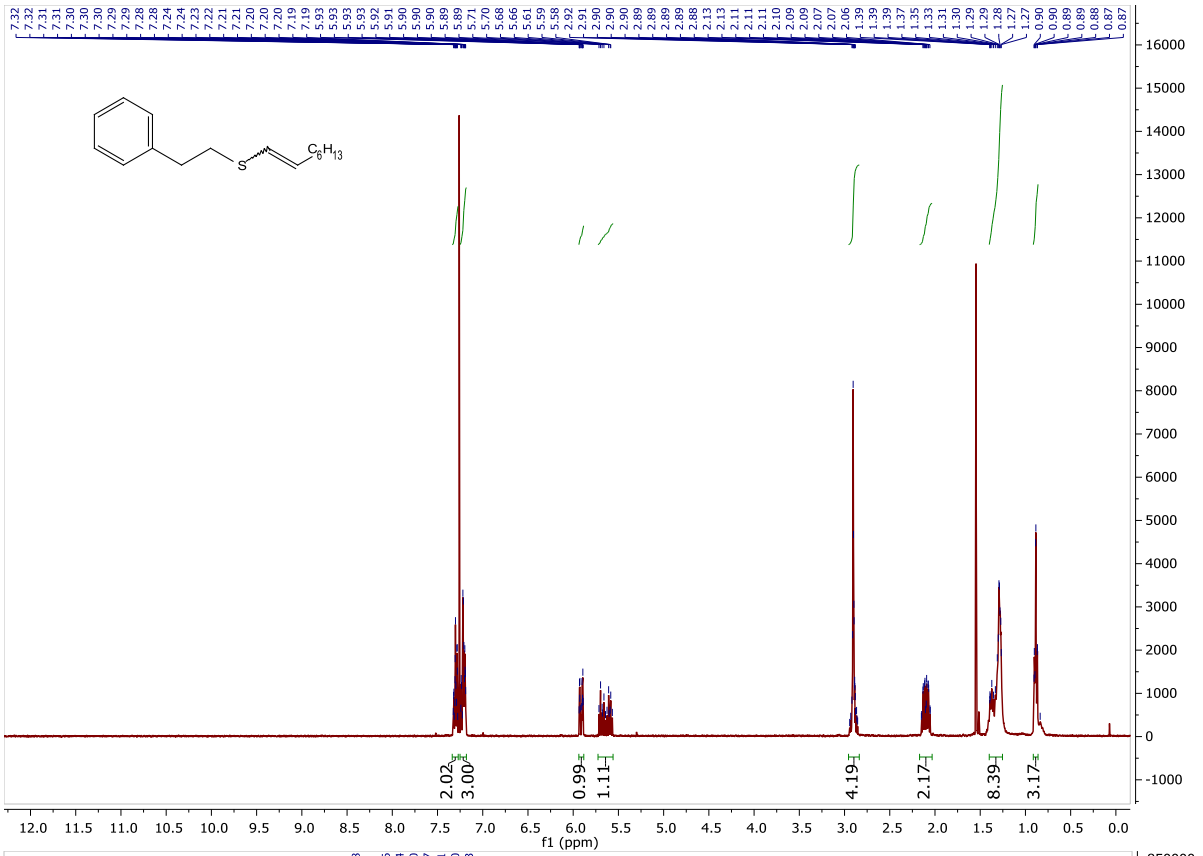
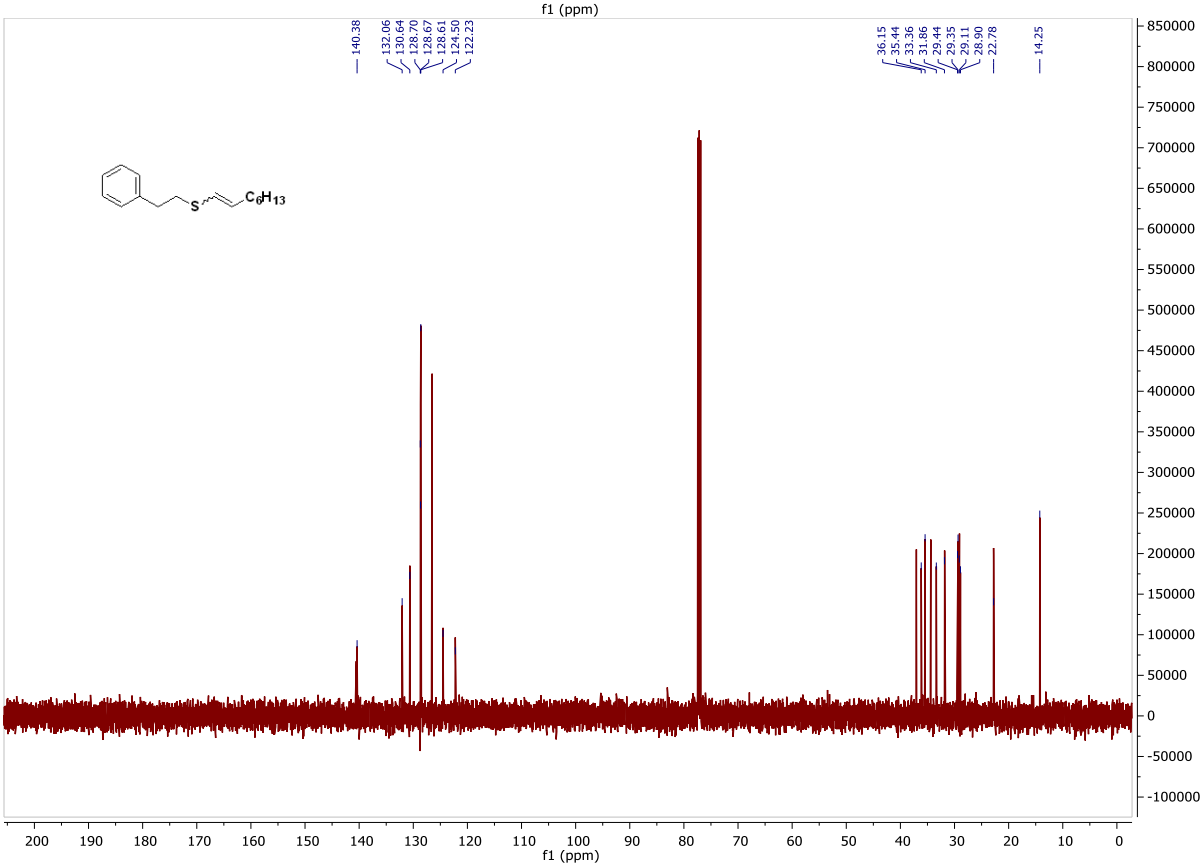
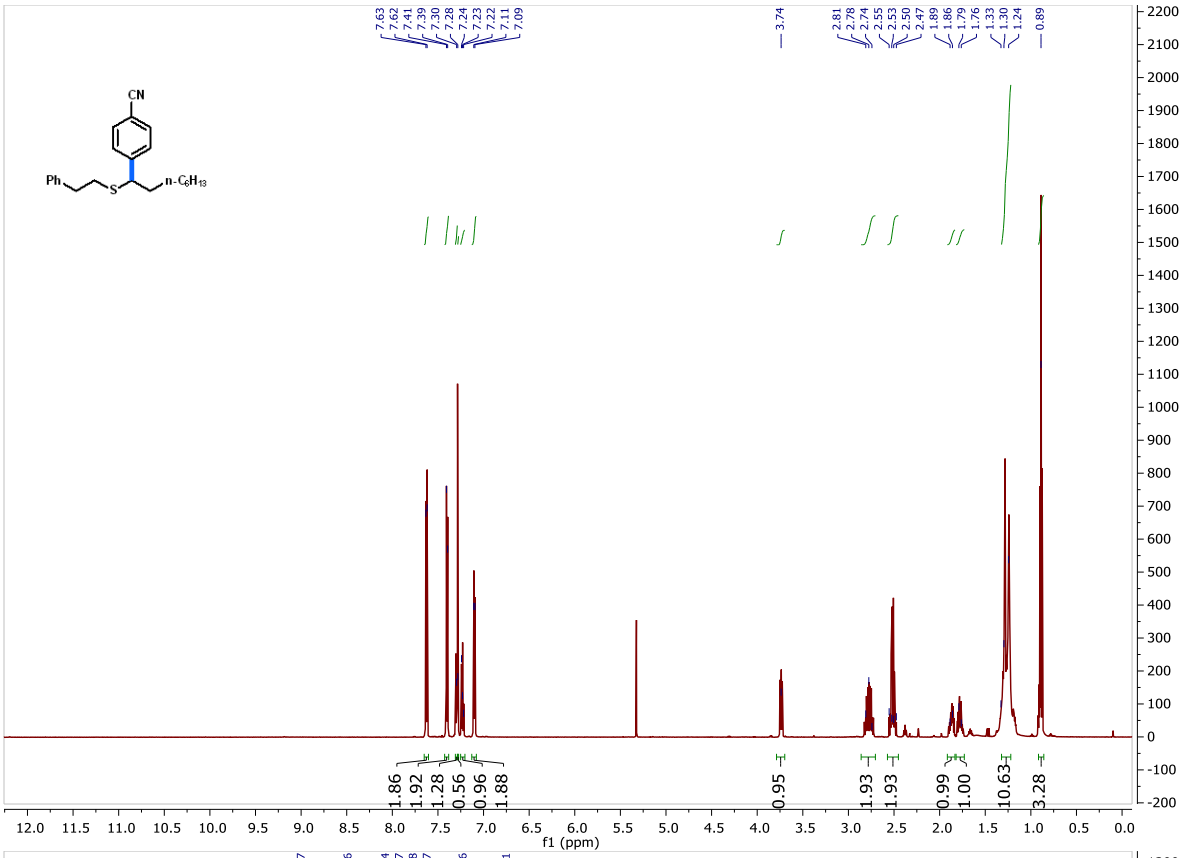
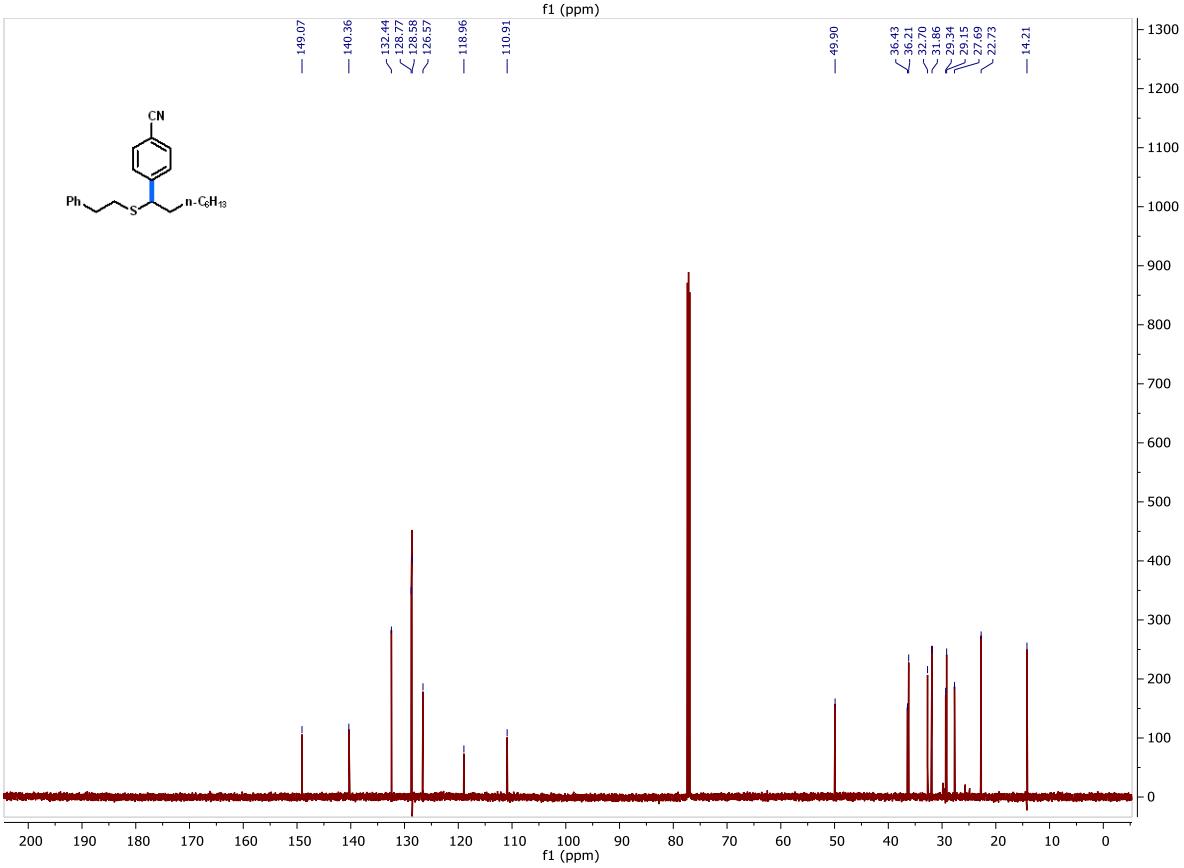
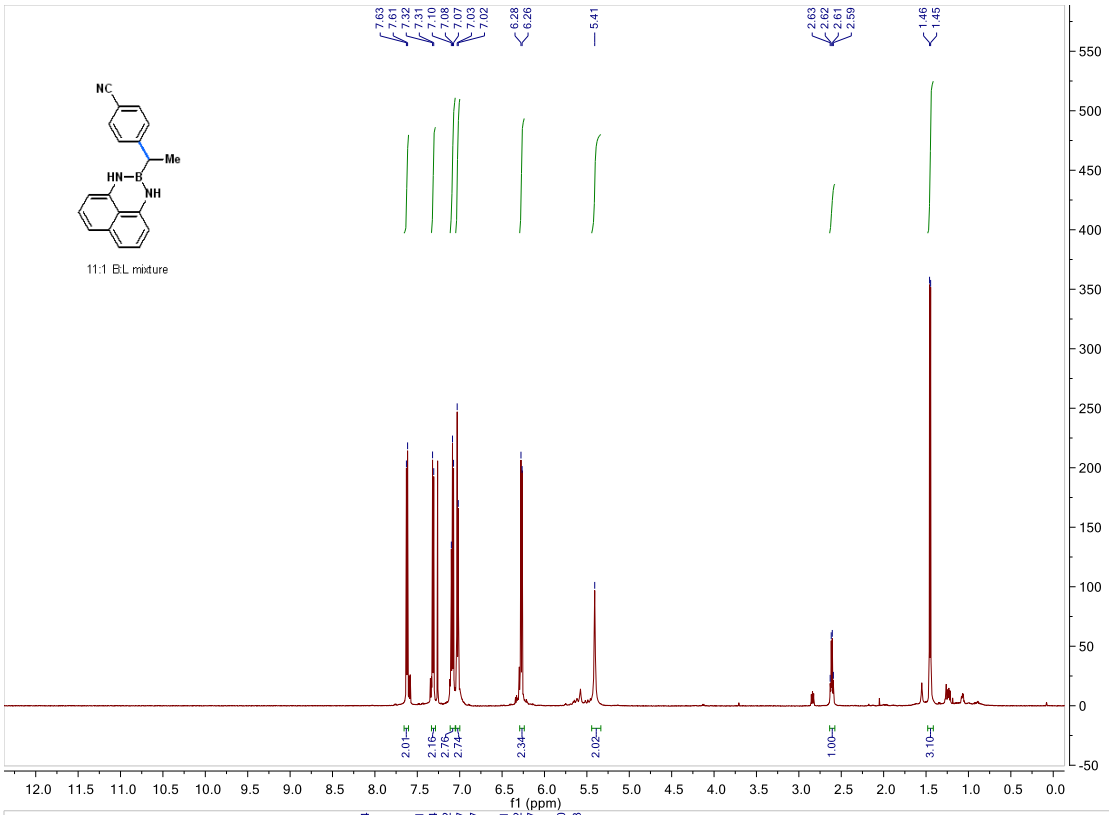
119.86
119.04
109.95
39.69
35.32
33.21
22.06
CN
PhHN
O
Me
f1 (ppm)

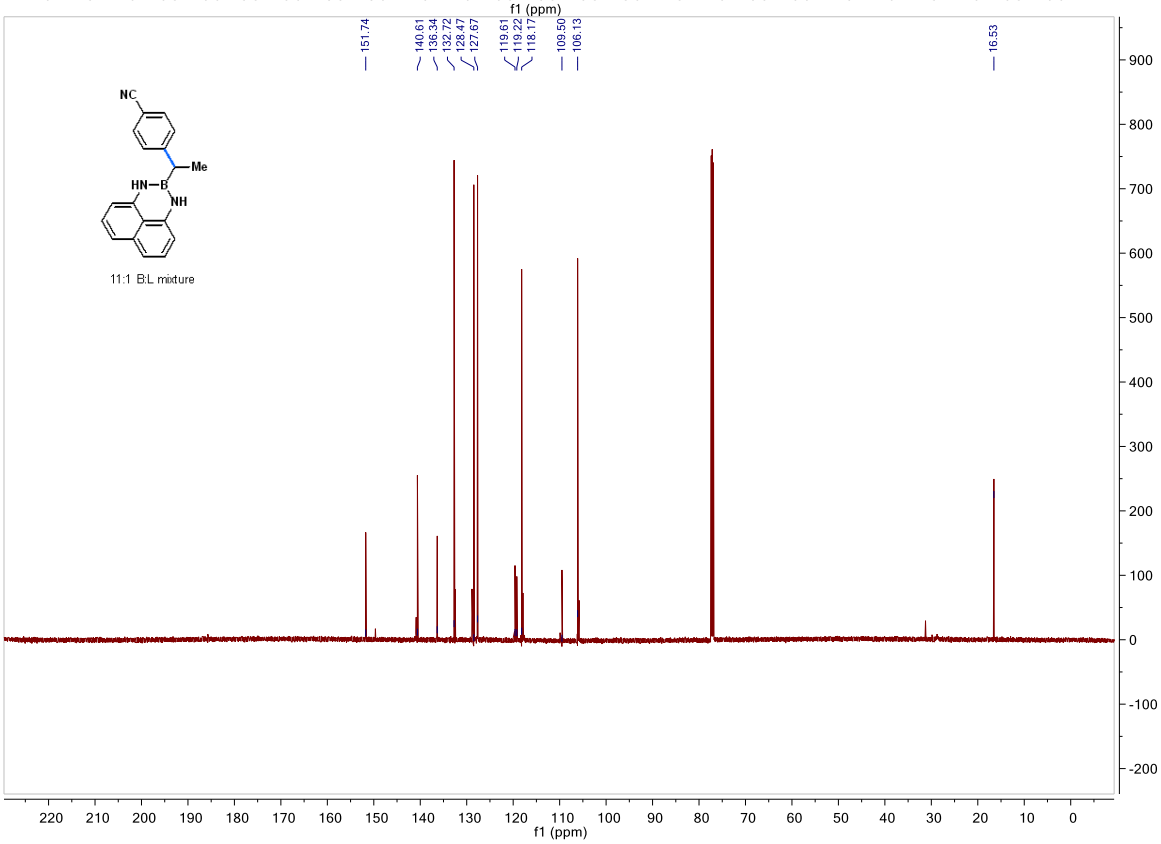

C6H13
S
2.02
3.00
0.99
1.11
4.19
2.17
8.39
3.17
f1 (ppm)

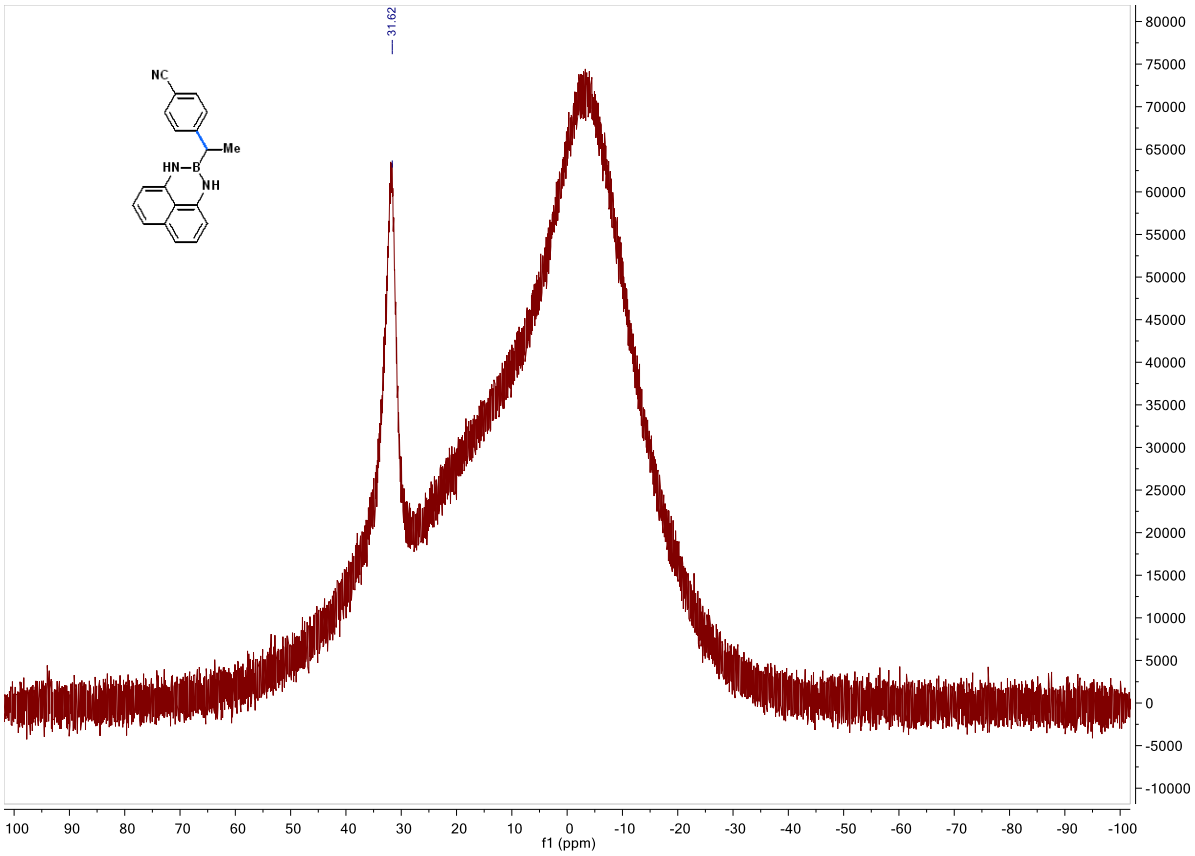

140.38
132.06
130.64
128.70
128.67
128.61
124.50
122.23
36.15
35.44
33.36
31.86
29.44
29.35
29.11
28.90
22.78
14.25
C6H13
S
f1 (ppm)

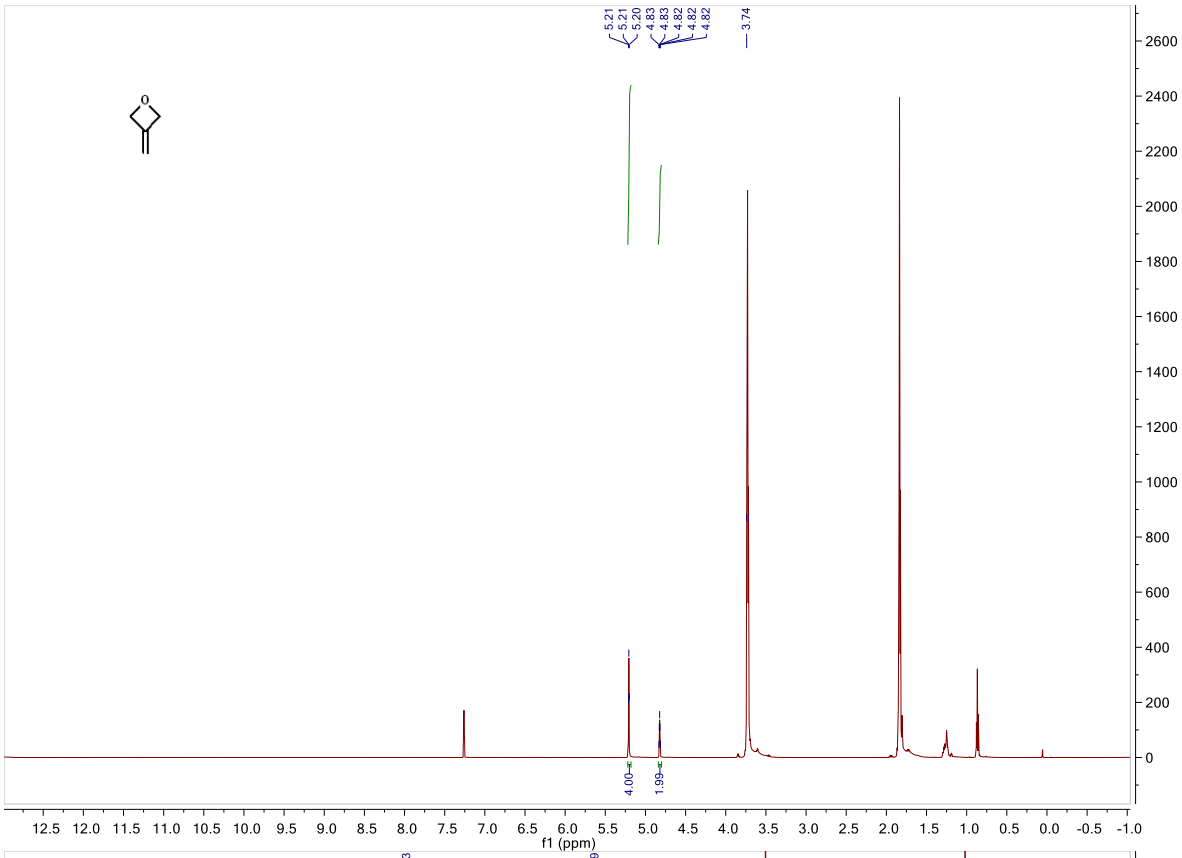

7.63
7.62
7.41
7.39
7.30
7.28
7.24
7.23
7.22
7.11
7.09
3.74
2.81
2.78
2.74
2.55
2.53
2.50
2.47
1.89
1.86
1.79
1.76
1.33
1.30
1.24
0.89
CN
Ph
S
n-C6H13
1.86
1.92
1.28
0.56
0.96
1.88
0.95
1.93
1.93
0.99
1.00
10.63
3.28
f1 (ppm)

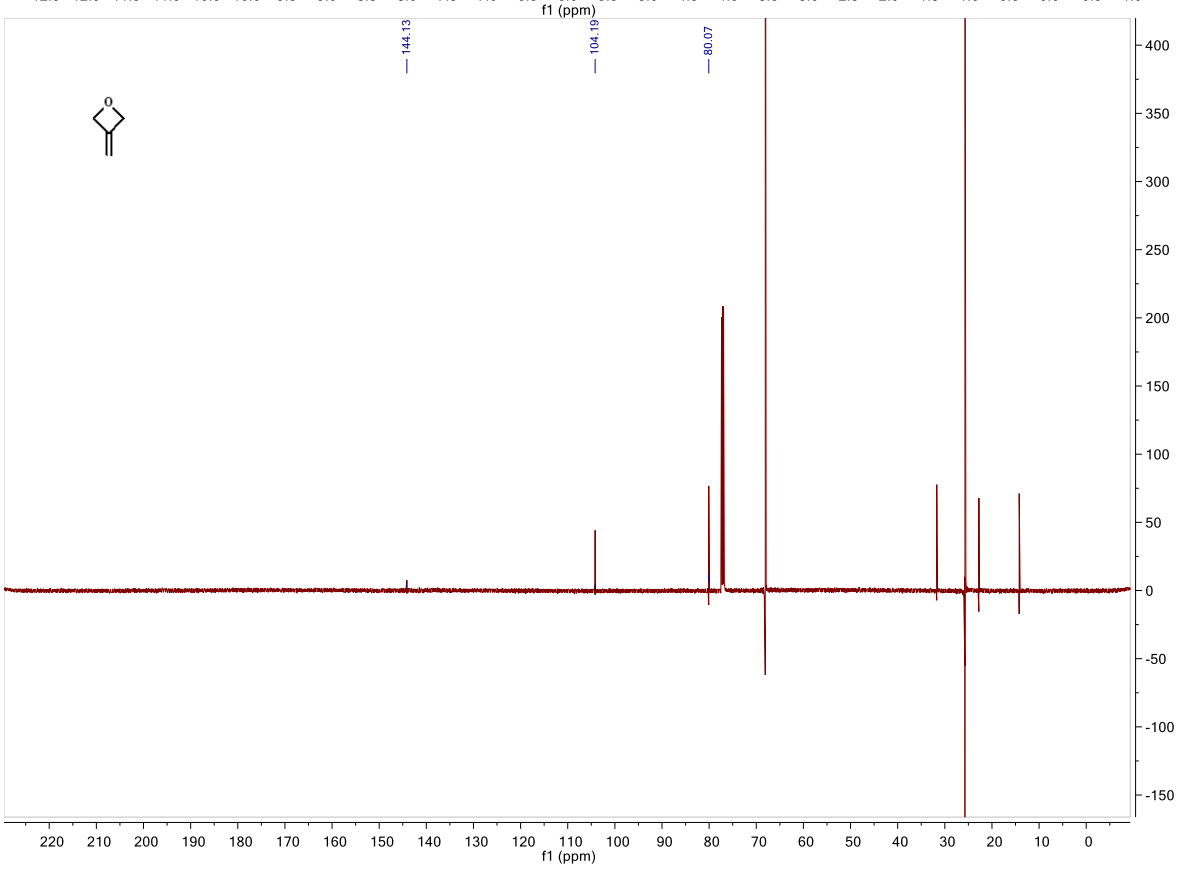

149.07
140.36
132.44
128.77
128.58
126.57
118.96
110.91
49.90
36.43
36.21
32.70
31.86
29.34
29.15
27.69
22.73
14.21
CN
Ph
S
n-C6H13
f1 (ppm)

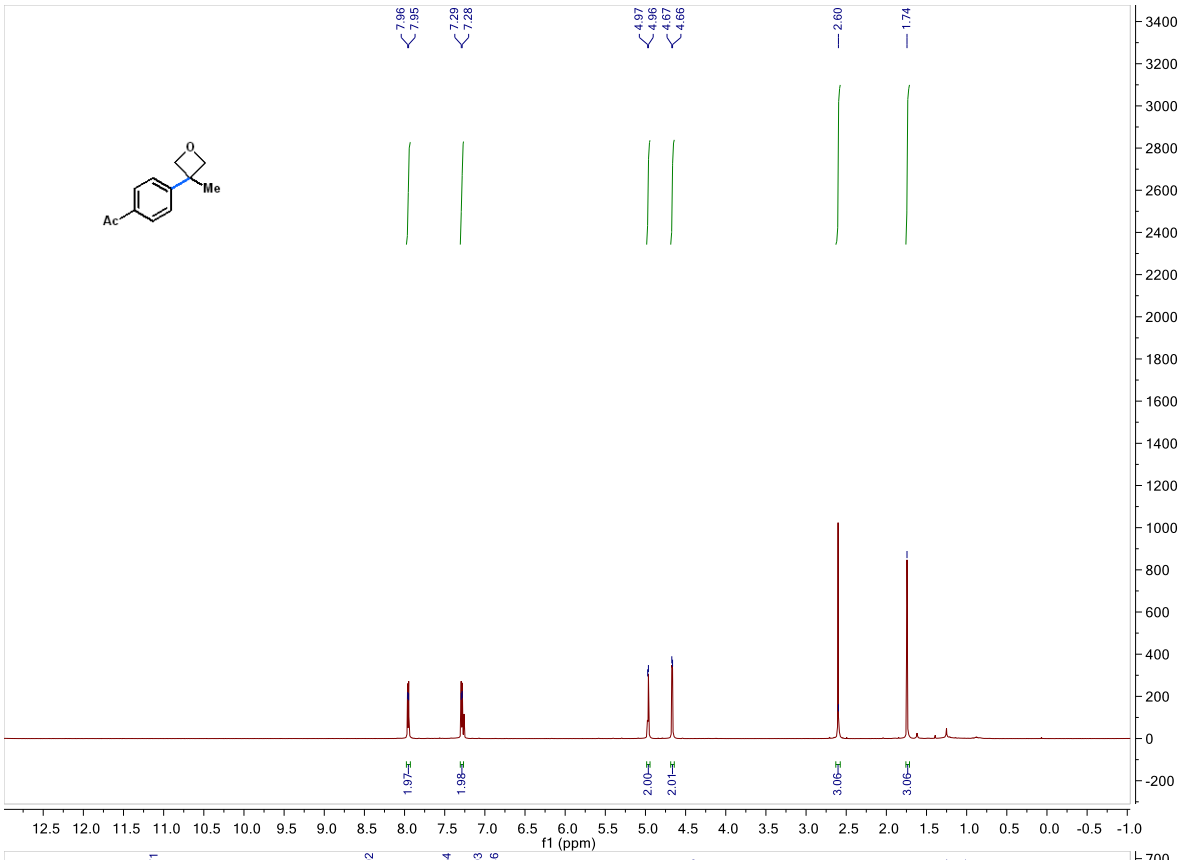

7.63
7.61
7.32
7.31
7.10
7.08
7.07
7.03
7.02
6.28
6.26
5.41
2.63
2.62
2.61
2.59
1.46
1.45
NC
Me
HN
B
NH
11:1 B:L mixture
2.01
2.16
2.76
2.74
2.34
2.02
1.00
3.10
f1 (ppm)

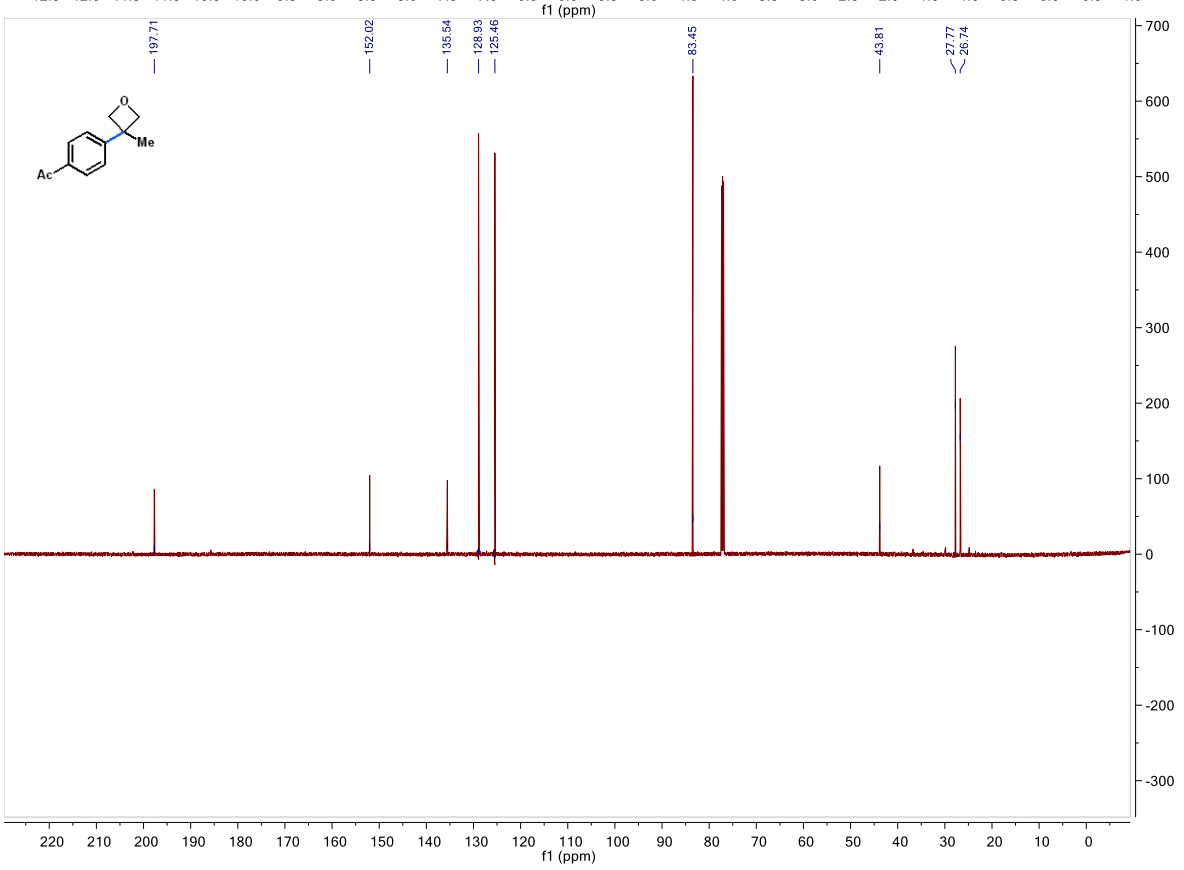

151.74
140.61
136.34
132.72
128.47
127.67
119.61
119.22
118.17
109.50
106.13
16.53
NC
Me
HN
B
NH
11:1 B:L mixture
f1 (ppm)

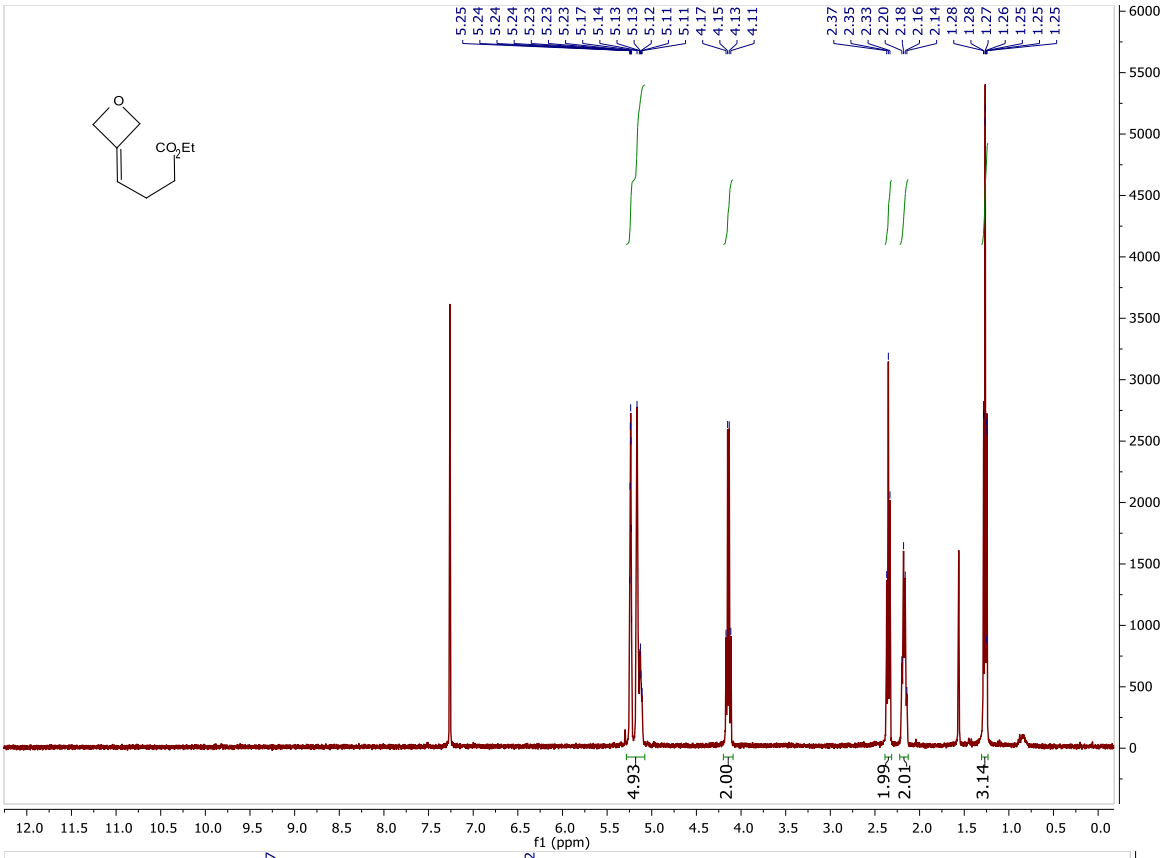

31.62
NC
Me
HN
B
NH
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)

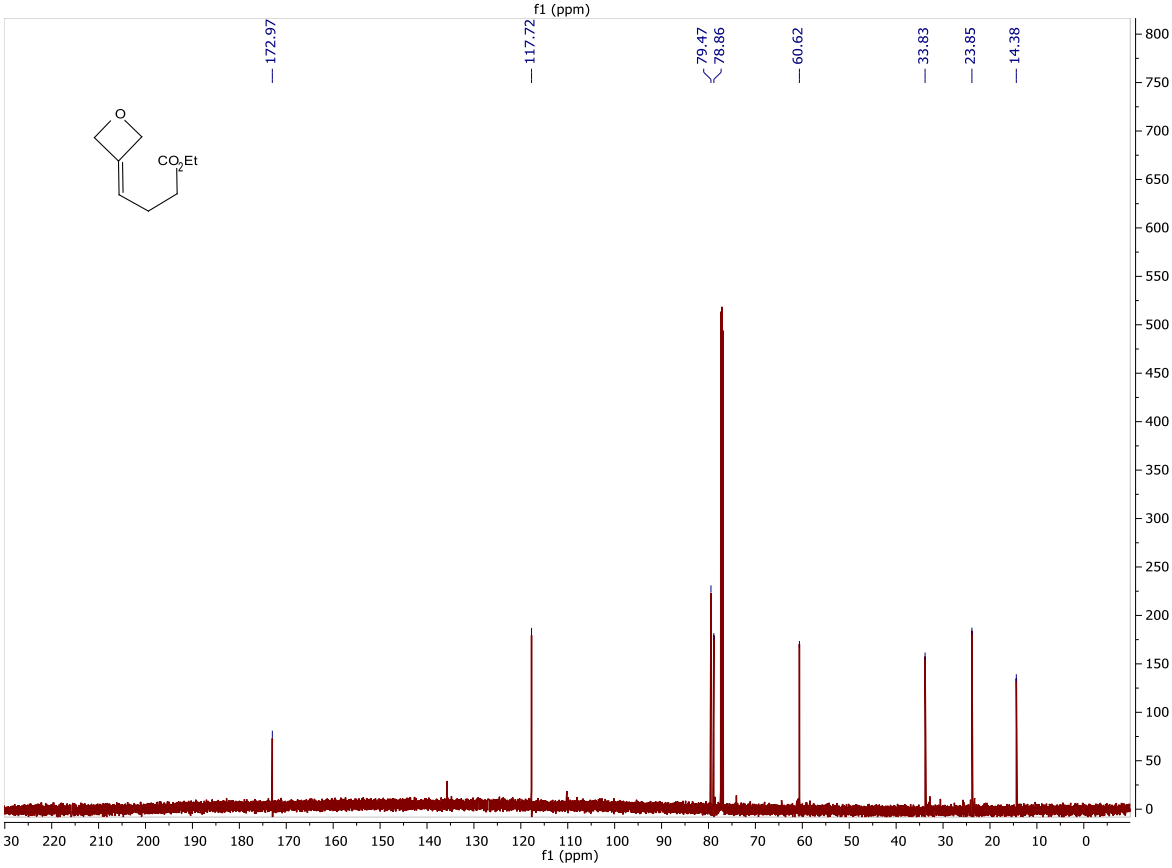

5.21
5.21
5.20
4.83
4.83
4.82
4.82
4.82
3.74
4.00
1.99
f1 (ppm)

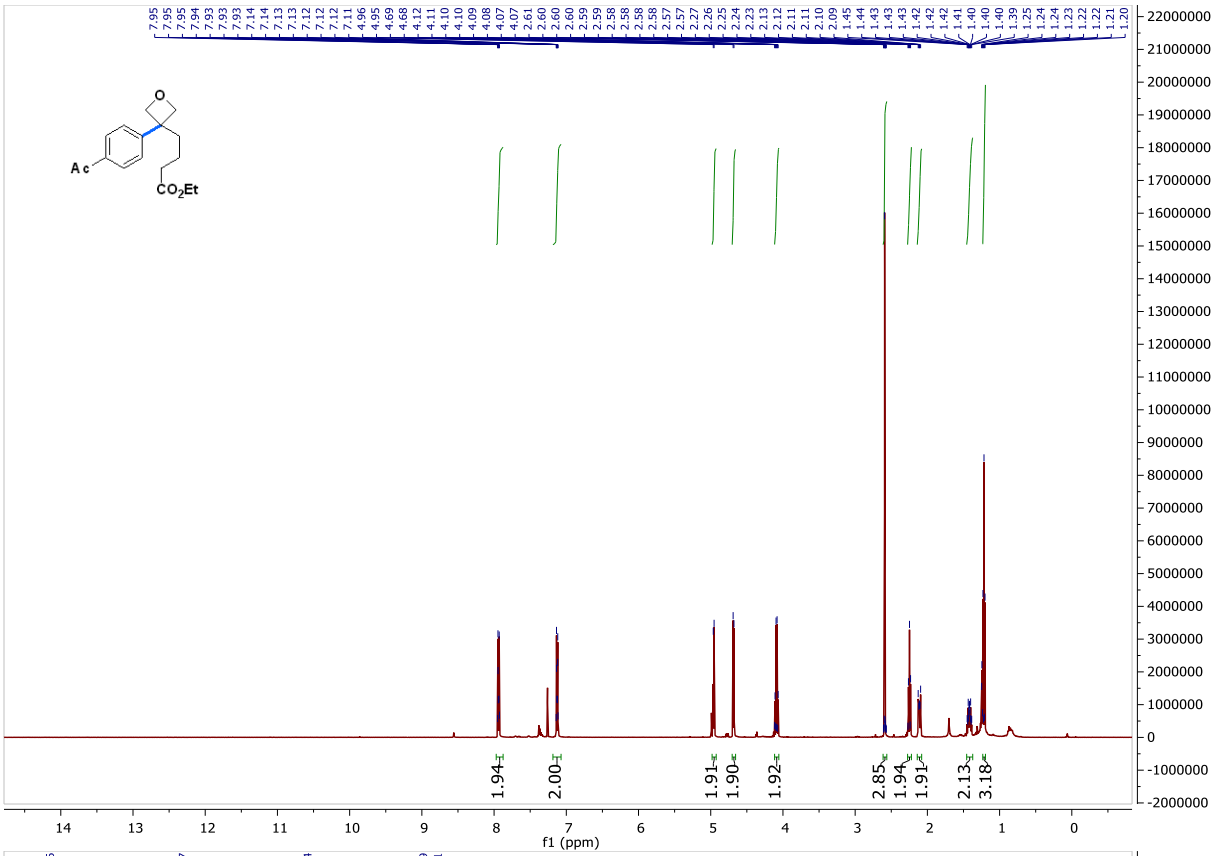

144.13
104.19
80.07
f1 (ppm)

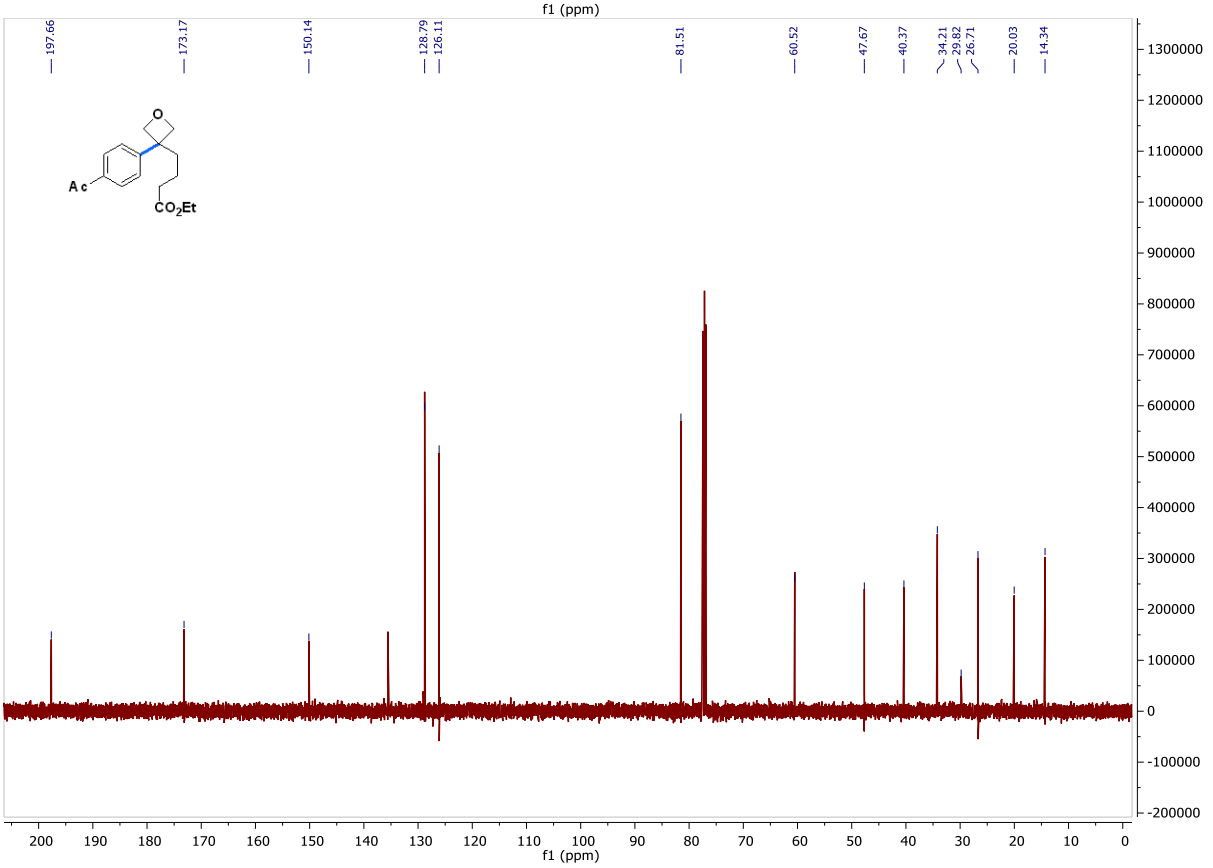

7.96
7.95
7.29
7.28
4.97
4.96
4.67
4.66
2.60
1.74
Me
Ac
1.97
1.98
2.00
2.01
3.06
3.06
f1 (ppm)

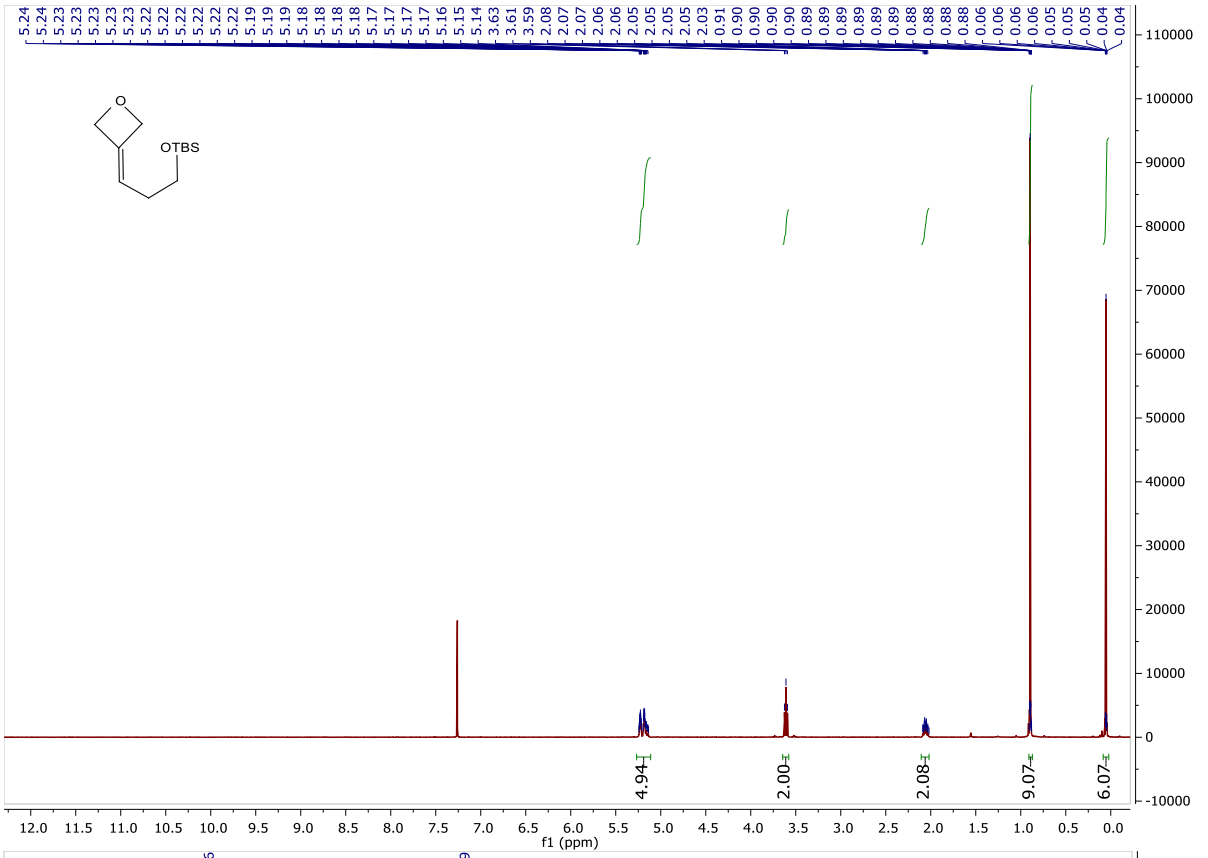

197.71
152.02
135.54
128.93
125.46
83.45
43.81
27.77
26.74
Me
Ac
f1 (ppm)

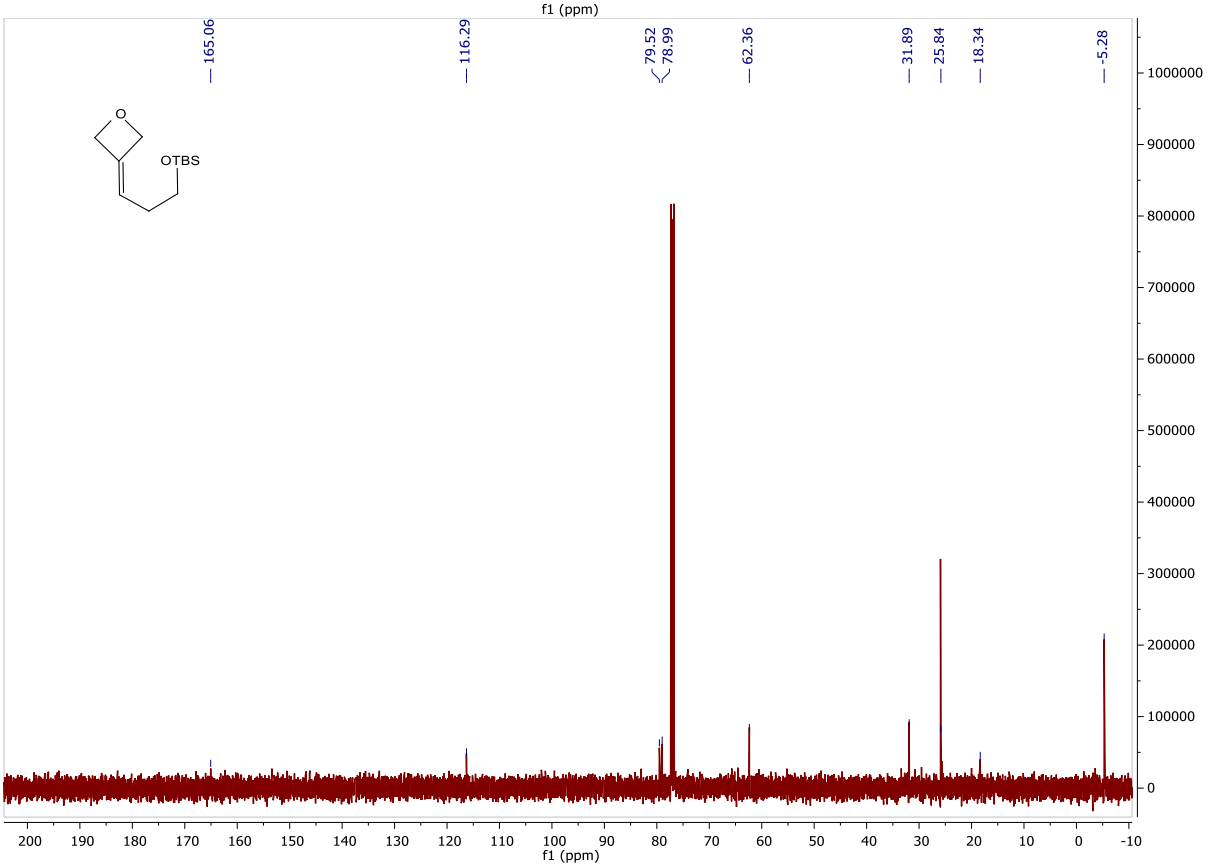

5.25
5.24
5.24
5.24
5.23
5.23
5.23
5.17
5.14
5.13
5.13
5.12
5.11
5.11
4.17
4.15
4.13
4.11
2.37
2.35
2.33
2.20
2.18
2.16
2.14
1.28
1.28
1.27
1.26
1.25
1.25
1.25
O
CO2Et
4.93
2.00
1.99
2.01
3.14
f1 (ppm)

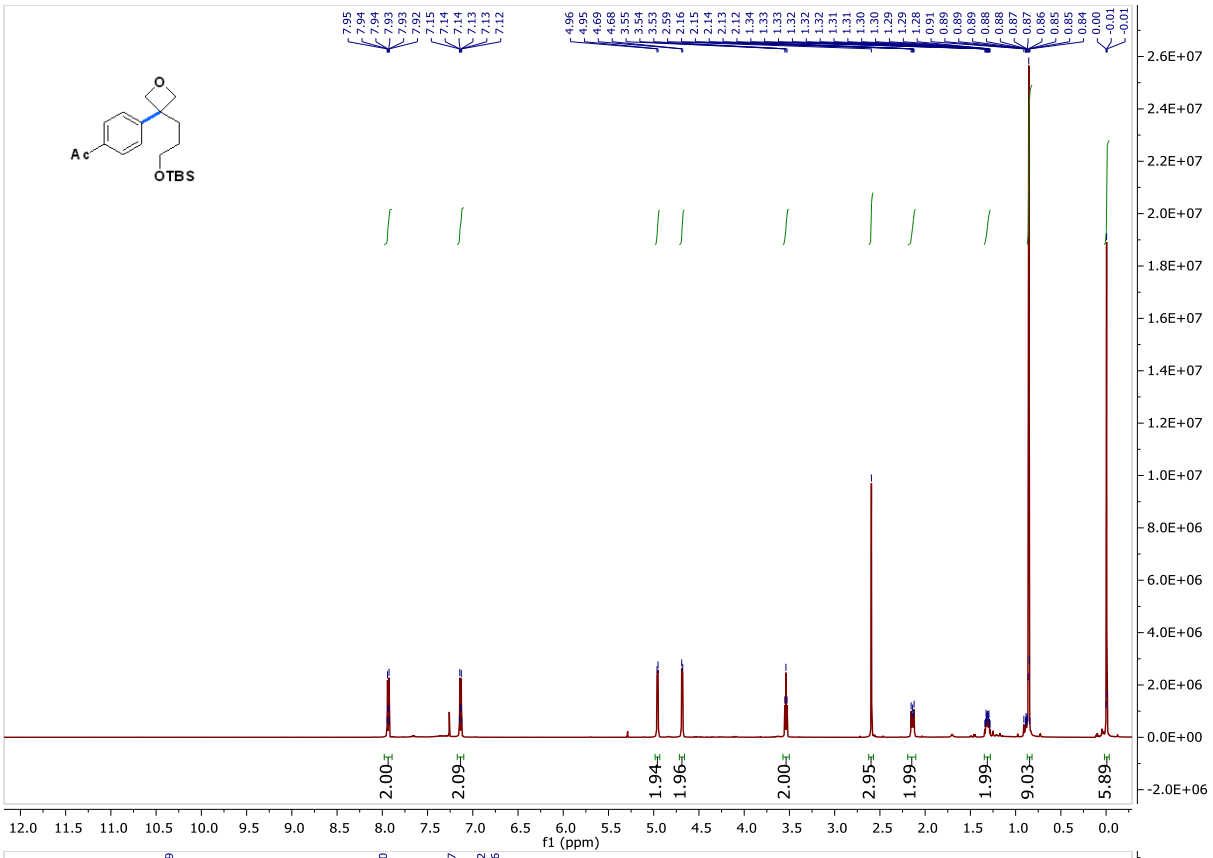

172.97
117.72
79.47
78.86
60.62
33.83
23.85
14.38
O
CO2Et
f1 (ppm)

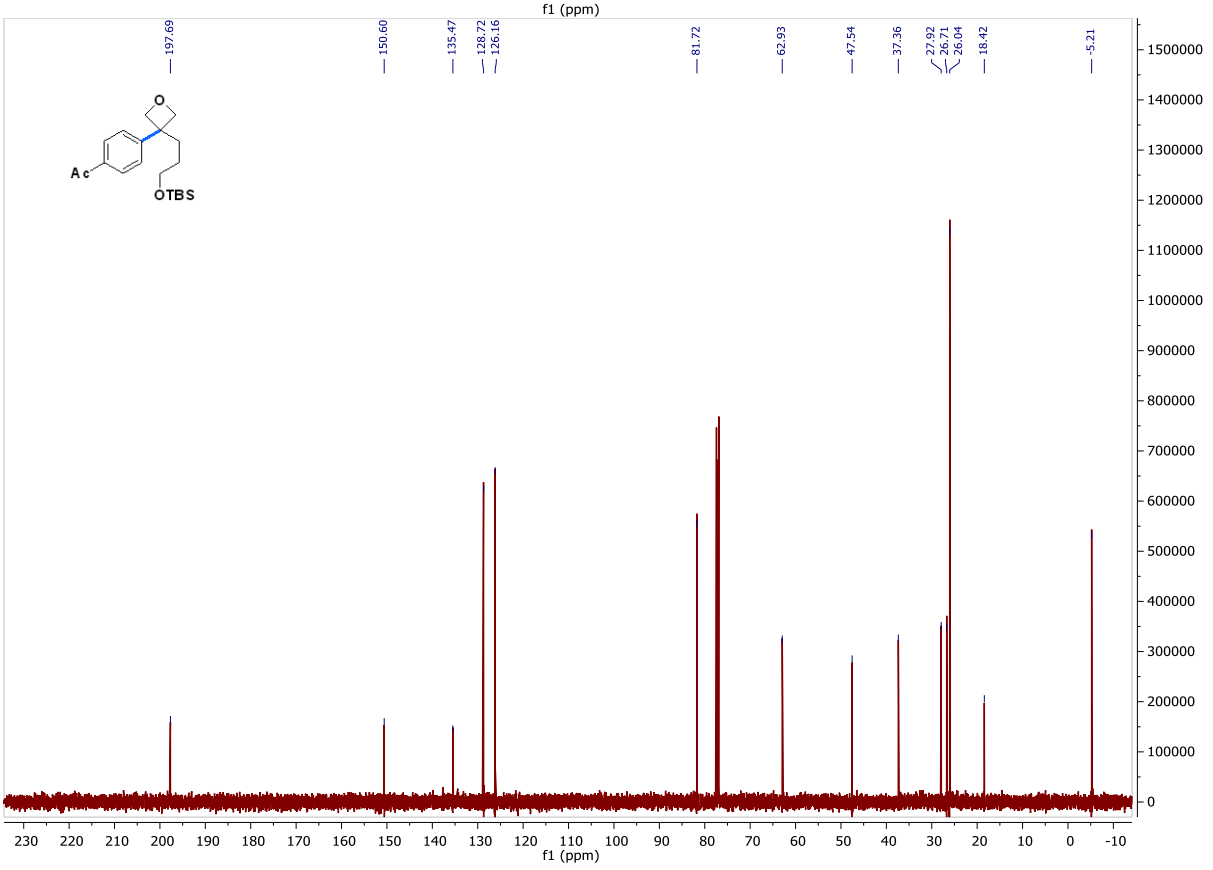

Ac
CO2Et
1.94
2.00
1.91
1.90
1.92
2.85
1.94
1.91
2.13
3.18
f1 (ppm)

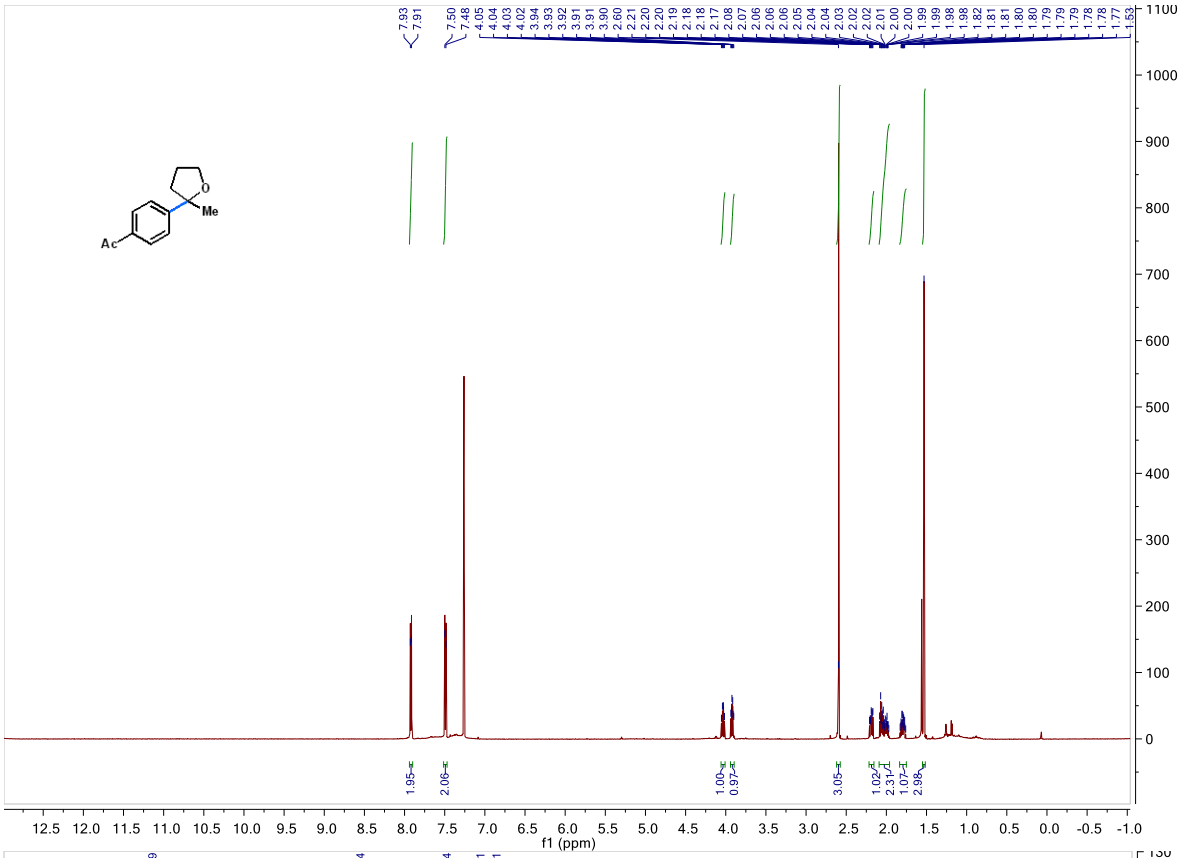

197.66
173.17
150.14
128.79
126.11
81.51
60.52
47.67
40.37
34.21
29.82
26.71
20.03
14.34
Ac
CO2Et
f1 (ppm)

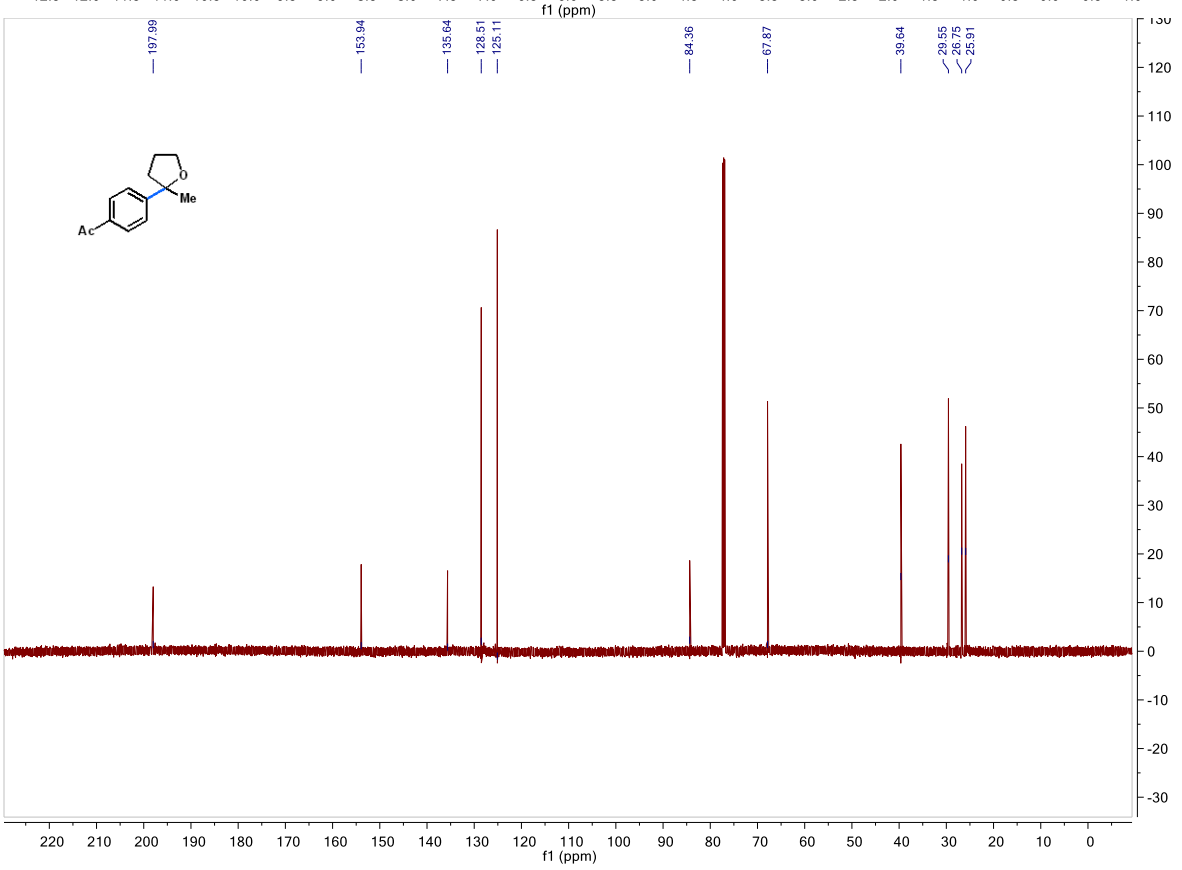

OTBS
4.94
2.00
2.08
9.07
6.07
f1 (ppm)

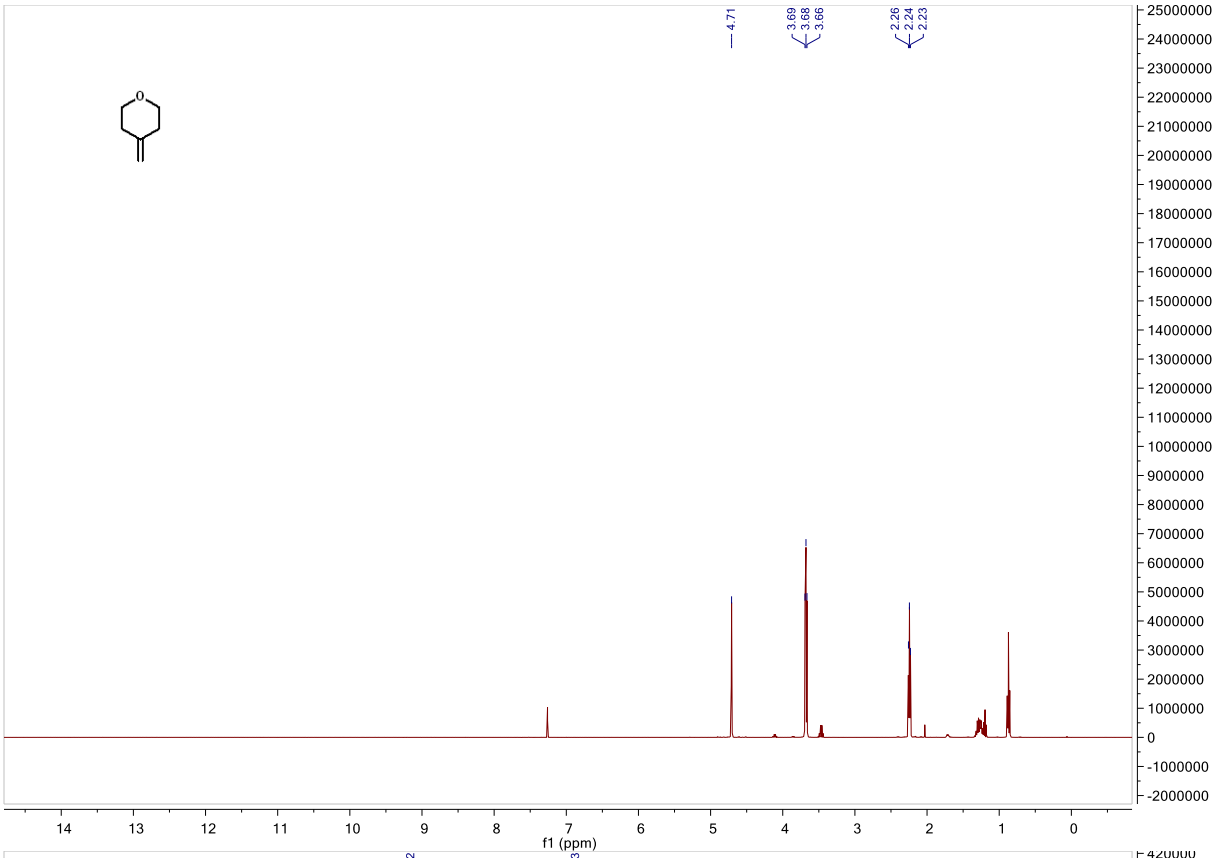

165.06
116.29
79.52
78.99
62.36
31.89
25.84
18.34
-5.28
OTBS
f1 (ppm)

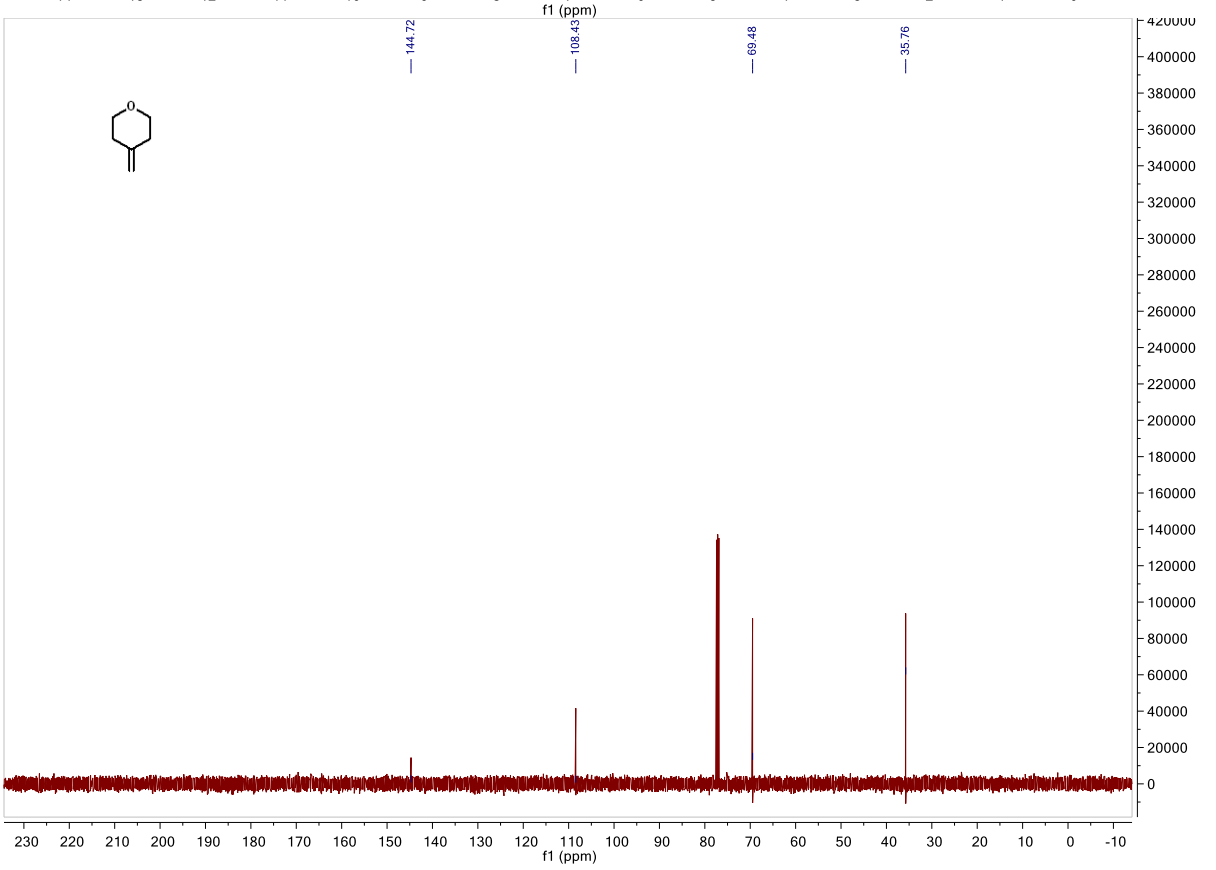

Ac
OTBS
f1 (ppm)

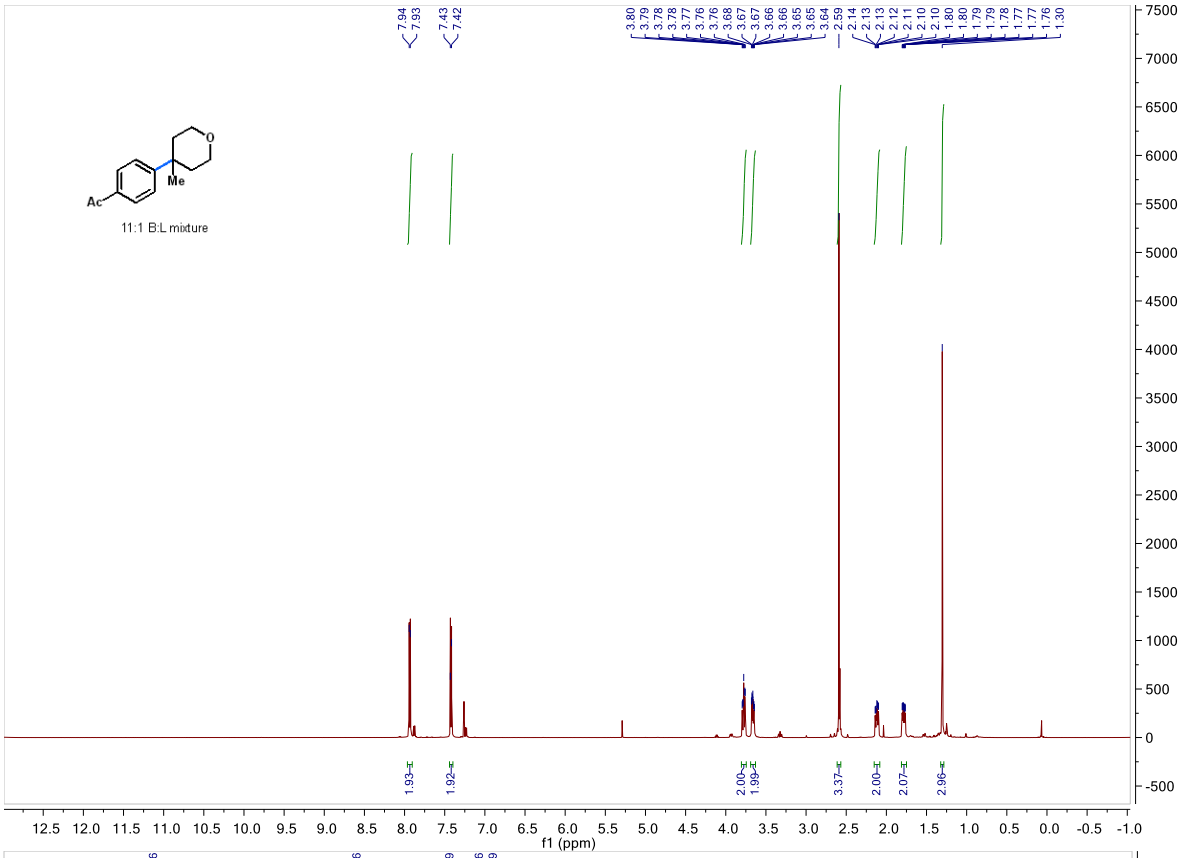

Ac
OTBS
f1 (ppm)

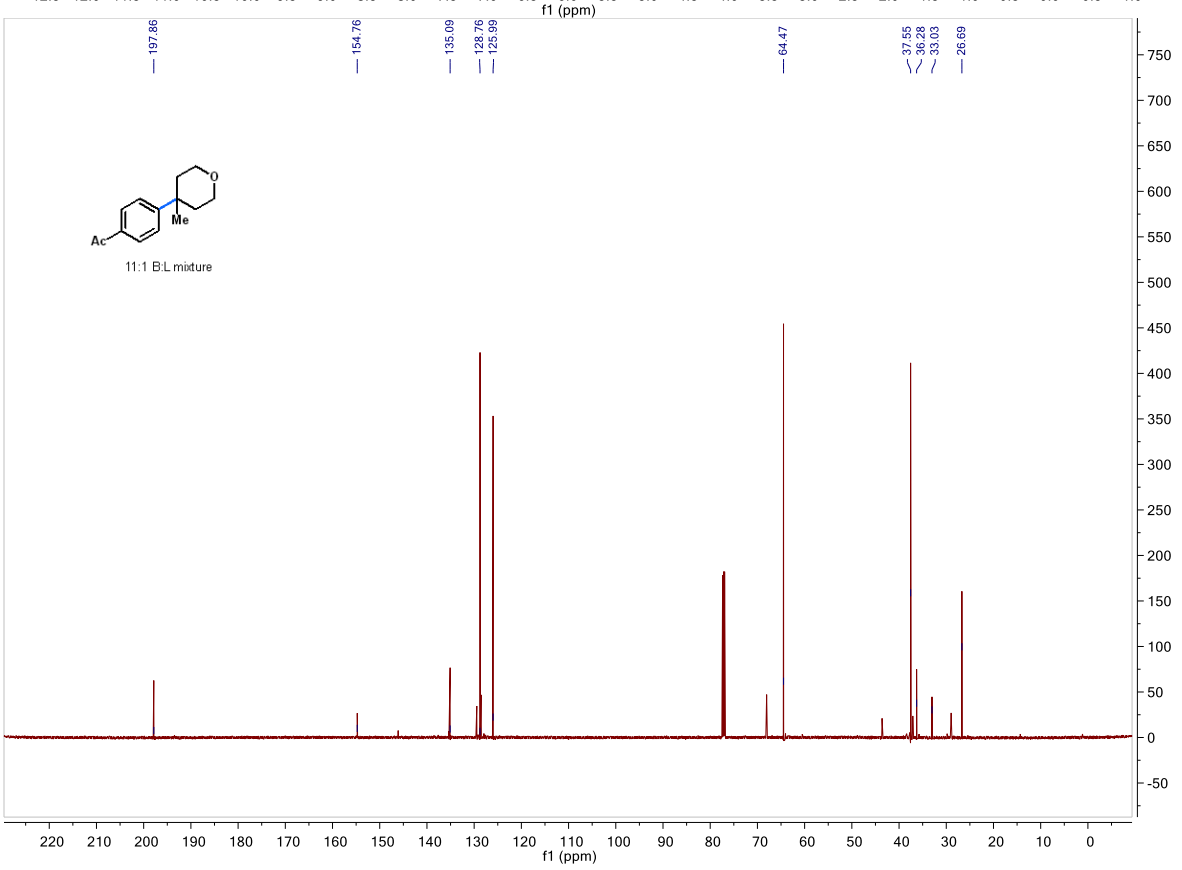

Ac
Me
f1 (ppm)

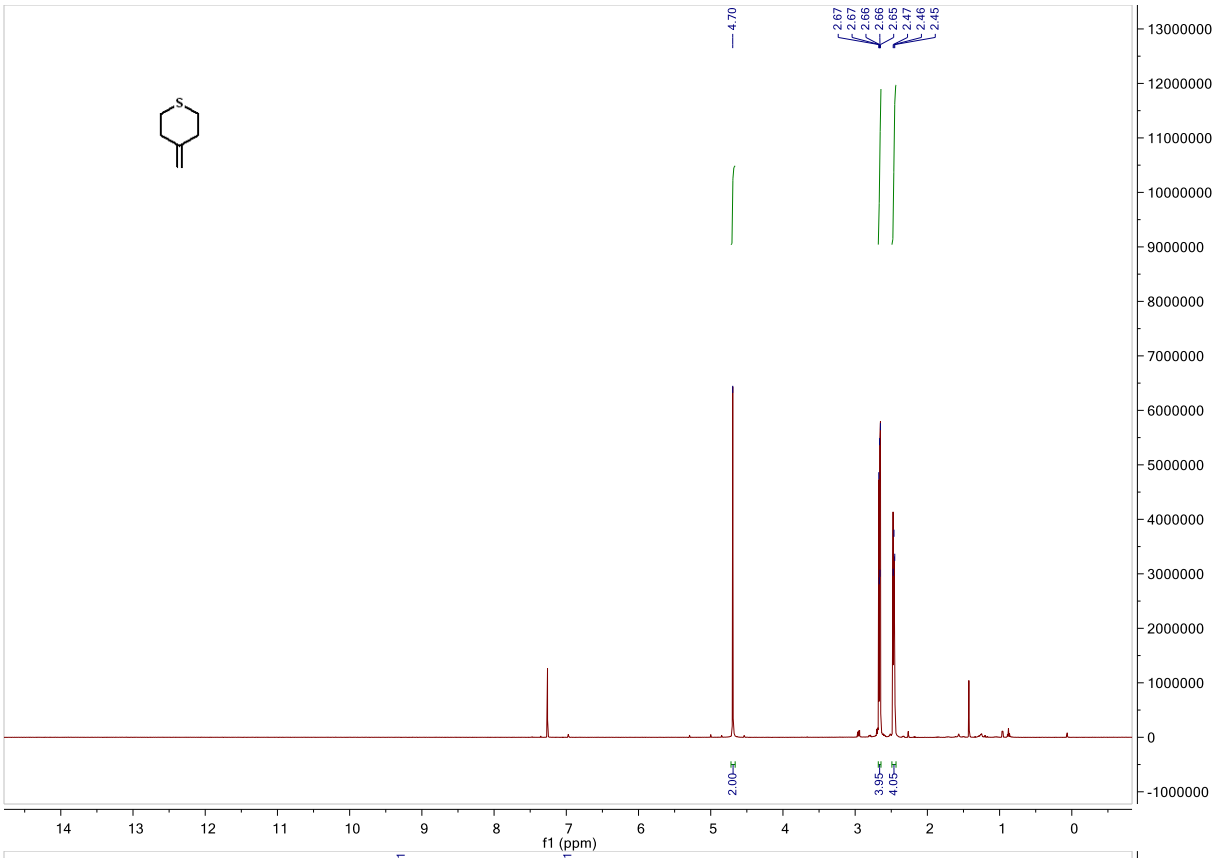

Ac
Me
f1 (ppm)

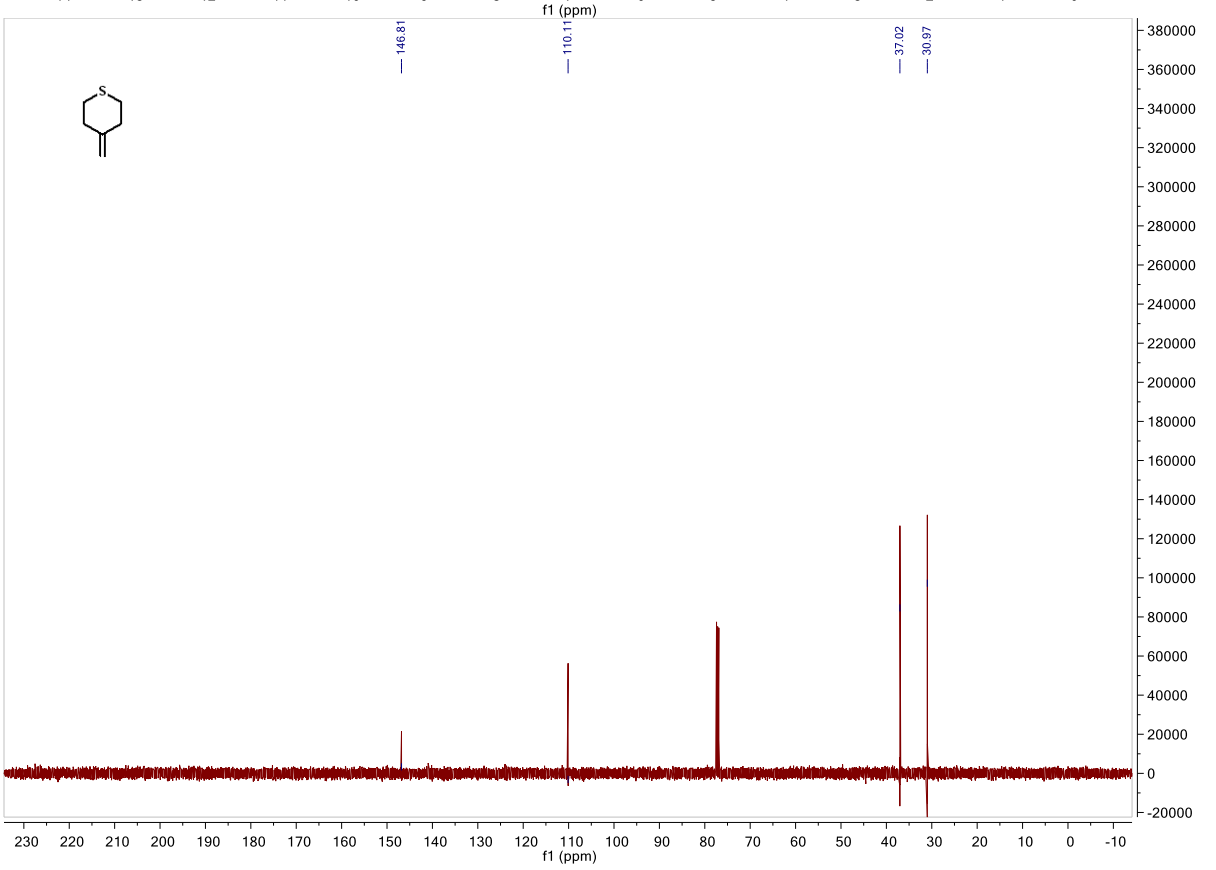

4.71
3.69
3.68
3.66
2.26
2.24
2.23
f1 (ppm)

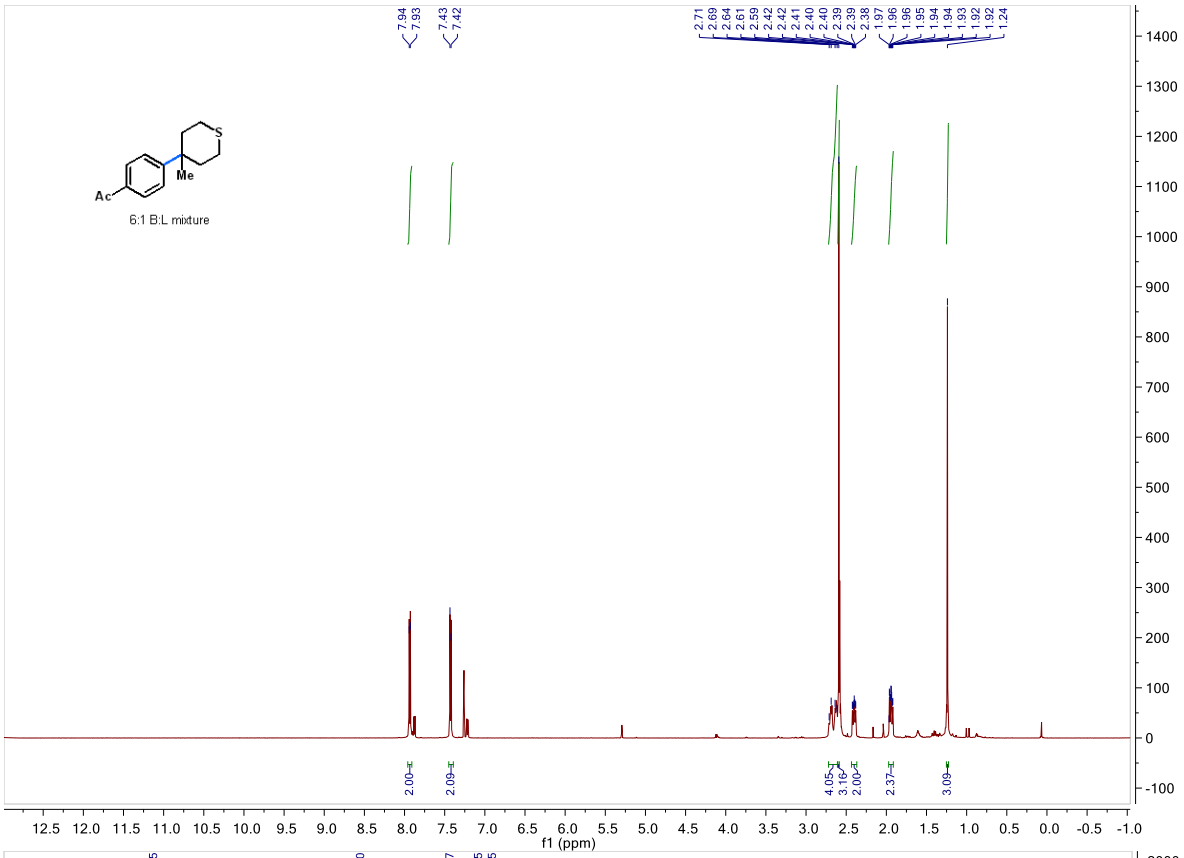

144.72
108.43
69.48
35.76
f1 (ppm)

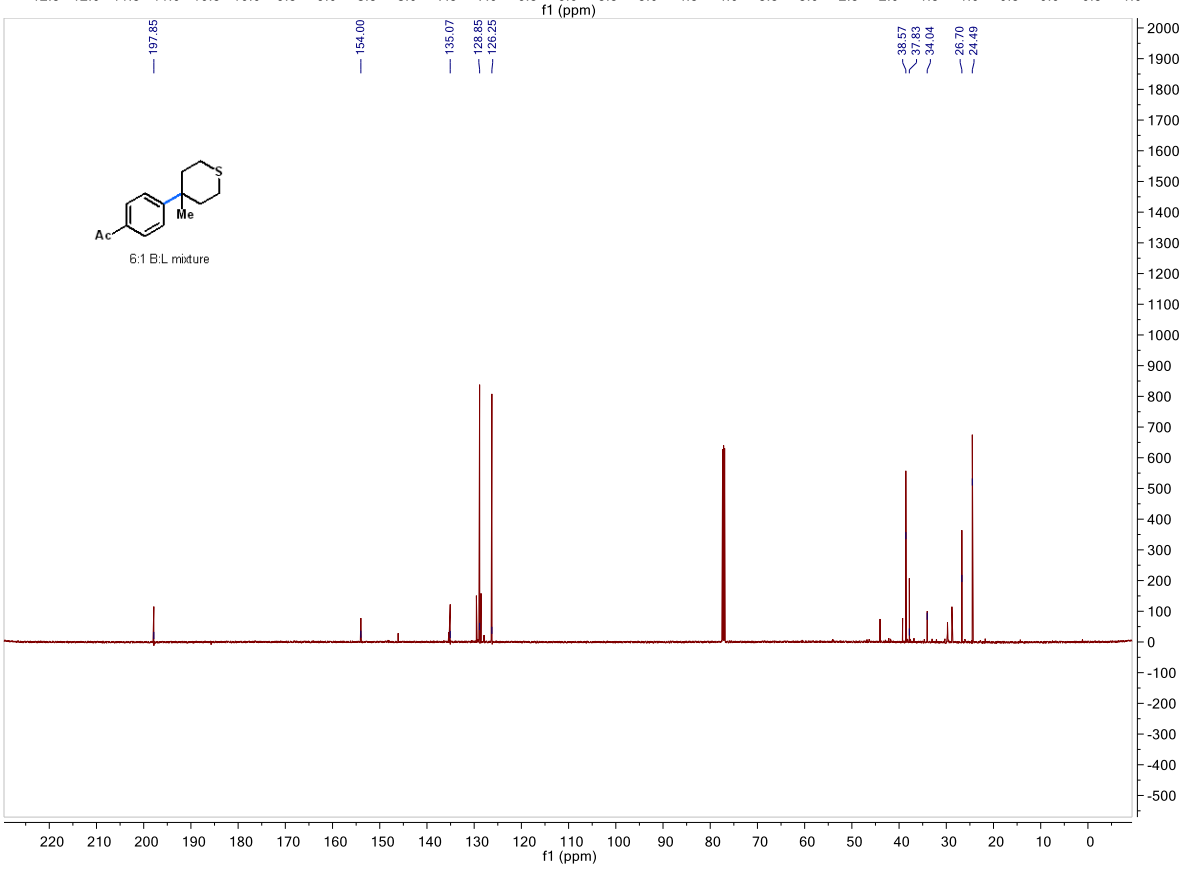

7.94
7.93
7.43
7.42
3.80
3.79
3.78
3.78
3.77
3.76
3.76
3.68
3.67
3.67
3.66
3.66
3.65
3.65
3.64
2.59
2.14
2.13
2.13
2.12
2.11
2.10
2.10
1.80
1.80
1.79
1.79
1.78
1.77
1.77
1.76
1.30
O
Me
Ac
11:1 B:L mixture
1.93
1.92
2.00
1.99
3.37
2.00
2.07
2.96
f1 (ppm)

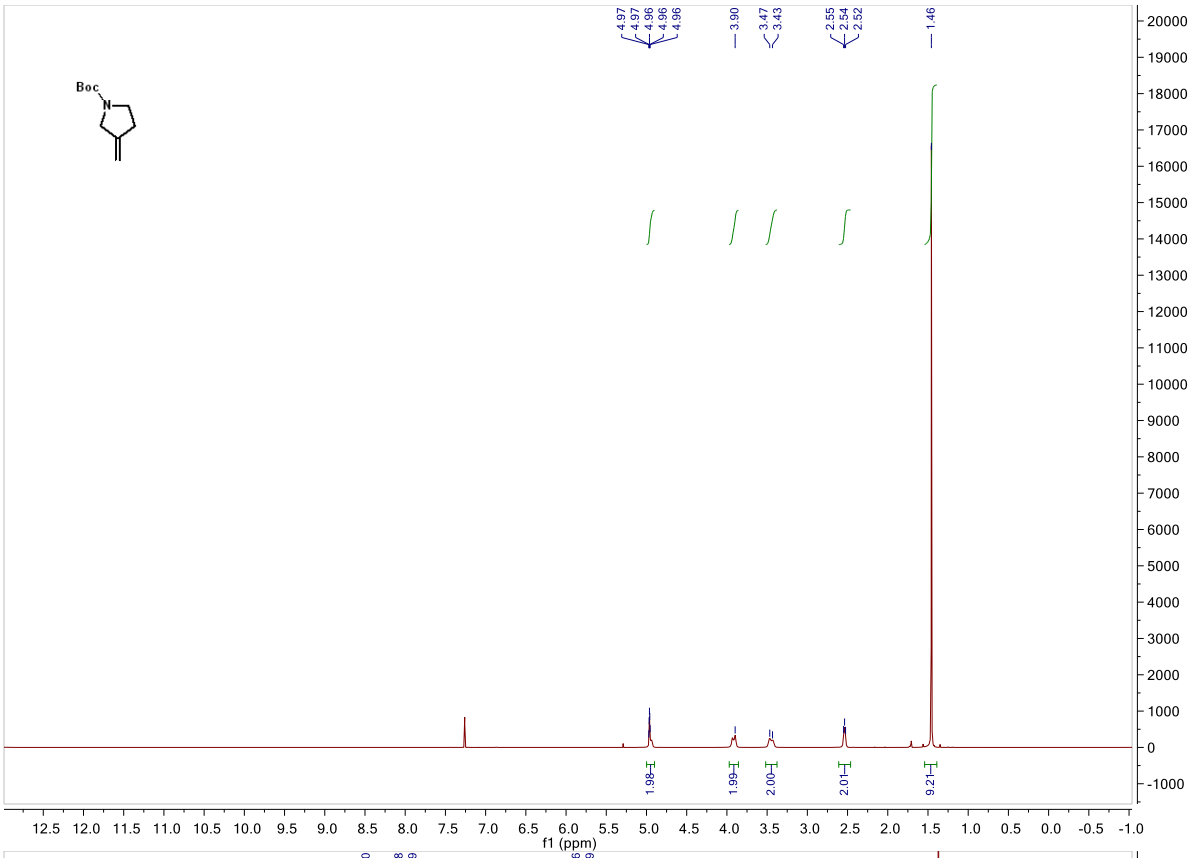

197.86
154.76
135.09
128.76
125.99
64.47
37.55
36.28
33.03
26.69
O
Me
Ac
11:1 B:L mixture
f1 (ppm)

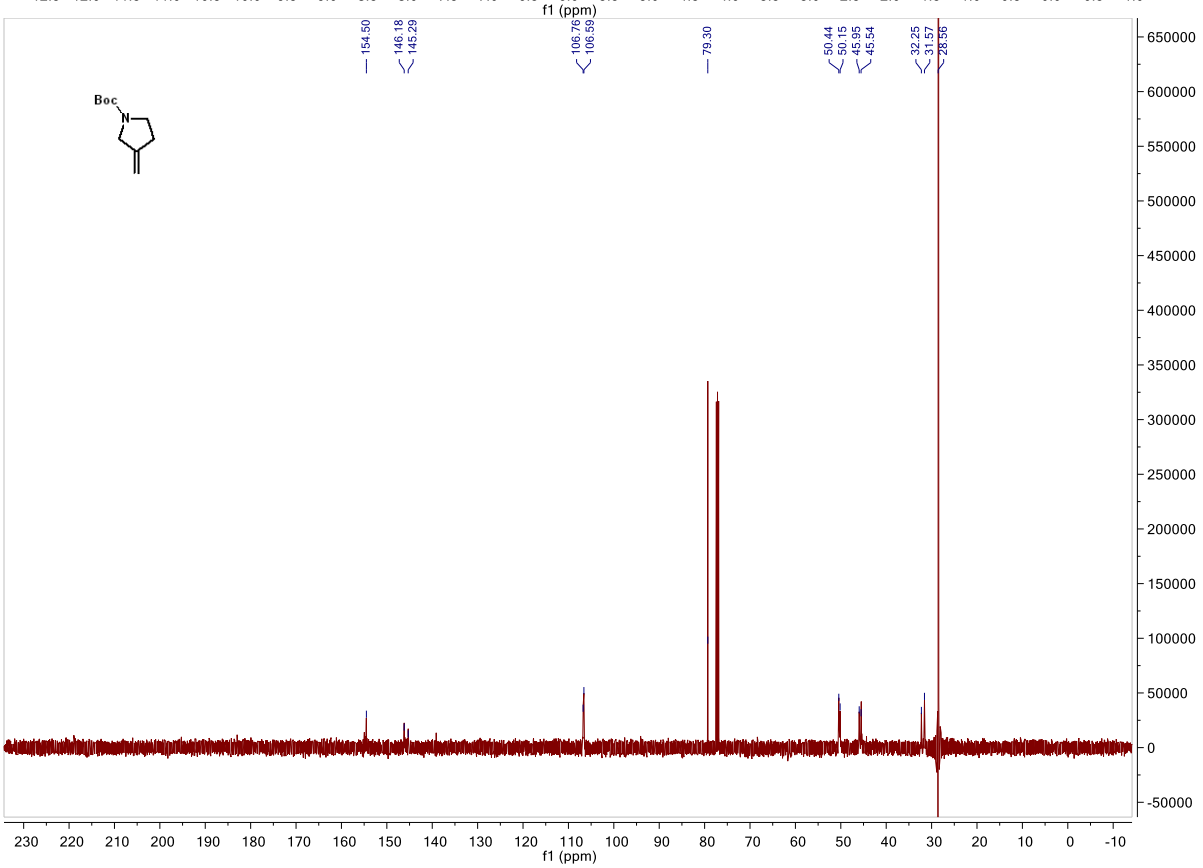

4.70
2.67
2.67
2.66
2.66
2.65
2.47
2.46
2.45
2.00
3.95
4.05
f1 (ppm)

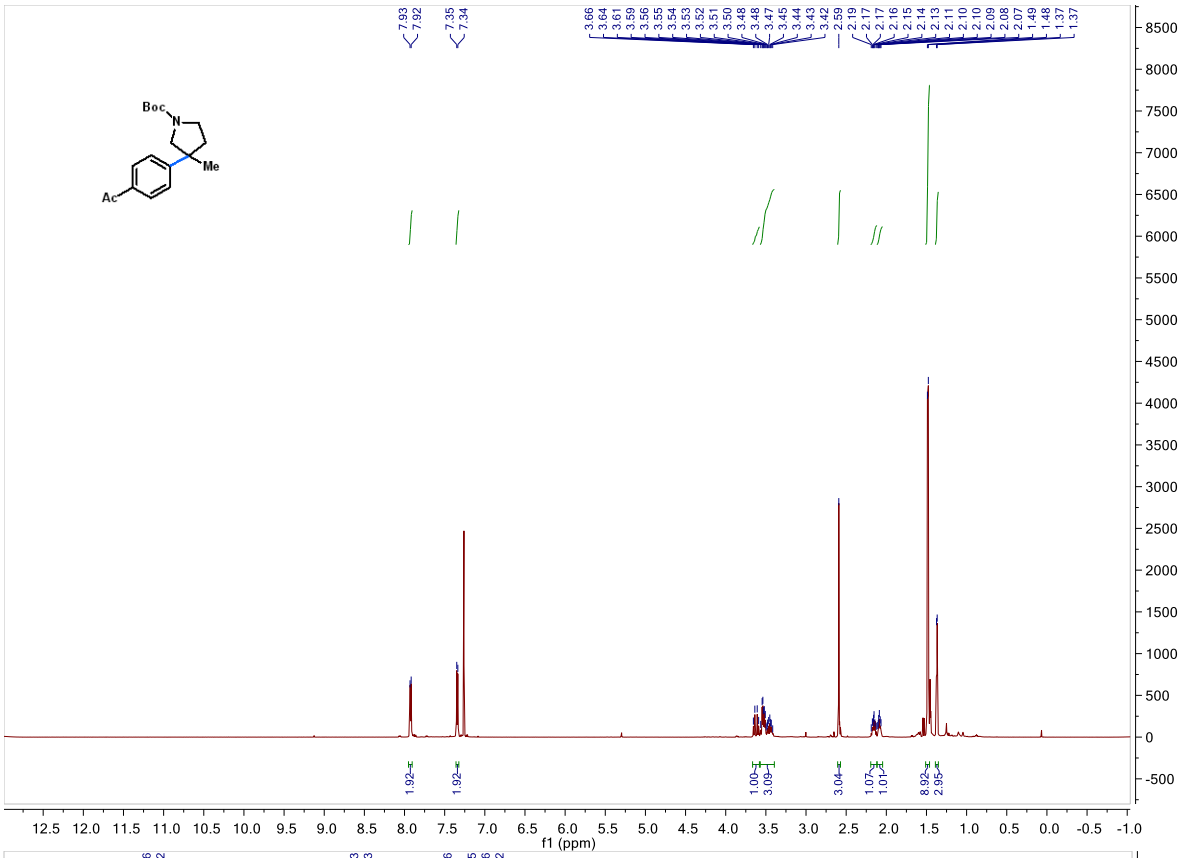

146.81
110.11
37.02
30.97
f1 (ppm)

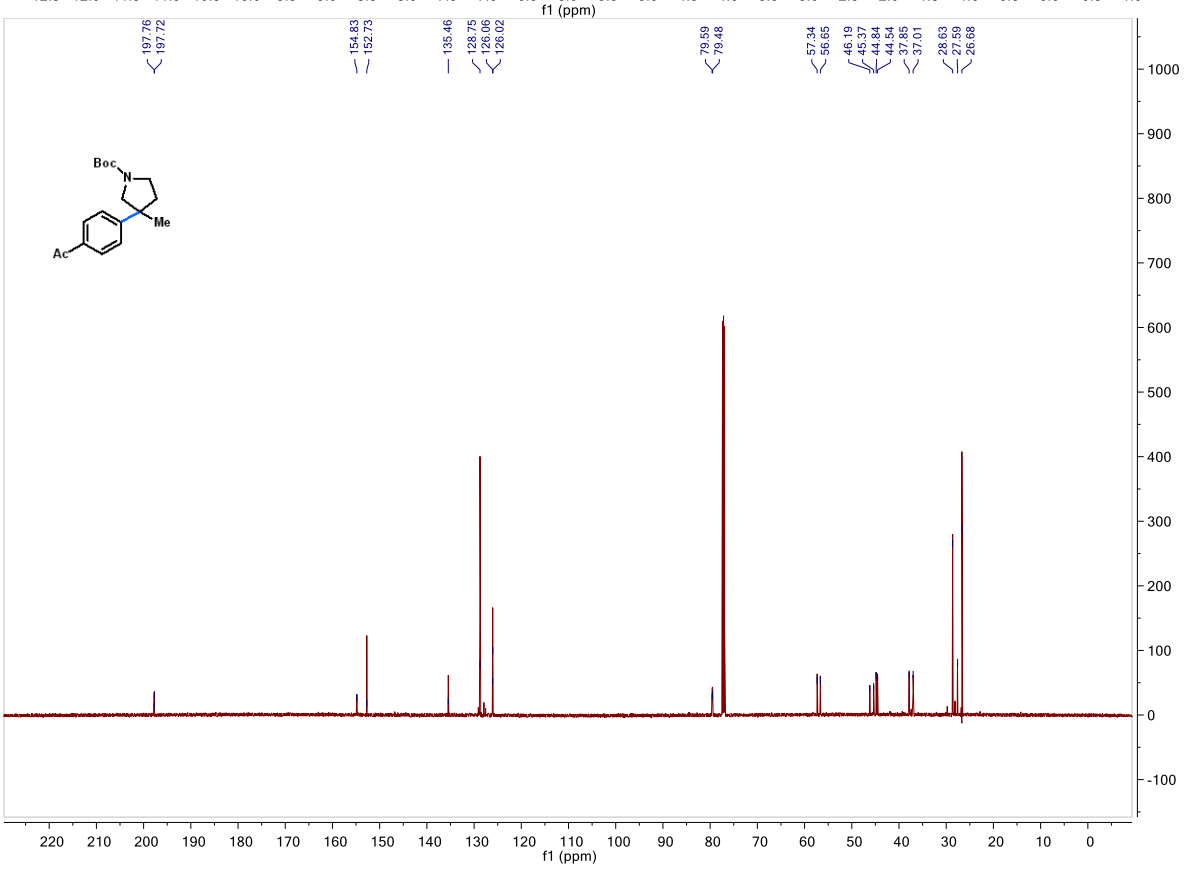

7.94
7.93
7.43
7.42
2.71
2.69
2.64
2.61
2.59
2.42
2.42
2.41
2.40
2.40
2.39
2.39
2.38
1.97
1.96
1.96
1.95
1.94
1.94
1.93
1.92
1.92
1.24
S
Me
Ac
6:1 B:L mixture
2.00
2.09
4.05
3.16
2.00
2.37
3.09
f1 (ppm)

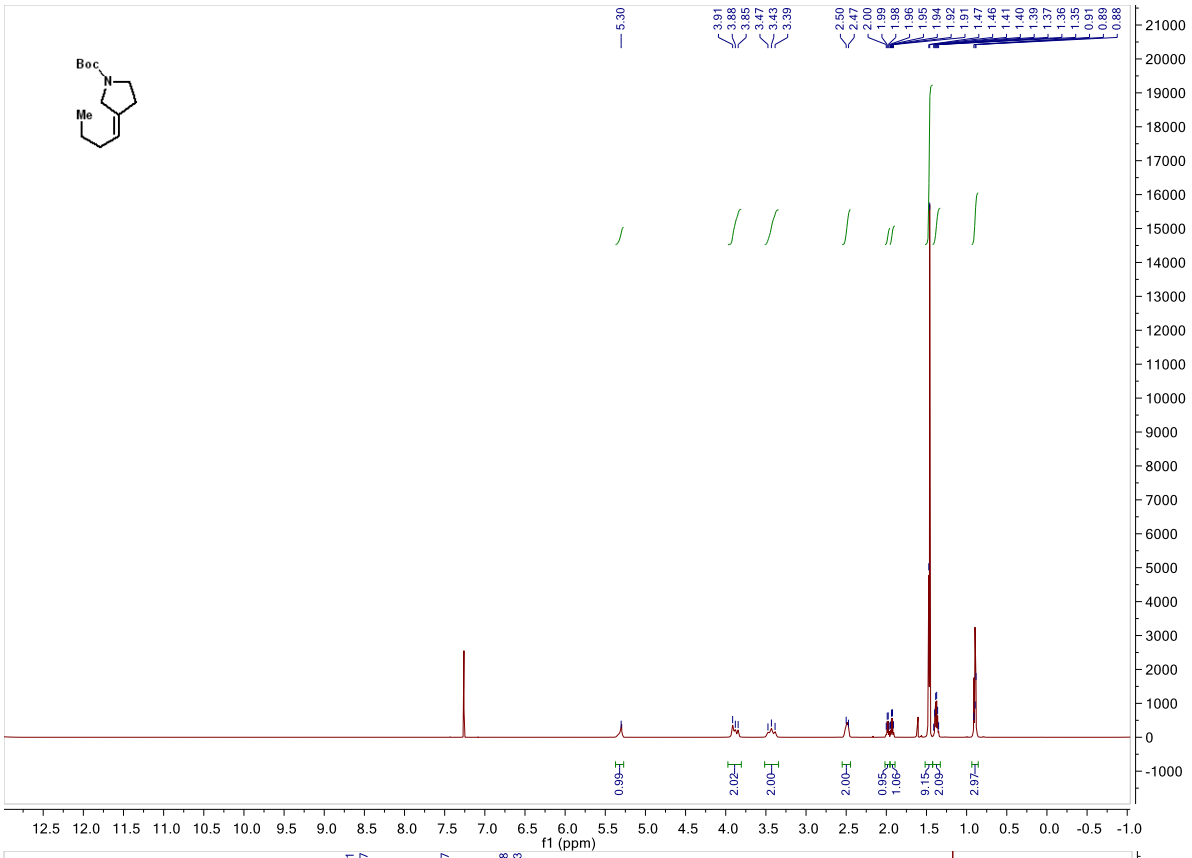

197.85
154.00
135.07
128.85
126.25
38.57
37.83
34.04
26.70
24.49
S
Me
Ac
6:1 B:L mixture
f1 (ppm)

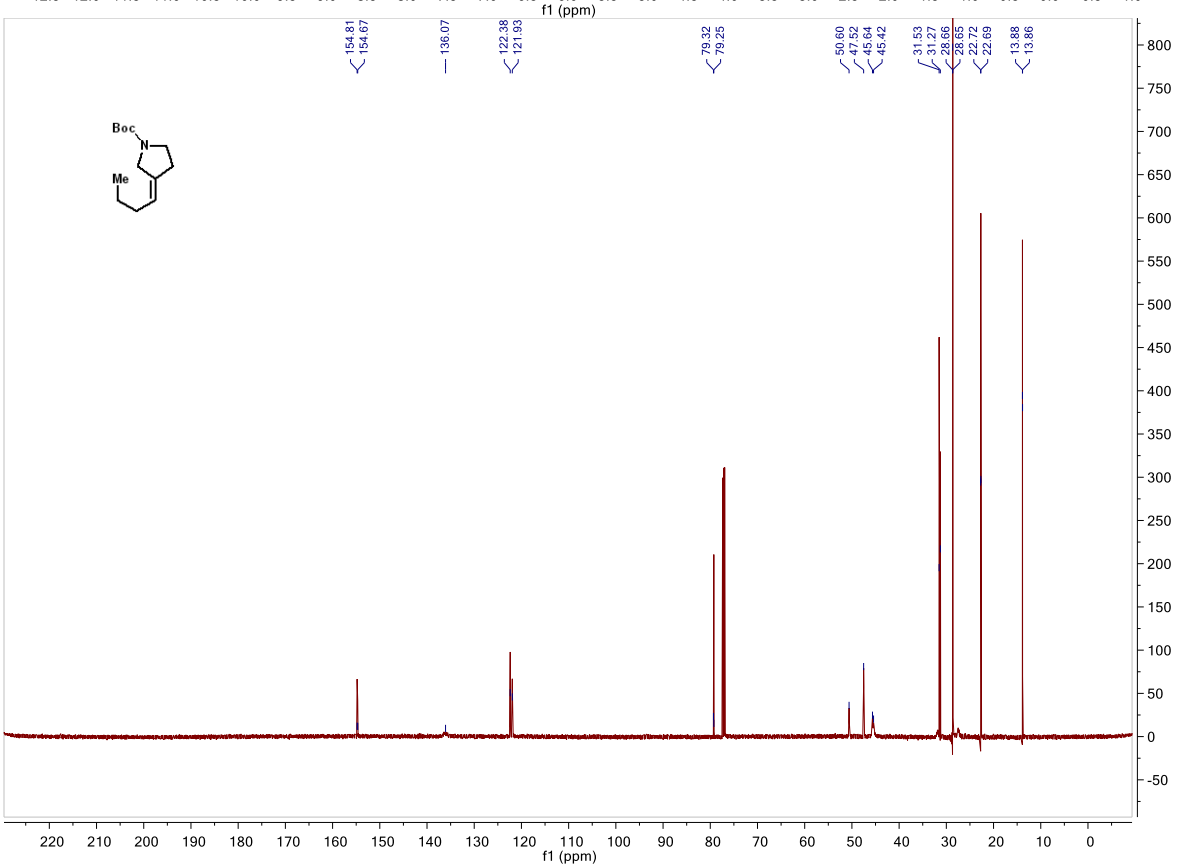

4.97
4.97
4.96
4.96
4.96
3.90
3.47
3.43
2.55
2.54
2.52
1.46
Boc
N
1.98
1.99
2.00
2.01
9.21
f1 (ppm)

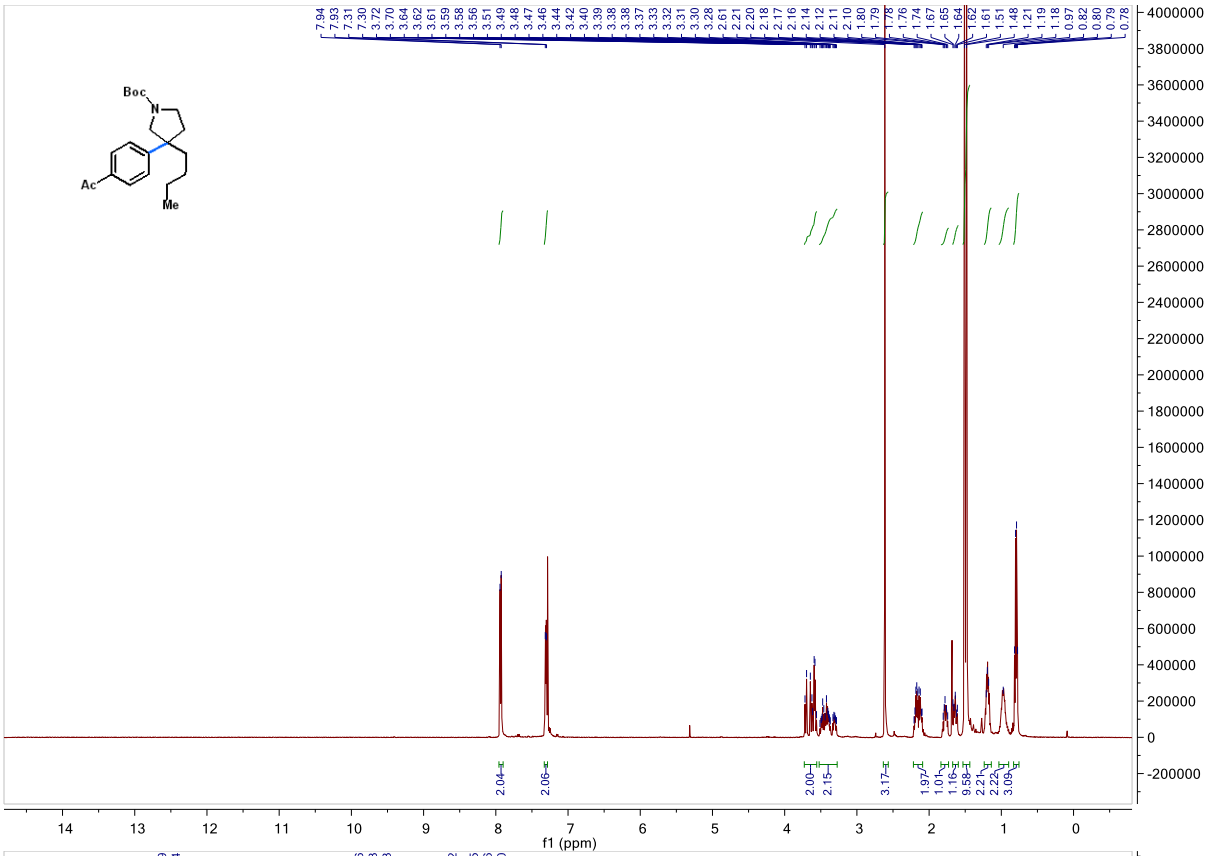

154.50
146.18
145.29
106.76
106.59
79.30
50.44
50.15
45.95
45.54
32.25
31.57
28.56
Boc
N
f1 (ppm)

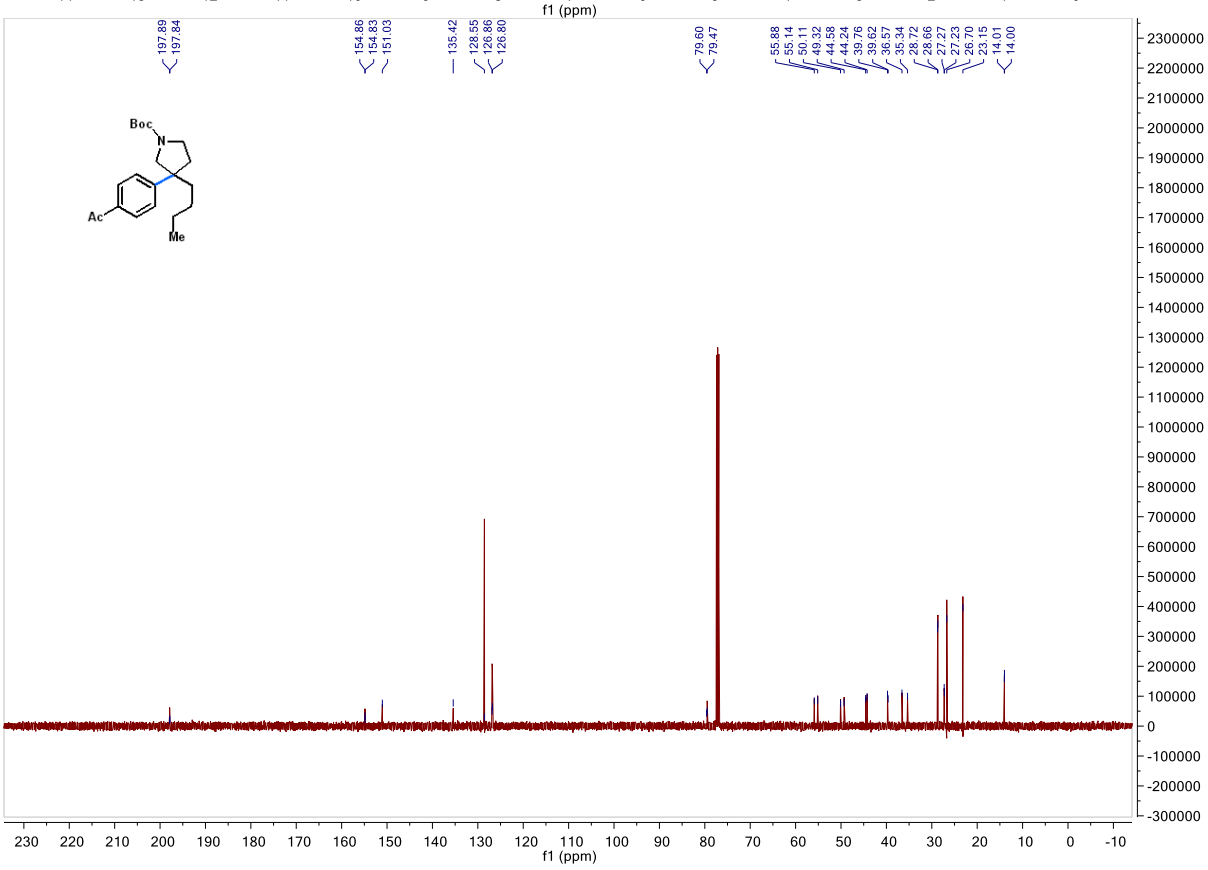

Boc
N
Me
Ac
7.93
7.92
7.35
7.34
3.66
3.64
3.61
3.59
3.56
3.55
3.54
3.53
3.52
3.51
3.50
3.48
3.47
3.45
3.44
3.43
3.42
2.59
2.19
2.17
2.17
2.16
2.15
2.14
2.13
2.11
2.10
2.10
2.09
2.08
2.07
1.49
1.48
1.37
1.37
1.92
1.92
1.00
3.09
3.04
1.07
1.01
8.92
2.95
f1 (ppm)

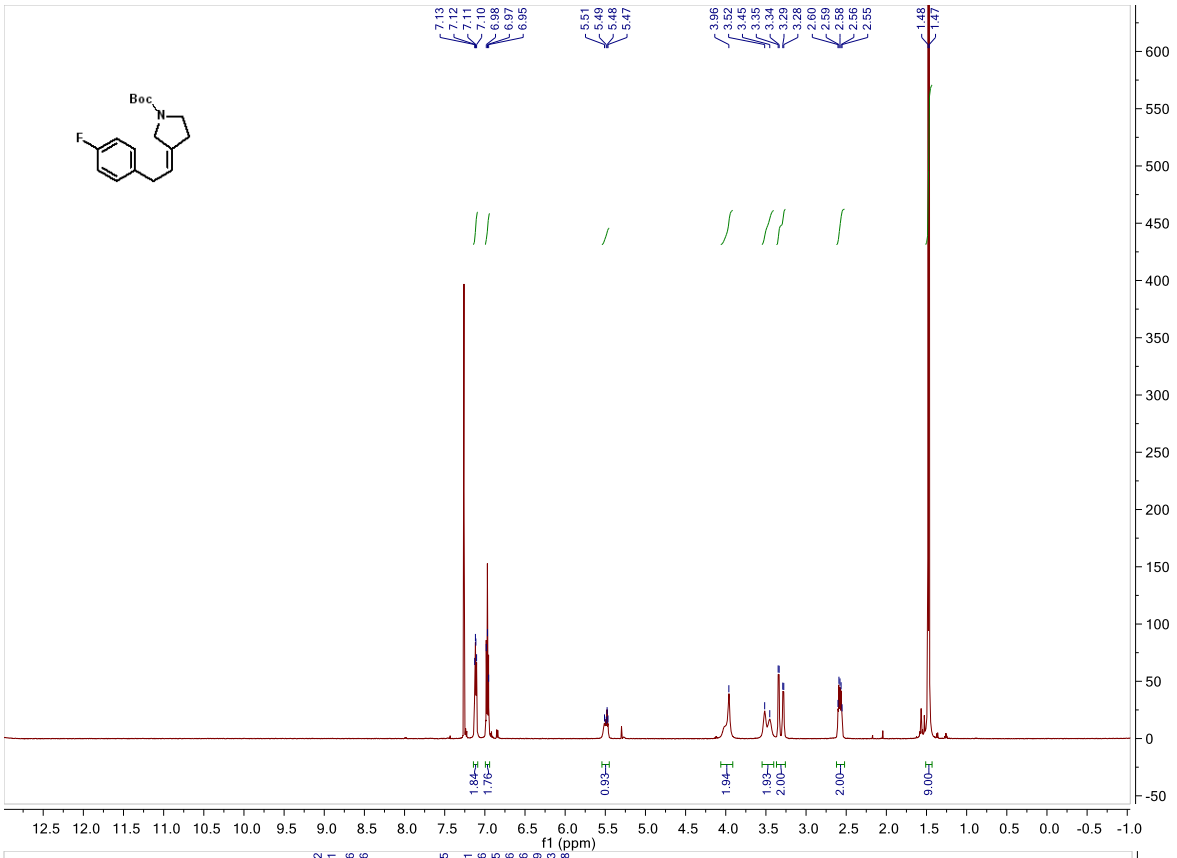

Boc
N
Me
Ac
197.76
197.72
154.83
152.73
135.46
128.75
126.06
126.02
79.59
79.48
57.34
56.65
46.19
45.37
44.84
44.54
37.85
37.01
28.63
27.59
26.68
f1 (ppm)

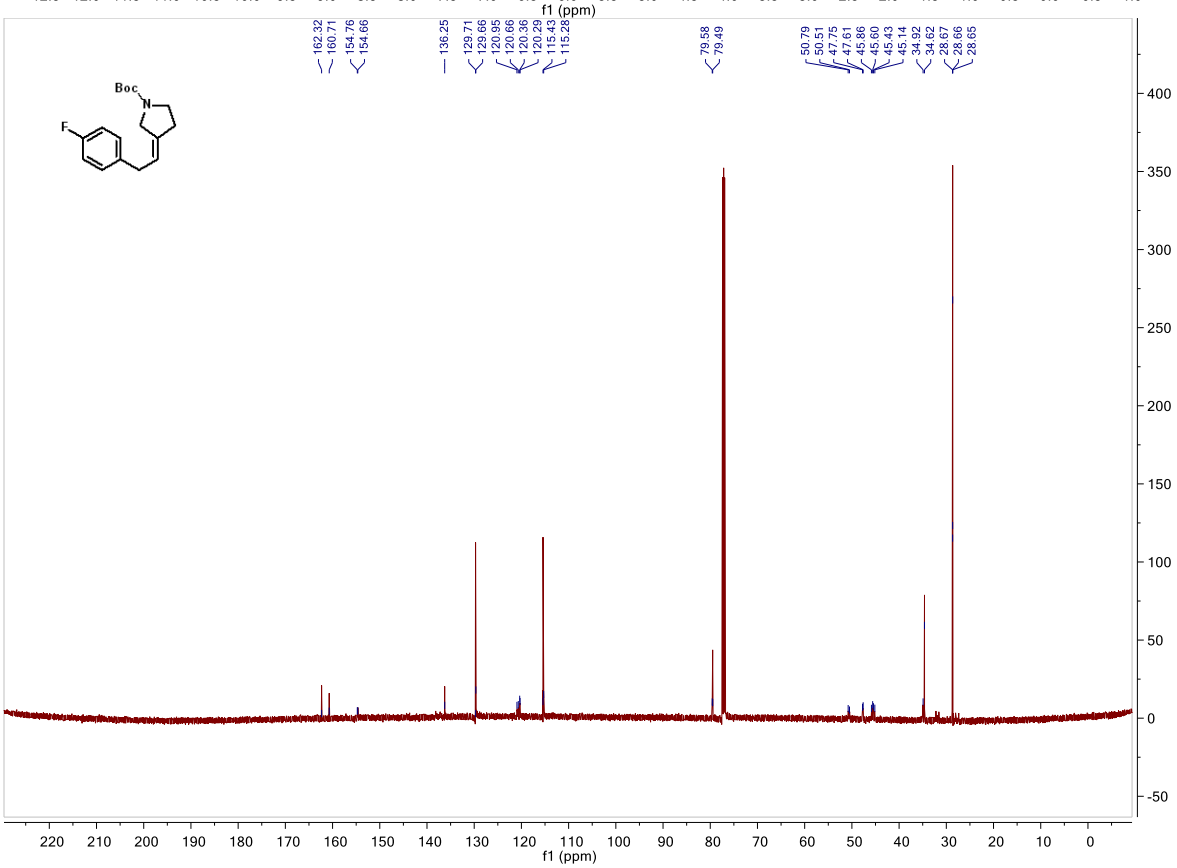

Boc
N
Me
5.30
3.91
3.88
3.85
3.47
3.43
3.39
2.50
2.47
2.00
1.99
1.98
1.96
1.95
1.94
1.92
1.91
1.47
1.46
1.41
1.40
1.39
1.37
1.36
1.35
0.91
0.89
0.88
0.99
2.02
2.00
2.00
0.95
1.06
9.15
2.09
2.97
f1 (ppm)

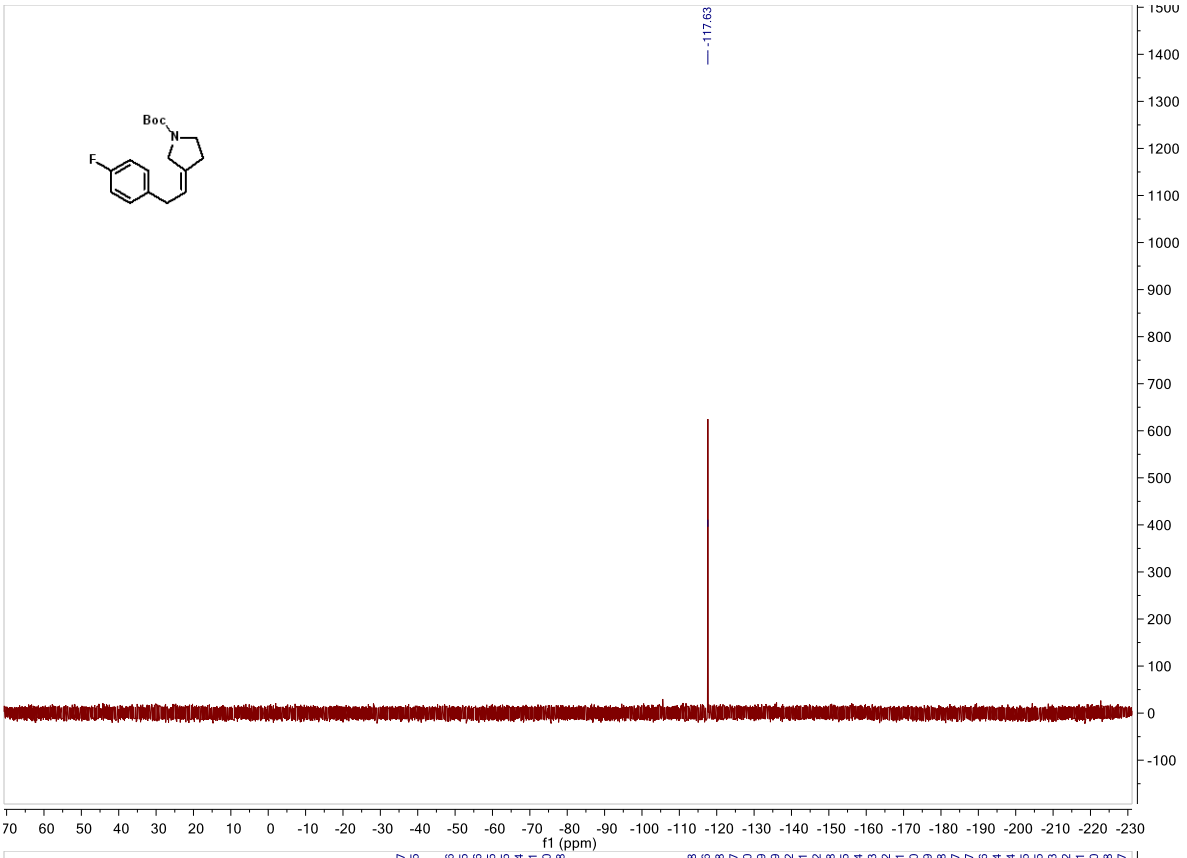

Boc
N
Me
154.81
154.67
136.07
122.38
121.93
79.32
79.25
50.60
47.52
45.64
45.42
31.53
31.27
28.66
28.65
22.72
22.69
13.88
13.86
f1 (ppm)

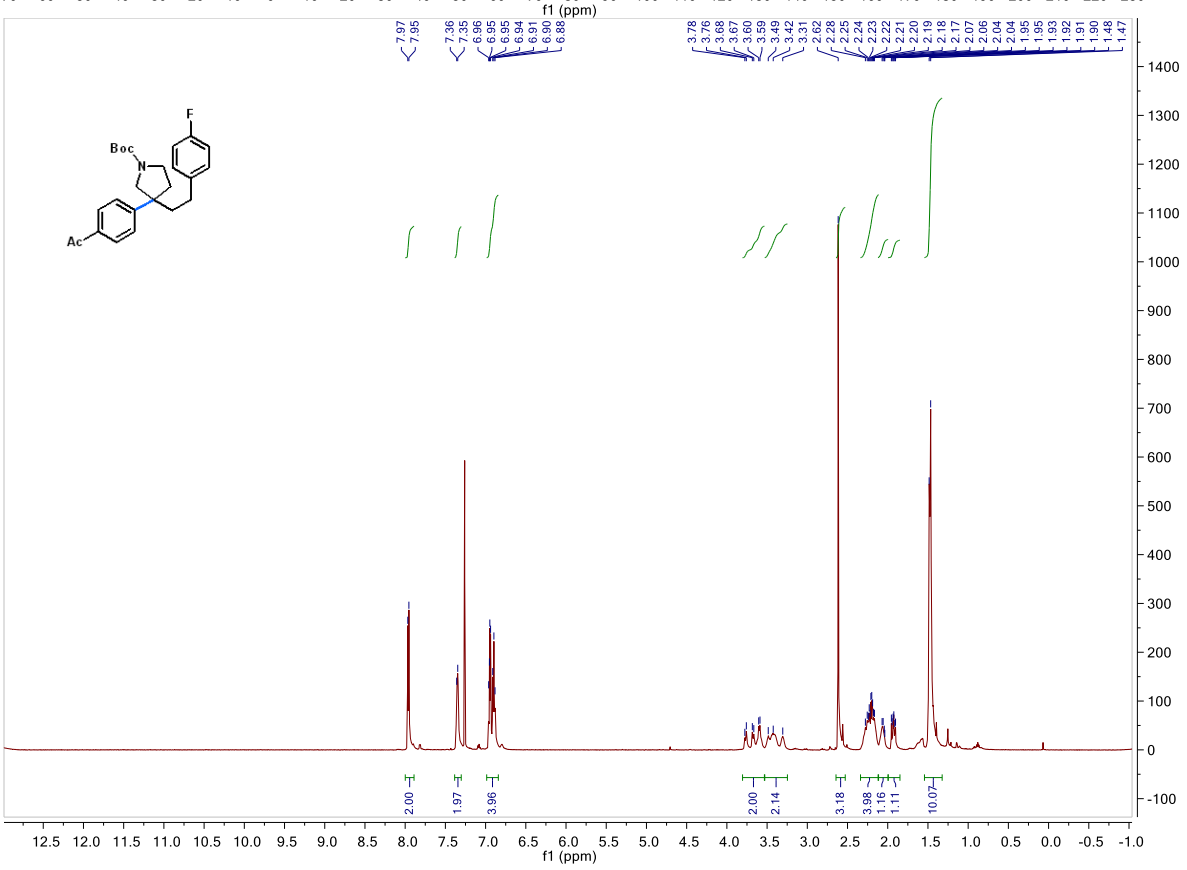

Boc
N
Ac
Me
f1 (ppm)

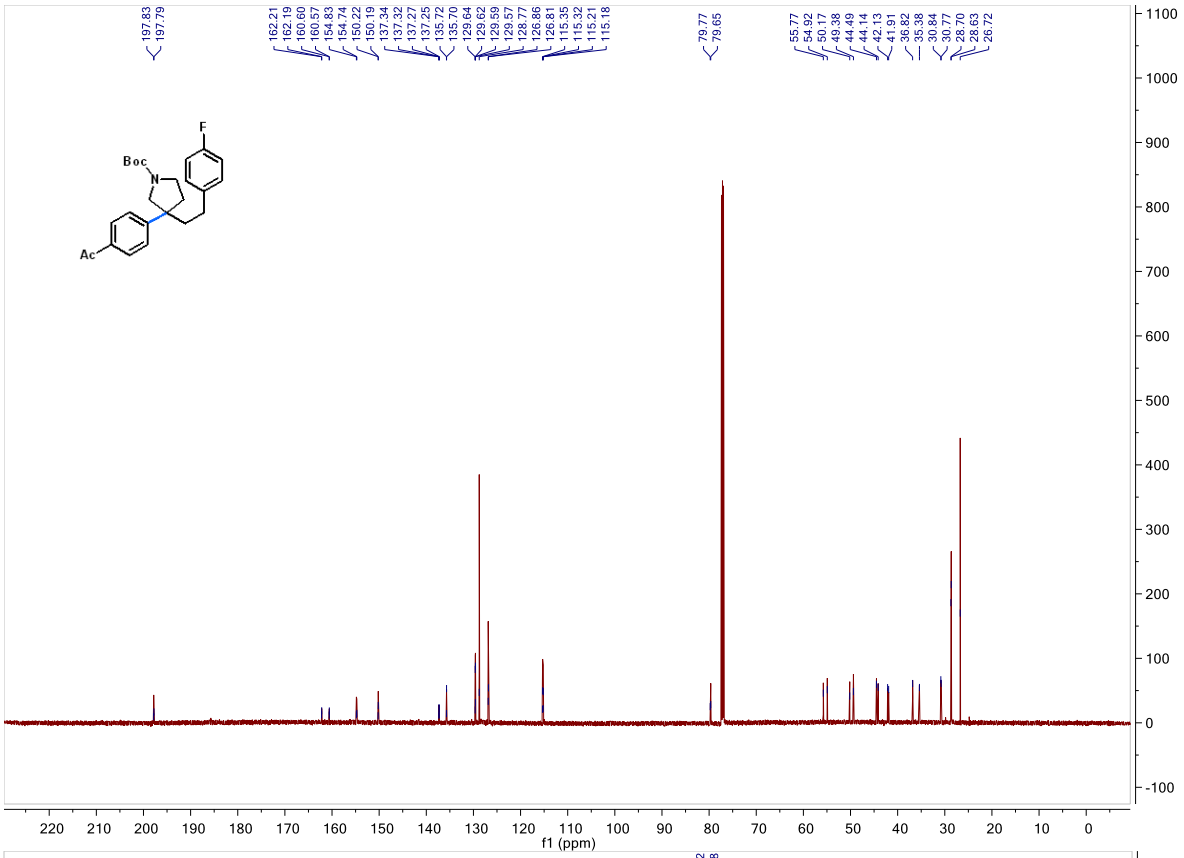

Boc
N
Ac
Me
f1 (ppm)

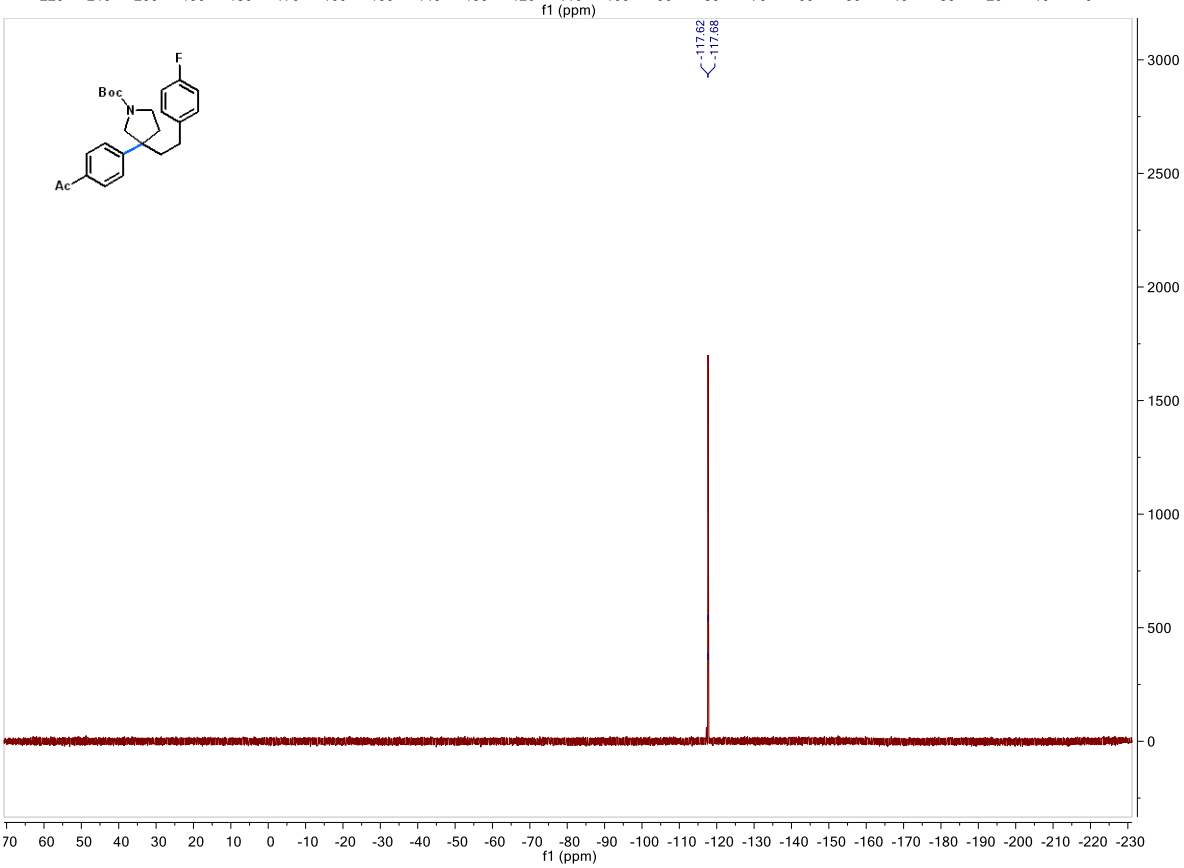

Boc
N
F
7.13
7.12
7.11
7.10
6.98
6.97
6.95
5.51
5.49
5.48
5.47
3.96
3.52
3.45
3.35
3.34
3.29
3.28
2.60
2.59
2.58
2.56
2.55
1.48
1.47
1.84
1.76
0.93
1.94
1.93
2.00
2.00
9.00
f1 (ppm)

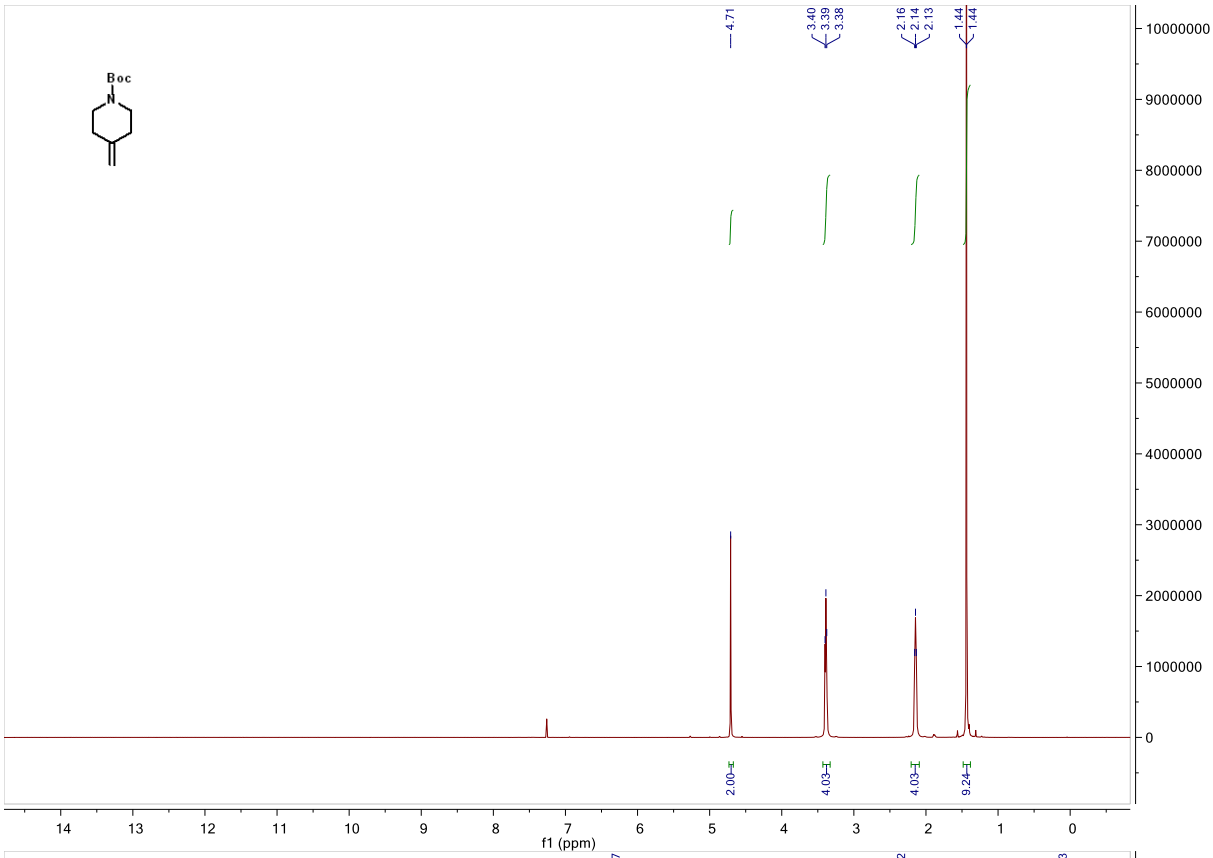

Boc
N
F
162.32
160.71
154.76
154.66
136.25
129.71
129.66
120.95
120.66
120.36
120.29
115.43
115.28
79.58
79.49
50.79
50.51
47.75
47.61
45.86
45.60
45.43
45.14
34.92
34.62
28.67
28.66
28.65
f1 (ppm)

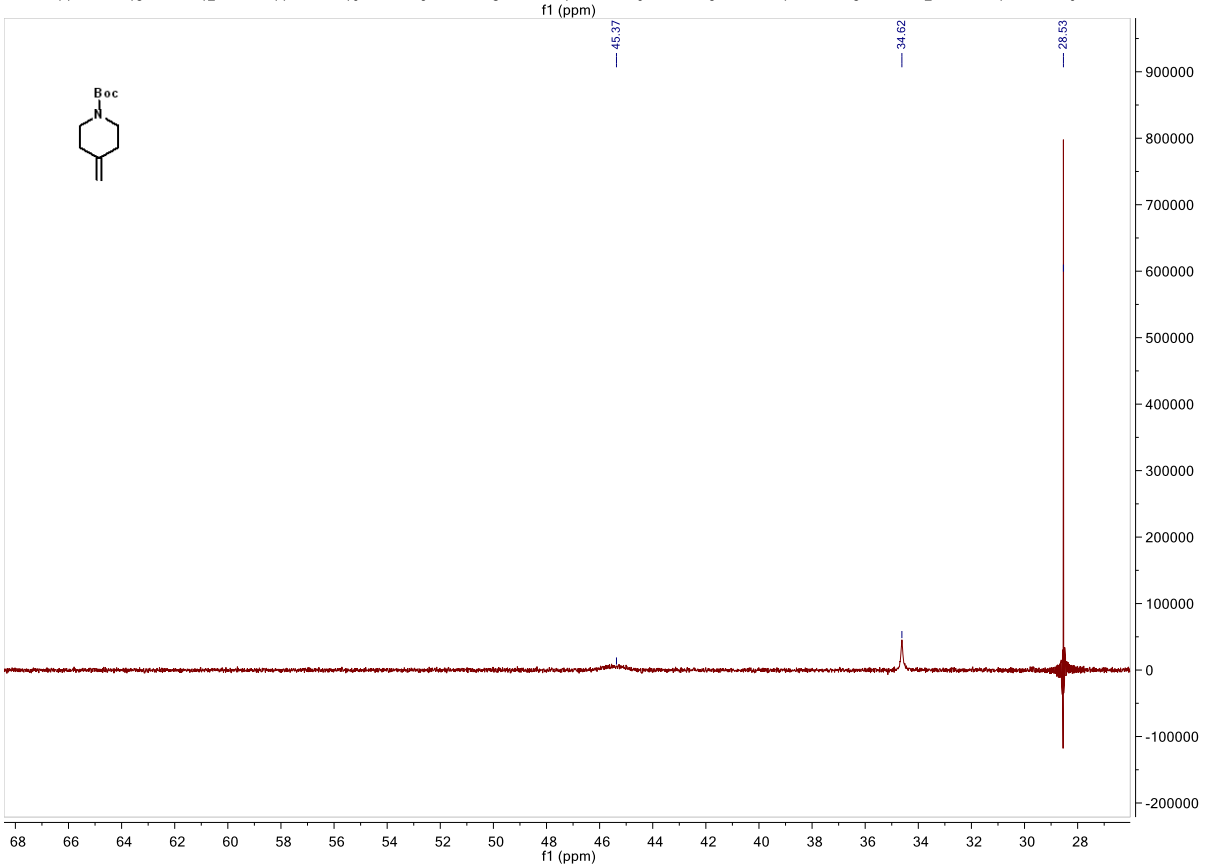

-117.63
Boc
N
F
f1 (ppm)

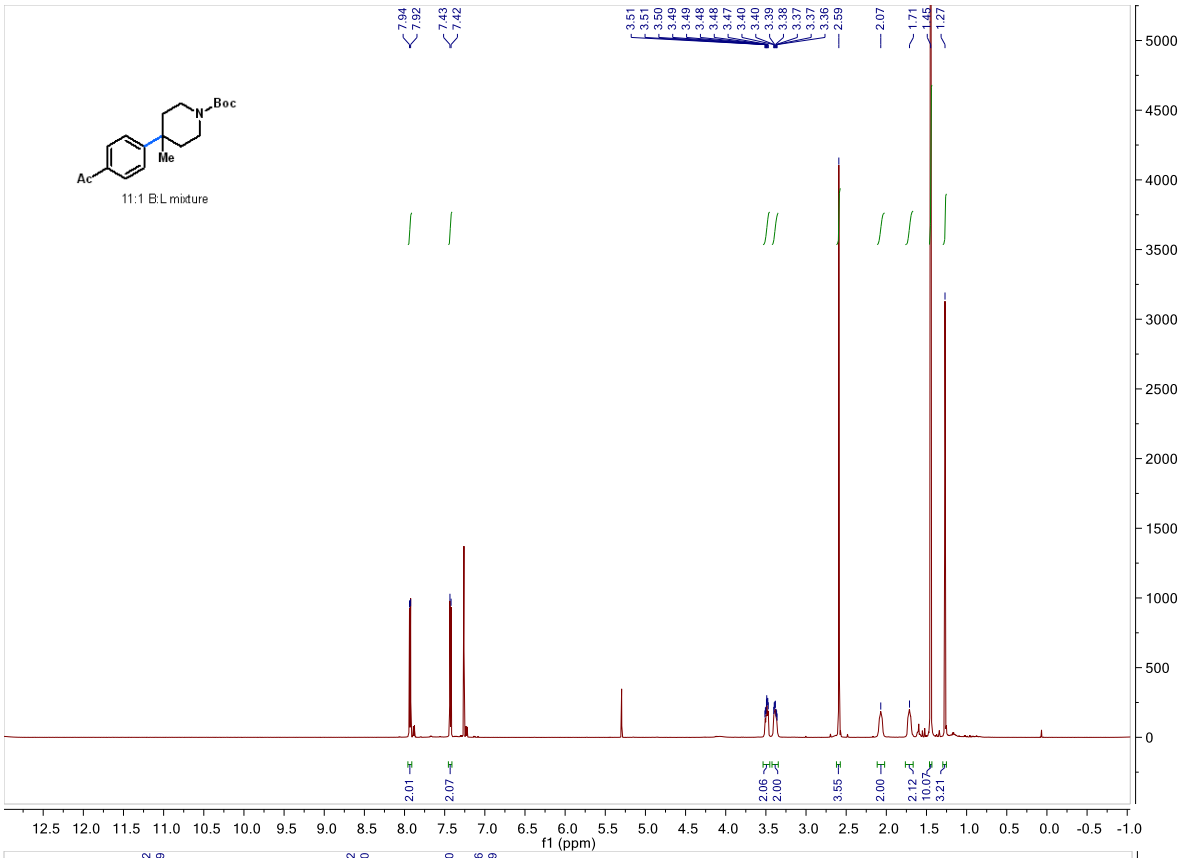

7.97
7.95
7.36
7.35
6.96
6.95
6.95
6.94
6.91
6.90
6.88
3.78
3.76
3.68
3.67
3.60
3.59
3.49
3.42
3.31
2.62
2.28
2.25
2.24
2.23
2.22
2.21
2.20
2.19
2.18
2.17
2.07
2.06
2.04
2.04
1.95
1.95
1.93
1.92
1.91
1.90
1.48
1.47
F
Boc
N
Ac
2.00
1.97
3.96
2.00
2.14
3.18
3.98
1.16
1.11
10.07
f1 (ppm)

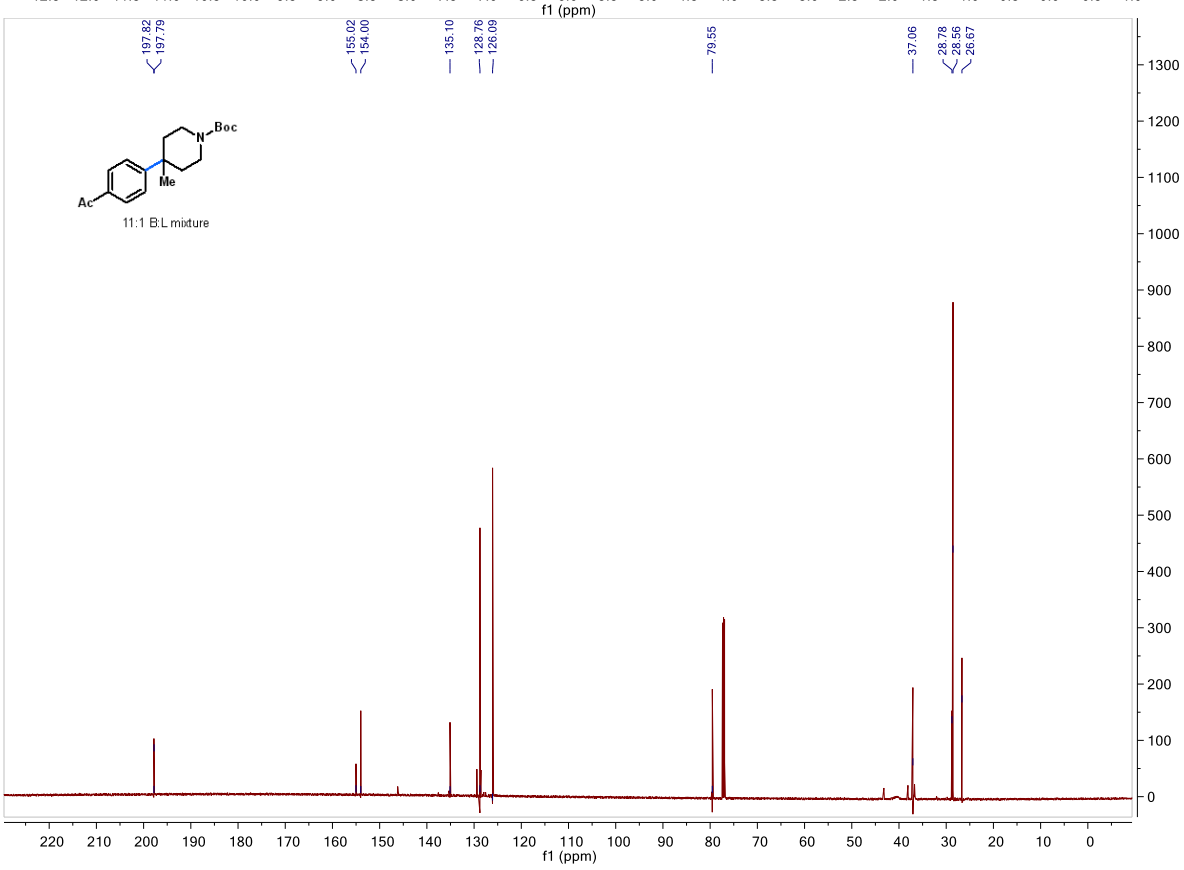

197.83
197.79
162.21
162.19
160.60
160.57
154.83
154.74
150.22
150.19
137.34
137.32
137.27
137.25
135.72
135.70
129.64
129.62
129.59
129.57
128.77
126.86
126.81
115.35
115.32
115.21
115.18
79.77
79.65
55.77
54.92
50.17
49.38
44.49
44.14
42.13
41.91
36.82
35.38
30.84
30.77
28.70
28.63
26.72
Boc
N
F
Ac
f1 (ppm)

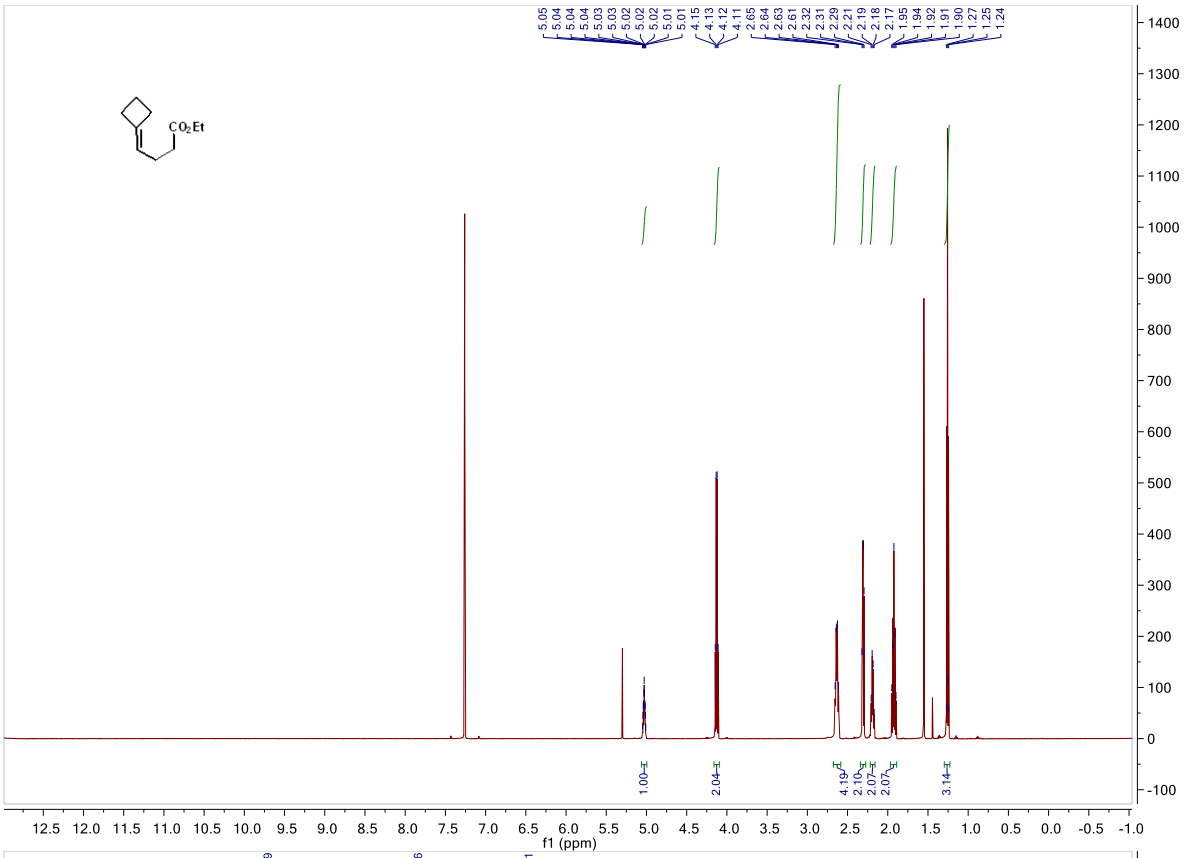

-117.62
-117.68
Boc
N
F
Ac
f1 (ppm)

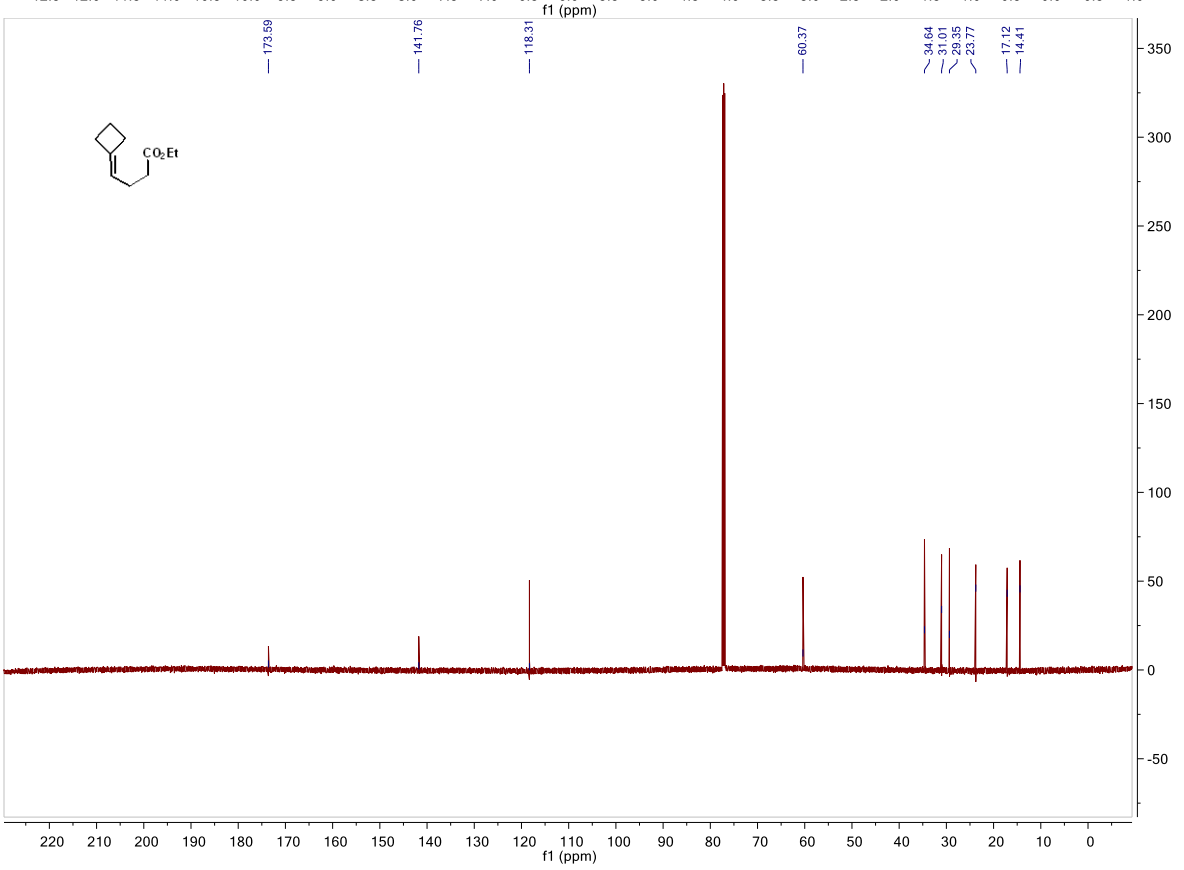

Boc
N
4.71
3.40
3.39
3.38
2.16
2.14
2.13
1.44
1.44
2.00
4.03
4.03
9.24
f1 (ppm)

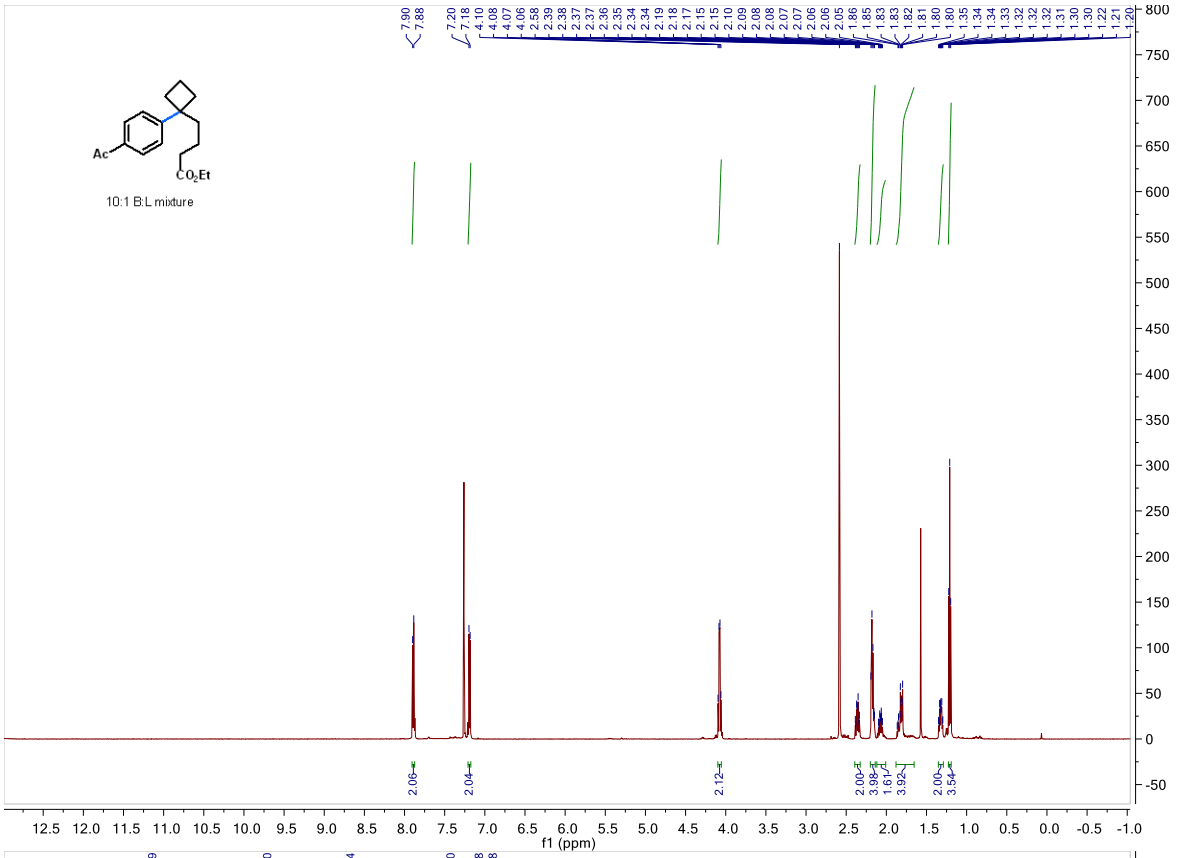

Boc
N
45.37
34.62
28.53
f1 (ppm)

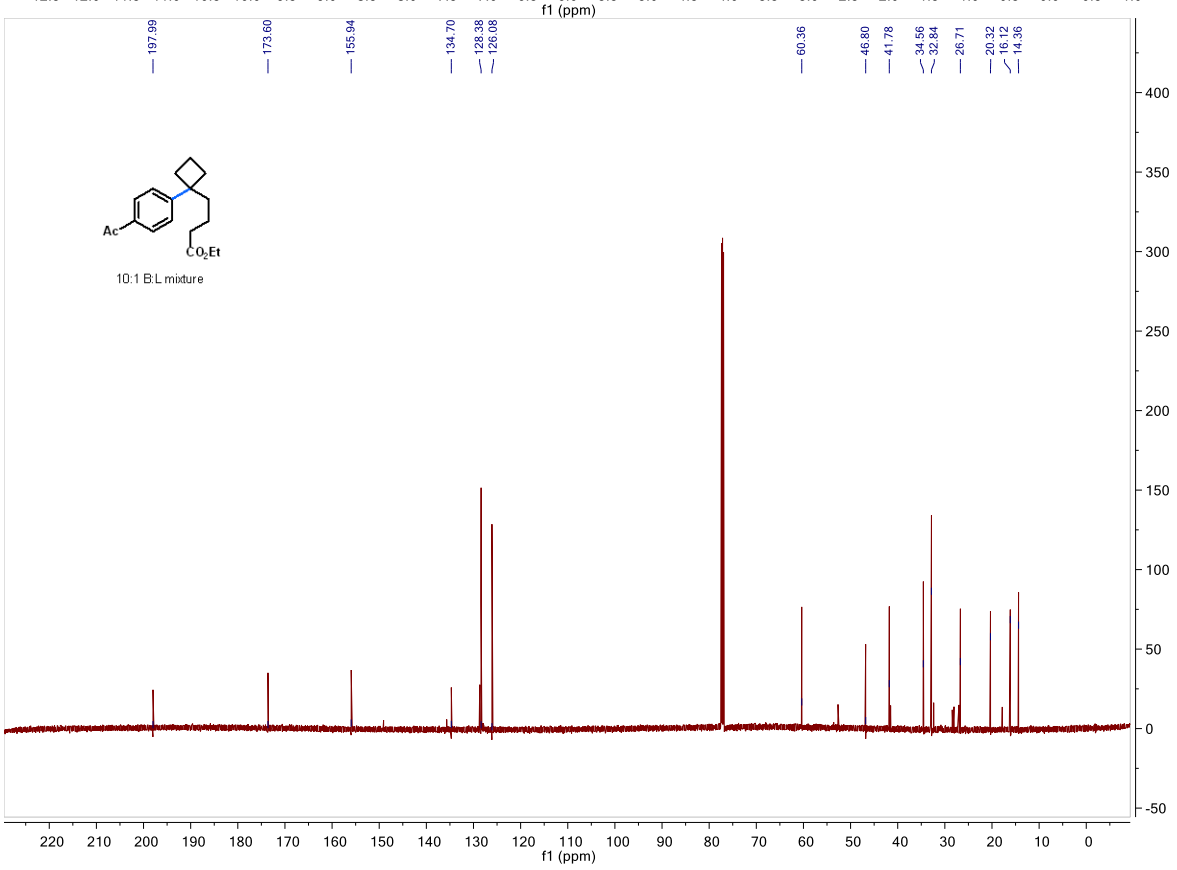

Boc
N
Me
Ac
11:1 B:L mixture
7.94
7.92
7.43
7.42
3.51
3.50
3.49
3.48
3.47
3.40
3.39
3.38
3.37
3.36
2.59
2.07
1.71
1.45
1.27
2.01
2.07
2.06
2.00
3.55
2.00
2.12
10.07
3.21
f1 (ppm)

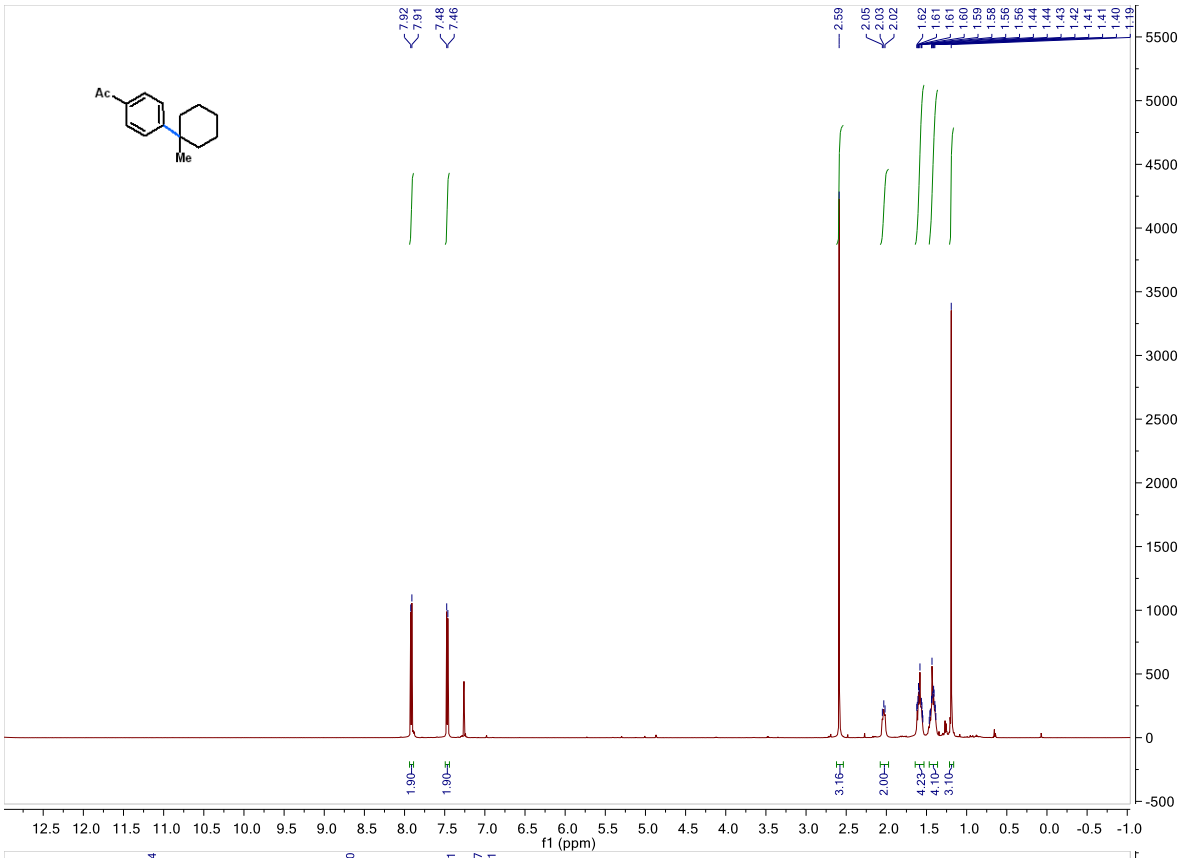

Boc
N
Me
Ac
11:1 B:L mixture
197.82
197.79
155.02
154.00
135.10
128.76
126.09
79.55
37.06
28.78
28.56
26.67
f1 (ppm)

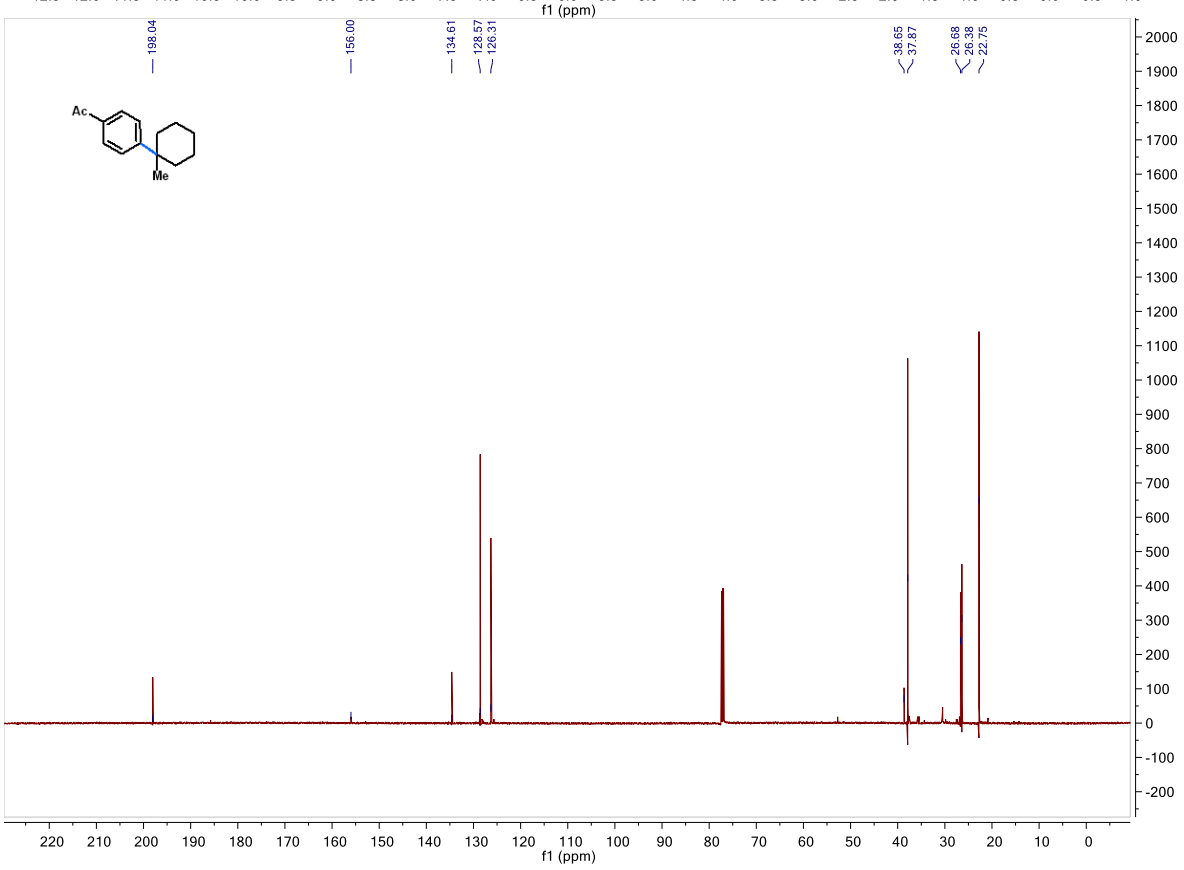

5.05
5.04
5.04
5.04
5.03
5.03
5.02
5.02
5.02
5.01
5.01
4.15
4.13
4.12
4.11
2.65
2.64
2.63
2.61
2.32
2.31
2.29
2.21
2.19
2.18
2.17
1.95
1.94
1.92
1.91
1.90
1.27
1.25
1.24
CO2Et
1.00
2.04
4.19
2.10
2.07
2.07
3.14
f1 (ppm)

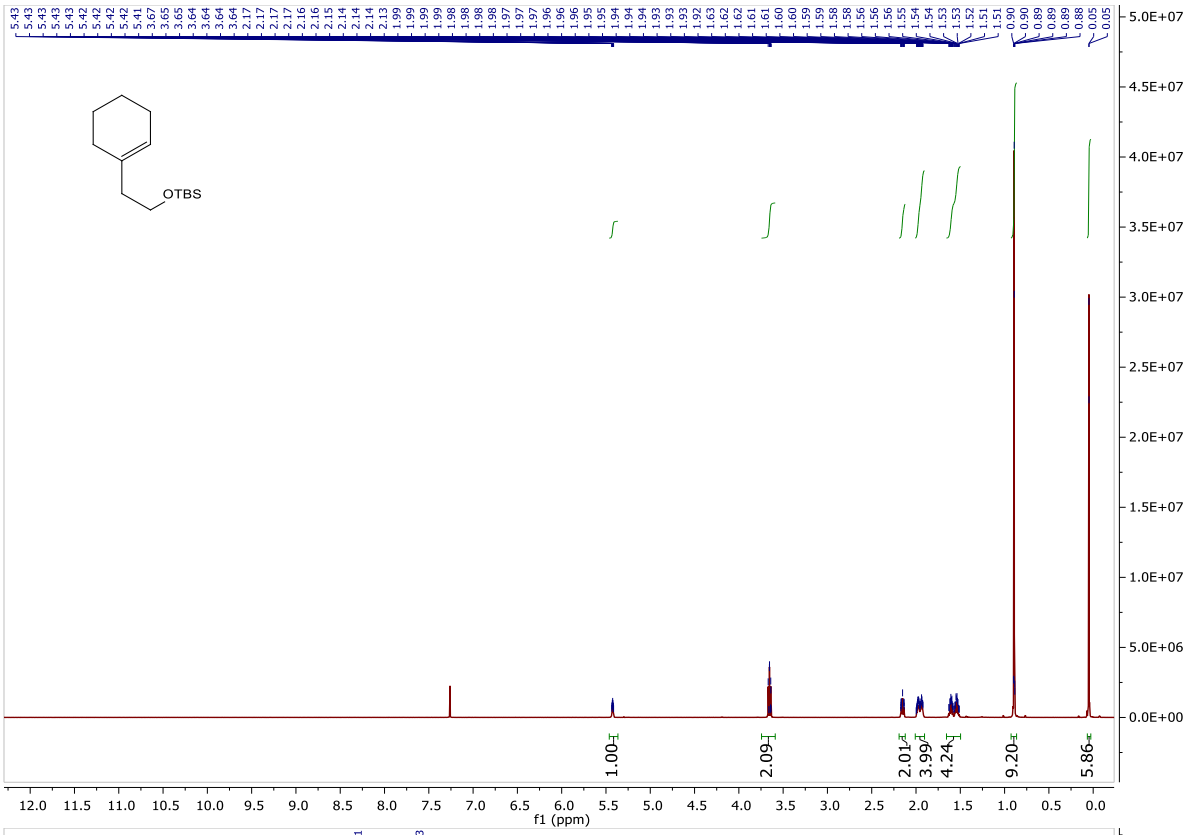

173.59
141.76
118.31
60.37
34.64
31.01
29.35
23.77
17.12
14.41
CO2Et
f1 (ppm)

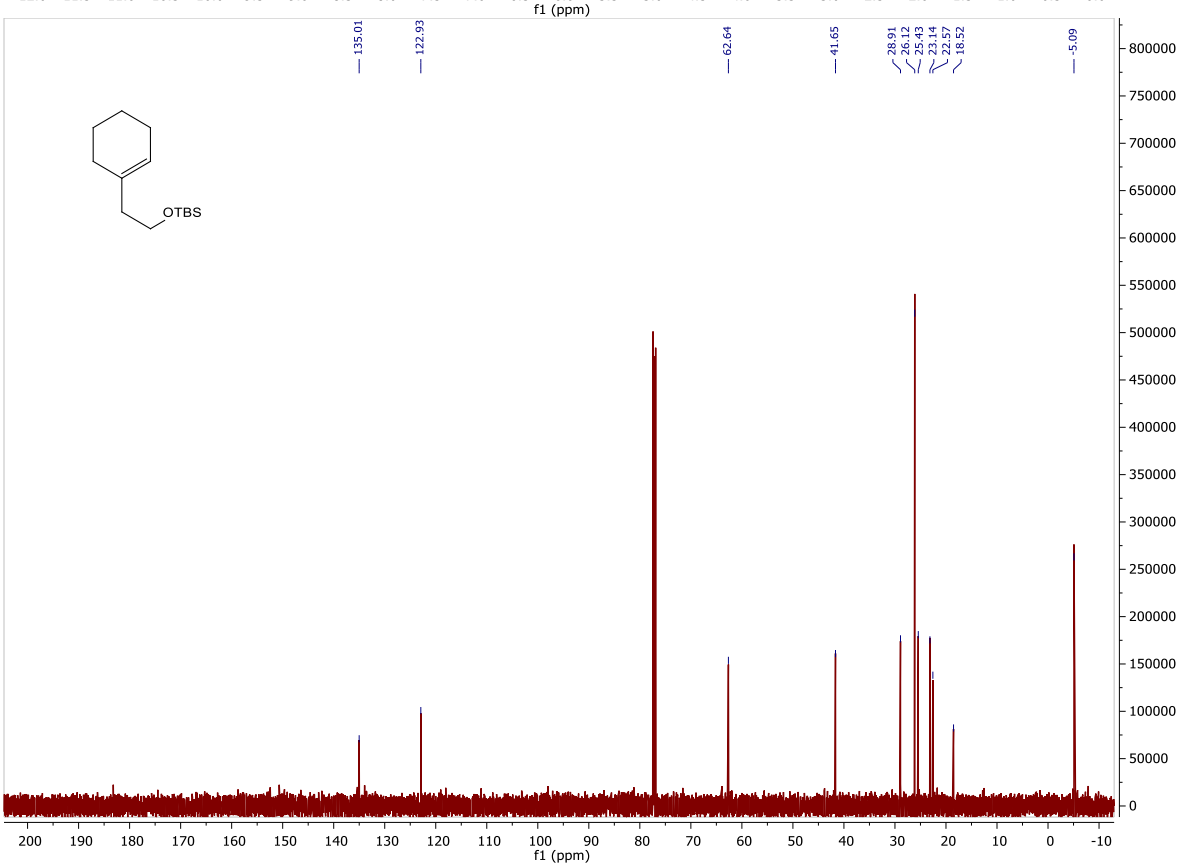

Ac
CO2Et
10:1 B:L mixture
f1 (ppm)

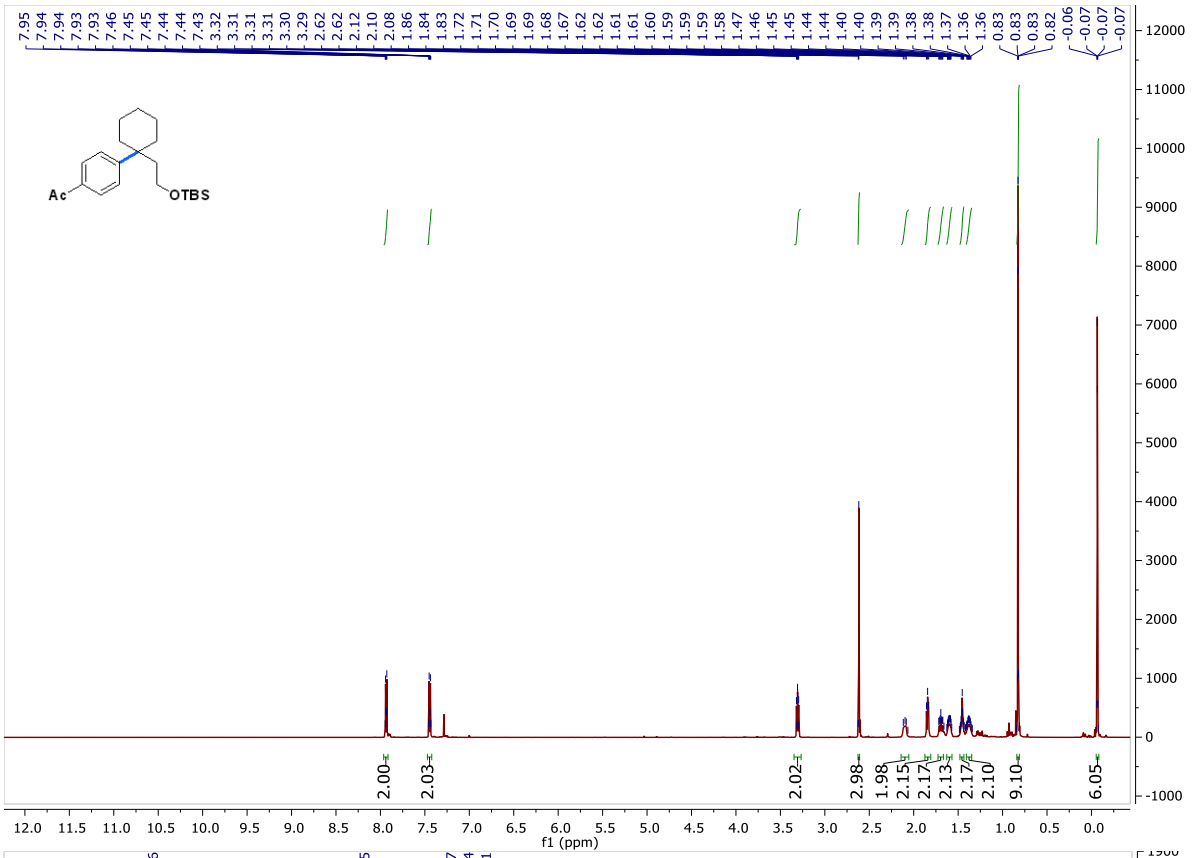

Ac
CO2Et
10:1 B:L mixture
f1 (ppm)

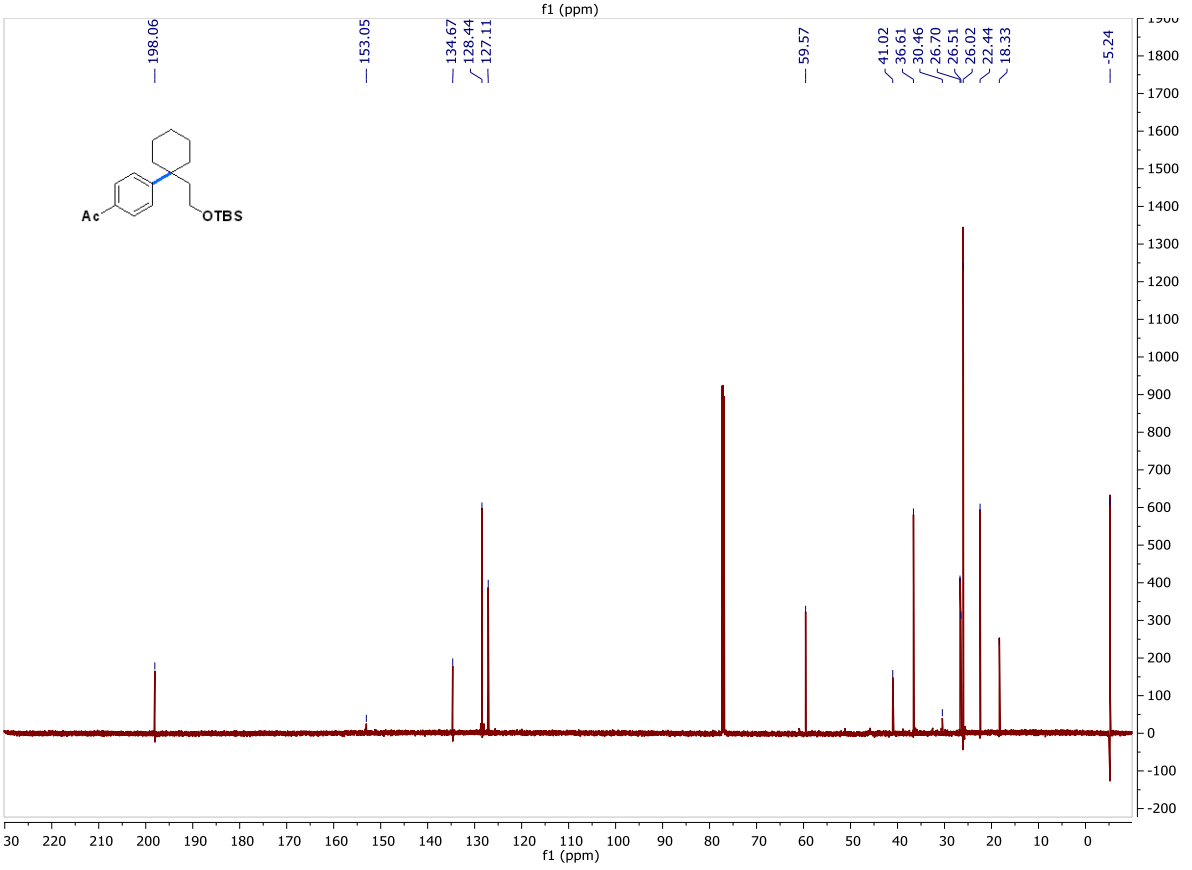

7.92
7.91
7.48
7.46
2.59
2.05
2.03
2.02
1.62
1.61
1.61
1.60
1.59
1.58
1.56
1.56
1.44
1.44
1.43
1.42
1.41
1.41
1.40
1.19
Ac
Me
1.90
1.90
3.16
2.00
4.23
4.10
3.10
f1 (ppm)

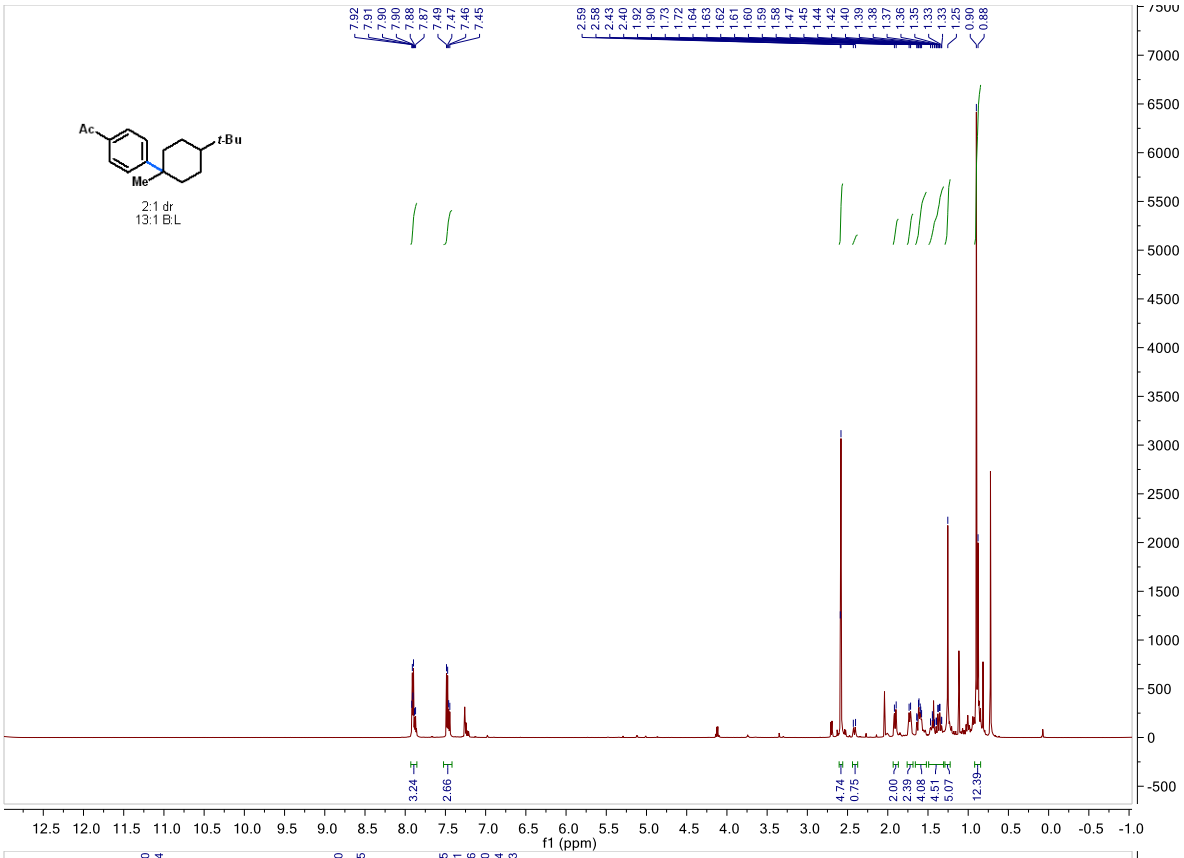

198.04
156.00
134.61
128.57
126.31
38.65
37.87
26.68
26.38
22.75
Ac
Me
f1 (ppm)

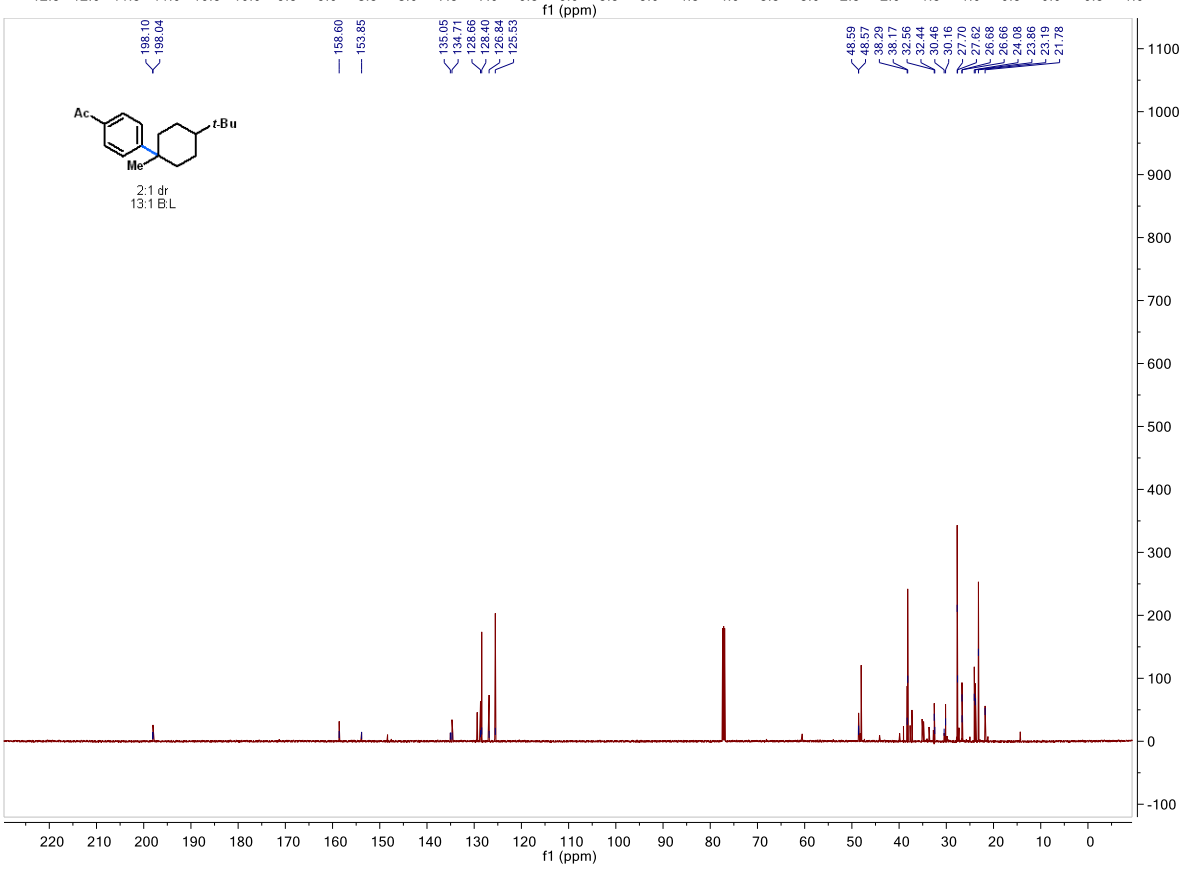

OTBS
1.00
2.09
2.01
3.99
4.24
9.20
5.86
f1 (ppm)

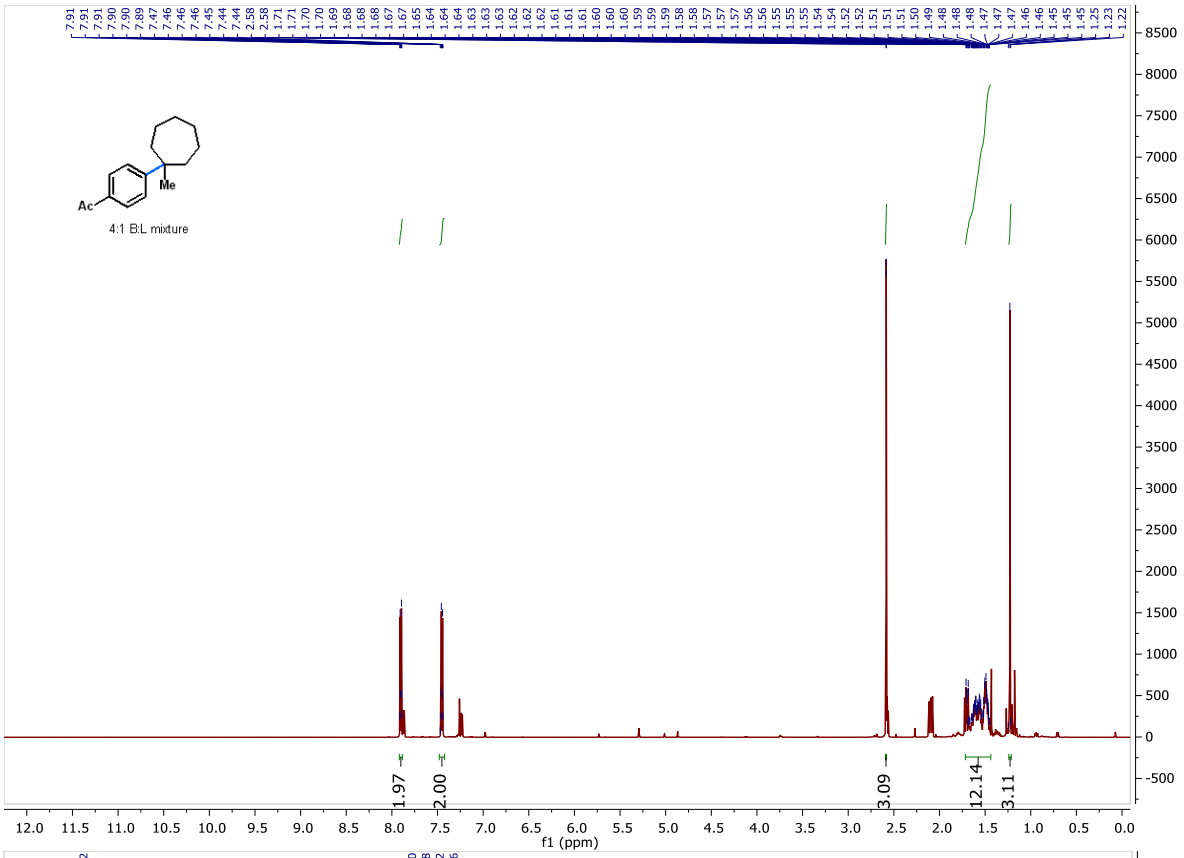

OTBS
135.01
122.93
62.64
41.65
28.91
26.12
25.43
23.14
22.57
18.52
-5.09
f1 (ppm)

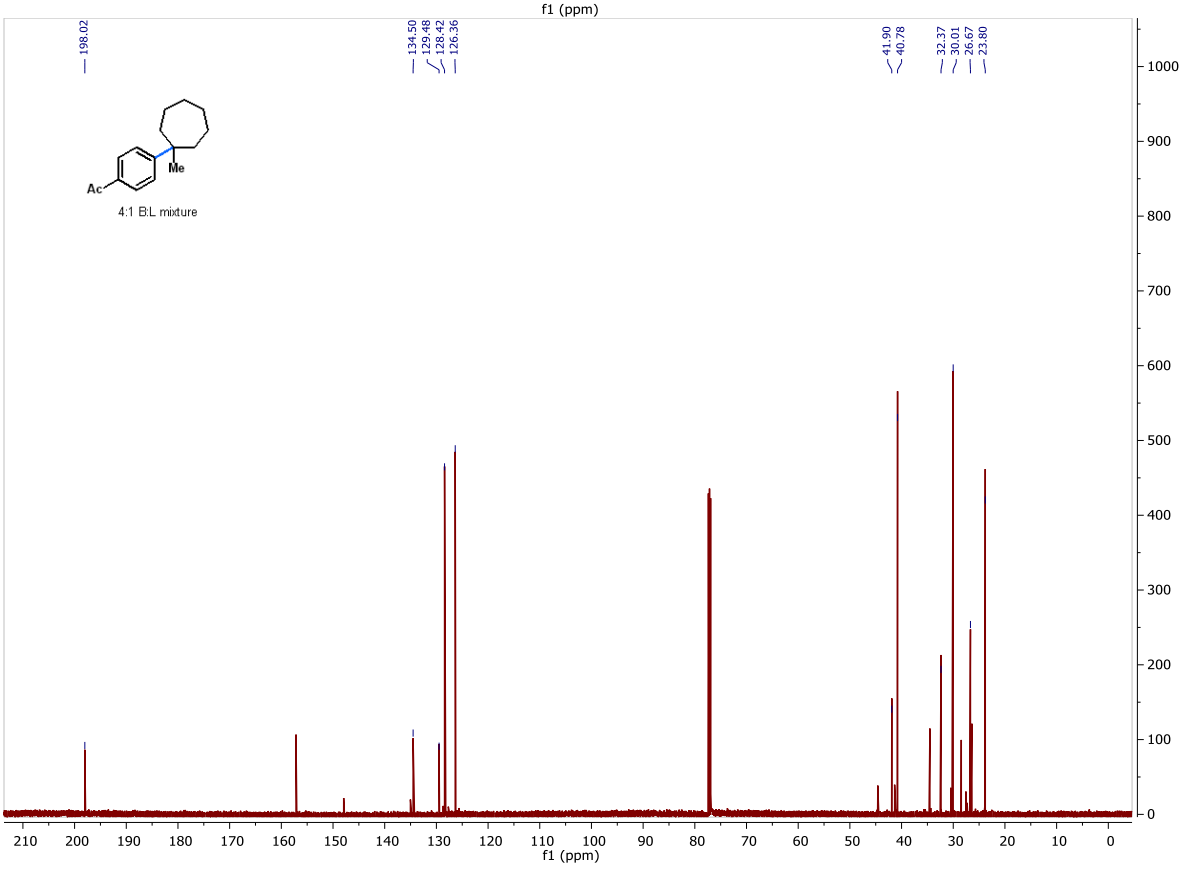

Ac
OTBS
f1 (ppm)

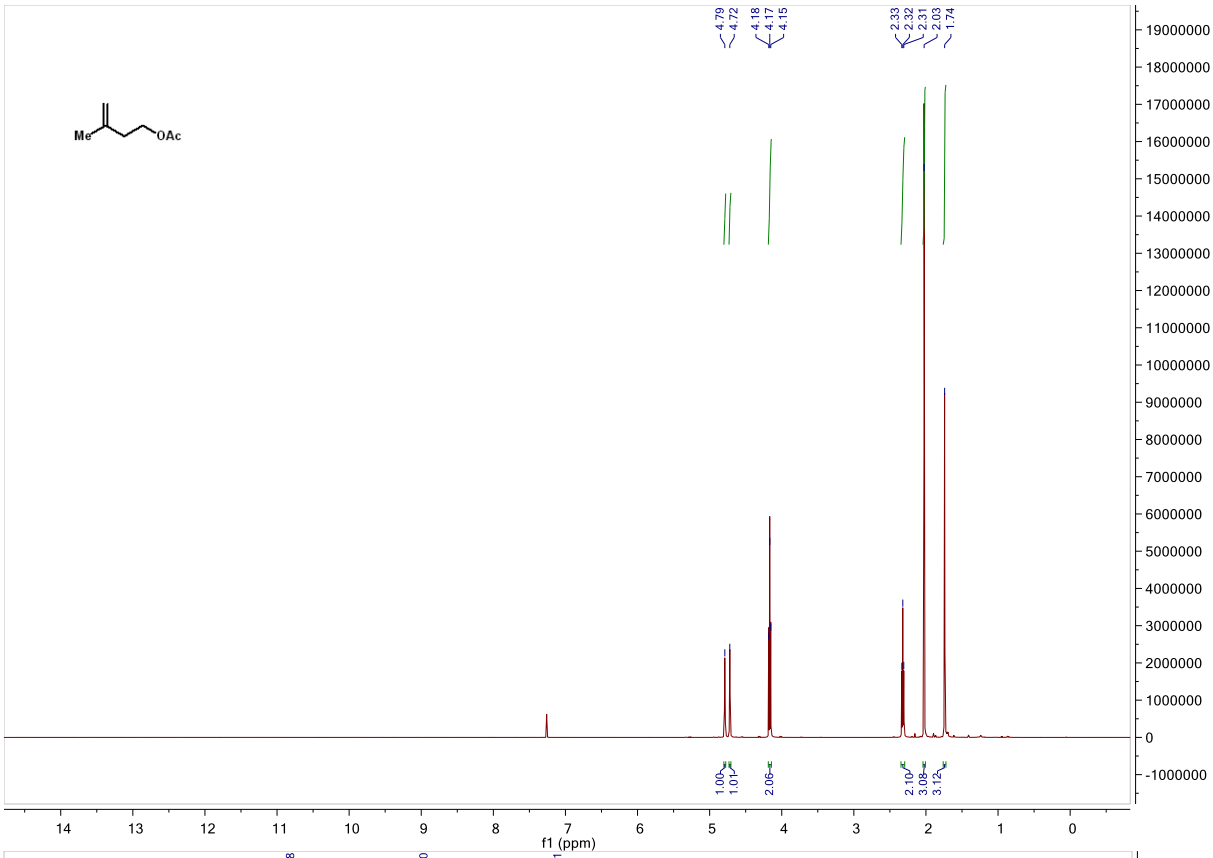

Ac
OTBS
f1 (ppm)

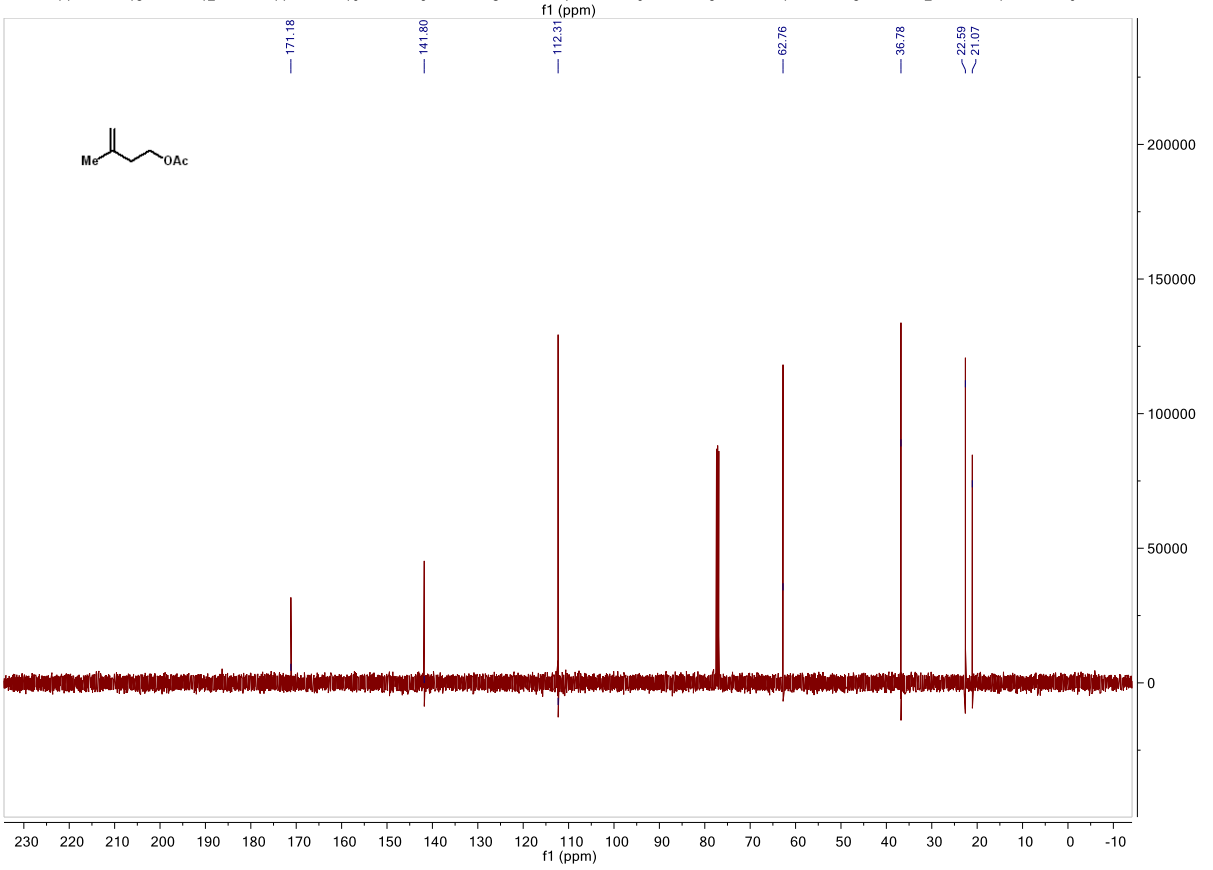

Ac
t-Bu
Me
2:1 dr
13:1 B:L
f1 (ppm)

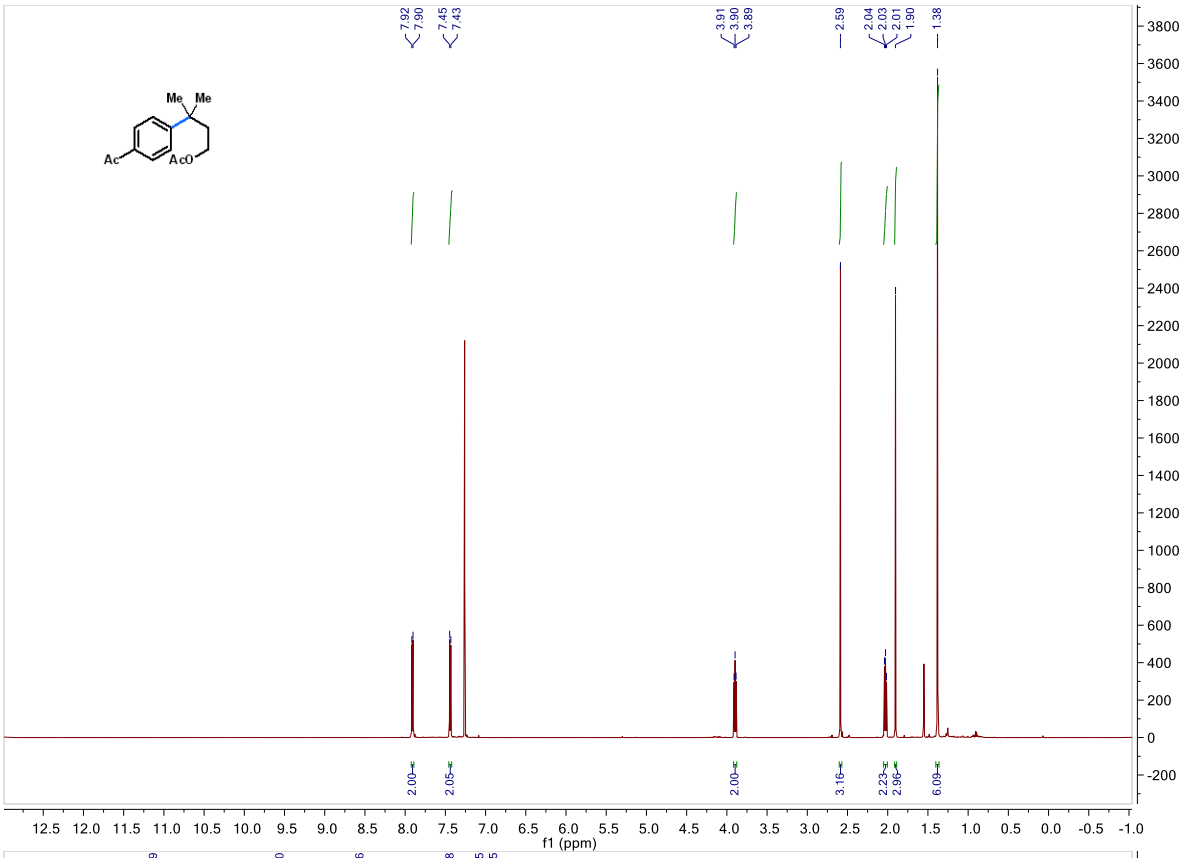

Ac
t-Bu
Me
2:1 dr
13:1 B:L
f1 (ppm)

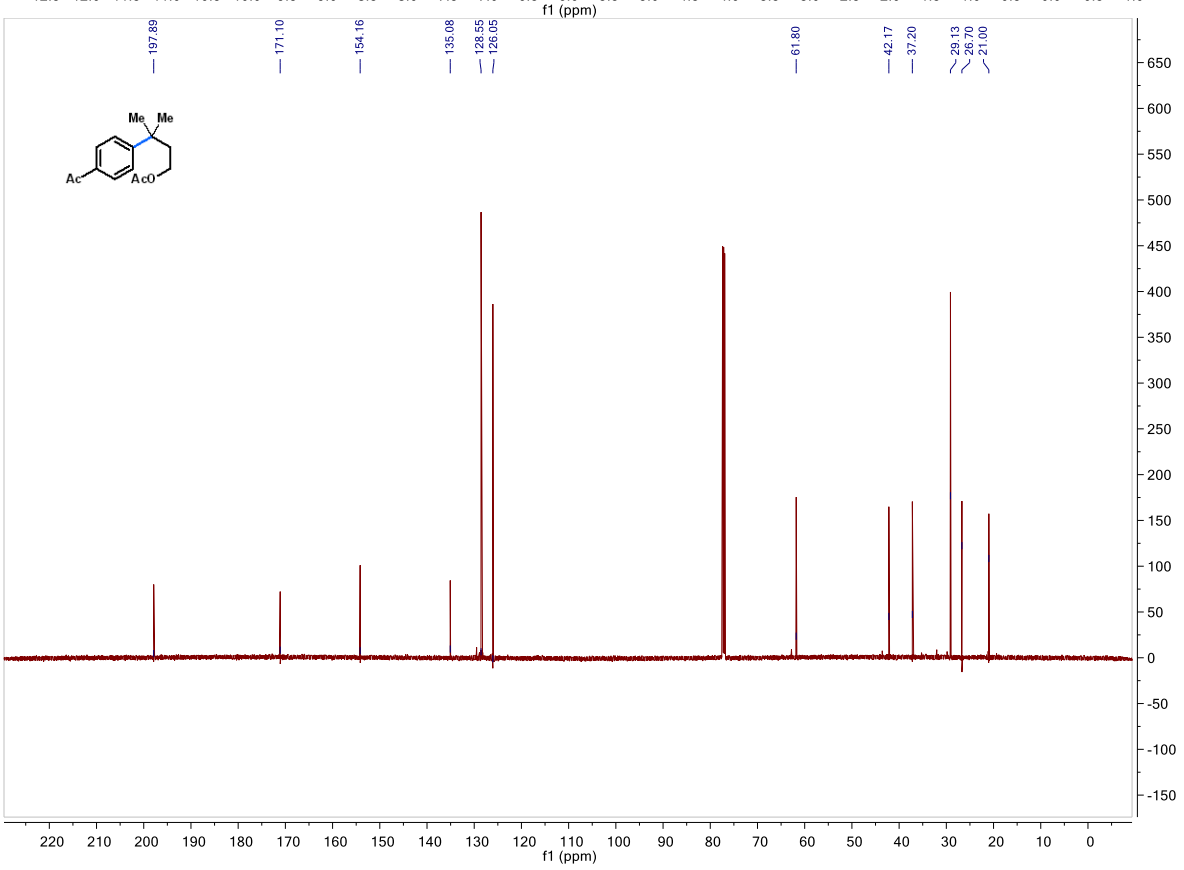

Me
Ac
4:1 B:L mixture
1.97
2.00
3.09
12.14
3.11
f1 (ppm)

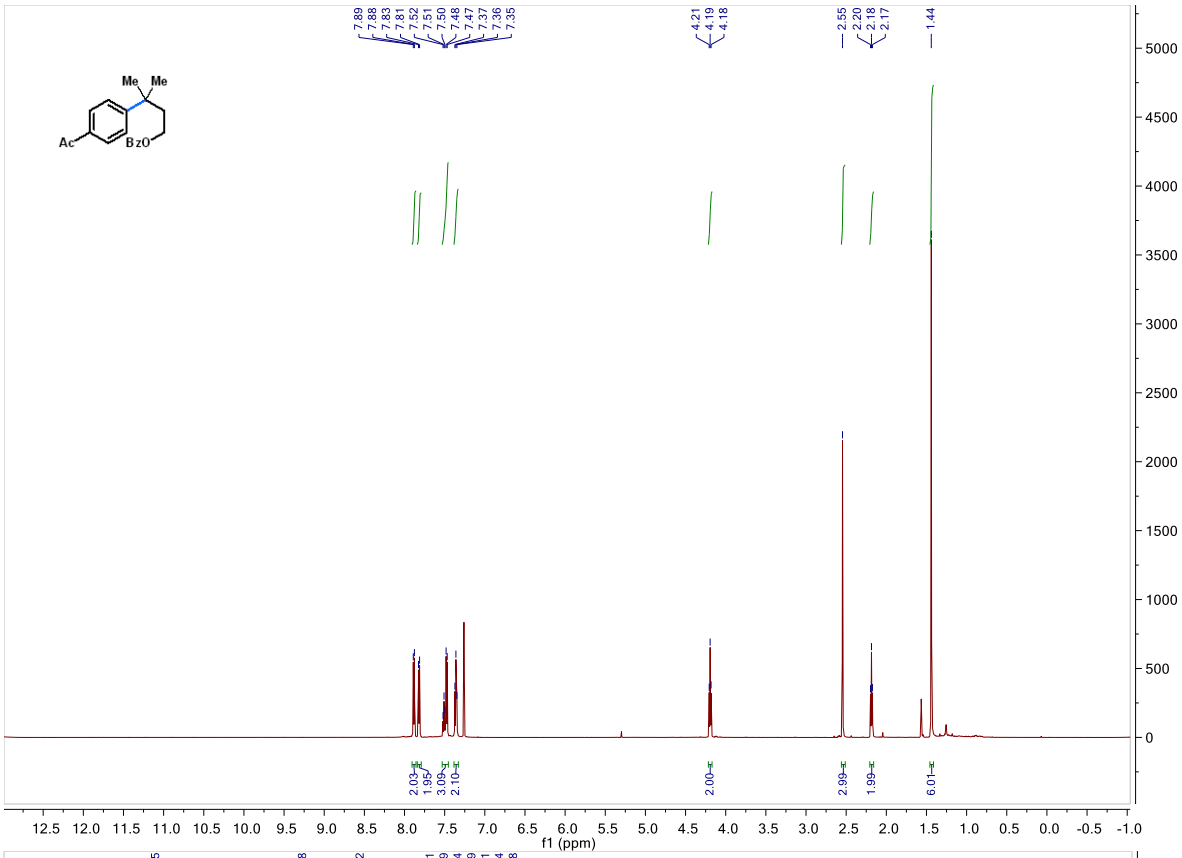

198.02
134.50
129.48
128.42
126.36
41.90
40.78
32.37
30.01
26.67
23.80
Me
Ac
4:1 B:L mixture
f1 (ppm)

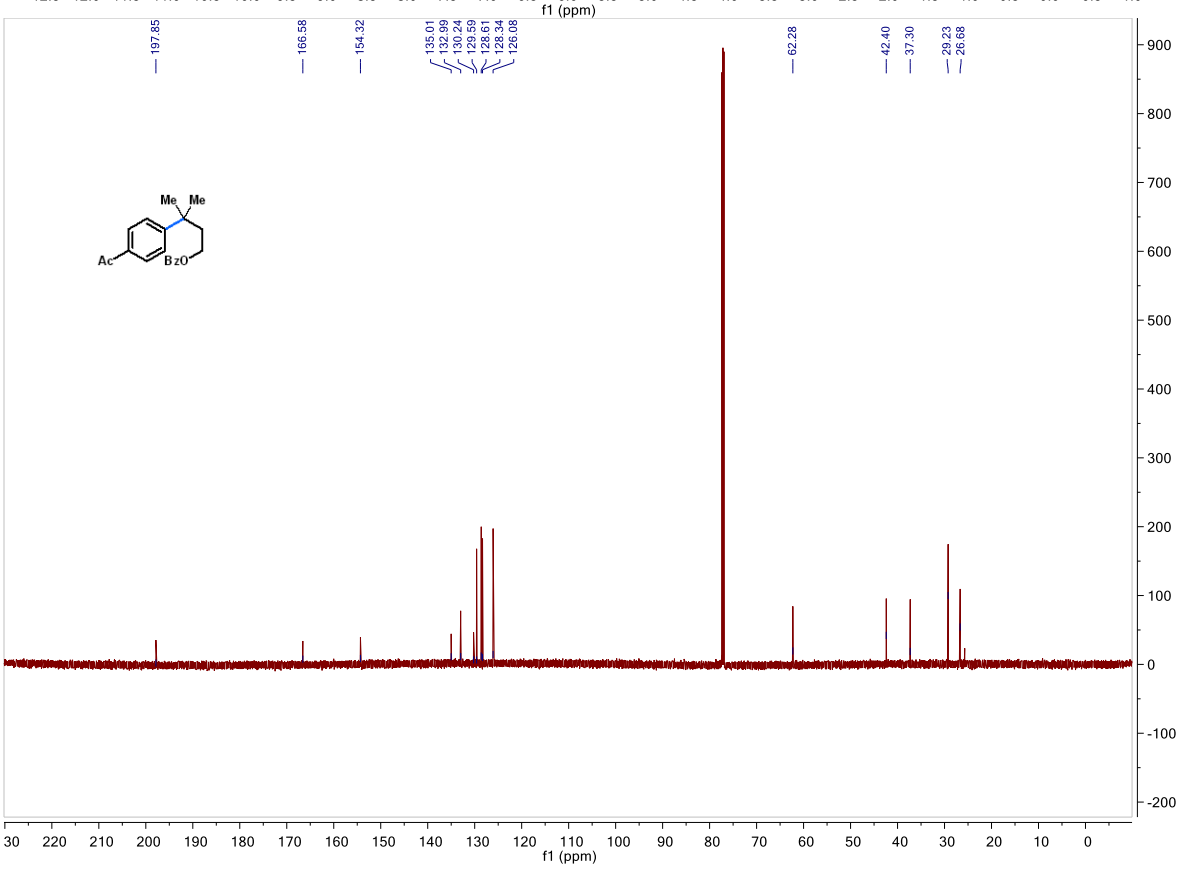

4.79
4.72
4.18
4.17
4.15
2.33
2.32
2.31
2.03
1.74
Me
OAc
1.00
1.01
2.06
2.10
3.08
3.12
f1 (ppm)

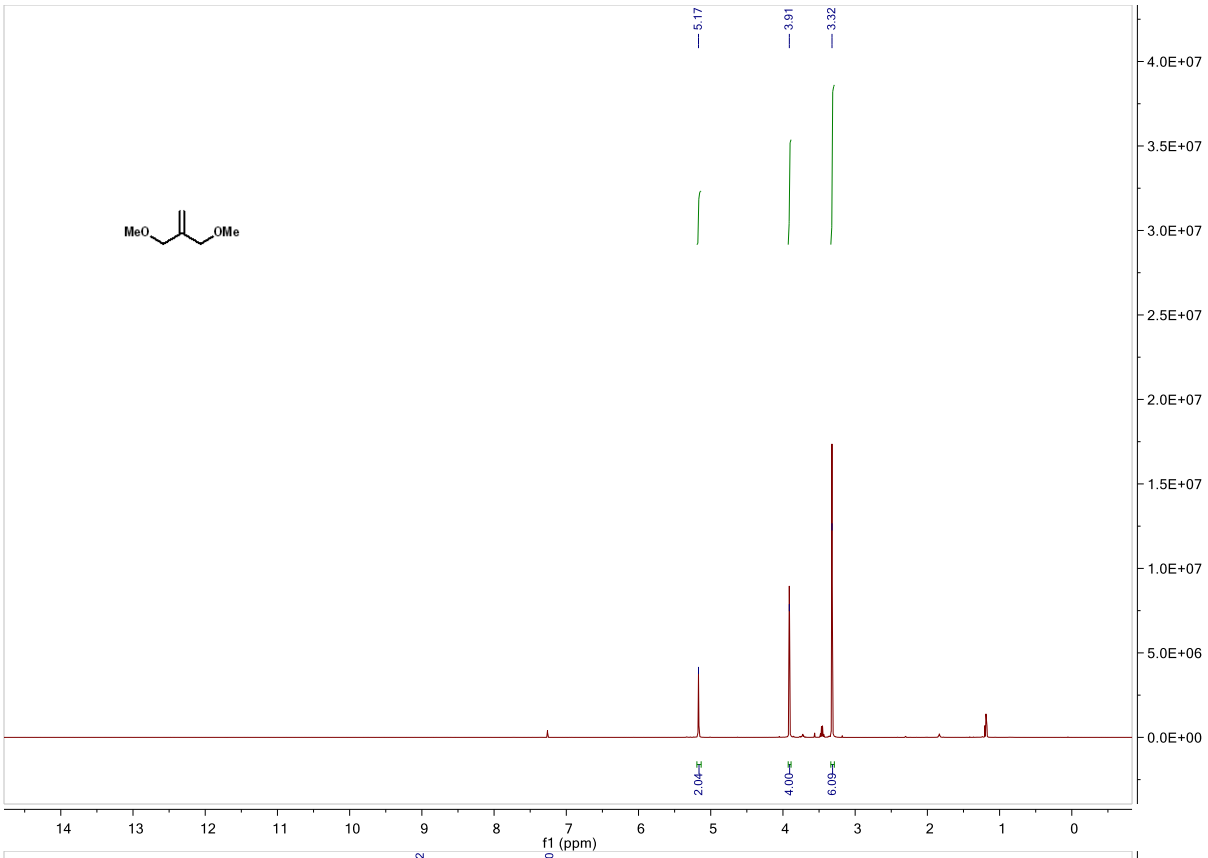

171.18
141.80
112.31
62.76
36.78
22.59
21.07
Me
OAc
f1 (ppm)

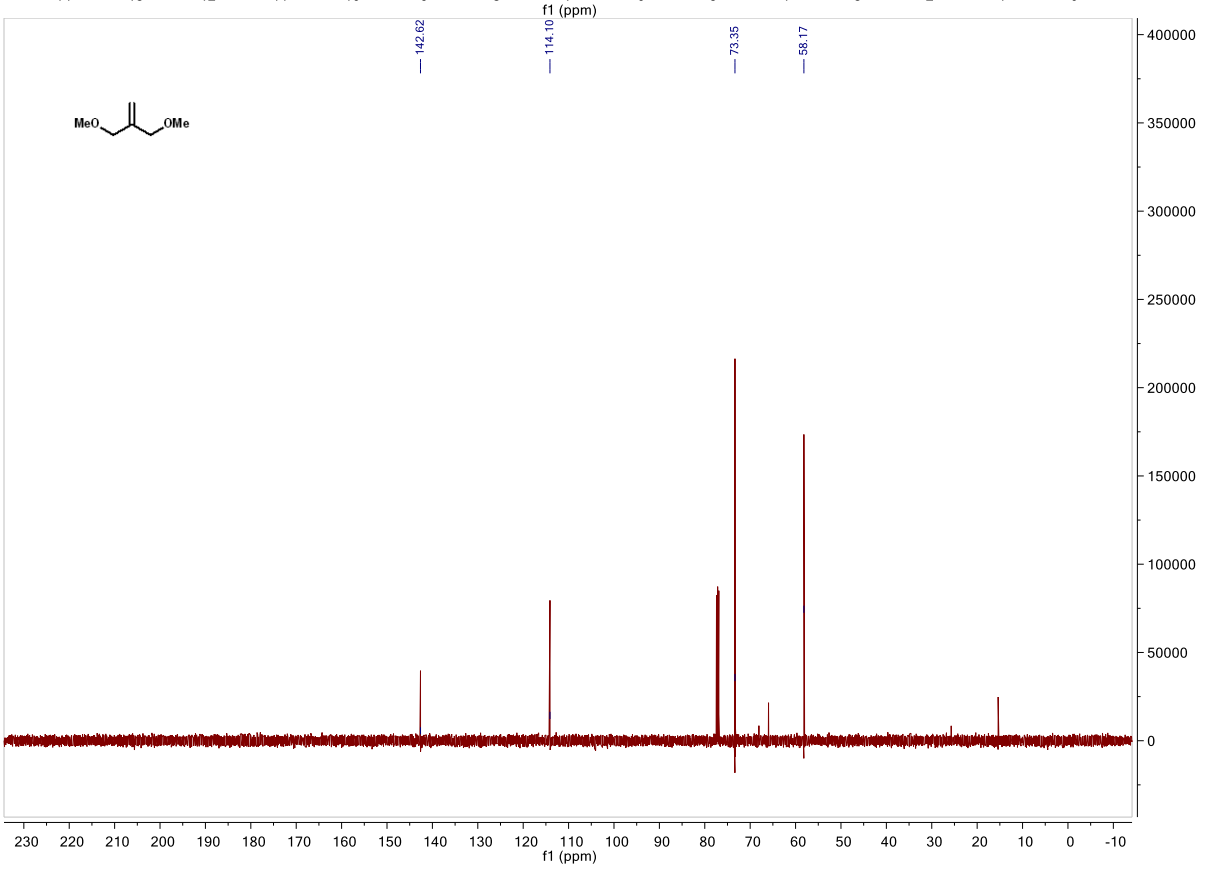

7.92
7.90
7.45
7.43
3.91
3.90
3.89
2.59
2.04
2.03
2.01
1.90
1.38
Me
Me
Ac
AcO
2.00
2.05
2.00
3.16
2.23
2.96
6.09
f1 (ppm)

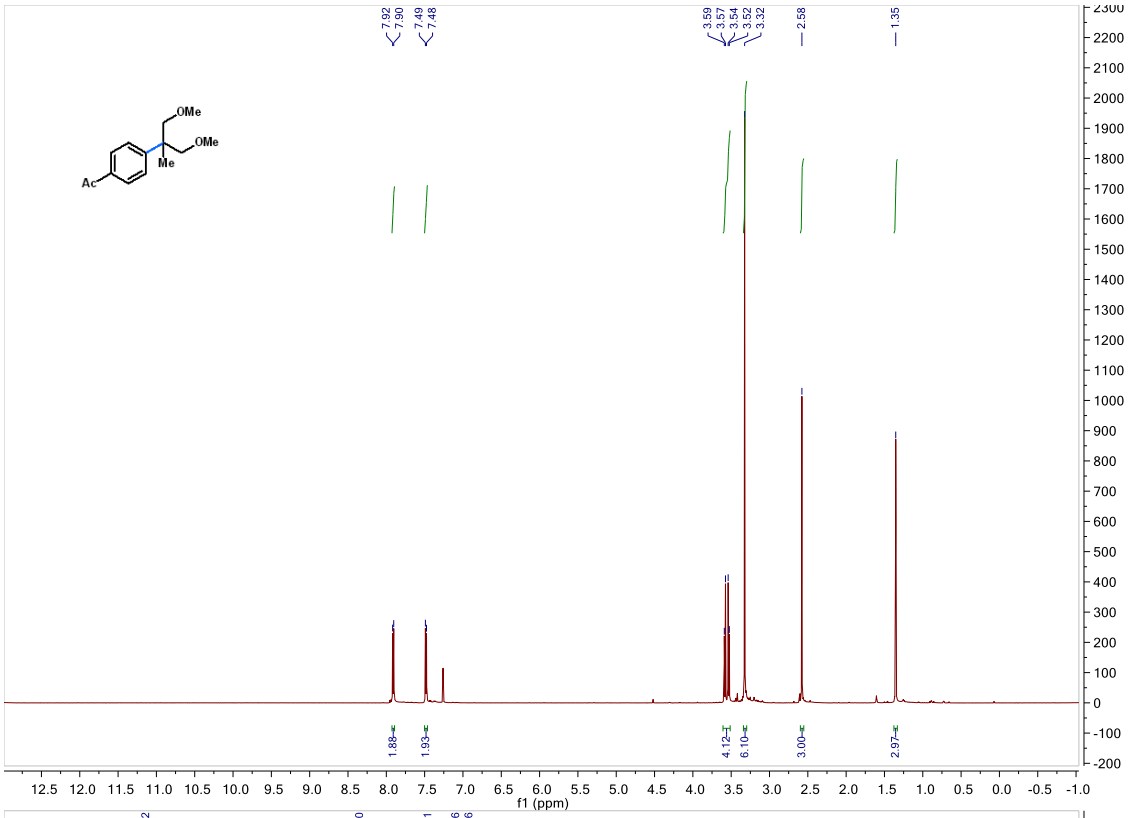

197.89
171.10
154.16
135.08
128.55
126.05
61.80
42.17
37.20
29.13
26.70
21.00
Me
Me
Ac
AcO
f1 (ppm)

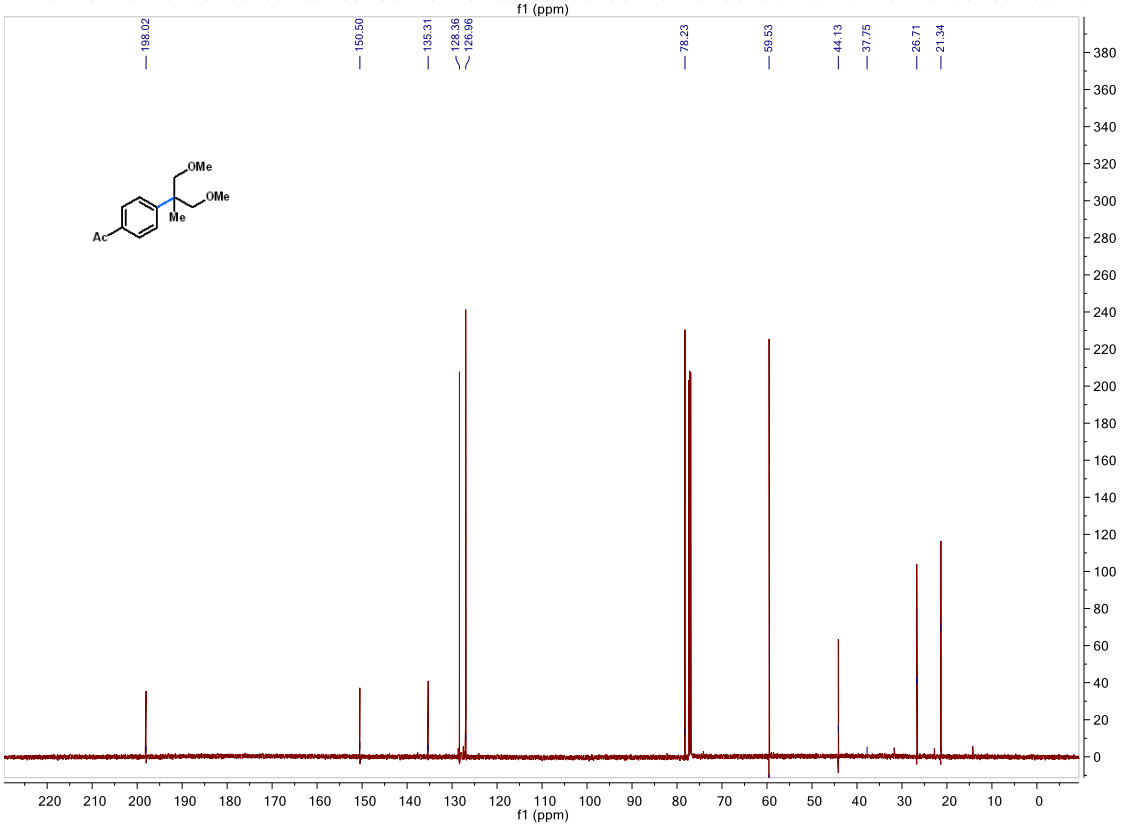

Me
Me
Ac
BzO
7.89
7.88
7.83
7.81
7.52
7.51
7.50
7.48
7.47
7.37
7.36
7.35
4.21
4.19
4.18
2.55
2.20
2.18
2.17
1.44
2.03
1.95
3.09
2.10
2.00
2.99
1.99
6.01
f1 (ppm)

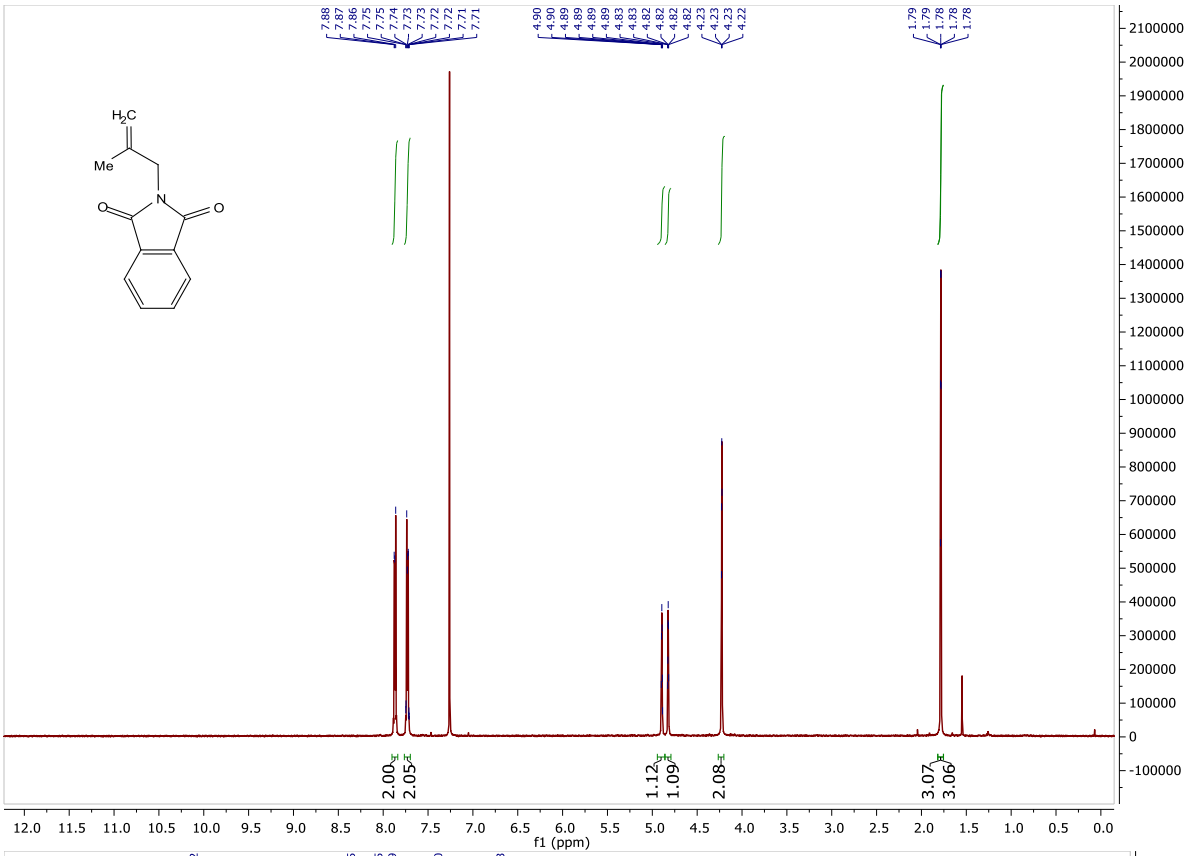

Me
Me
Ac
BzO
197.85
166.58
154.32
135.01
132.99
130.24
129.59
128.61
128.34
126.08
62.28
42.40
37.30
29.23
26.68
f1 (ppm)

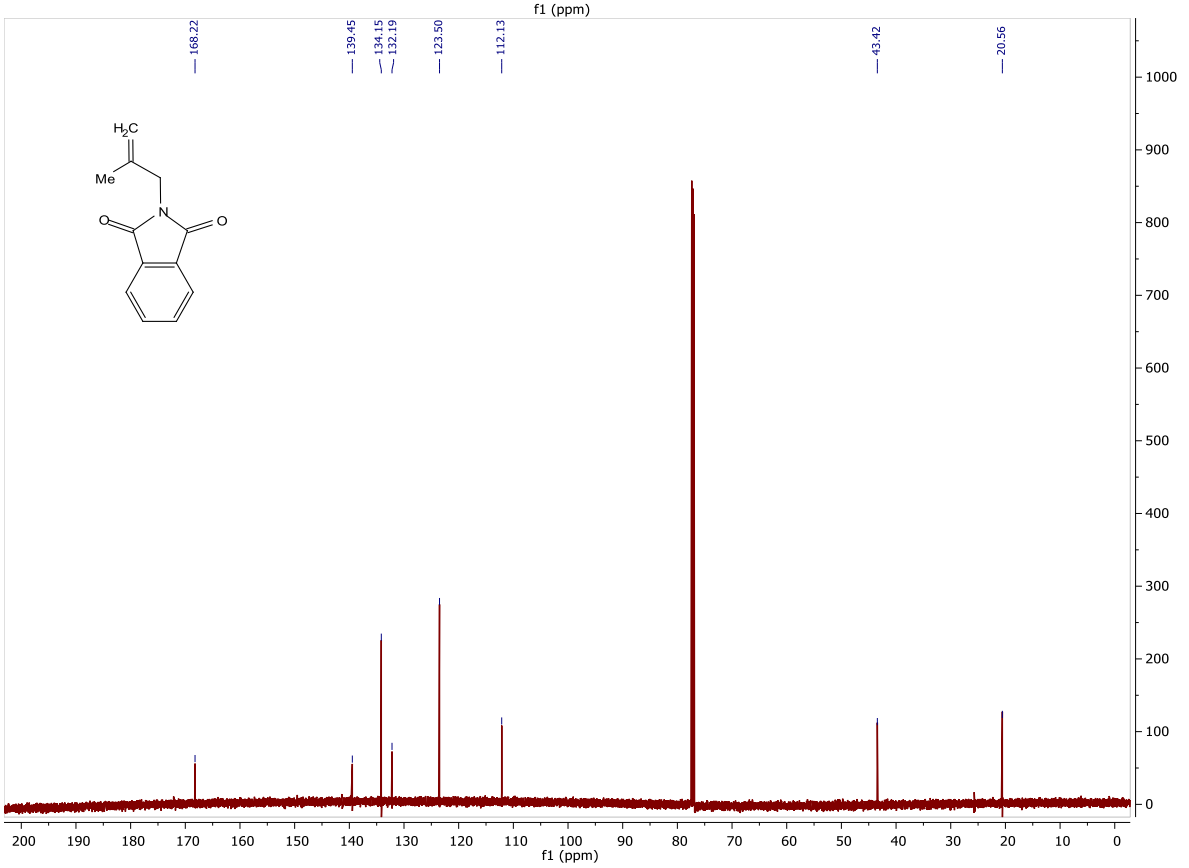

5.17
3.91
3.32
MeO
OMe
2.04
4.00
6.09
f1 (ppm)

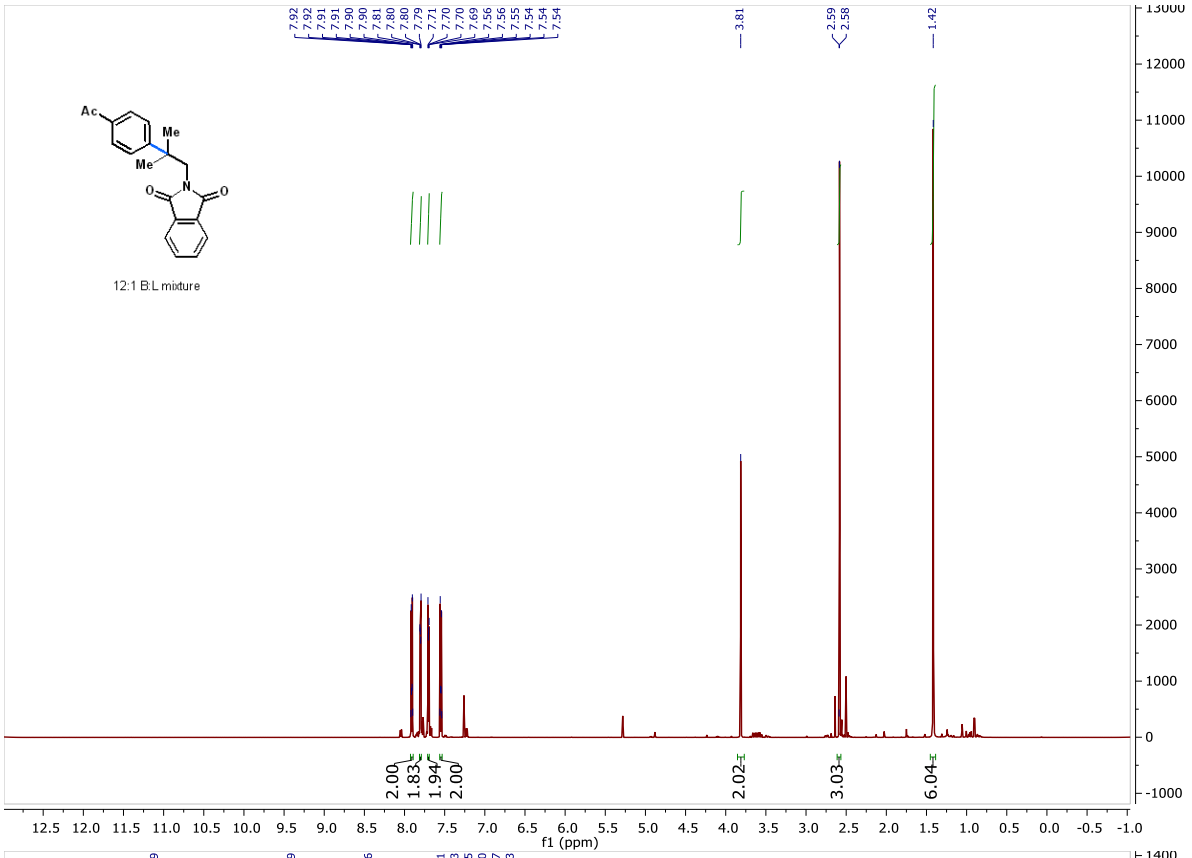

142.62
114.10
73.35
58.17
MeO
OMe
f1 (ppm)

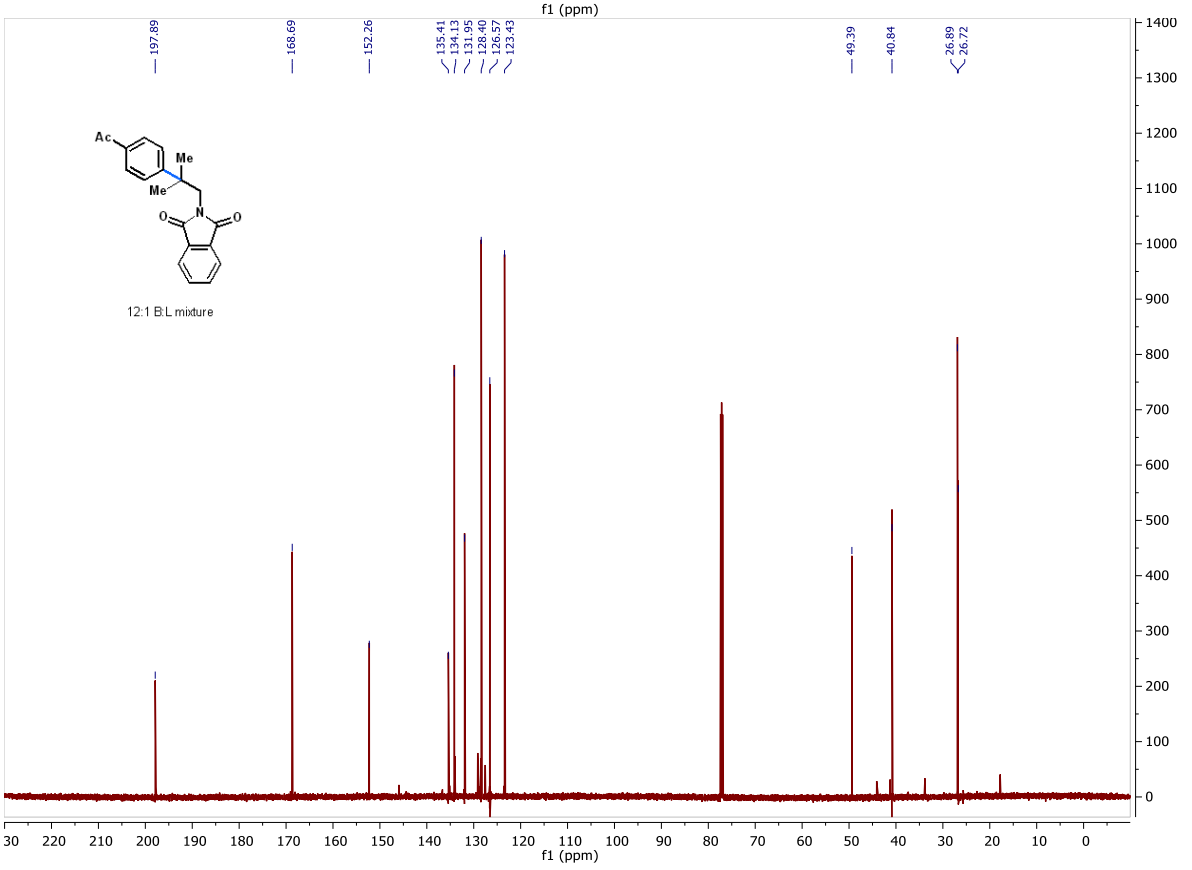

7.92
7.90
7.49
7.48
3.59
3.57
3.54
3.52
3.32
2.58
1.35
OMe
OMe
Me
Ac
1.88
1.93
4.12
6.10
3.00
2.97
f1 (ppm)

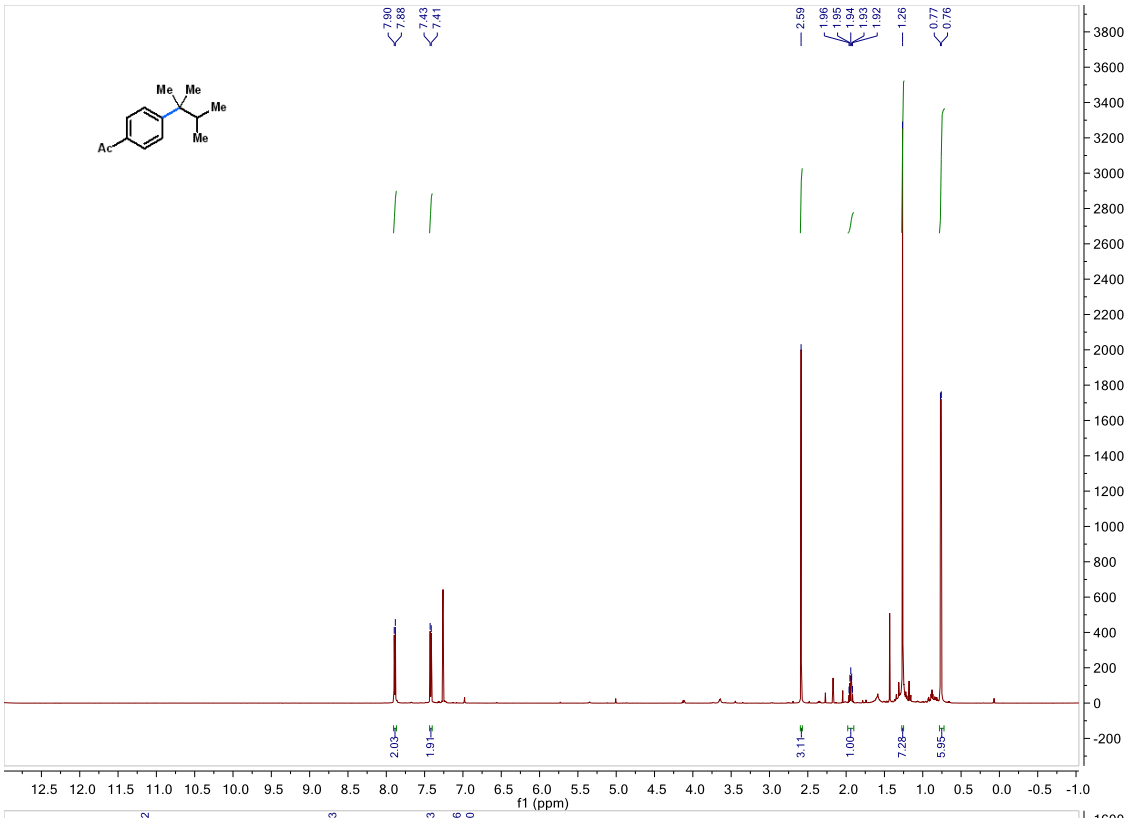

198.02
150.50
135.31
128.36
126.96
78.23
59.53
44.13
37.75
26.71
21.34
OMe
OMe
Me
Ac
f1 (ppm)

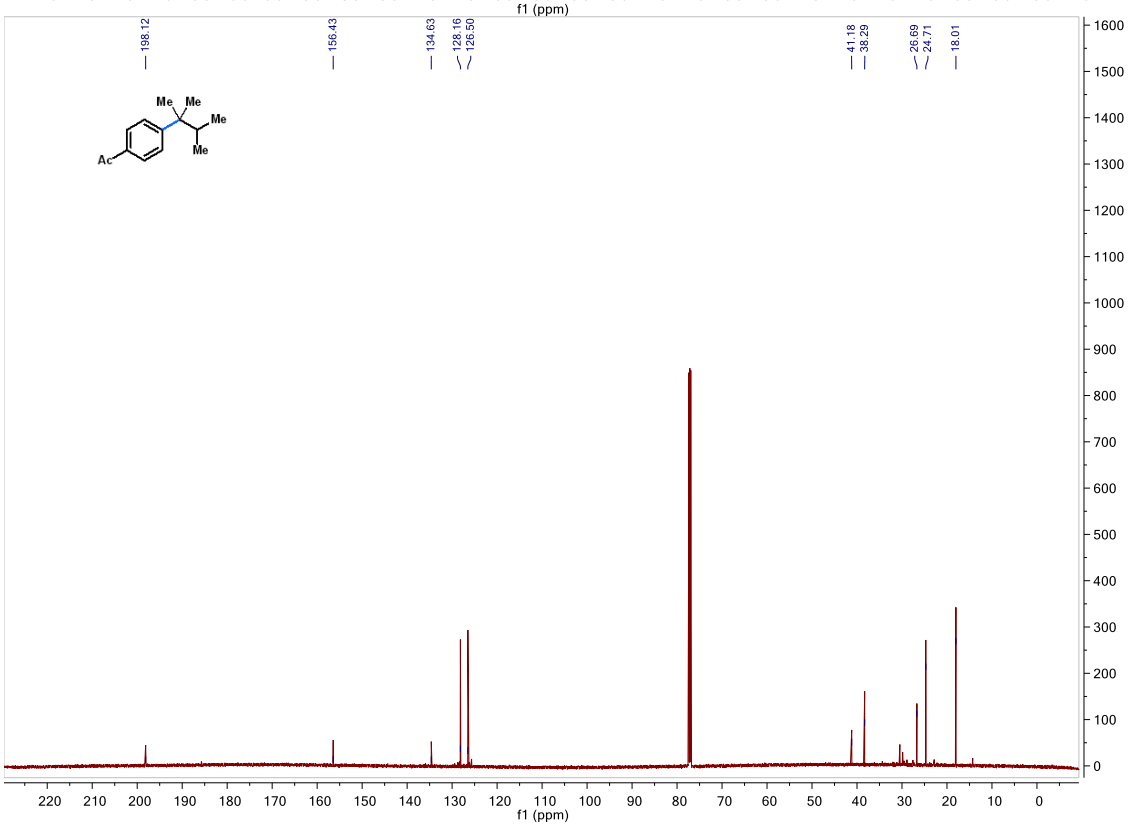

7.88
7.87
7.86
7.75
7.74
7.73
7.73
7.72
7.72
7.71
7.71
4.90
4.90
4.89
4.89
4.89
4.89
4.83
4.83
4.82
4.82
4.82
4.82
4.23
4.23
4.23
4.22
1.79
1.79
1.78
1.78
1.78
1.78
H2C
Me
N
O
O
2.00
2.05
1.12
1.09
2.08
3.07
3.06
f1 (ppm)

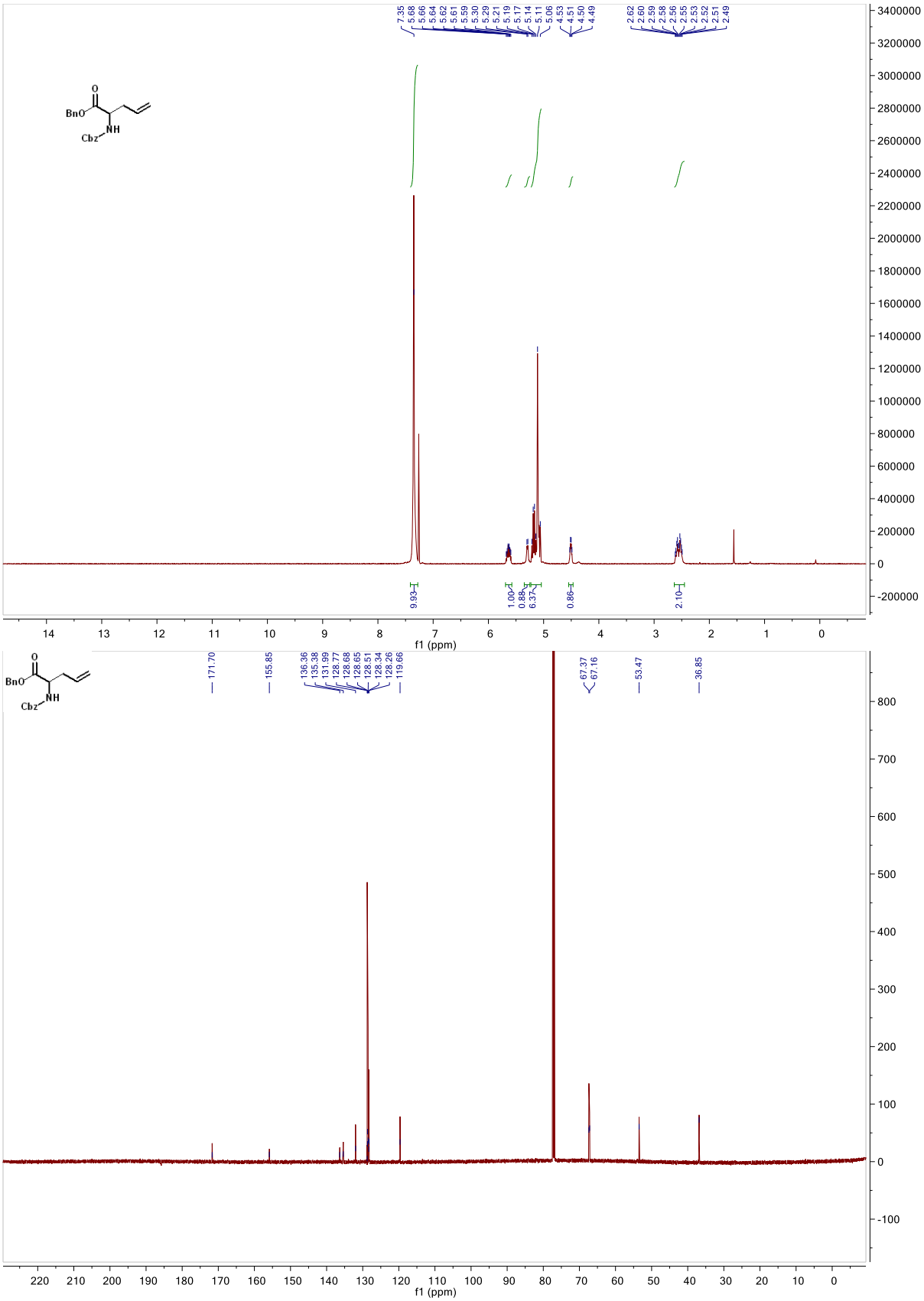

168.22
139.45
134.15
132.19
123.50
112.13
43.42
20.56
H2C
Me
N
O
O
f1 (ppm)

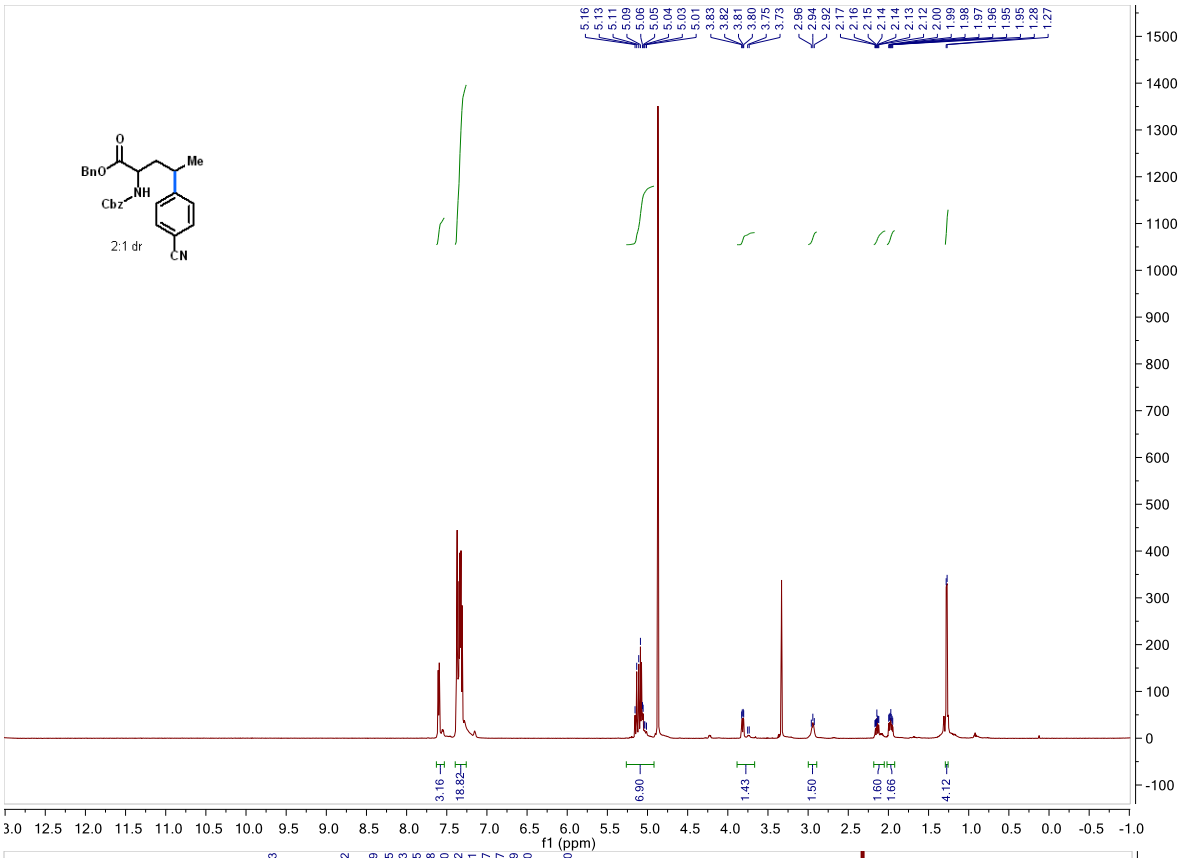

7.92
7.92
7.91
7.91
7.90
7.90
7.81
7.80
7.80
7.79
7.71
7.70
7.70
7.69
7.56
7.56
7.55
7.54
7.54
7.54
3.81
2.59
2.58
1.42
Ac
Me
Me
O
N
O
12:1 B:L mixture
2.00
1.83
1.94
2.00
2.02
3.03
6.04
f1 (ppm)

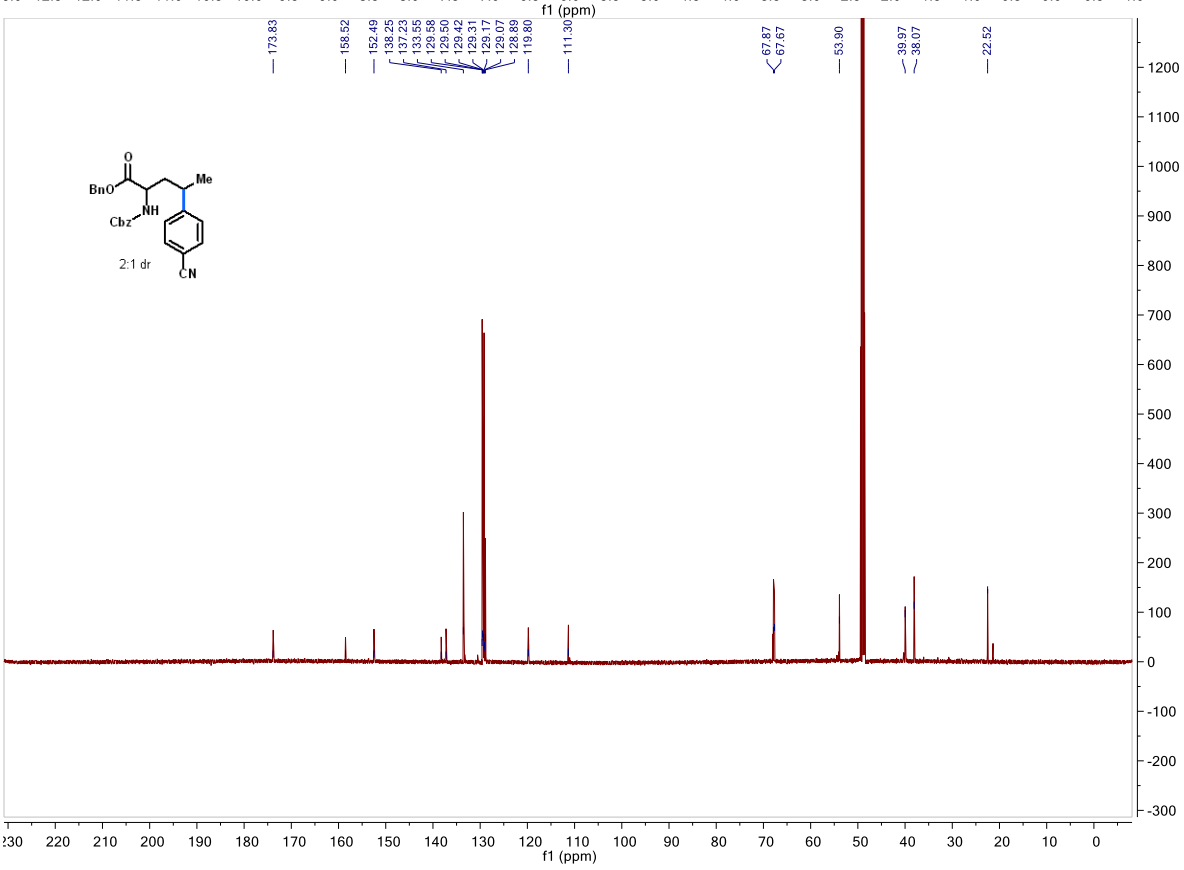

197.89
168.69
152.26
135.41
134.13
131.95
128.40
126.57
123.43
49.39
40.84
26.89
26.72
Ac
Me
Me
O
N
O
12:1 B:L mixture
f1 (ppm)

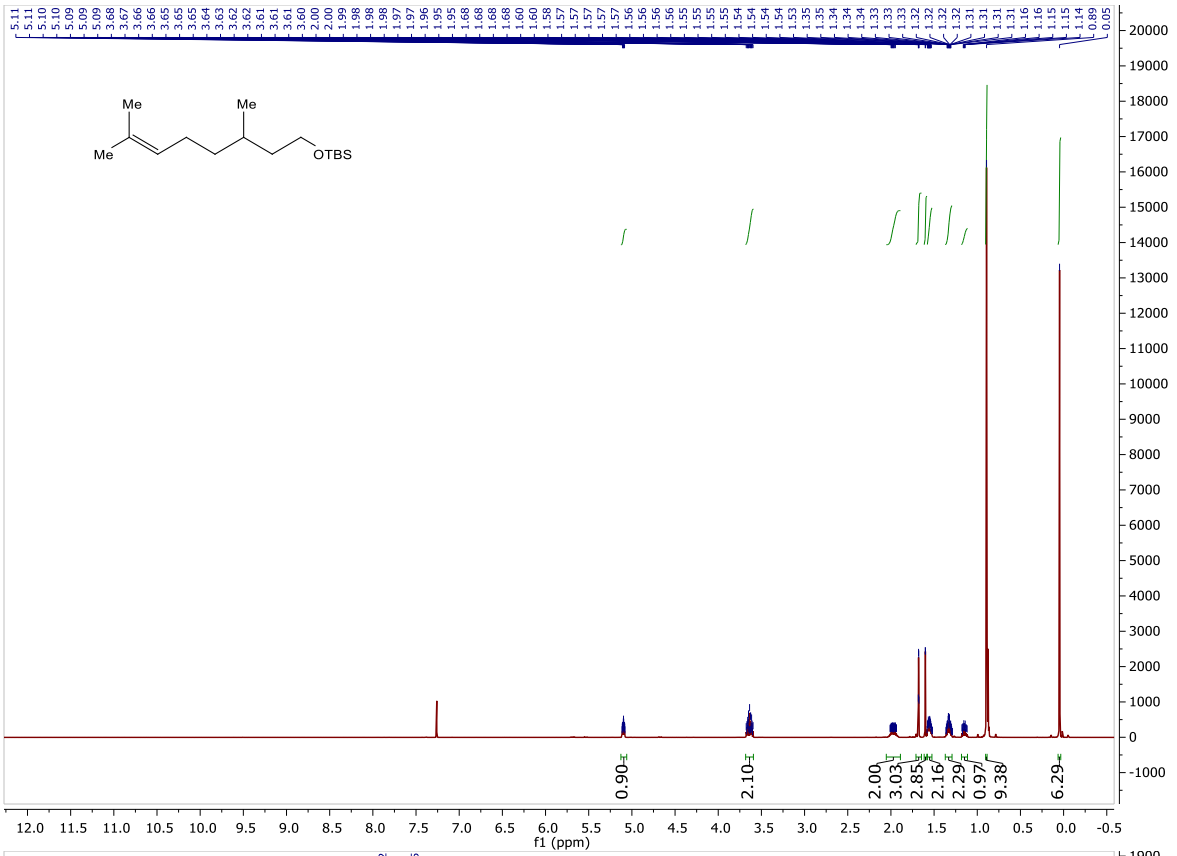

7.90
7.88
7.43
7.41
2.59
1.96
1.95
1.94
1.93
1.92
1.26
0.77
0.76
Me
Me
Me
Me
Ac
2.03
1.91
3.11
1.00
7.28
5.95
f1 (ppm)

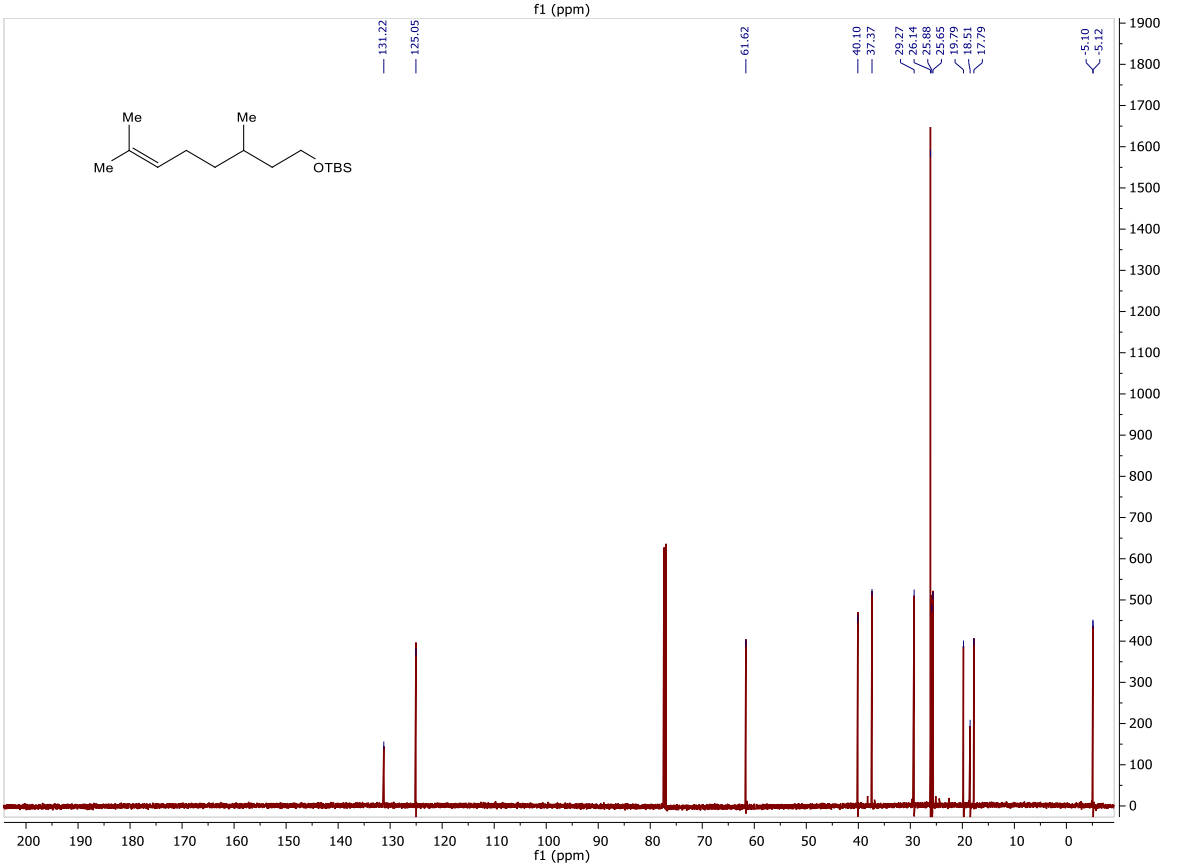

198.12
156.43
134.63
128.16
126.50
41.18
38.29
26.69
24.71
18.01
Me
Me
Me
Me
Ac
f1 (ppm)

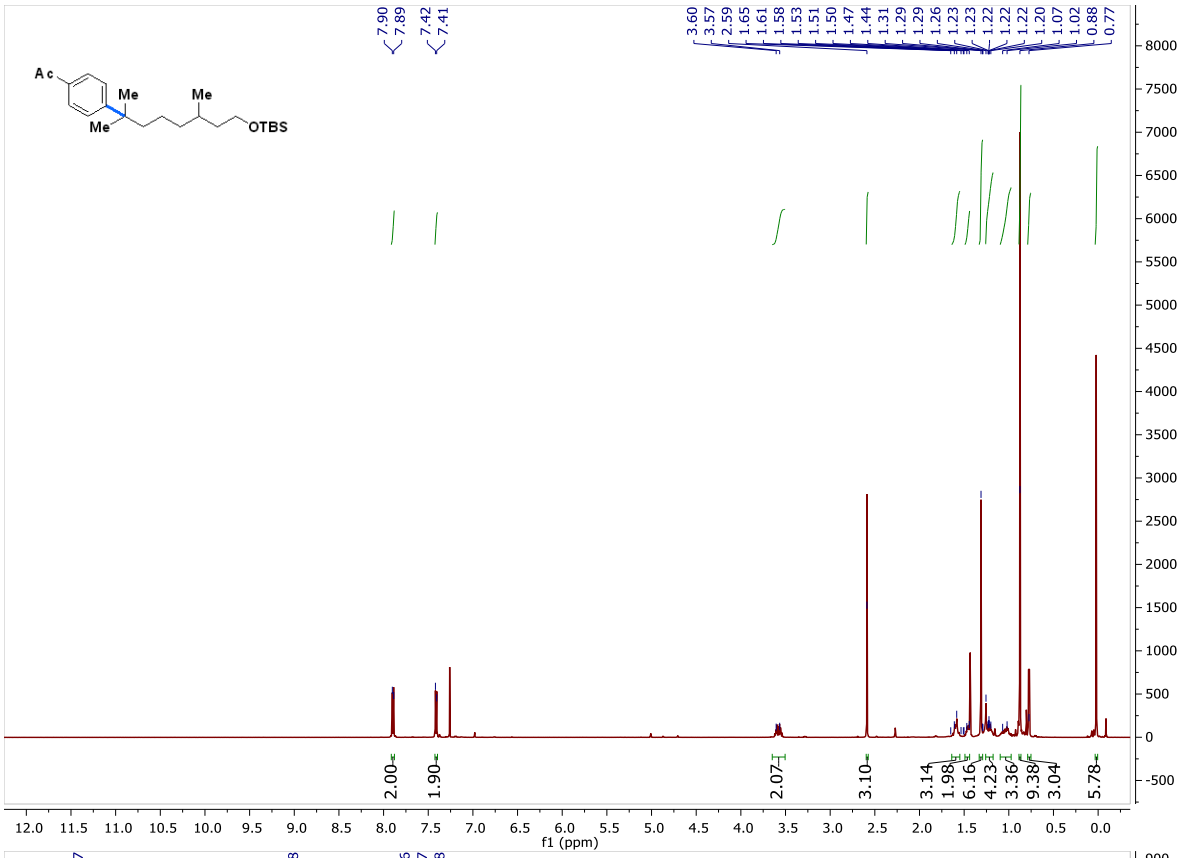

7.35
5.68
5.66
5.64
5.62
5.61
5.59
5.30
5.29
5.21
5.19
5.17
5.14
5.11
5.06
4.53
4.51
4.50
4.49
2.62
2.60
2.59
2.58
2.56
2.55
2.53
2.52
2.51
2.49
9.93
1.00
0.88
6.37
0.86
2.10
f1 (ppm)
171.70
155.85
136.36
135.38
131.99
128.77
128.68
128.65
128.51
128.34
128.26
119.66
67.37
67.16
53.47
36.85
f1 (ppm)

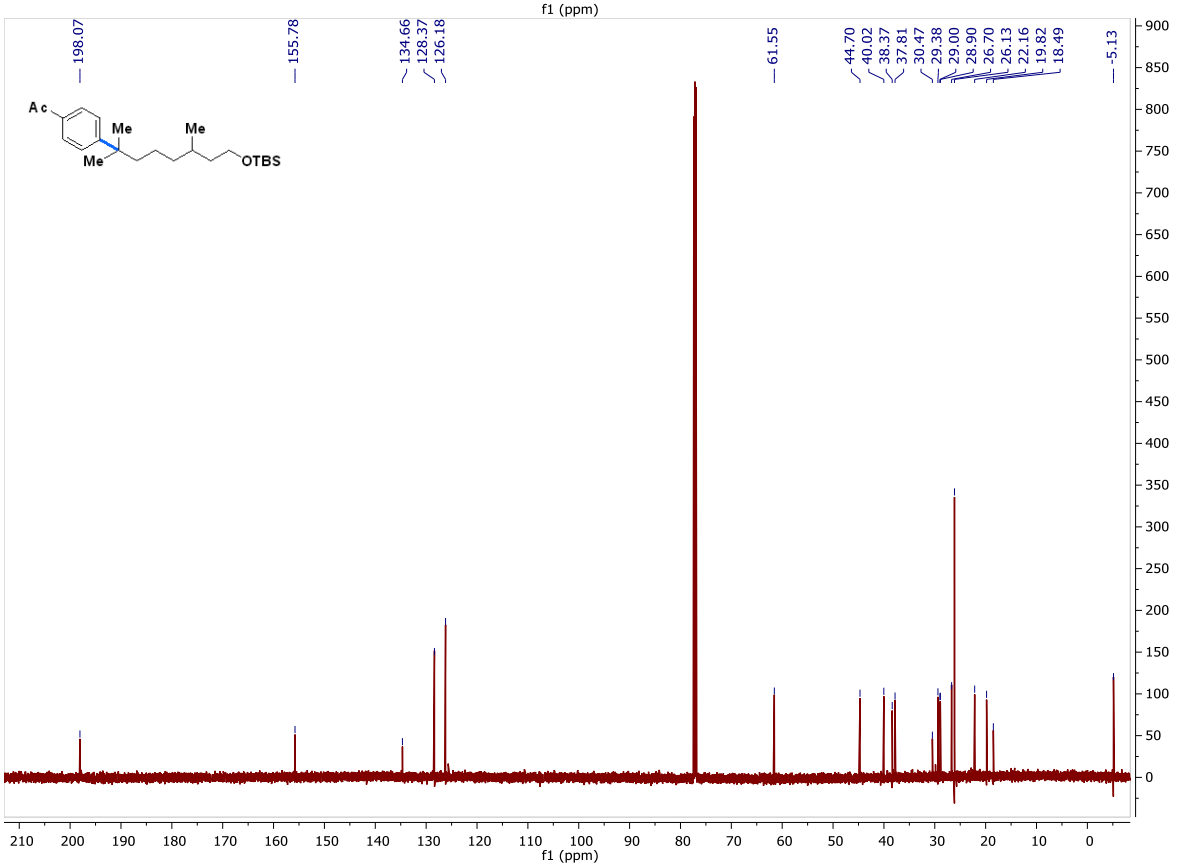

5.16
5.13
5.11
5.09
5.06
5.05
5.04
5.03
5.01
3.83
3.82
3.81
3.80
3.75
3.73
2.96
2.94
2.92
2.17
2.16
2.15
2.14
2.14
2.13
2.12
2.00
1.99
1.98
1.97
1.96
1.95
1.95
1.28
1.27
BnO
Me
NH
Cbz
2:1 dr
CN
3.16
18.82
6.90
1.43
1.50
1.60
1.66
4.12
f1 (ppm)

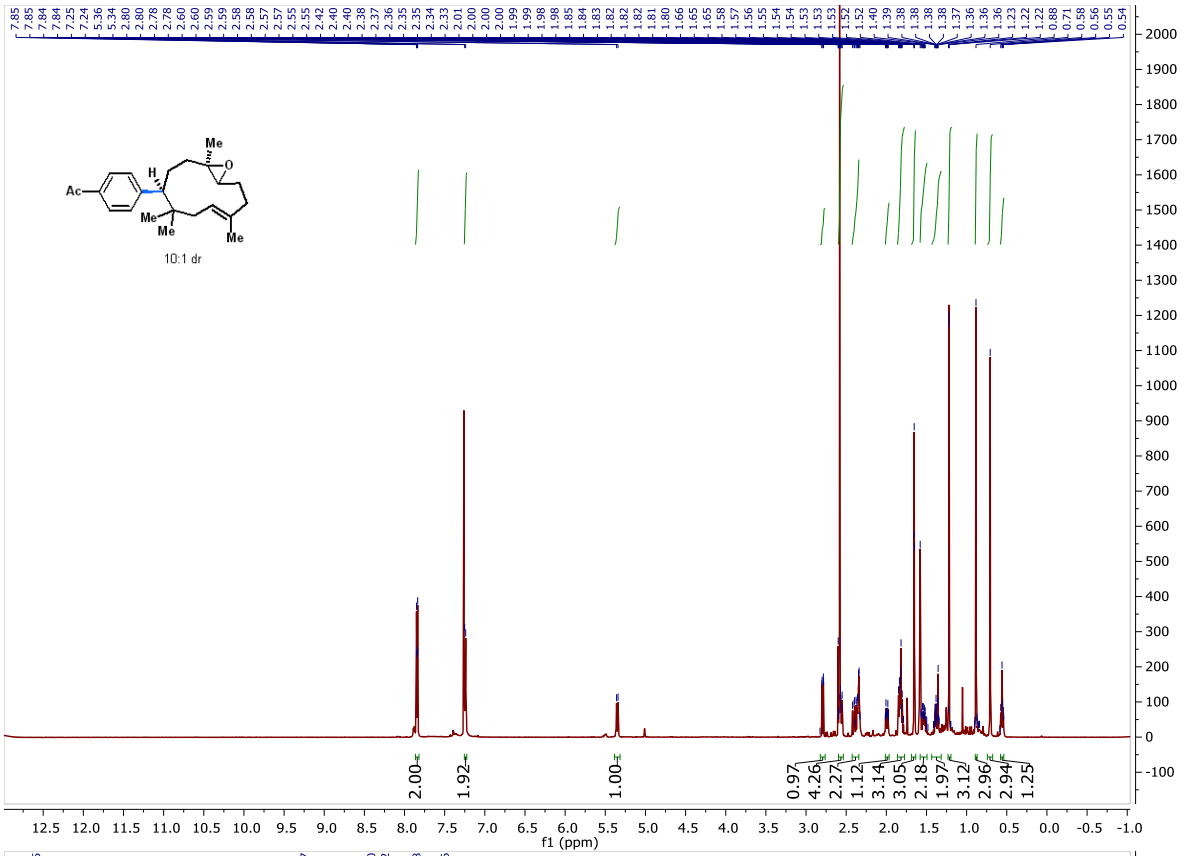

173.83
158.52
152.49
138.25
137.23
133.55
129.58
129.50
129.42
129.31
129.17
129.07
128.89
119.80
111.30
67.87
67.67
53.90
39.97
38.07
22.52
BnO
Me
NH
Cbz
2:1 dr
CN
f1 (ppm)

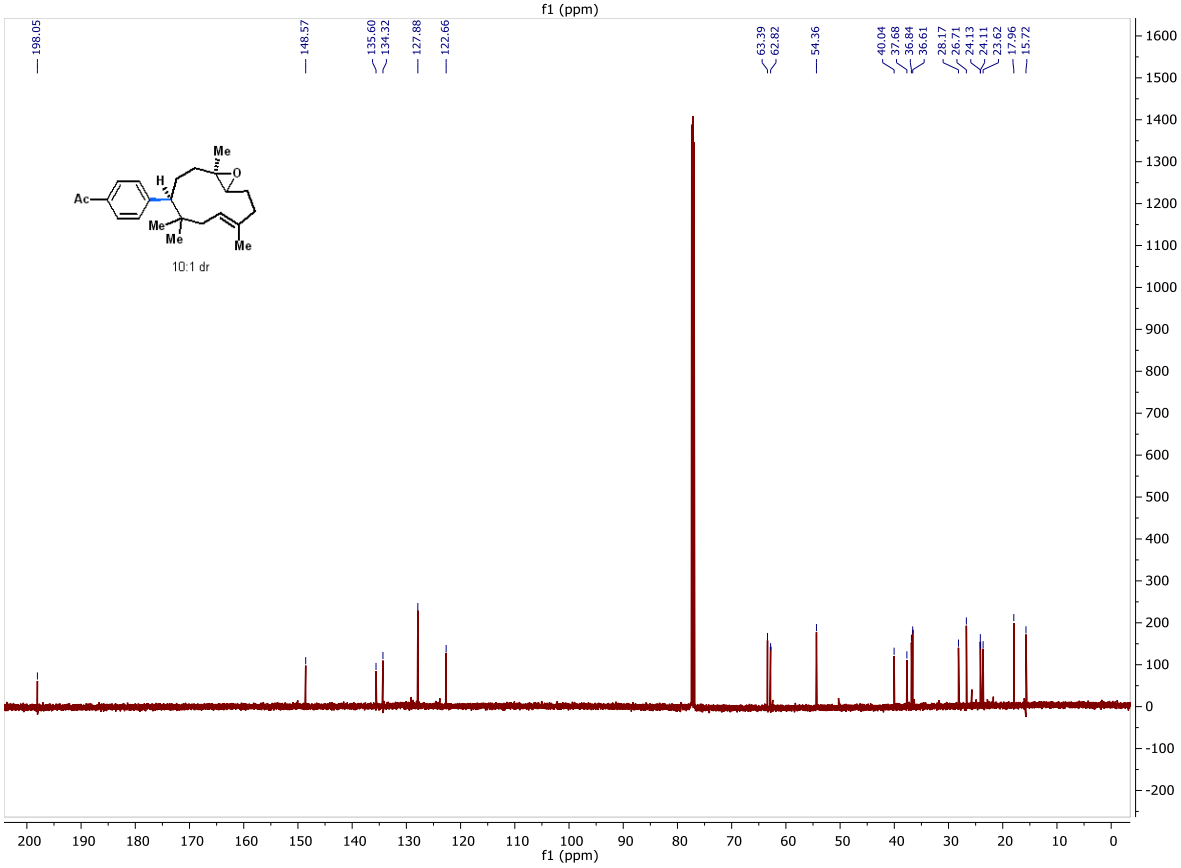

Me
Me
Me
OTBS
0.90
2.10
2.00
3.03
2.85
2.16
2.29
0.97
9.38
6.29
f1 (ppm)

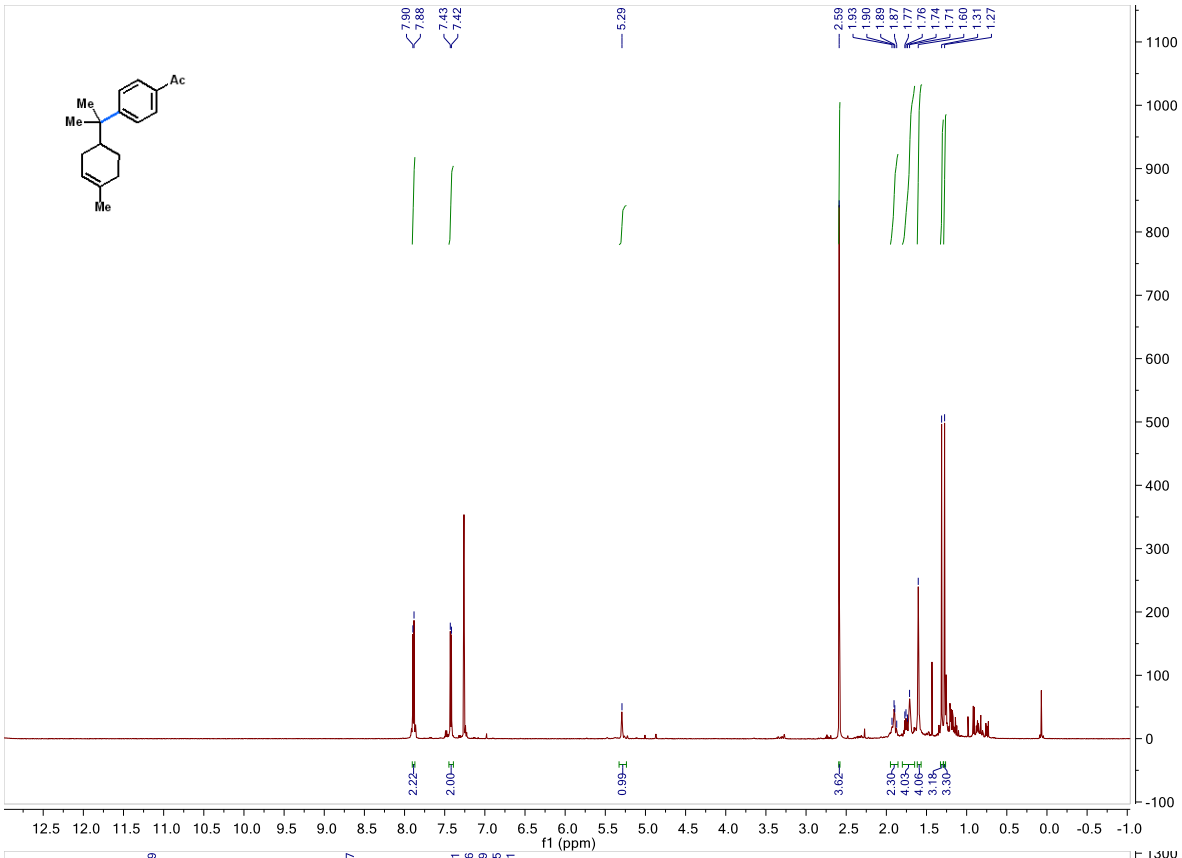

Me
Me
Me
OTBS
131.22
125.05
61.62
40.10
37.37
29.27
26.14
25.88
25.65
19.79
18.51
17.79
-5.10
-5.12
f1 (ppm)

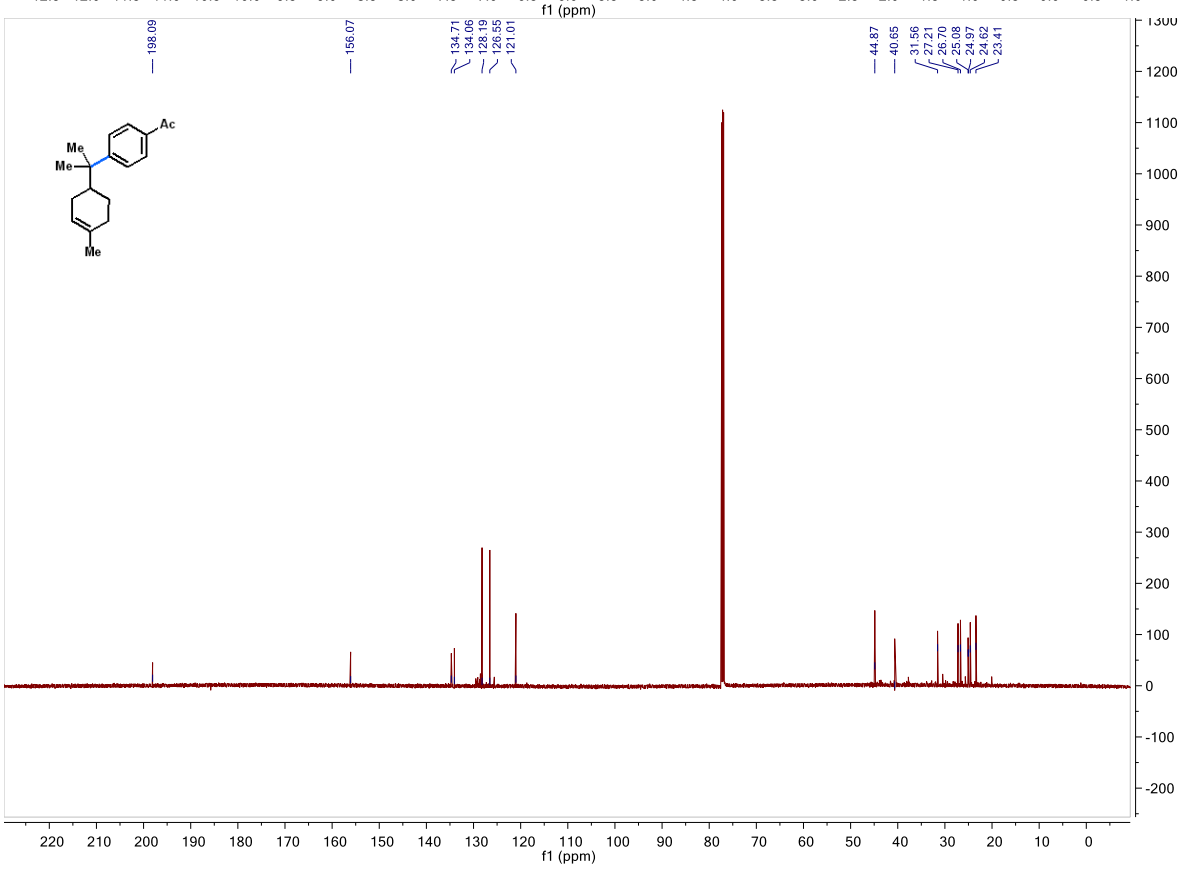

Ac
Me
Me
Me
OTBS
7.90
7.89
7.42
7.41
3.60
3.57
2.59
1.65
1.61
1.58
1.53
1.51
1.50
1.47
1.44
1.31
1.29
1.29
1.26
1.23
1.23
1.22
1.22
1.22
1.20
1.07
1.02
0.88
0.77
2.00
1.90
2.07
3.10
3.14
1.98
6.16
4.23
3.36
9.38
3.04
5.78
f1 (ppm)

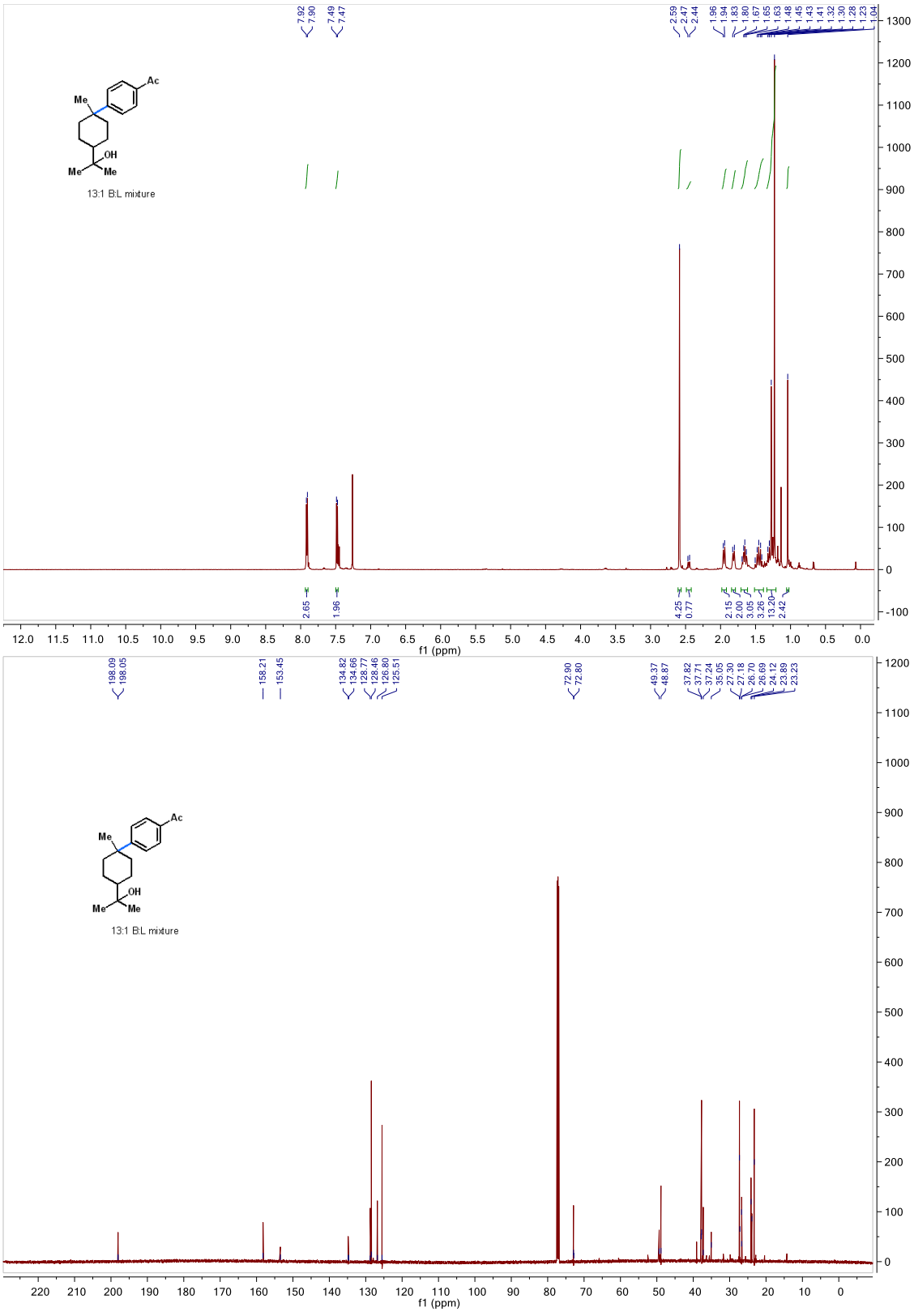

Ac
Me
Me
Me
OTBS
198.07
155.78
134.66
128.37
126.18
61.55
44.70
40.02
38.37
37.81
30.47
29.38
29.00
28.90
26.70
26.13
22.16
19.82
18.49
-5.13
f1 (ppm)

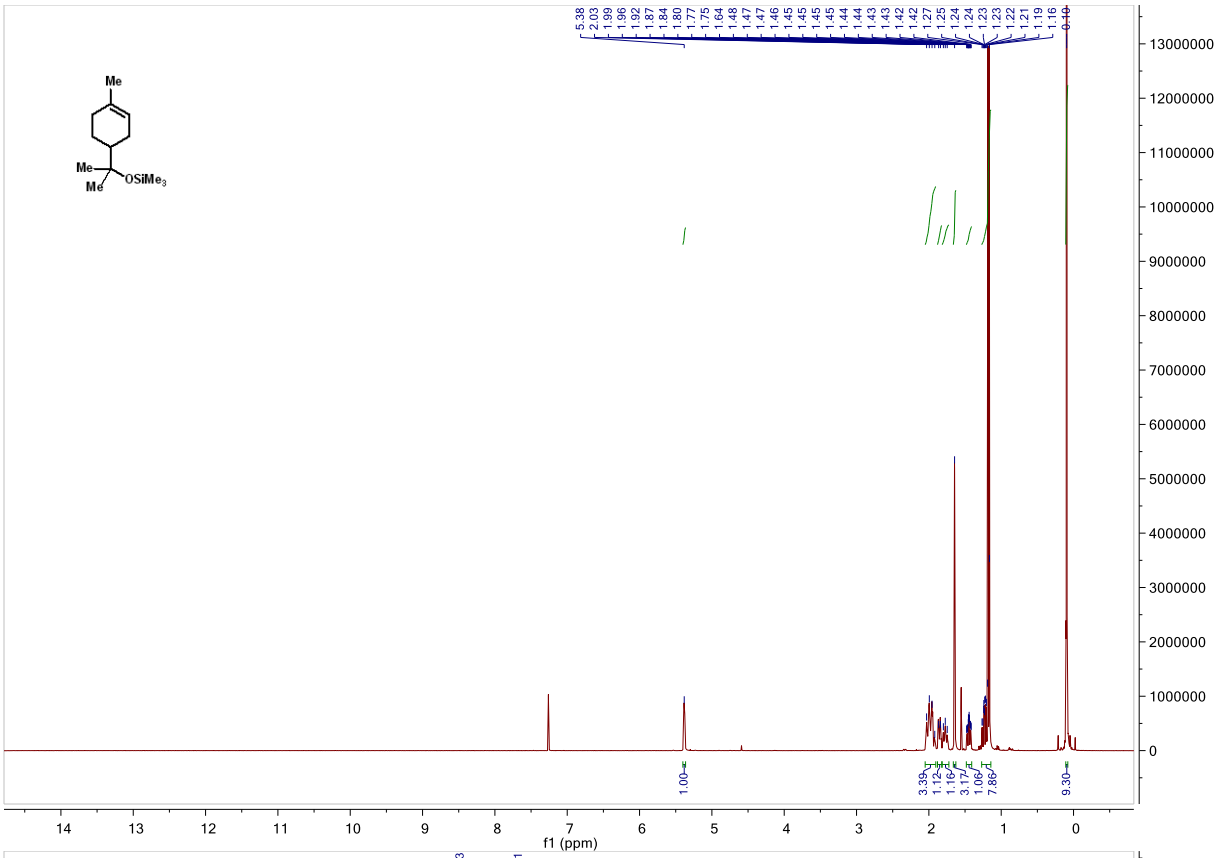

Me
O
H
Ac
Me
Me
Me
10:1 dr
2.00
1.92
1.00
0.97
4.26
2.27
1.12
3.14
3.05
2.18
1.97
3.12
2.96
2.94
1.25
f1 (ppm)

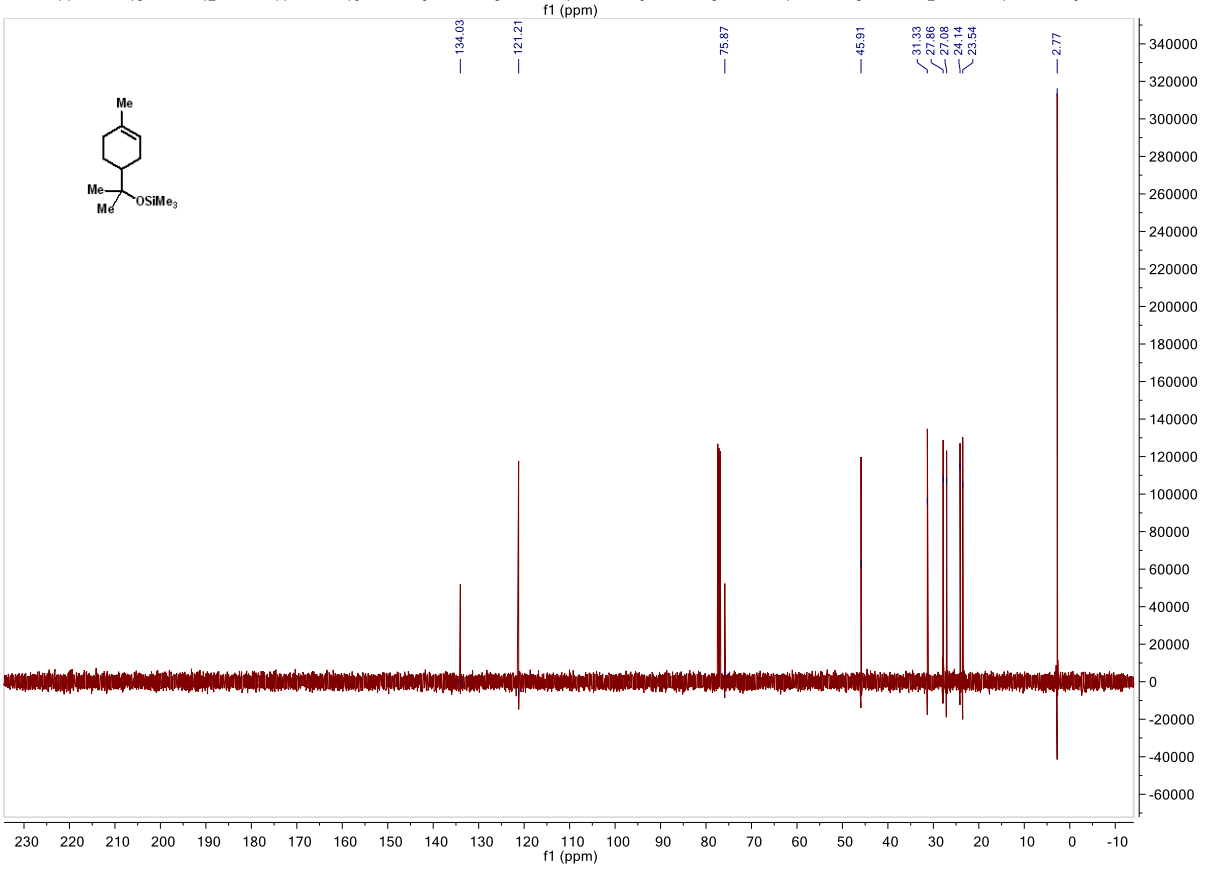

198.05
148.57
135.60
134.32
127.88
122.66
63.39
62.82
54.36
40.04
37.68
36.84
36.61
28.17
26.71
24.13
24.11
23.62
17.96
15.72
Me
O
H
Ac
Me
Me
Me
10:1 dr
f1 (ppm)

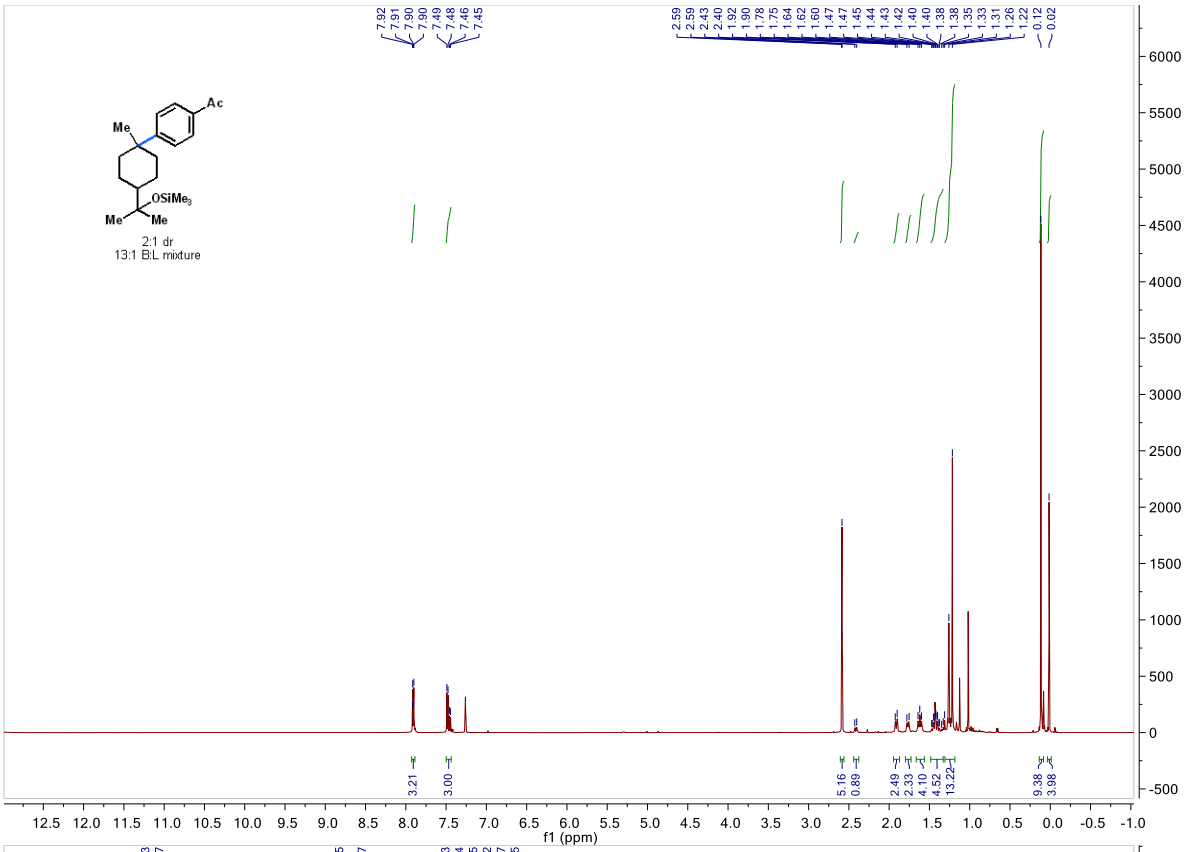

7.90
7.88
7.43
7.42
5.29
2.59
1.93
1.90
1.89
1.87
1.77
1.76
1.74
1.71
1.60
1.31
1.27
Ac
Me
Me
Me
2.22
2.00
0.99
3.62
2.30
4.03
4.06
3.18
3.30
f1 (ppm)

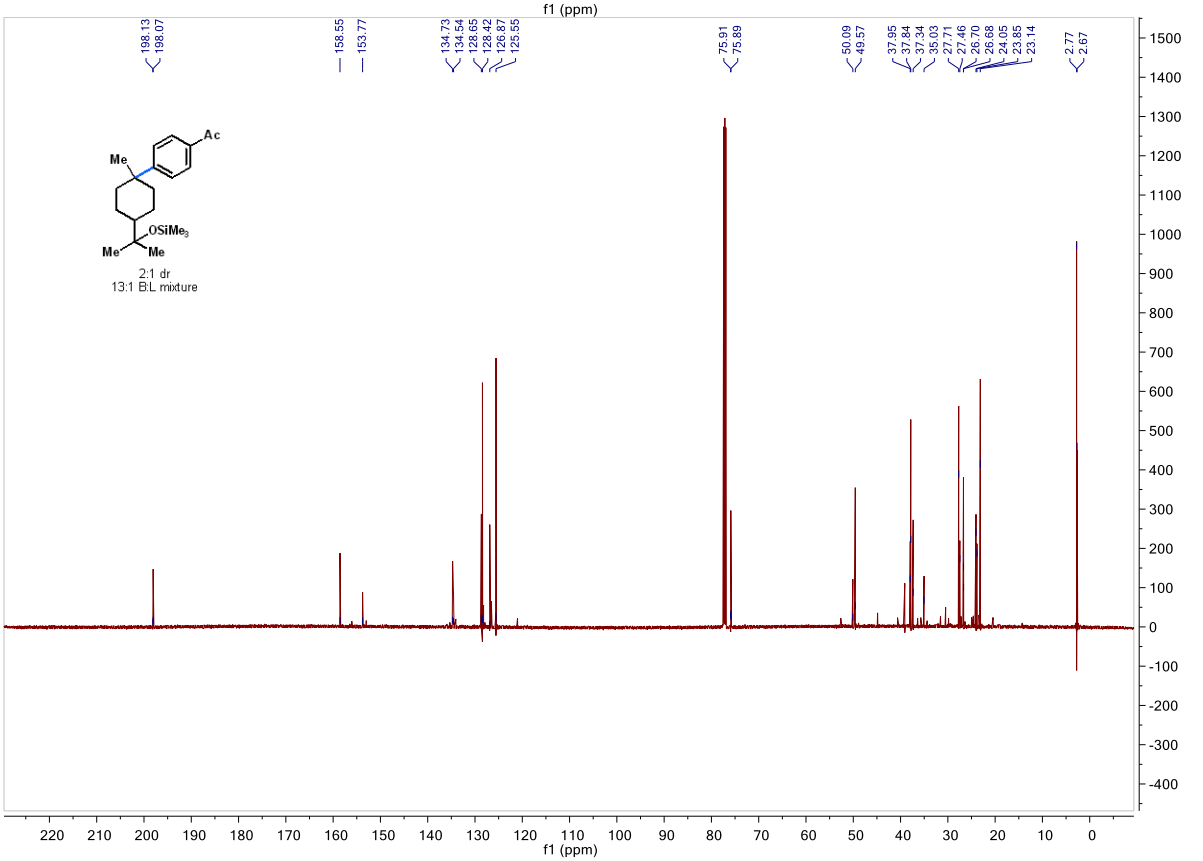

198.09
156.07
134.71
134.06
128.19
126.55
121.01
44.87
40.65
31.56
27.21
26.70
25.08
24.97
24.62
23.41
Ac
Me
Me
Me
f1 (ppm)

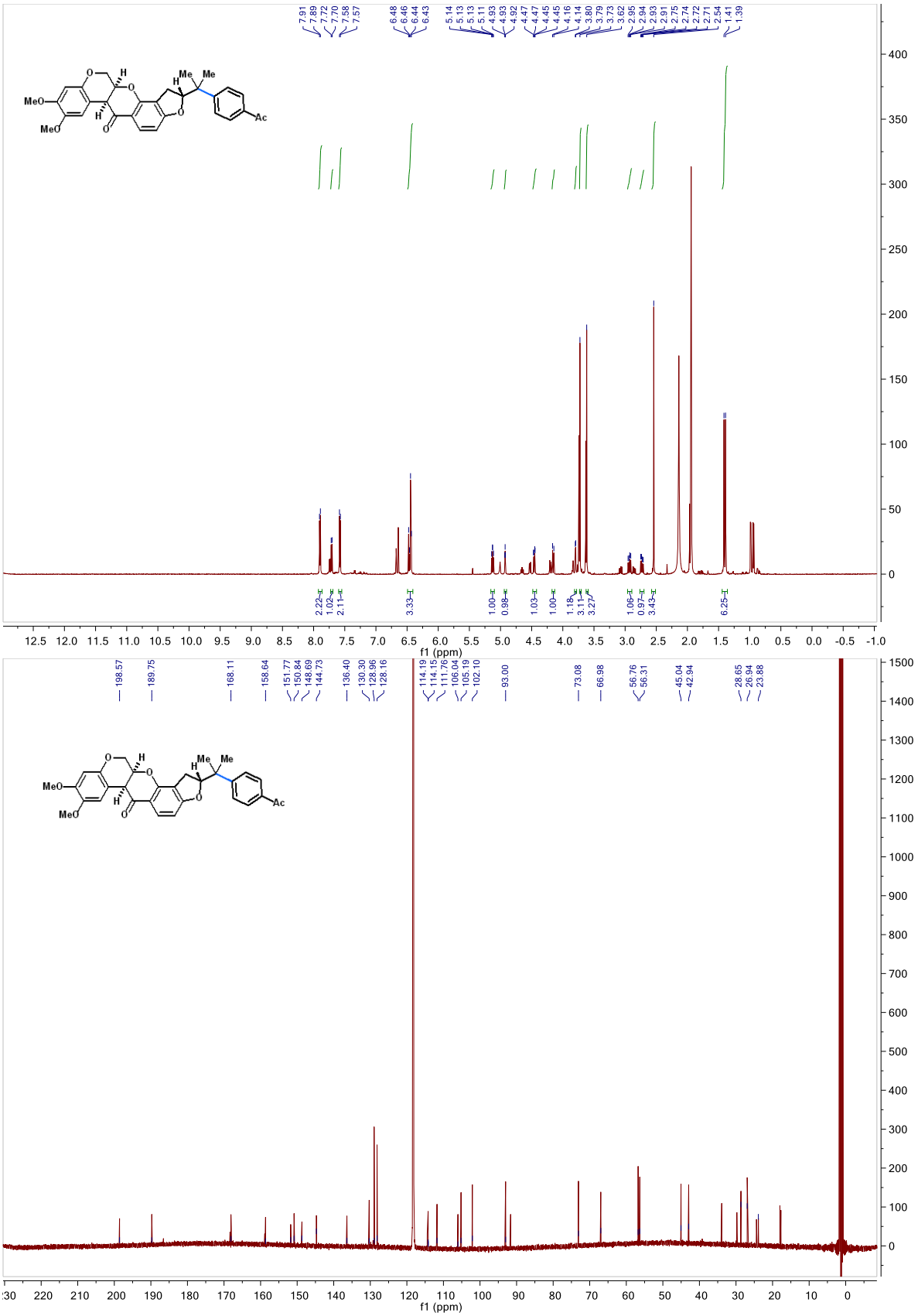

Ac
Me
OH
Me
Me
13:1 B:L mixture
f1 (ppm)
Ac
Me
OH
Me
Me
13:1 B:L mixture
f1 (ppm)


Me
Me
Me
OSiMe3
f1 (ppm)


134.03
121.21
75.87
45.91
31.33
27.86
27.08
24.14
23.54
2.77
Me
Me
Me
OSiMe3
f1 (ppm)


Ac
Me
OSiMe3
Me
Me
2:1 dr
13:1 B:L mixture
f1 (ppm)


Ac
Me
OSiMe3
Me
Me
2:1 dr
13:1 B:L mixture
f1 (ppm)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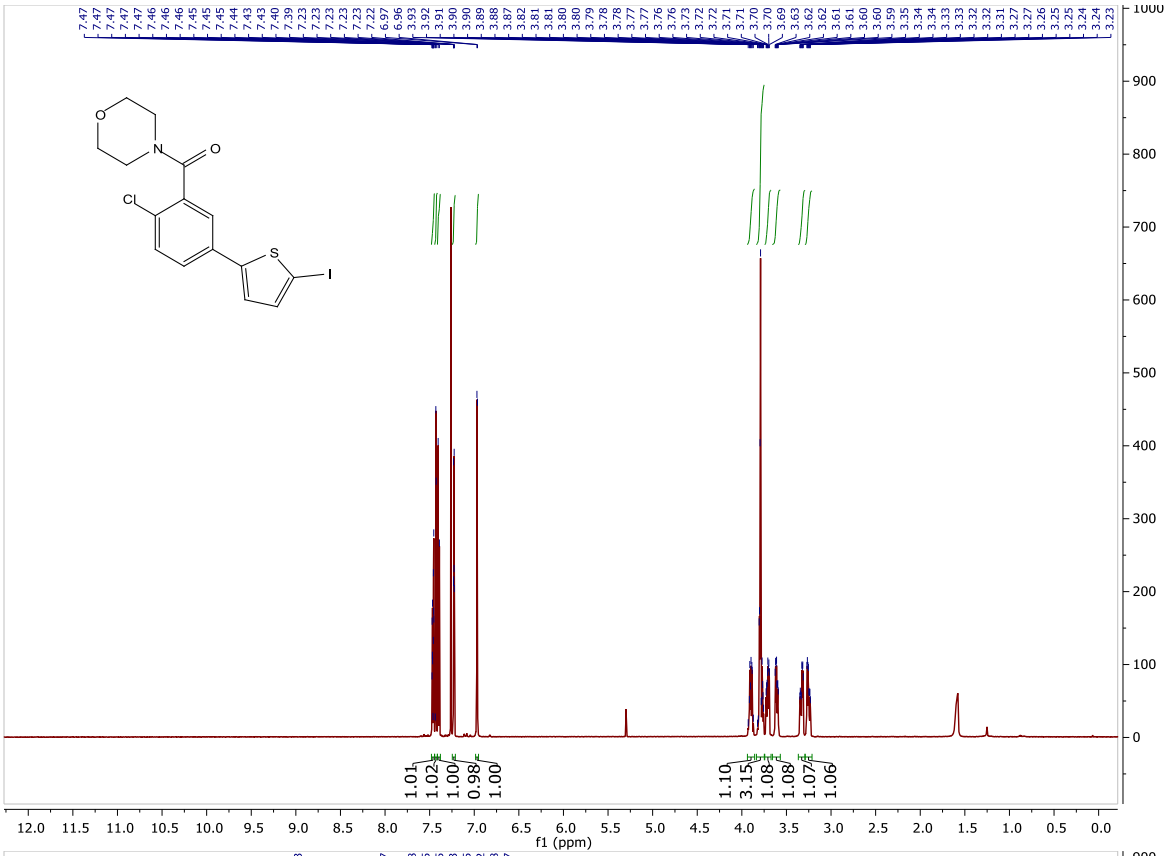
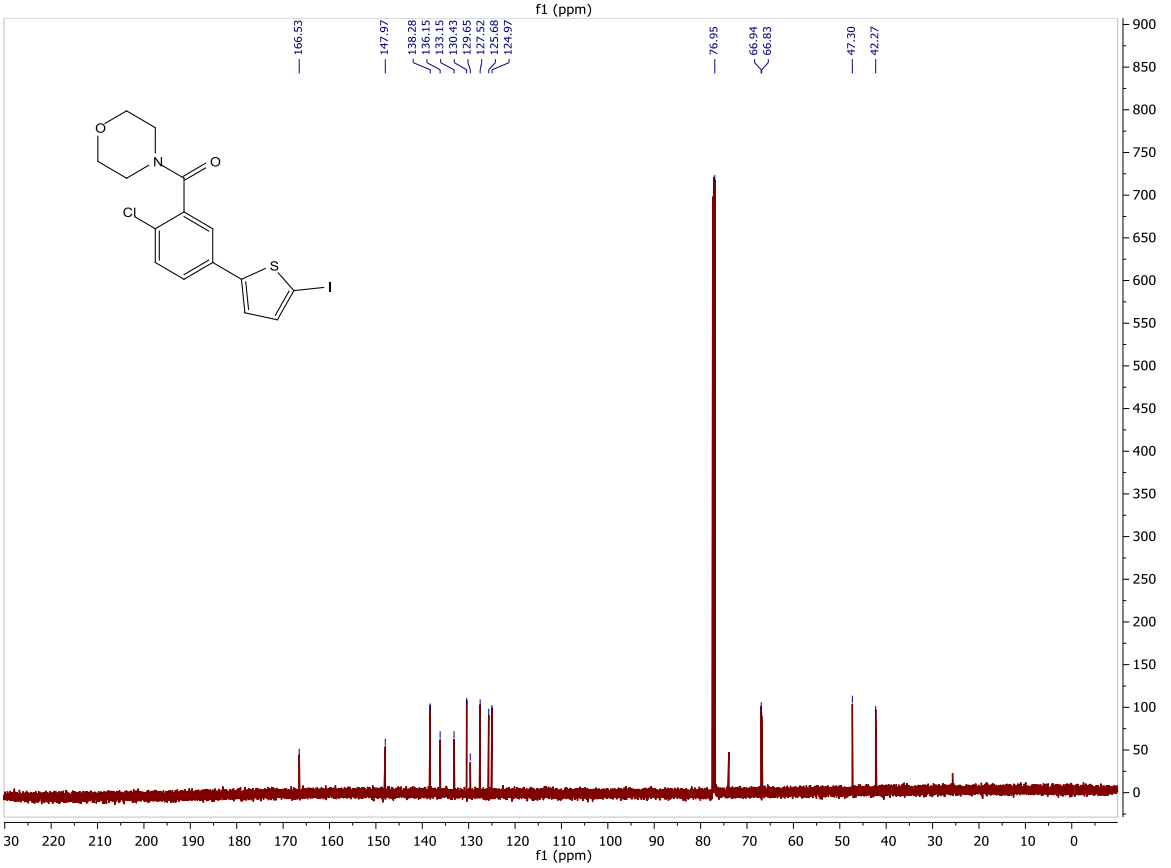
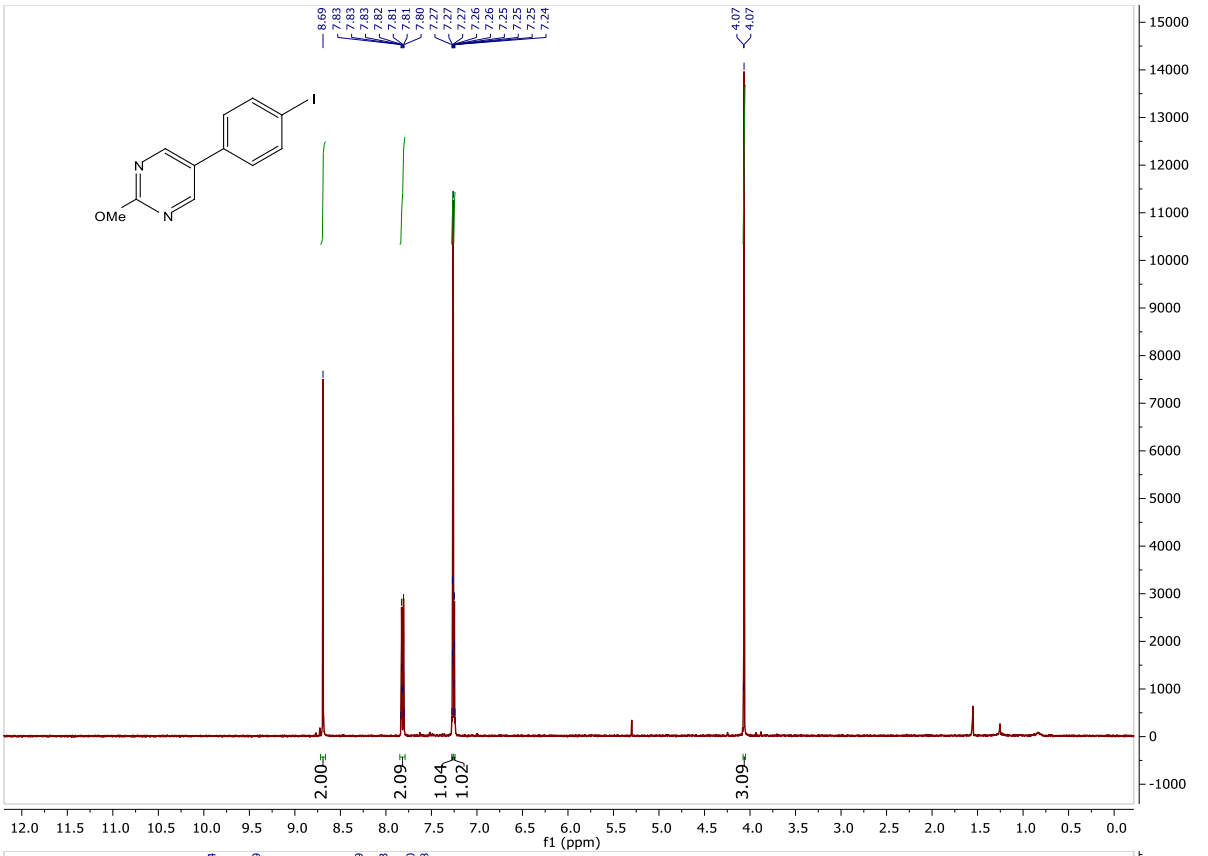
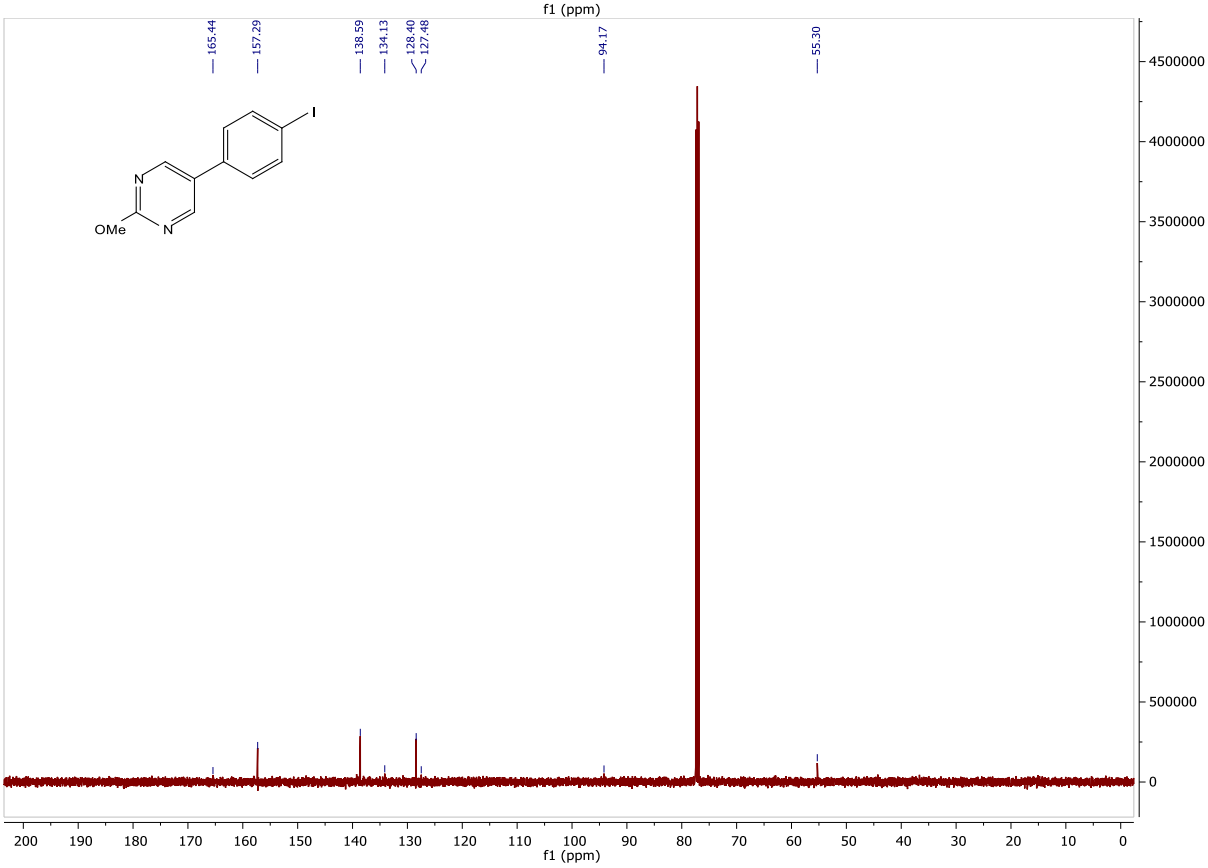
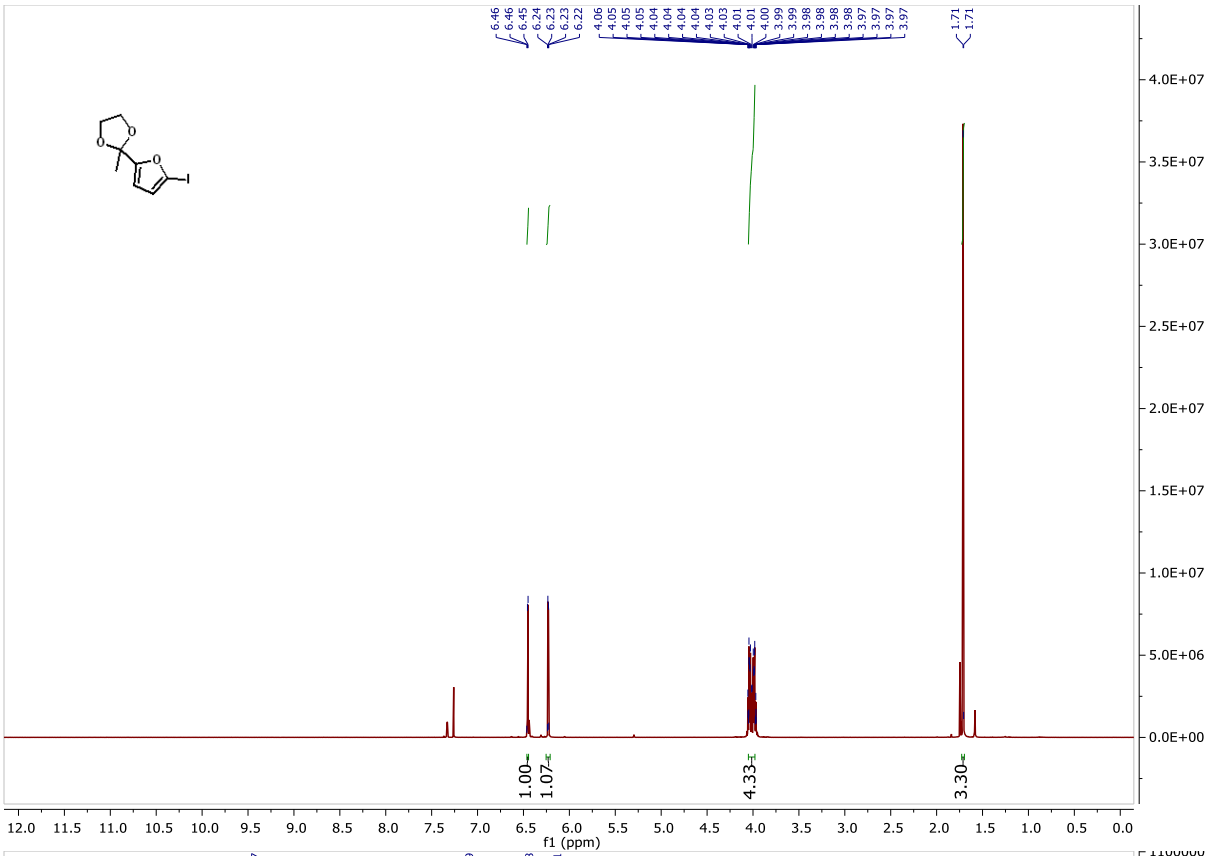
7.89
7.72
7.70
7.58
7.57
6.48
6.46
6.44
6.43
5.14
5.13
5.13
5.11
4.93
4.93
4.92
4.47
4.47
4.45
4.45
4.16
4.14
3.80
3.79
3.73
3.62
2.95
2.94
2.93
2.91
2.75
2.74
2.72
2.71
2.54
1.41
1.39
MeO
MeO
Me
Me
Ac
2.22
1.02
2.11
3.33
1.00
0.98
1.03
1.00
1.18
3.11
3.27
1.06
0.97
3.43
6.25
f1 (ppm)
198.57
189.75
168.11
158.64
151.77
150.84
148.69
144.73
136.40
130.30
128.96
128.16
114.19
114.15
111.76
106.04
105.19
102.10
93.00
73.08
66.98
56.76
56.31
45.04
42.94
28.65
26.94
23.88
f1 (ppm)

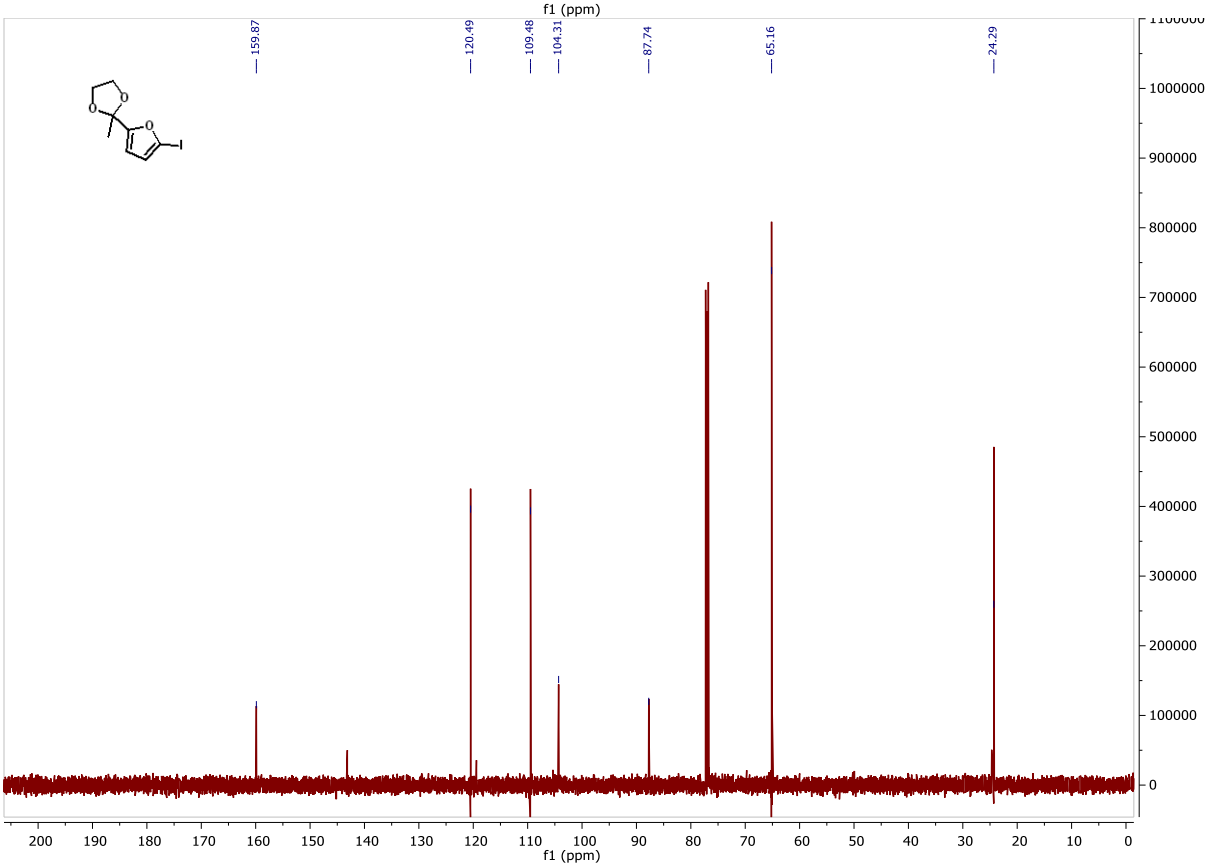

O
N
O
Cl
S
I
1.01
1.02
1.00
0.98
1.00
1.10
3.15
1.08
1.08
1.07
1.06
f1 (ppm)

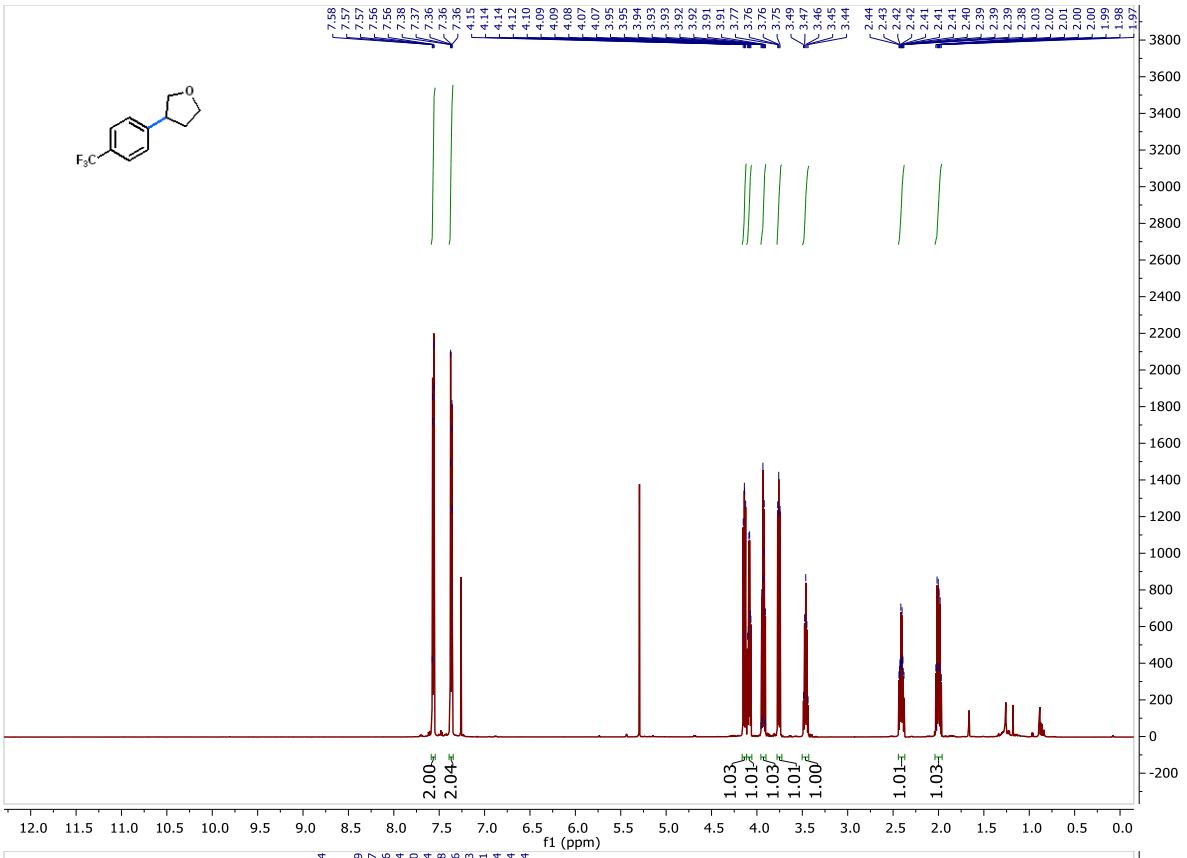

166.53
147.97
138.28
136.15
133.15
130.43
129.65
127.52
125.68
124.97
76.95
66.94
66.83
47.30
42.27
O
N
O
Cl
S
I
f1 (ppm)

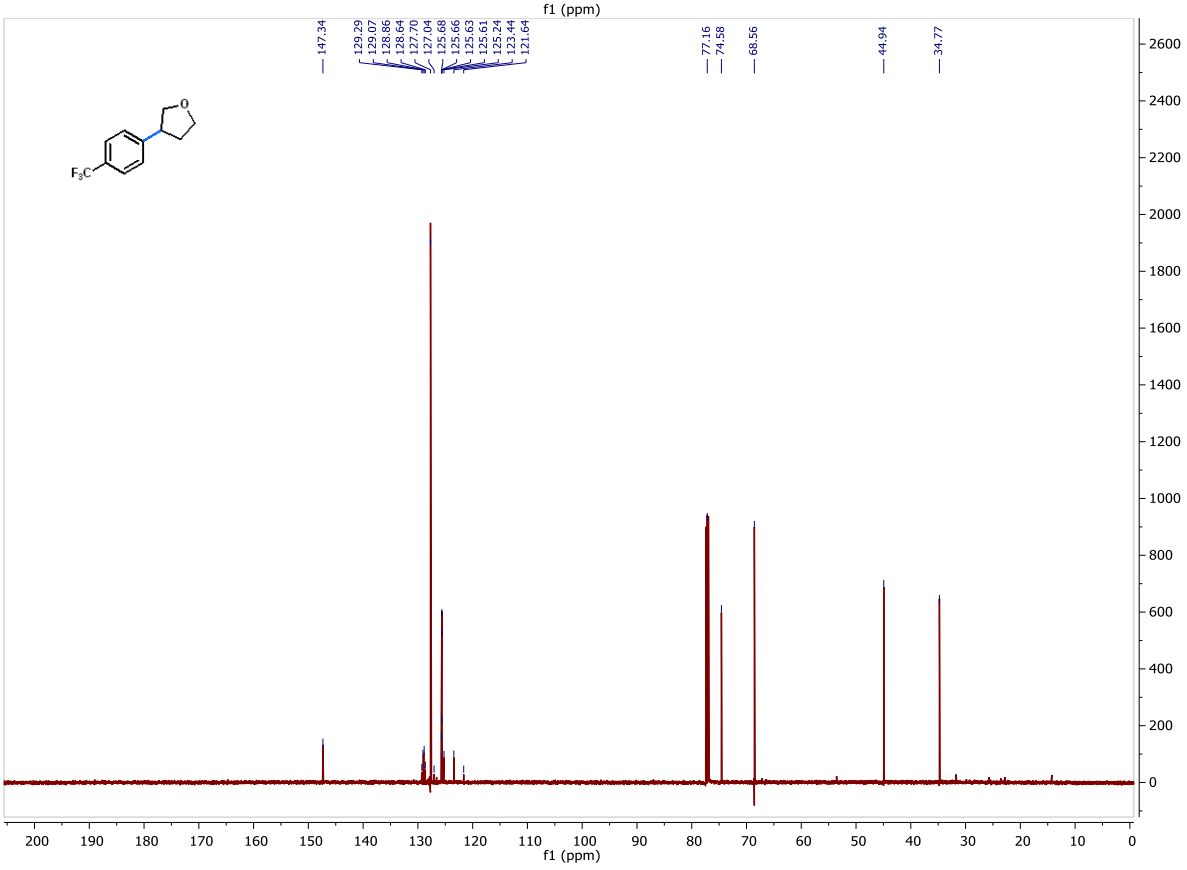

8.69
7.83
7.83
7.83
7.82
7.81
7.81
7.80
7.27
7.27
7.27
7.26
7.26
7.25
7.25
7.25
7.24
4.07
4.07
I
N
OMe
N
2.00
2.09
1.04
1.02
3.09
f1 (ppm)

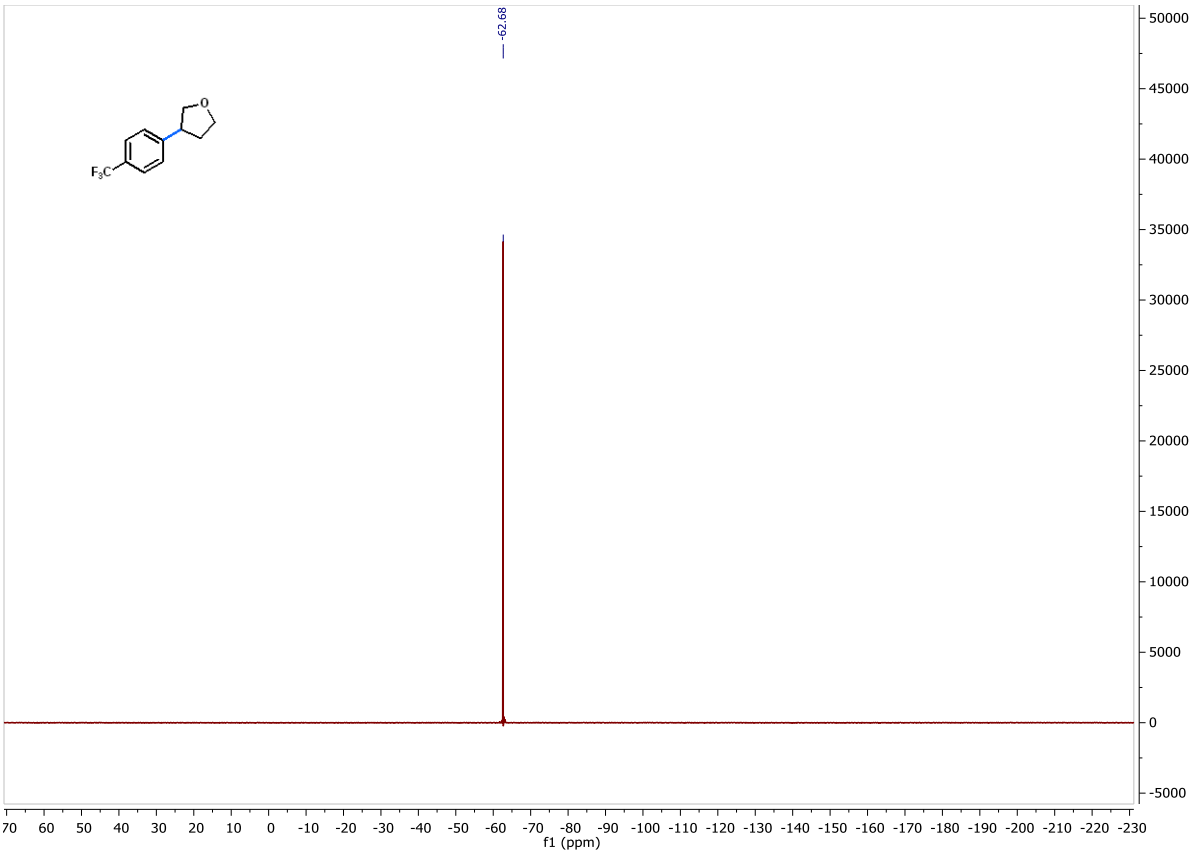

165.44
157.29
138.59
134.13
128.40
127.48
94.17
55.30
I
N
OMe
N
f1 (ppm)

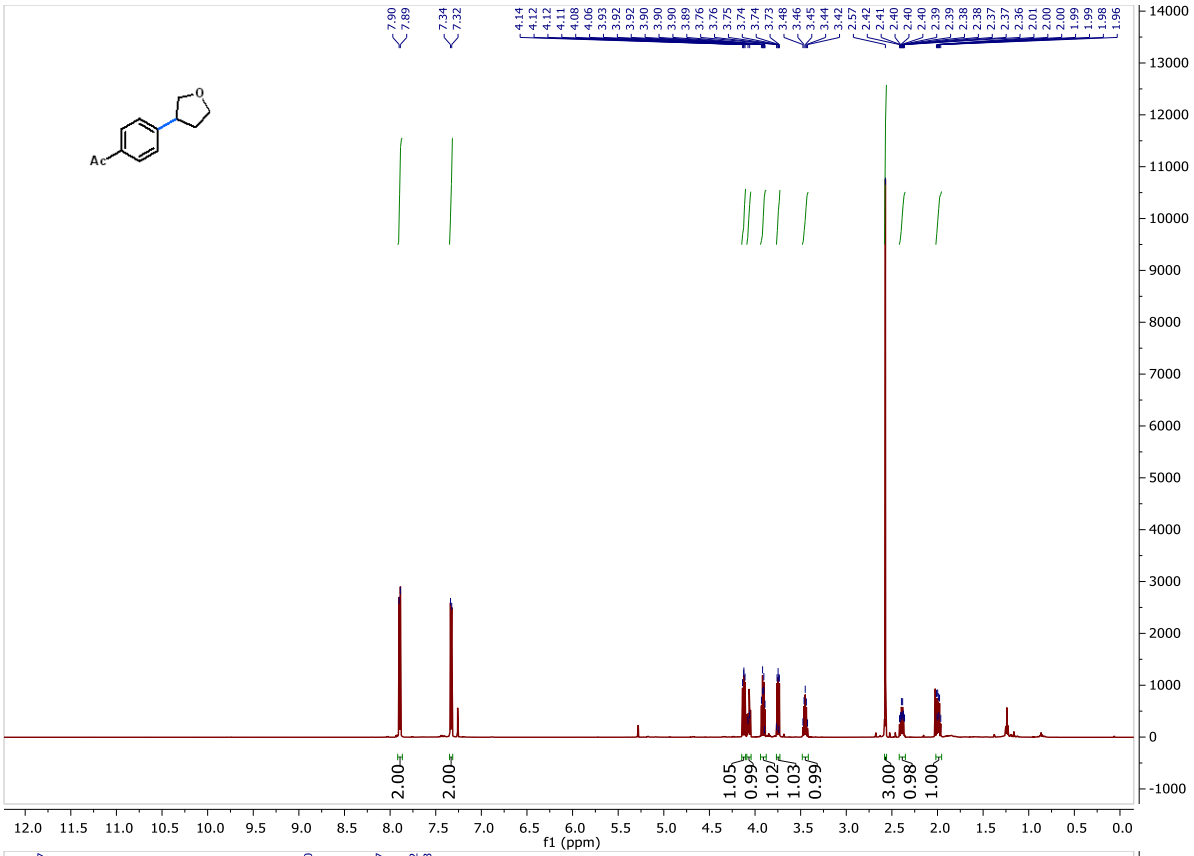

6.46
6.46
6.45
6.24
6.23
6.23
6.22
4.06
4.05
4.05
4.04
4.04
4.04
4.04
4.03
4.03
4.01
4.01
4.00
3.99
3.99
3.98
3.98
3.98
3.97
3.97
3.97
3.97
1.71
1.71
4.0E+07
3.5E+07
3.0E+07
2.5E+07
2.0E+07
1.5E+07
1.0E+07
5.0E+06
0.0E+00
1.00
1.07
4.33
3.30
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

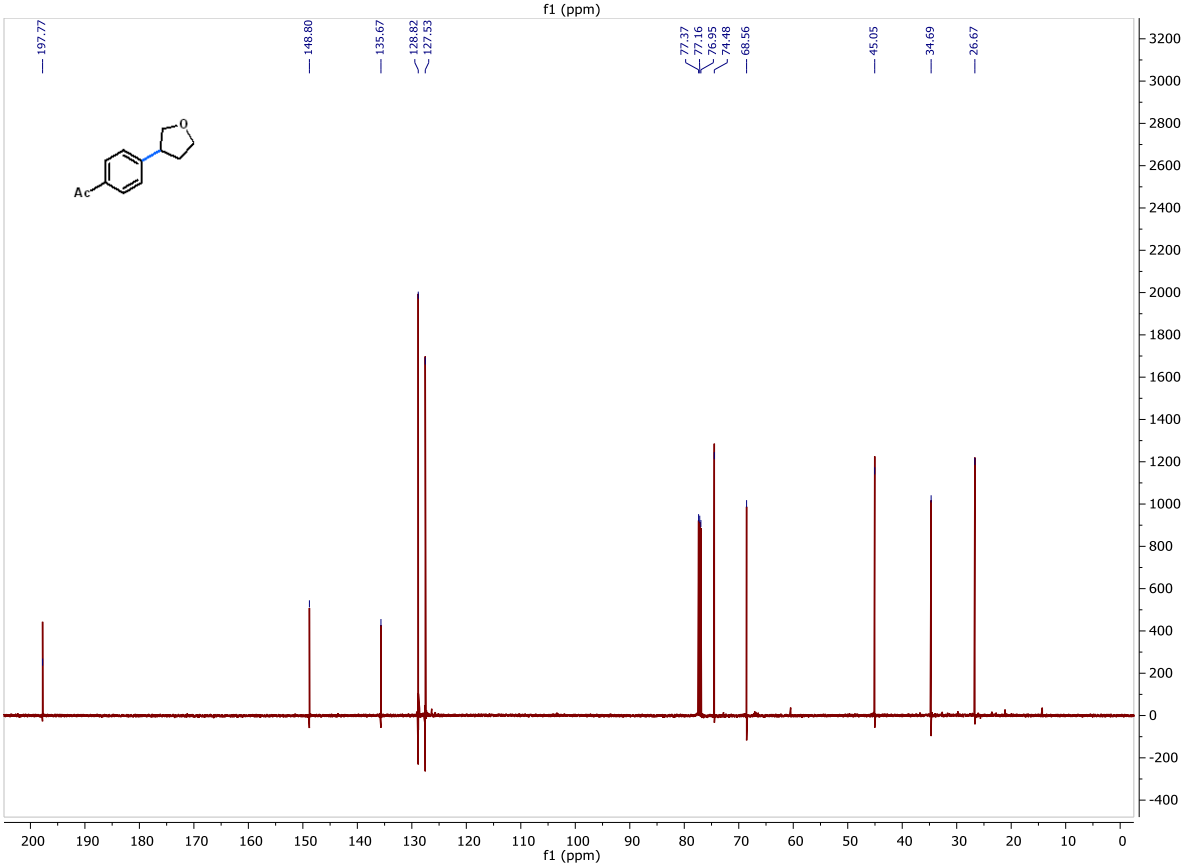

159.87
120.49
109.48
104.31
87.74
65.16
24.29
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

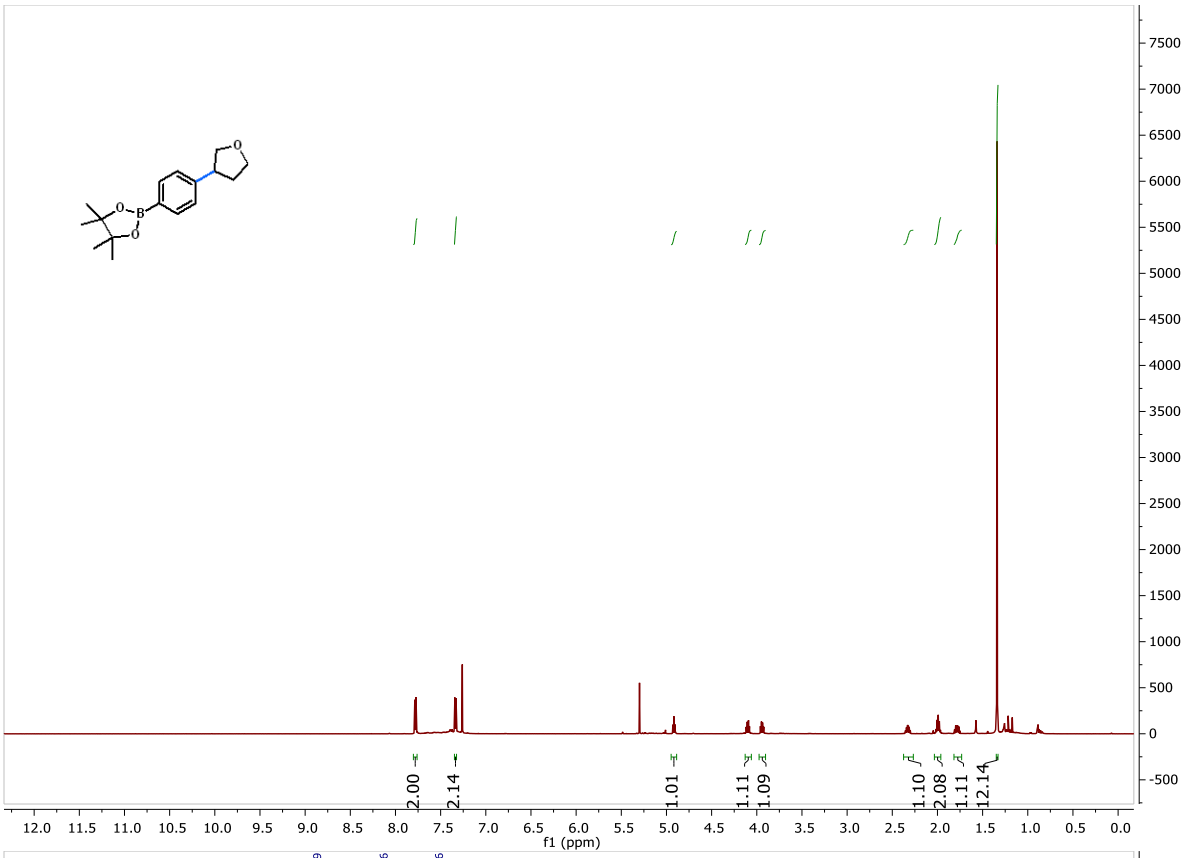

F3C
O
2.00
2.04
1.03
1.01
1.03
1.01
1.00
1.01
1.03
f1 (ppm)


F3C
O
147.34
129.29
129.07
128.86
128.64
127.70
127.04
125.68
125.66
125.63
125.61
125.24
123.44
121.64
77.16
74.58
68.56
44.94
34.77
f1 (ppm)


-62.68
O
F3C
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)


7.90
7.89
7.34
7.32
4.14
4.12
4.12
4.11
4.08
4.06
3.93
3.92
3.92
3.90
3.90
3.90
3.89
3.76
3.76
3.75
3.74
3.74
3.73
3.48
3.46
3.45
3.44
3.42
2.57
2.42
2.41
2.40
2.40
2.40
2.39
2.39
2.38
2.38
2.37
2.37
2.36
2.01
2.00
2.00
1.99
1.99
1.98
1.96
Ac
2.00
2.00
1.05
0.99
1.02
1.03
0.99
3.00
0.98
1.00
f1 (ppm)


197.77
148.80
135.67
128.82
127.53
77.37
77.16
76.95
74.48
68.56
45.05
34.69
26.67
Ac
f1 (ppm)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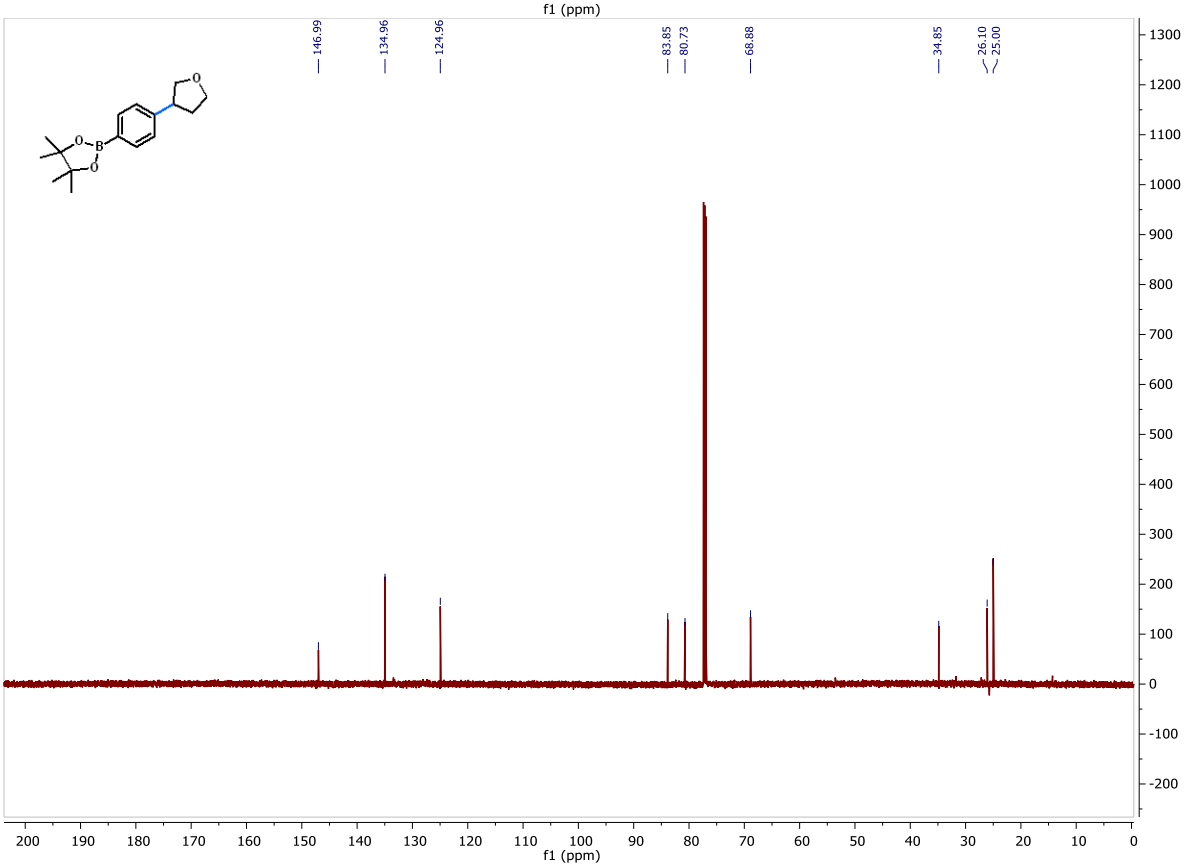
2.14
1.01
1.11
1.09
1.10
2.08
1.11
12.14
f1 (ppm)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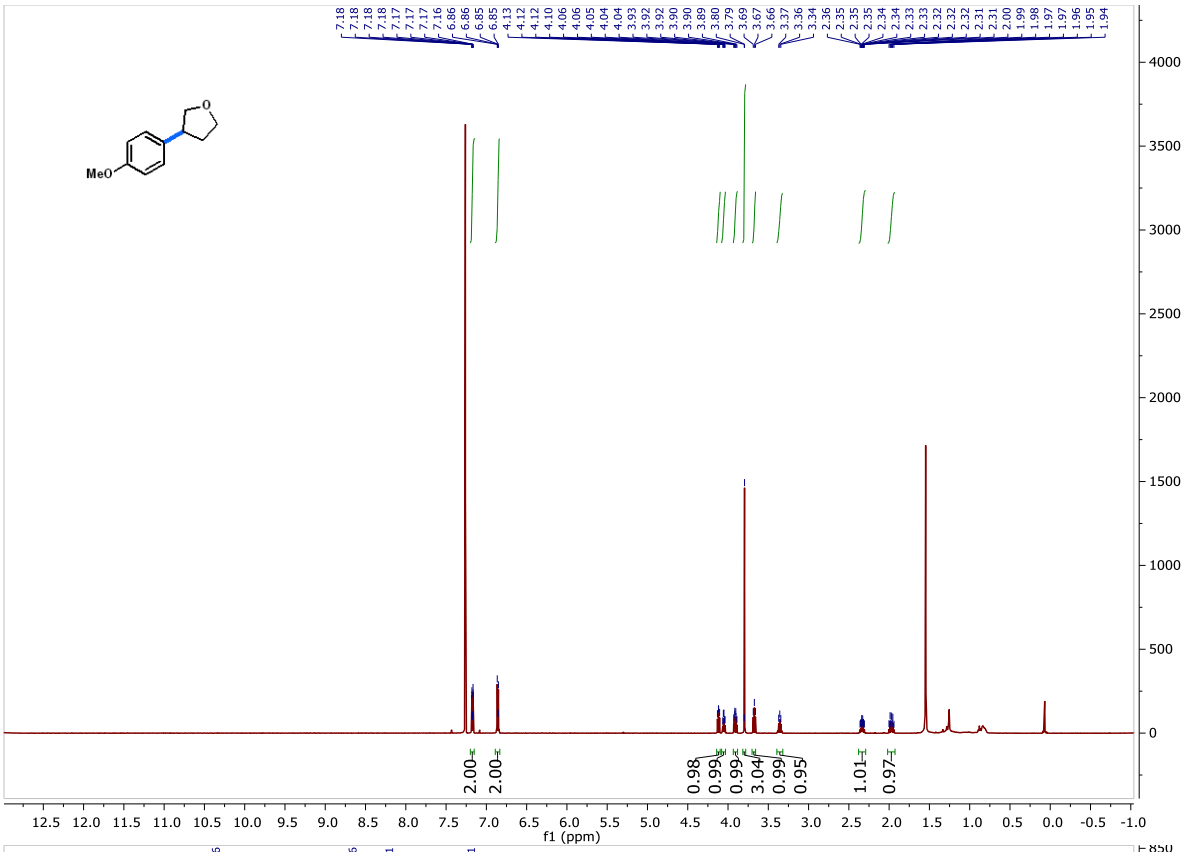
134.96
124.96
83.85
80.73
68.88
34.85
26.10
25.00
f1 (ppm)


MeO
2.00
2.00
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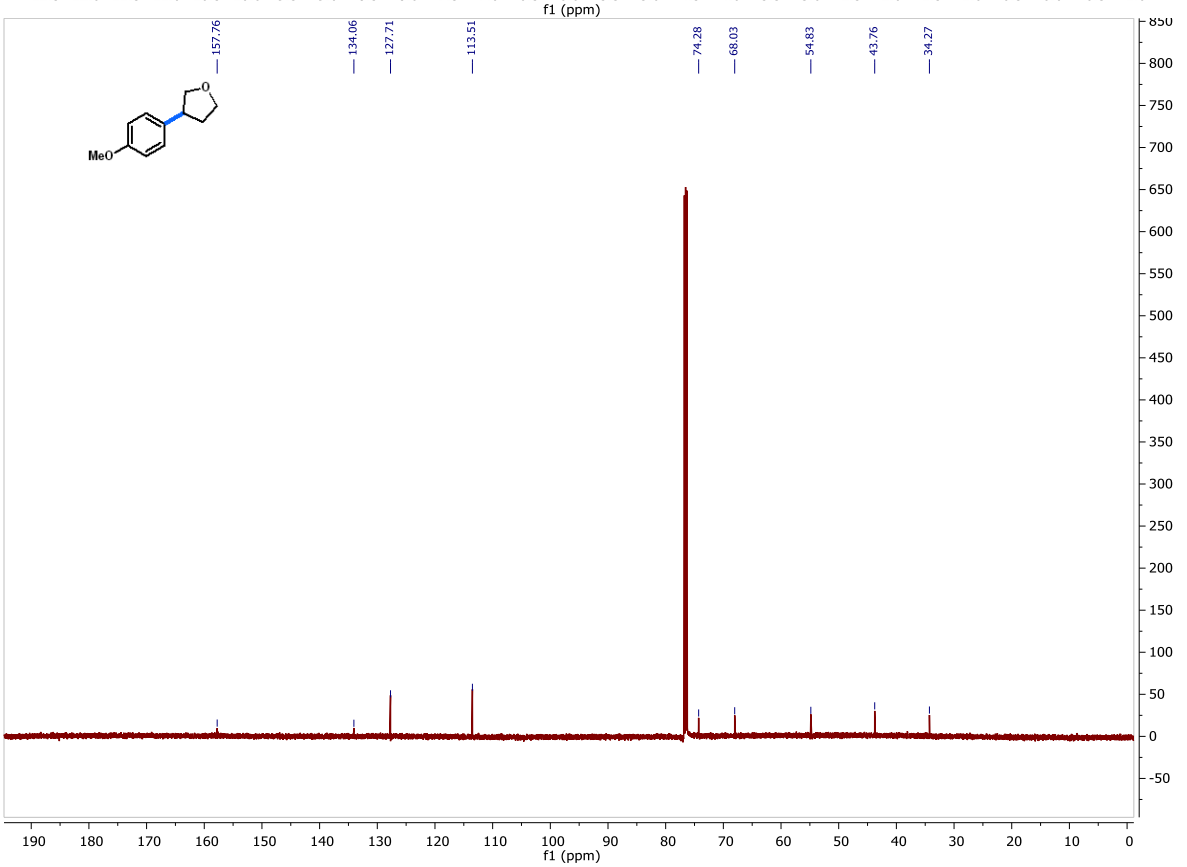
0.99
0.99
3.04
0.99
0.95
1.01
0.97
f1 (ppm)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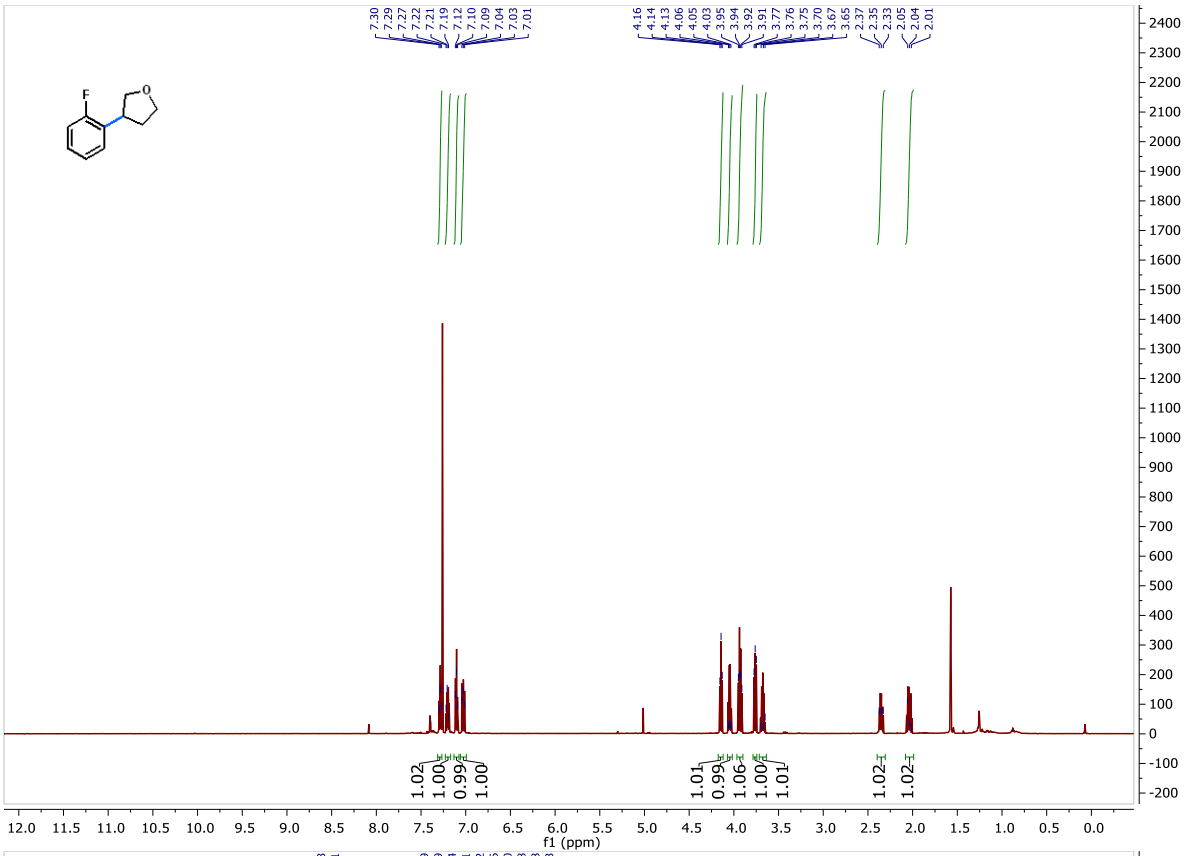
134.06
127.71
113.51
74.28
68.03
54.83
43.76
34.27
MeO
f1 (ppm)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7.10
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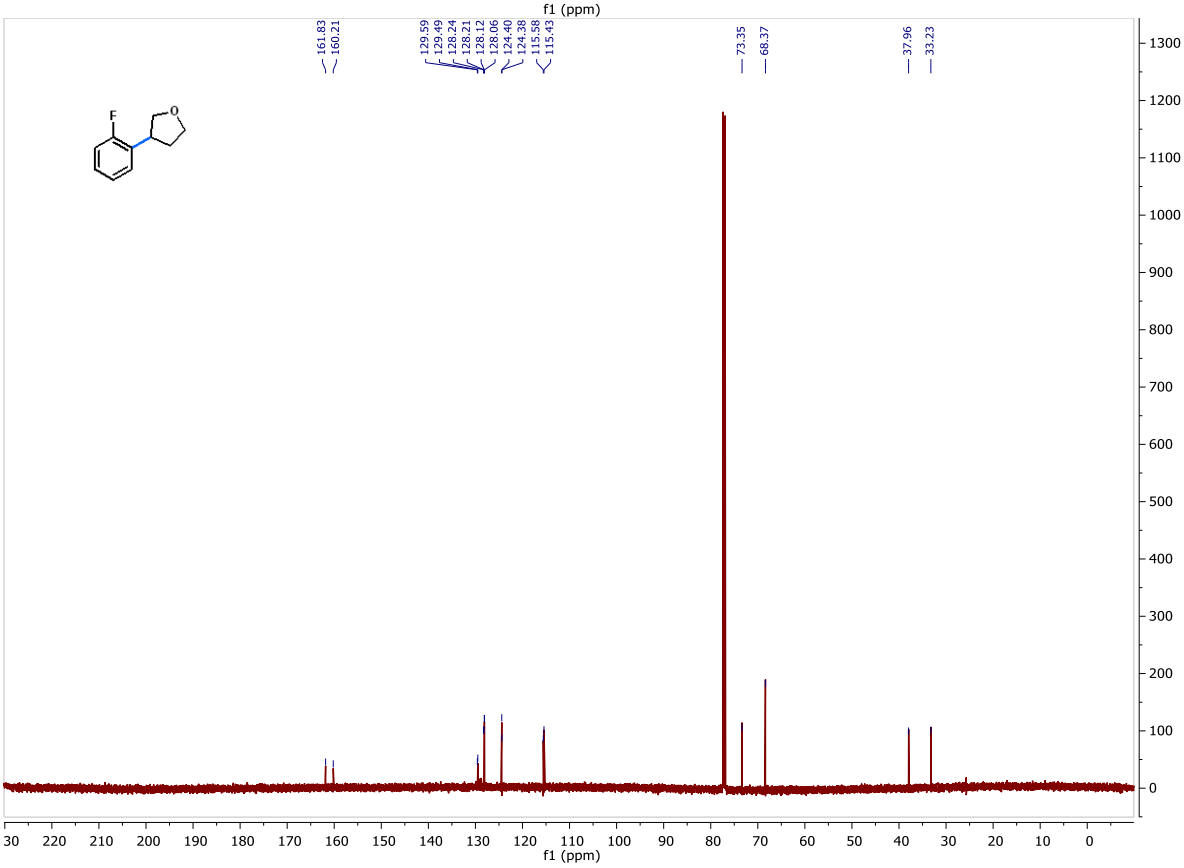
7.04
7.03
7.01
4.16
4.14
4.13
4.06
4.05
4.03
3.95
3.94
3.92
3.91
3.77
3.76
3.75
3.70
3.67
3.65
2.37
2.35
2.33
2.05
2.04
2.01
F
O
1.02
1.00
0.99
1.00
1.01
0.99
1.06
1.00
1.01
1.02
1.02
f1 (ppm)


161.83
160.21
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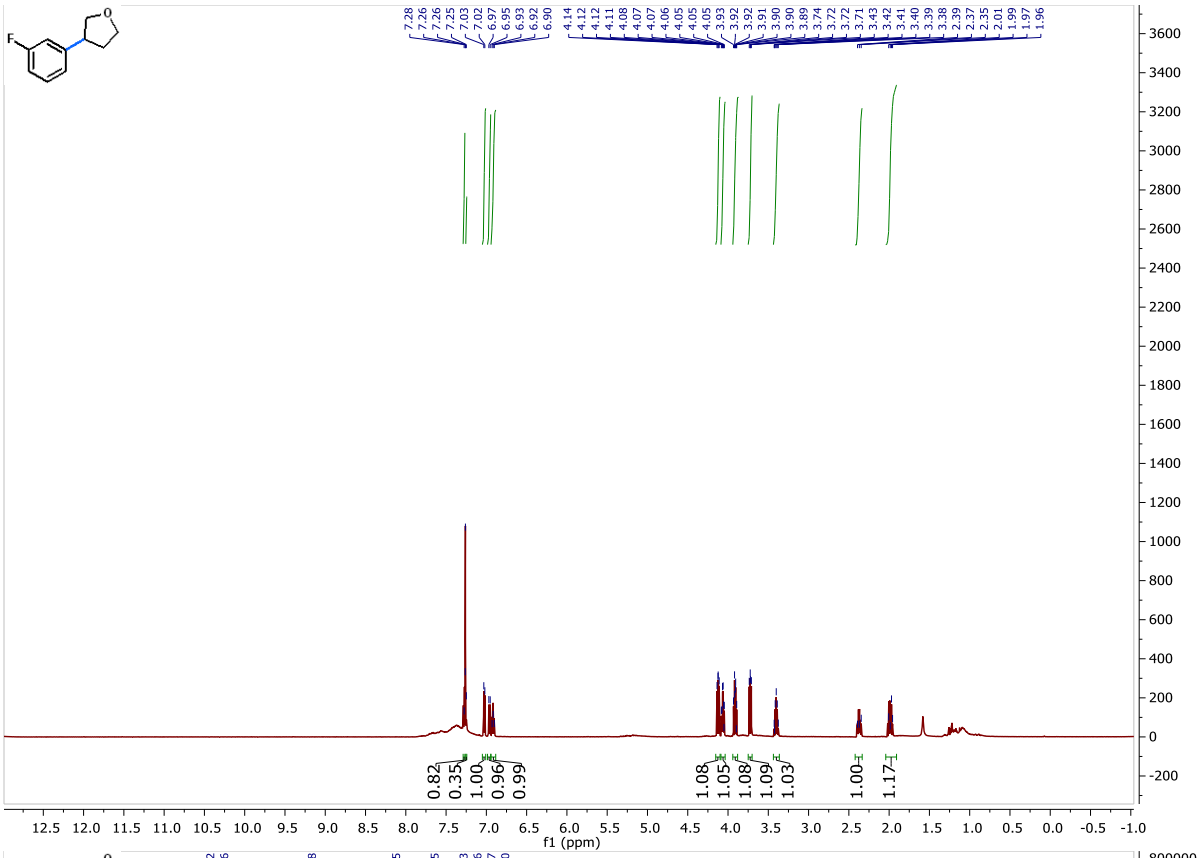
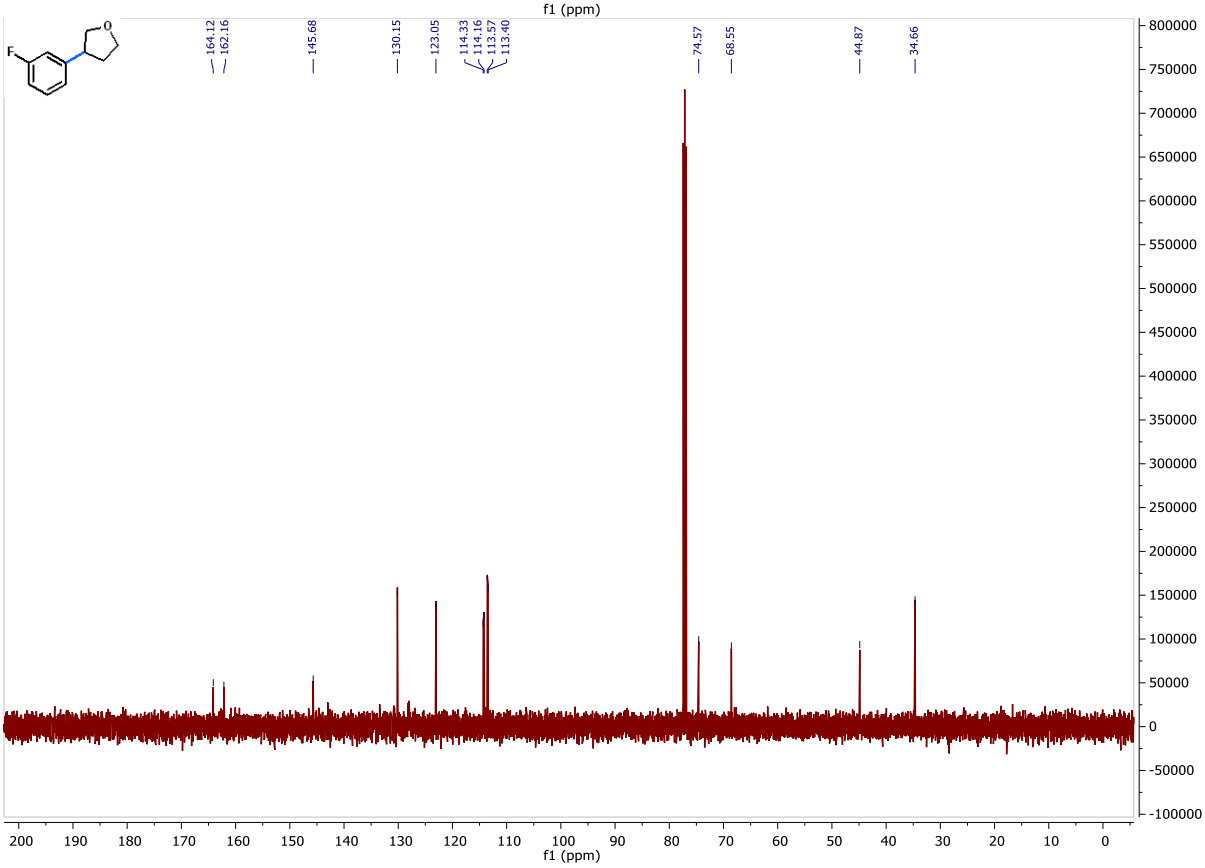
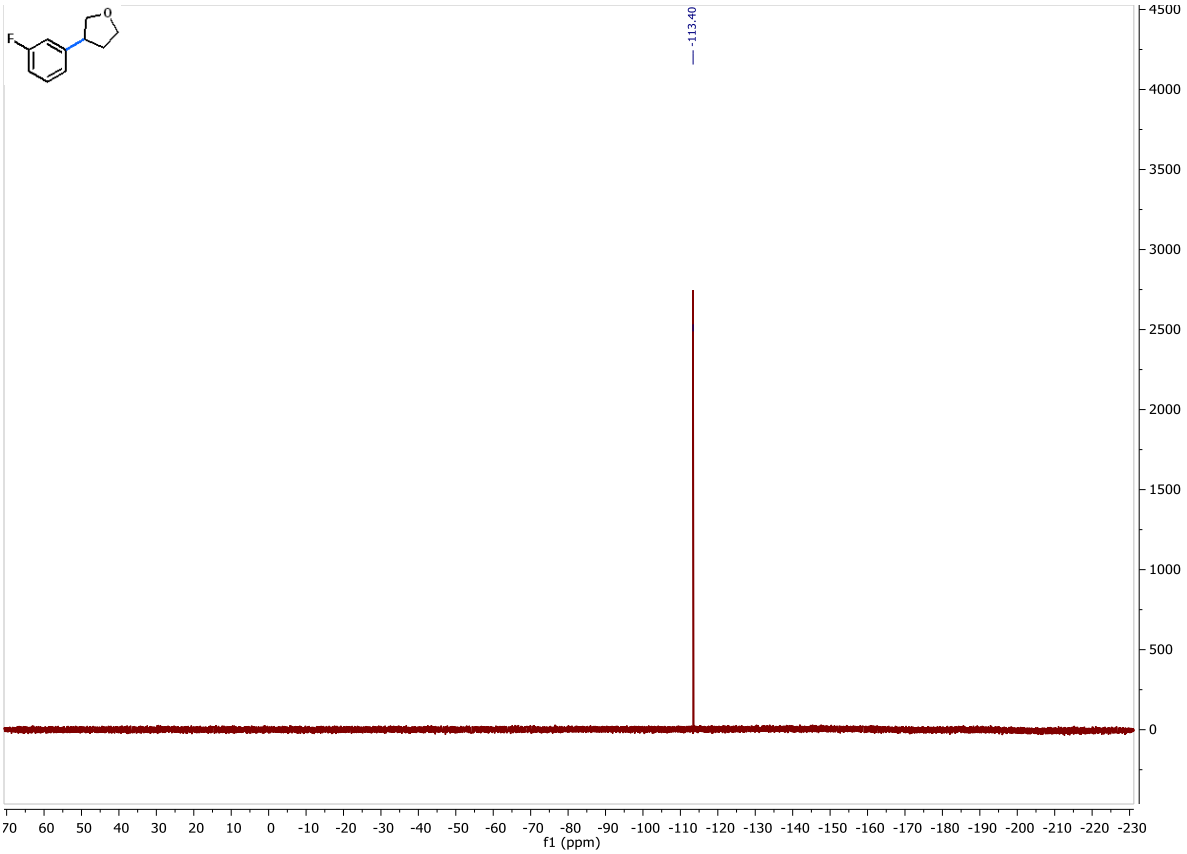
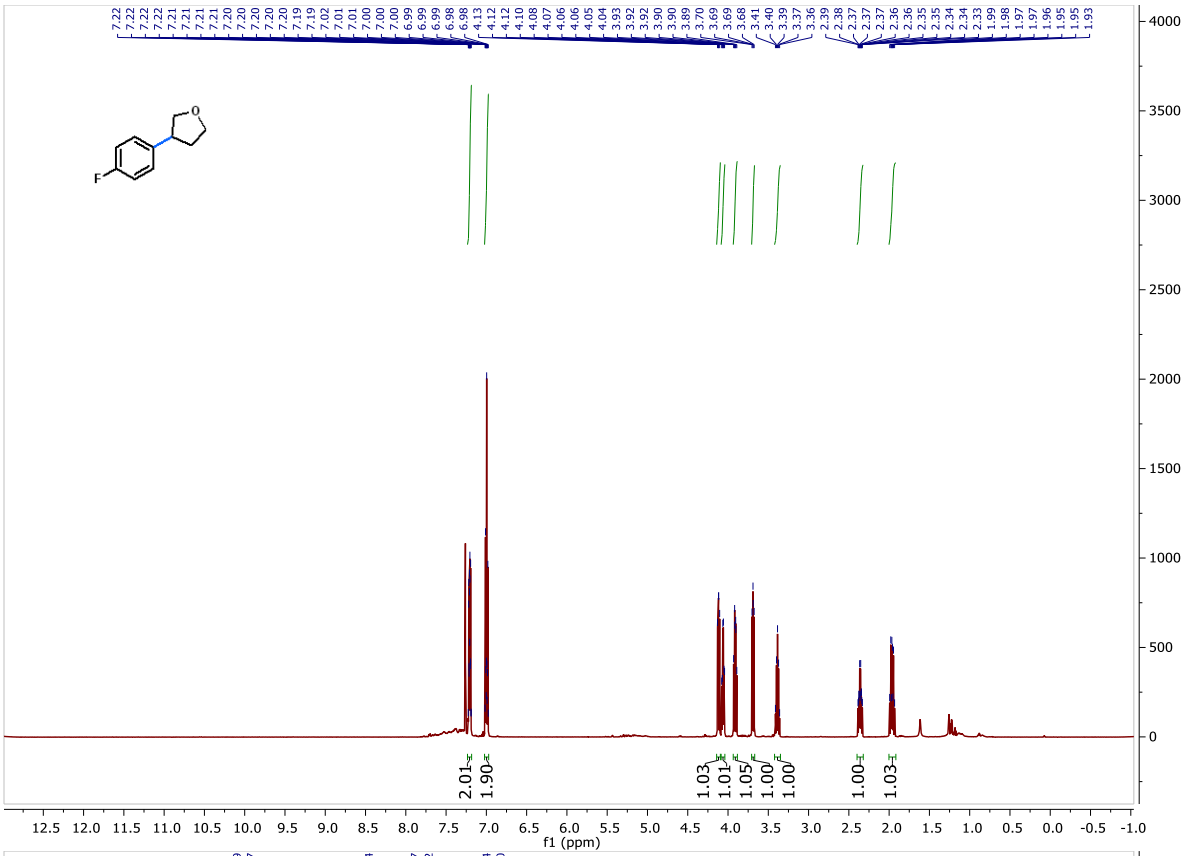
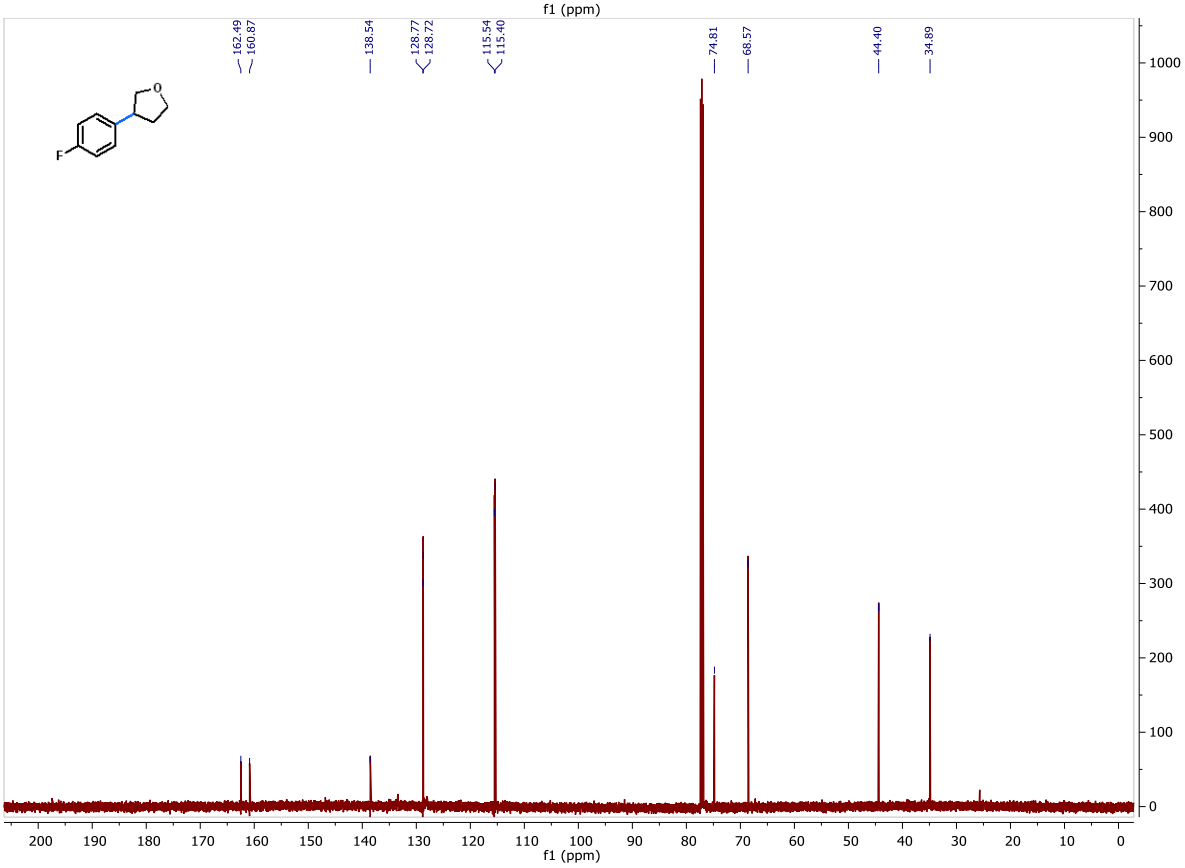
129.49
128.24
128.21
128.12
128.06
124.40
124.38
115.58
115.43
73.35
68.37
37.96
33.23
F
O
f1 (ppm)

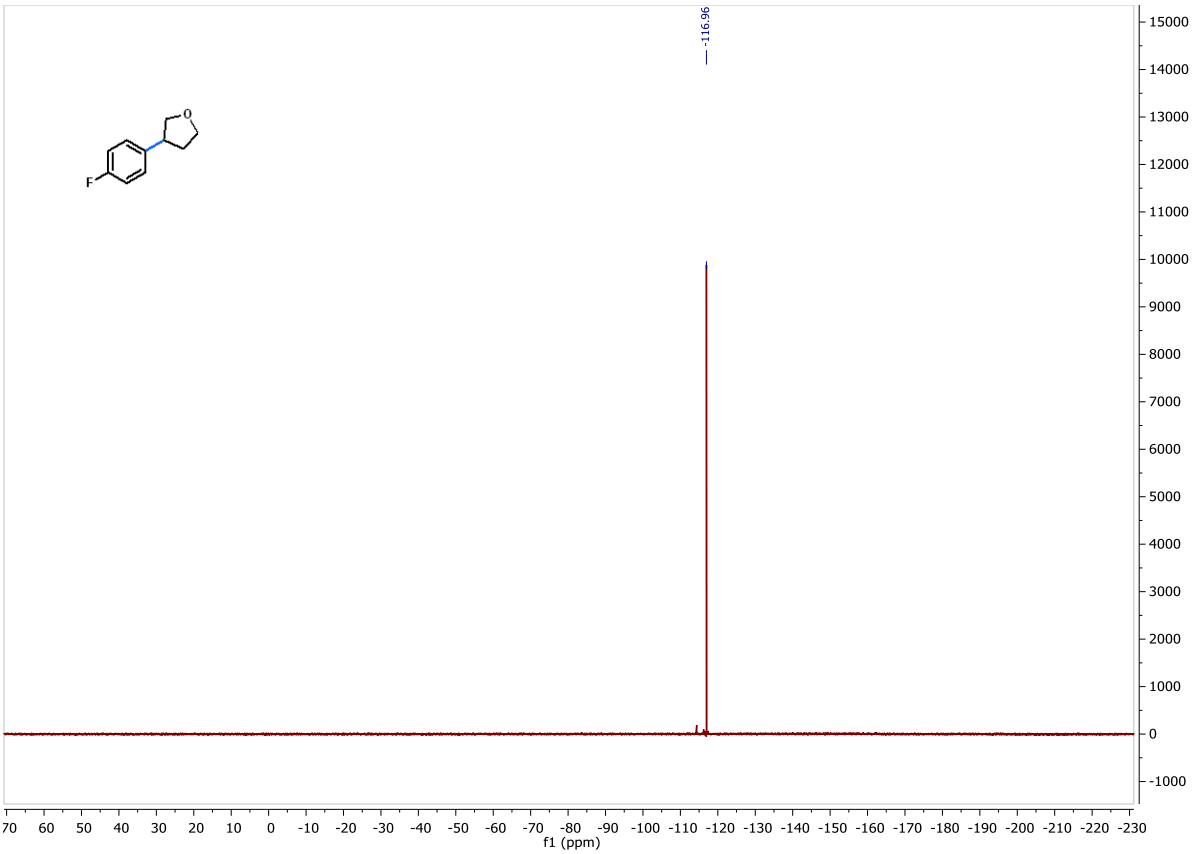

7.28 7.26 7.26 7.26 7.25 7.03 7.02 6.97 6.95 6.93 6.92 6.90
4.14 4.12 4.12 4.11 4.08 4.07 4.07 4.06 4.05 4.05 4.05 3.93 3.92 3.92 3.91 3.90 3.90 3.89 3.74 3.72 3.72 3.71 3.43 3.42 3.41 3.40 3.39 3.38 2.39 2.37 2.35 2.01 1.99 1.97 1.96
0.82 0.35 1.00 0.96 0.99 1.08 1.05 1.08 1.09 1.03 1.00 1.17
f1 (ppm)

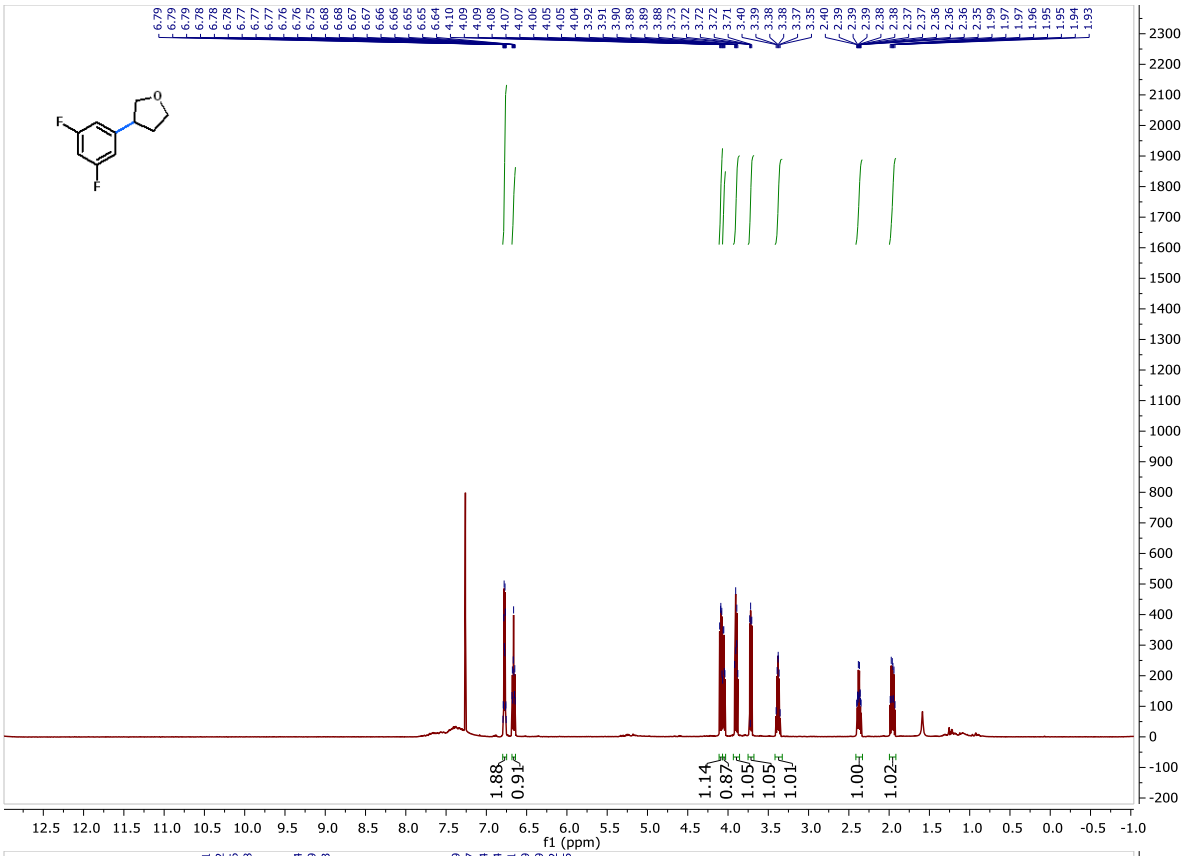

164.12 162.16 145.68 130.15 123.05 114.33 114.16 113.57 113.40 74.57 68.55 44.87 34.66
f1 (ppm)

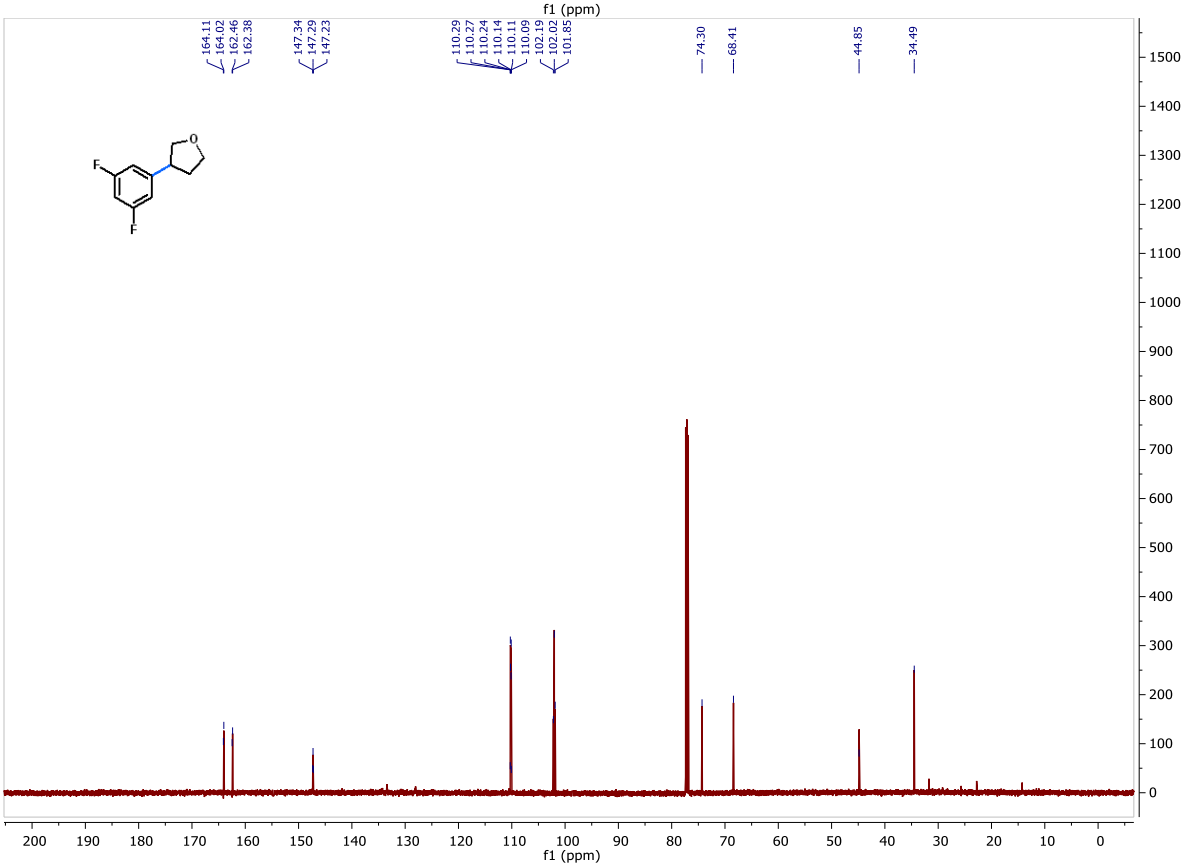

-113.40
4500
4000
3500
3000
2500
2000
1500
1000
500
0
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

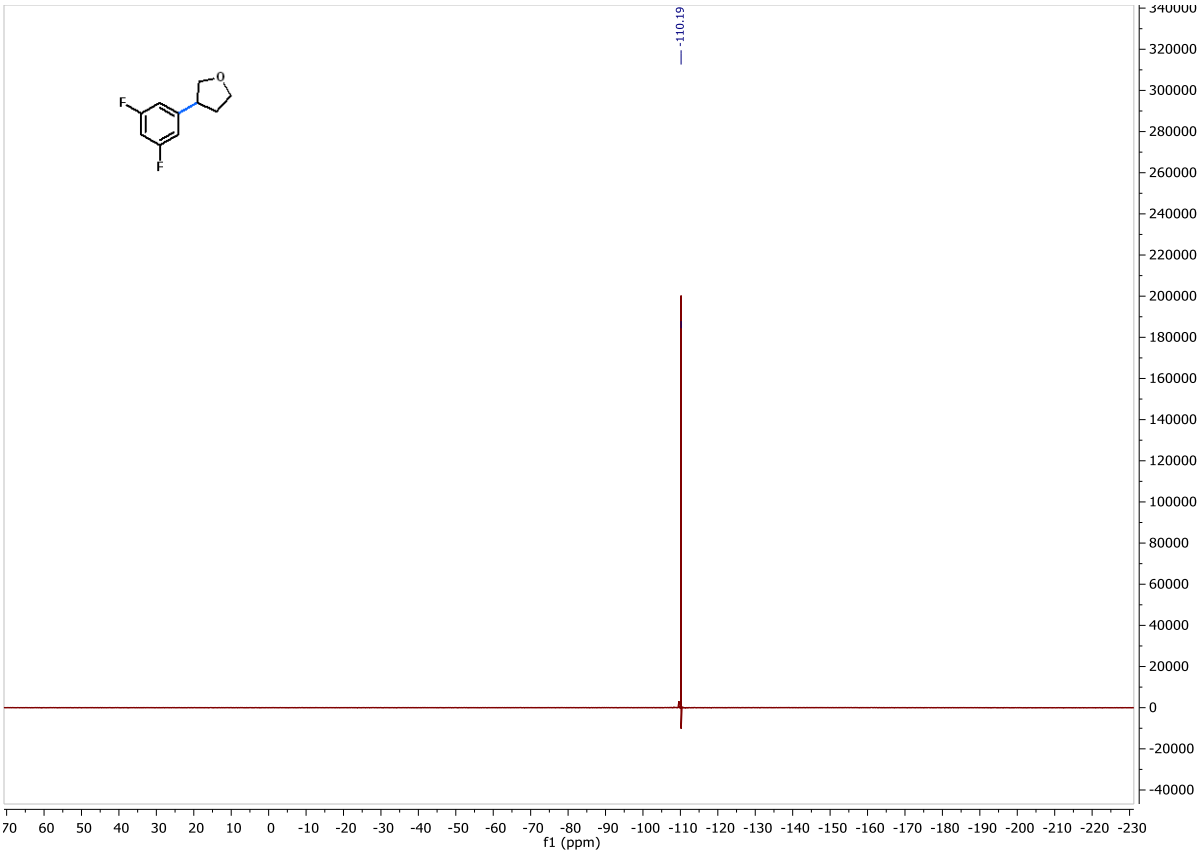

7.22 7.22 7.22 7.22 7.21 7.21 7.21 7.21 7.20 7.20 7.20 7.20 7.20 7.19 7.19 7.02 7.01 7.01 7.00 7.00 7.00 6.99 6.99 6.99 6.98 6.98 4.13 4.12 4.10 4.08 4.07 4.06 4.06 4.05 4.04 3.93 3.92 3.92 3.90 3.90 3.89 3.70 3.69 3.68 3.41 3.40 3.39 3.37 3.36 2.39 2.38 2.37 2.37 2.37 2.36 2.36 2.35 2.35 2.34 2.34 2.33 1.99 1.98 1.97 1.97 1.96 1.95 1.95 1.95 1.93
F
O
2.01 1.90 1.03 1.01 1.05 1.00 1.00 1.00 1.03
f1 (ppm)


162.49 160.87 138.54 128.77 128.72 115.54 115.40 74.81 68.57 44.40 34.89
F
O
f1 (ppm)


-116.96
O
F
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)


F
F
O
6.79 6.79 6.79 6.78 6.78 6.78 6.77 6.77 6.77 6.76 6.76 6.75 6.68 6.68 6.67 6.67 6.66 6.66 6.65 6.65 6.64 4.10 4.09 4.09 4.08 4.07 4.07 4.06 4.05 4.05 4.04 3.92 3.91 3.90 3.89 3.89 3.88 3.73 3.72 3.72 3.72 3.71 3.40 3.39 3.38 3.38 3.37 3.35 2.40 2.39 2.39 2.39 2.38 2.38 2.37 2.37 2.36 2.36 2.36 2.35 1.99 1.97 1.97 1.96 1.95 1.95 1.94 1.93
1.88
0.91
1.14
0.87
1.05
1.05
1.01
1.00
1.02
f1 (ppm)


F
F
O
164.11 164.02 162.46 162.38 147.34 147.29 147.23 110.29 110.27 110.24 110.14 110.11 110.09 102.19 102.02 101.85 74.30 68.41 44.85 34.49
f1 (ppm)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F
F
O
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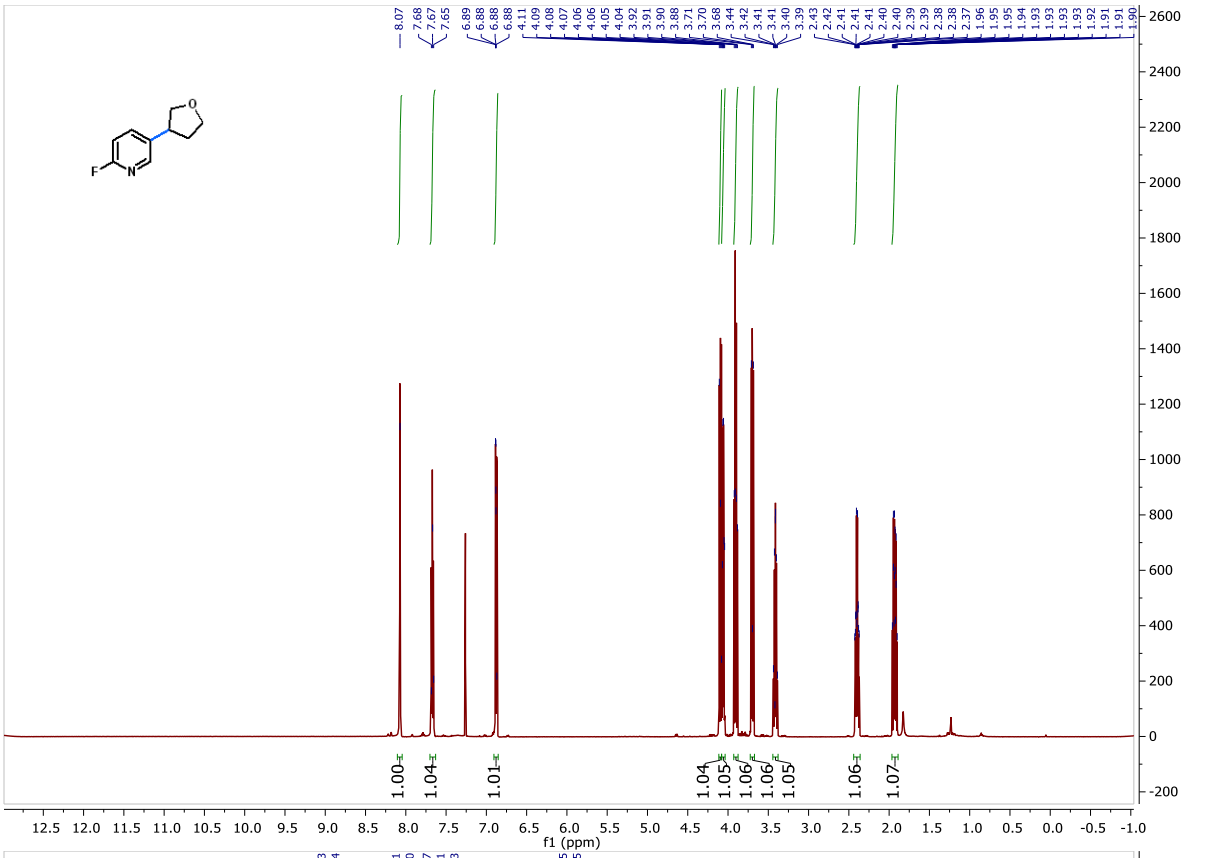
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
-40000
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)


8.07
7.68
7.67
7.65
6.89
6.88
6.88
6.88
4.11
4.09
4.08
4.07
4.06
4.06
4.05
4.04
3.92
3.91
3.90
3.88
3.71
3.70
3.68
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3.41
3.40
3.39
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2.39
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2.38
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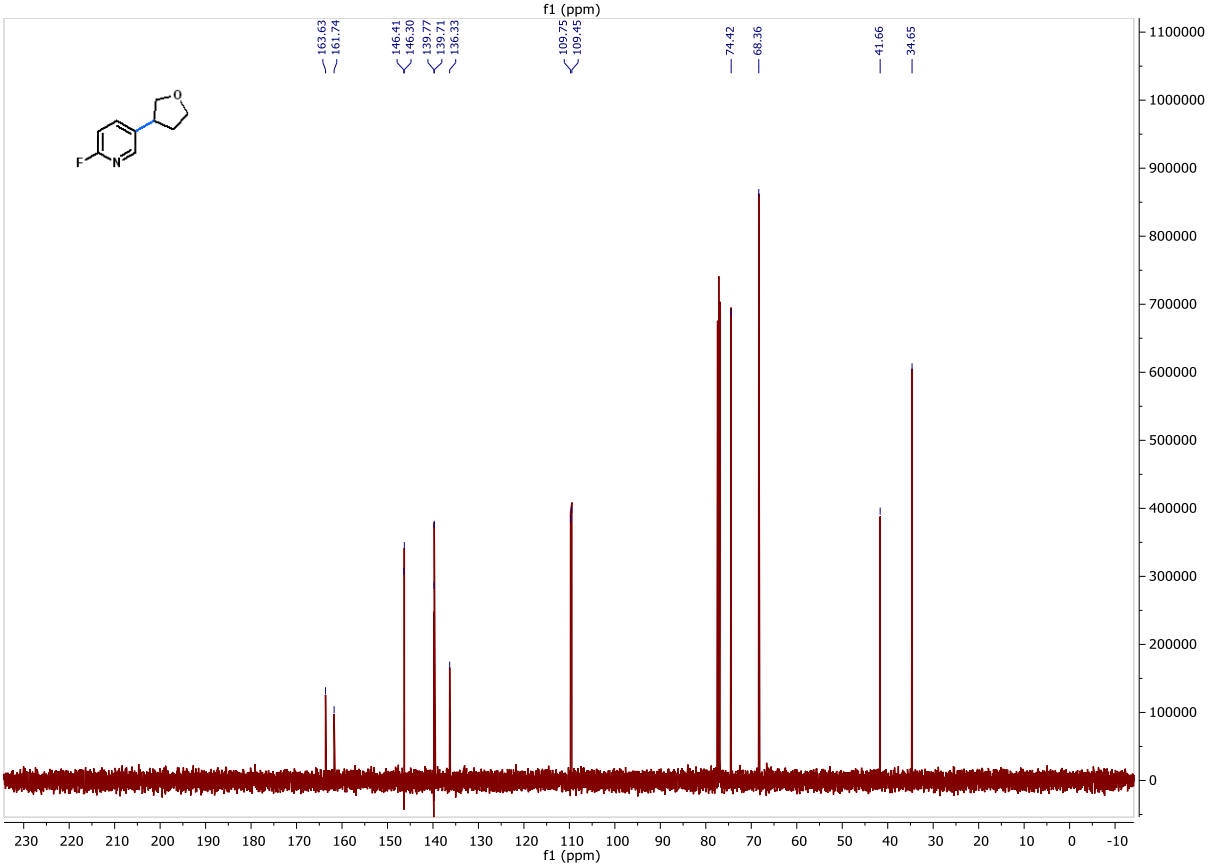
1.06
1.05
1.06
1.07
f1 (ppm)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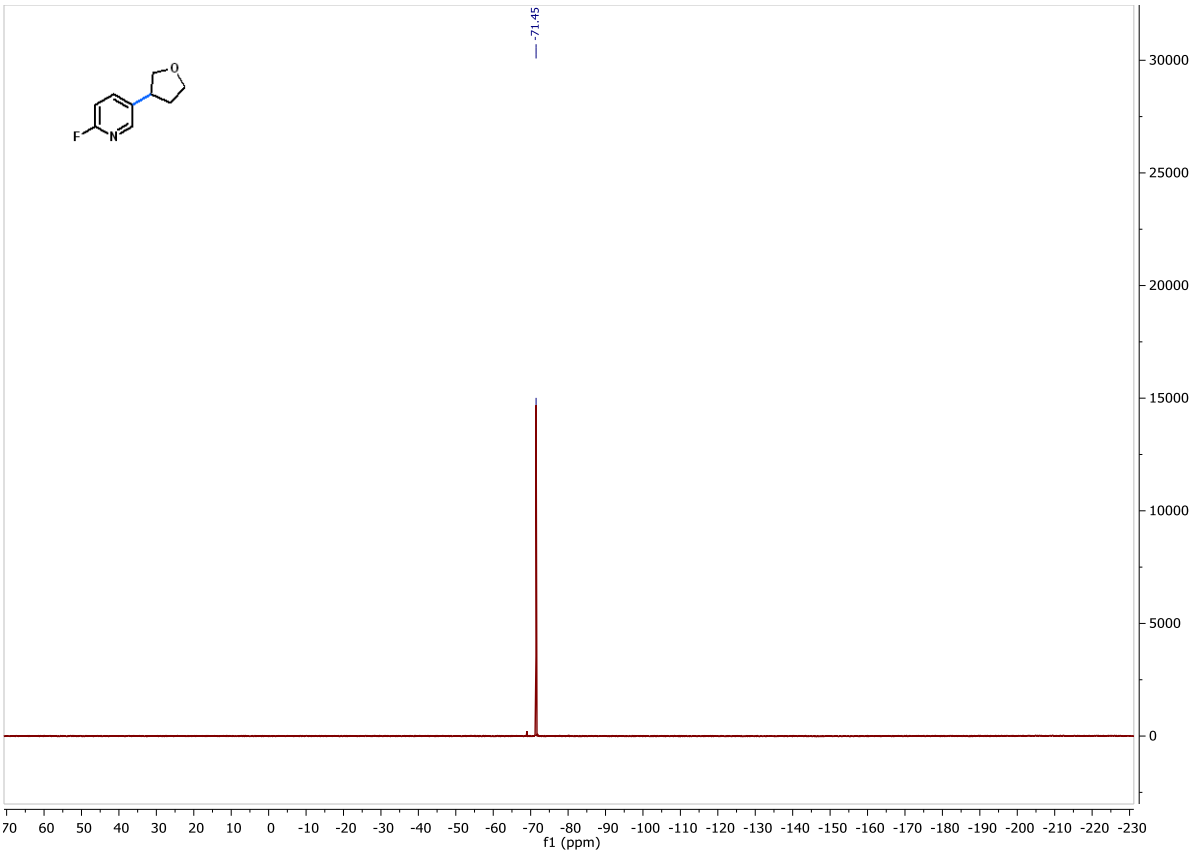
139.71
136.33
109.75
109.45
74.42
68.36
41.66
34.65
f1 (ppm)


-71.45
F
N
O
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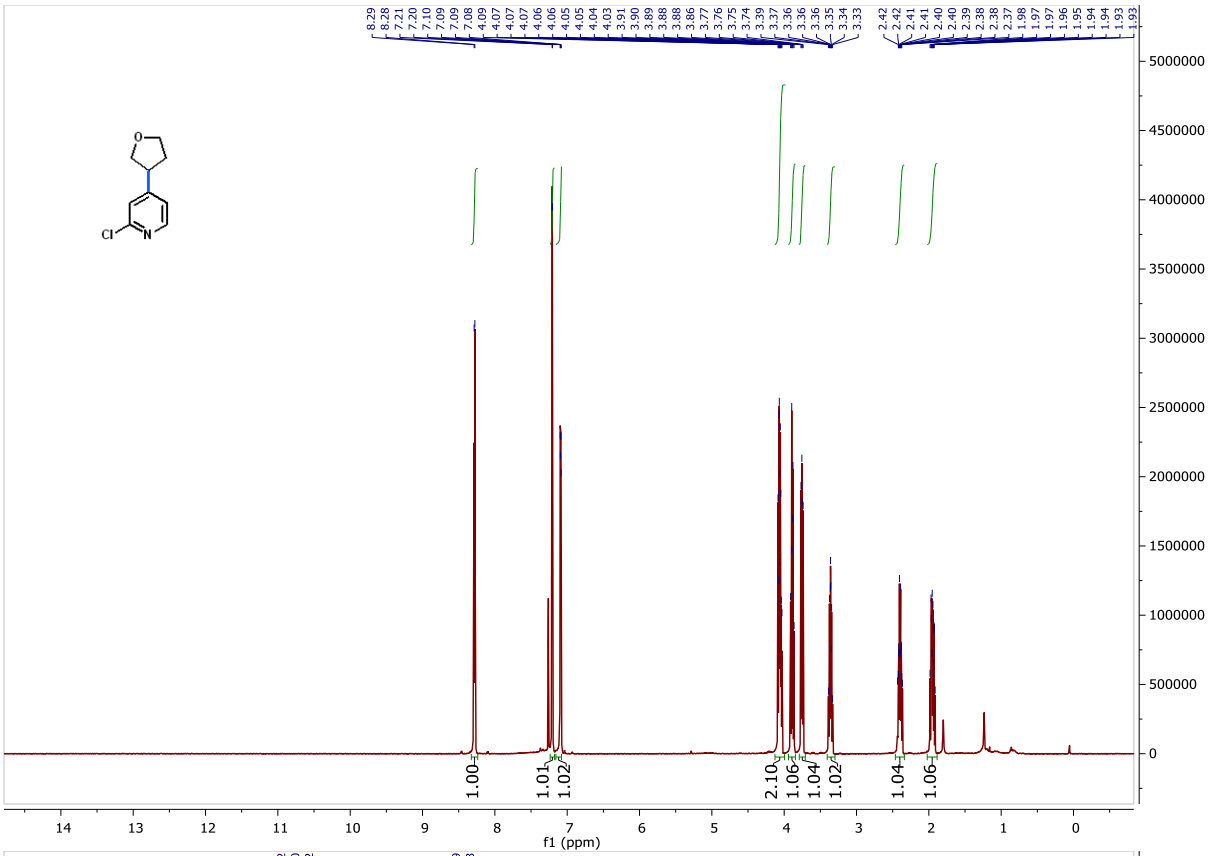
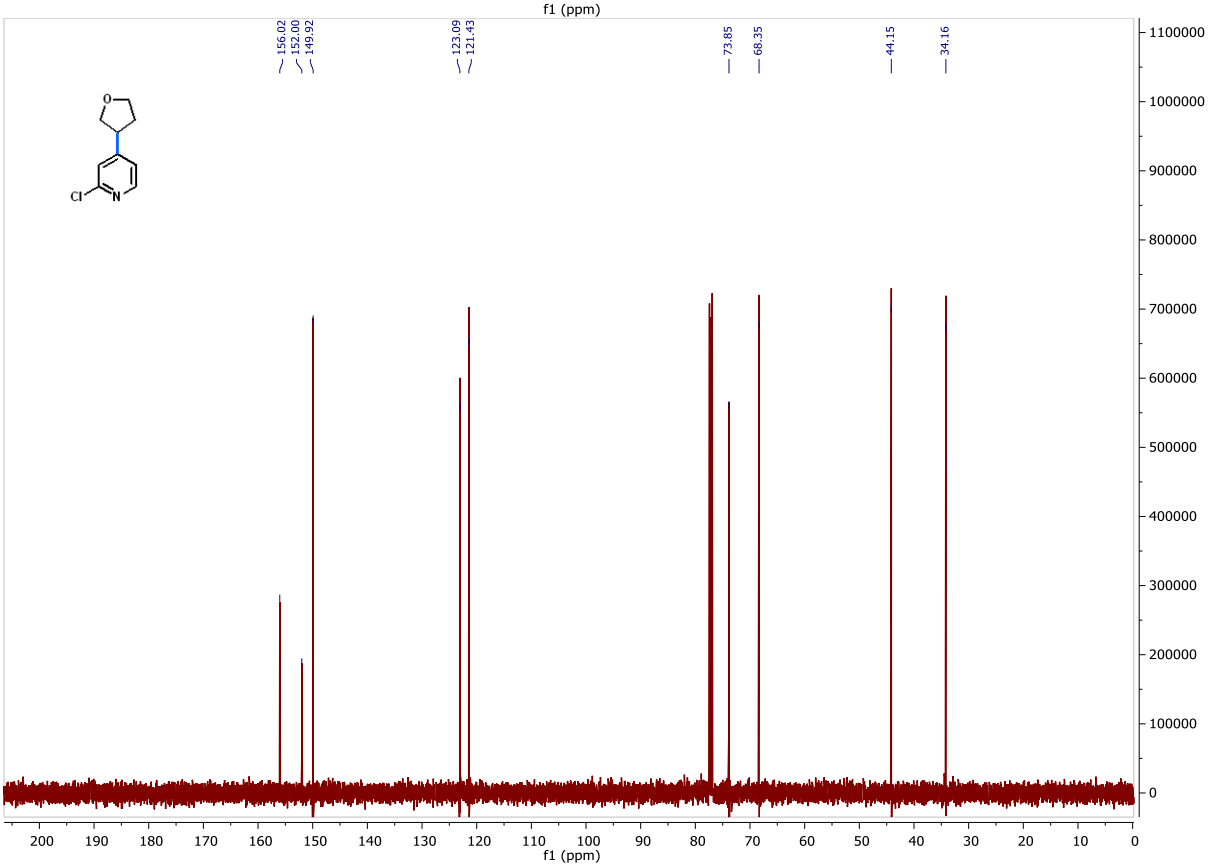
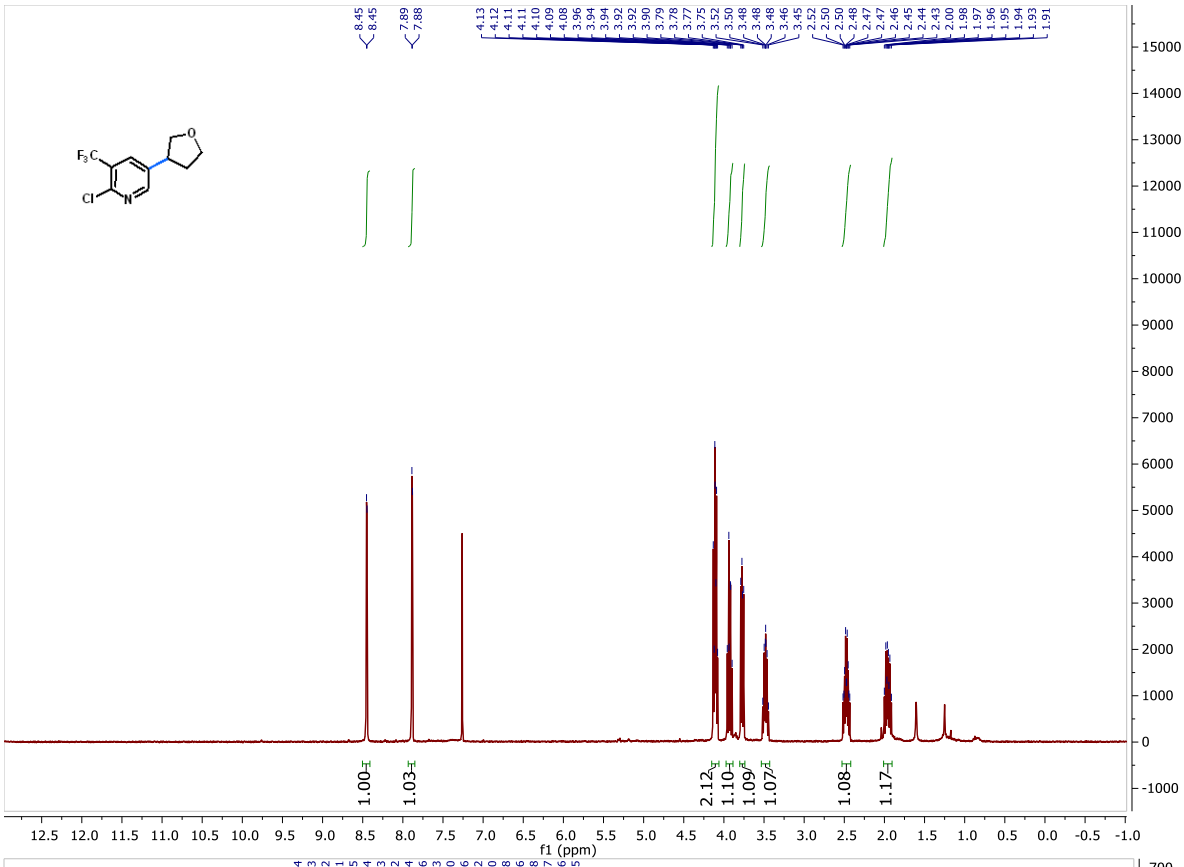
25000
20000
15000
10000
5000
0
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)


8.29 8.28 7.21 7.20 7.10 7.09 7.09 7.08 4.09 4.07 4.07 4.07 4.06 4.06 4.05 4.05 4.04 4.03 3.91 3.90 3.89 3.88 3.88 3.86 3.77 3.76 3.75 3.74 3.39 3.37 3.36 3.36 3.36 3.35 3.34 3.33 2.42 2.42 2.41 2.41 2.40 2.40 2.39 2.38 2.38 2.37 1.98 1.97 1.97 1.96 1.95 1.94 1.94 1.93 1.93
O
Cl
N
1.00 1.01 1.02 2.10 1.06 1.04 1.02 1.04 1.06
f1 (ppm)


156.02 152.00 149.92 123.09 121.43 73.85 68.35 44.15 34.16
O
Cl
N
f1 (ppm)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8.45
7.89
7.88
4.13
4.12
4.11
4.11
4.10
4.09
4.08
3.96
3.94
3.94
3.92
3.92
3.90
3.79
3.78
3.77
3.75
3.52
3.50
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3.48
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2.47
2.46
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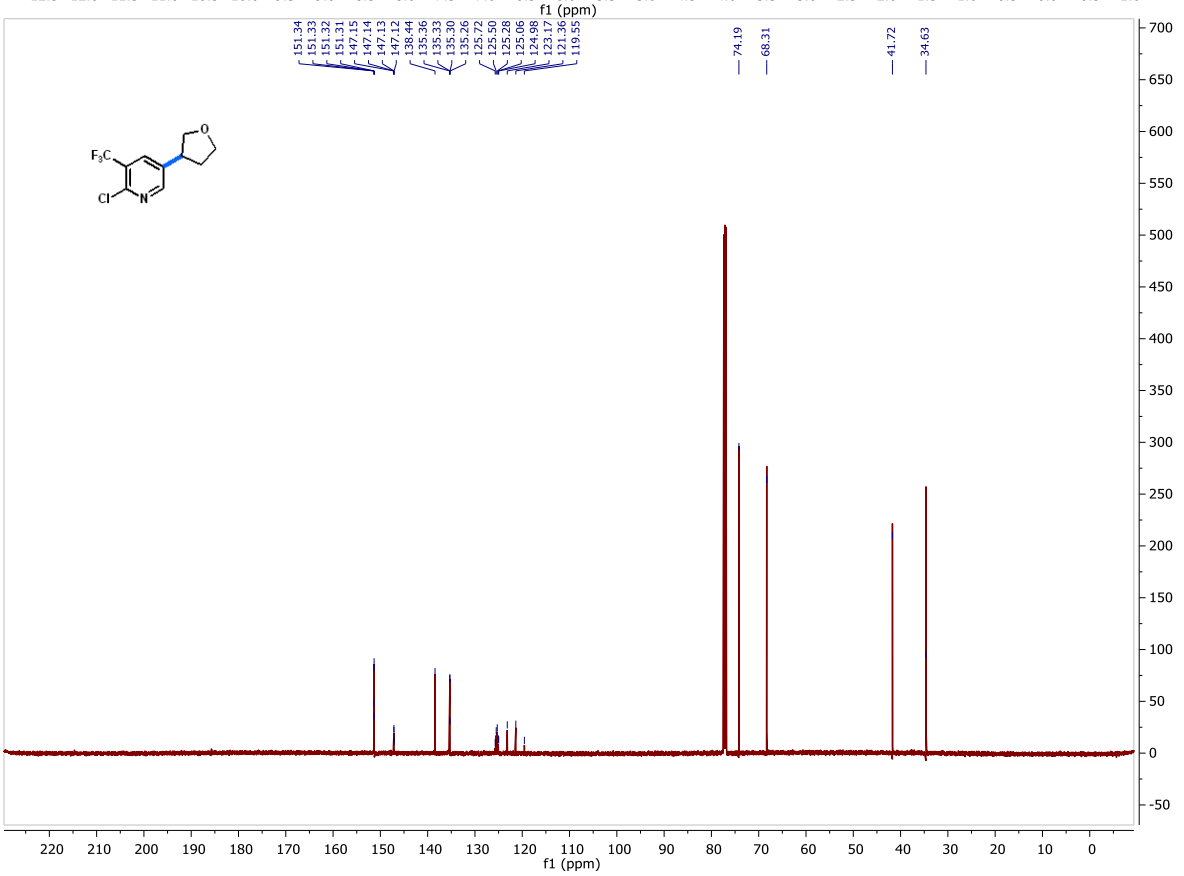
2.44
2.43
2.00
1.98
1.97
1.96
1.95
1.94
1.93
1.91
F3C
Cl
N
O
1.00
1.03
2.12
1.10
1.09
1.07
1.08
1.17
f1 (ppm)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151.33
151.32
151.31
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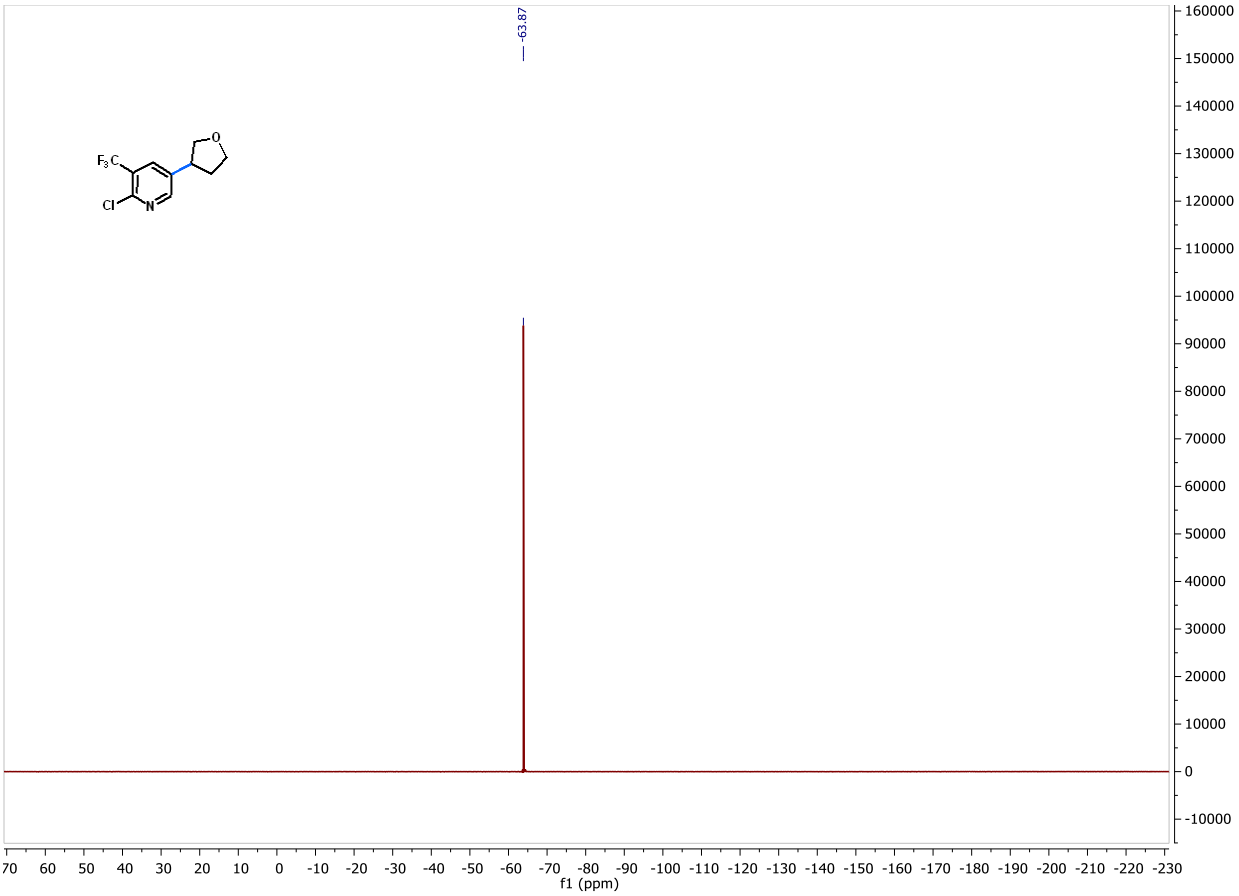
147.14
147.13
147.12
138.44
135.36
135.33
135.30
135.26
125.72
125.50
125.28
125.06
124.99
123.37
123.36
119.55
74.19
68.31
41.72
34.63
F3C
Cl
N
O
f1 (ppm)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F3C
Cl
N
O
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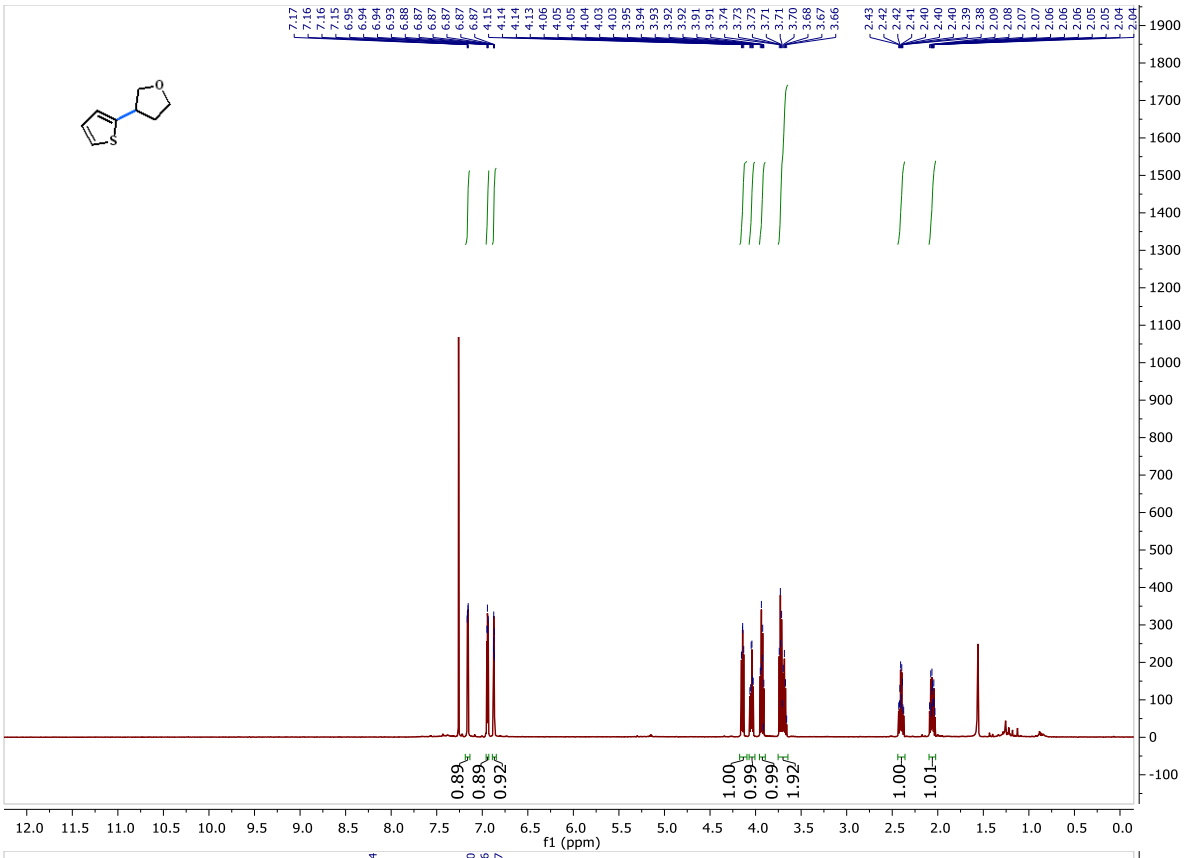
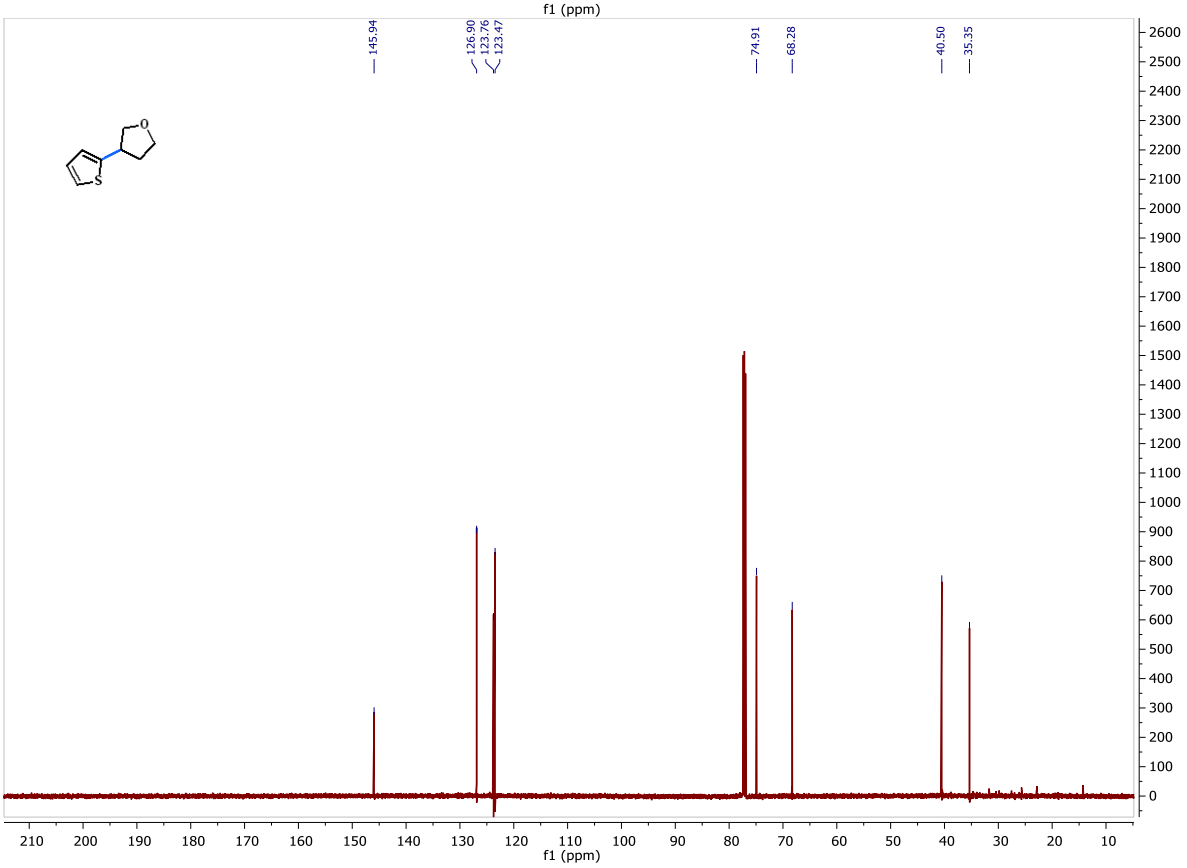
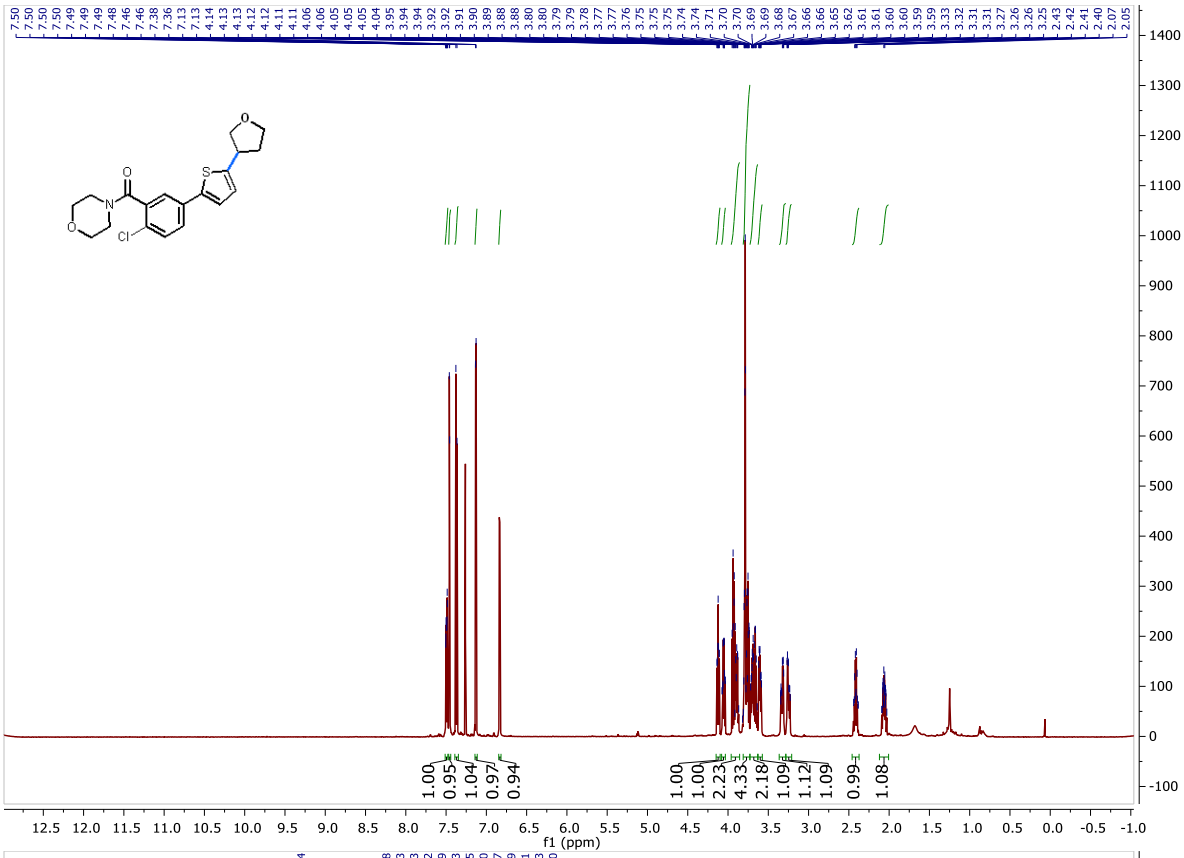
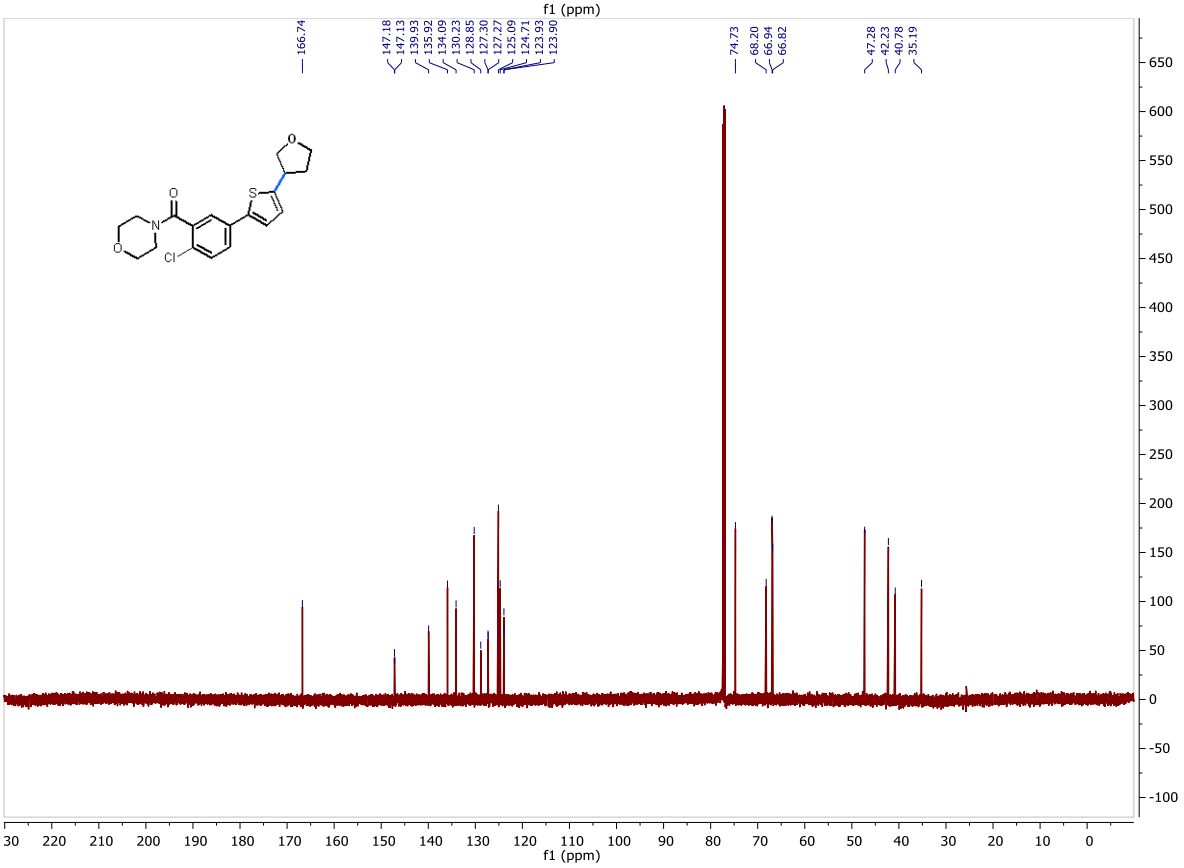
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)


7.17 7.16 7.16 7.15 6.95 6.94 6.94 6.93 6.88 6.87 6.87 6.87 6.87 6.87 4.15 4.14 4.14 4.13 4.06 4.05 4.05 4.04 4.03 4.03 3.95 3.94 3.93 3.92 3.92 3.91 3.91 3.74 3.73 3.73 3.71 3.71 3.70 3.68 3.67 3.66
2.43 2.42 2.42 2.41 2.40 2.40 2.39 2.38 2.09 2.08 2.07 2.07 2.06 2.06 2.06 2.05 2.05 2.04 2.04
0.89 0.89 0.92 1.00 0.99 0.99 1.92 1.00 1.01
f1 (ppm)


145.94
126.90
123.76
123.47
74.91
68.28
40.50
35.35
f1 (ppm)


1.00
0.95
1.04
0.97
0.94
1.00
1.00
2.23
4.33
2.18
1.09
1.12
1.09
0.99
1.08
f1 (ppm)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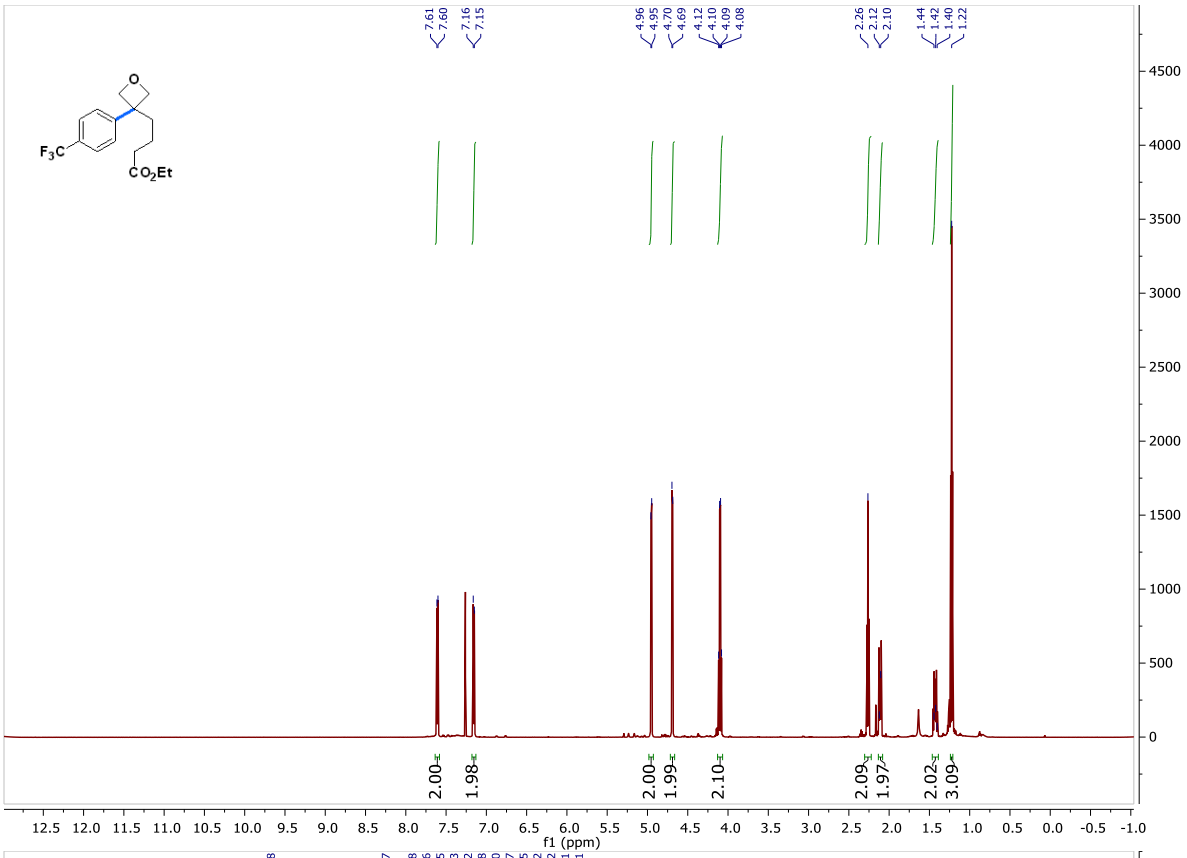
139.93
135.92
134.09
130.23
128.85
127.30
127.27
125.09
124.71
123.93
123.90
74.73
68.20
66.94
66.82
47.28
42.23
40.78
35.19
f1 (ppm)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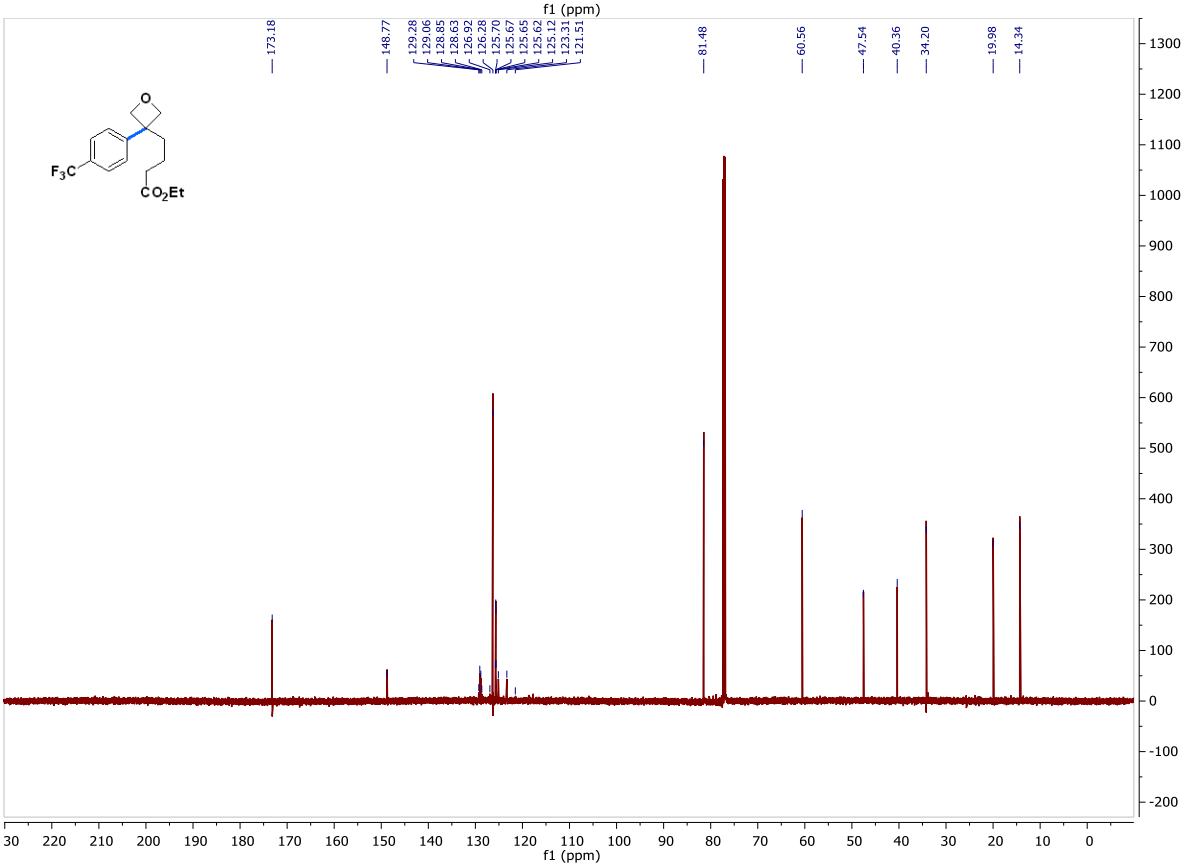
7.60
7.16
7.15
4.96
4.95
4.70
4.69
4.12
4.10
4.09
4.08
2.26
2.12
2.10
1.44
1.42
1.40
1.22
2.00
1.98
2.00
1.99
2.10
2.09
1.97
2.02
3.09
f1 (ppm)


173.18
148.77
129.28
129.06
128.85
128.63
126.92
126.28
125.70
125.67
125.65
125.62
125.12
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121.51
81.48
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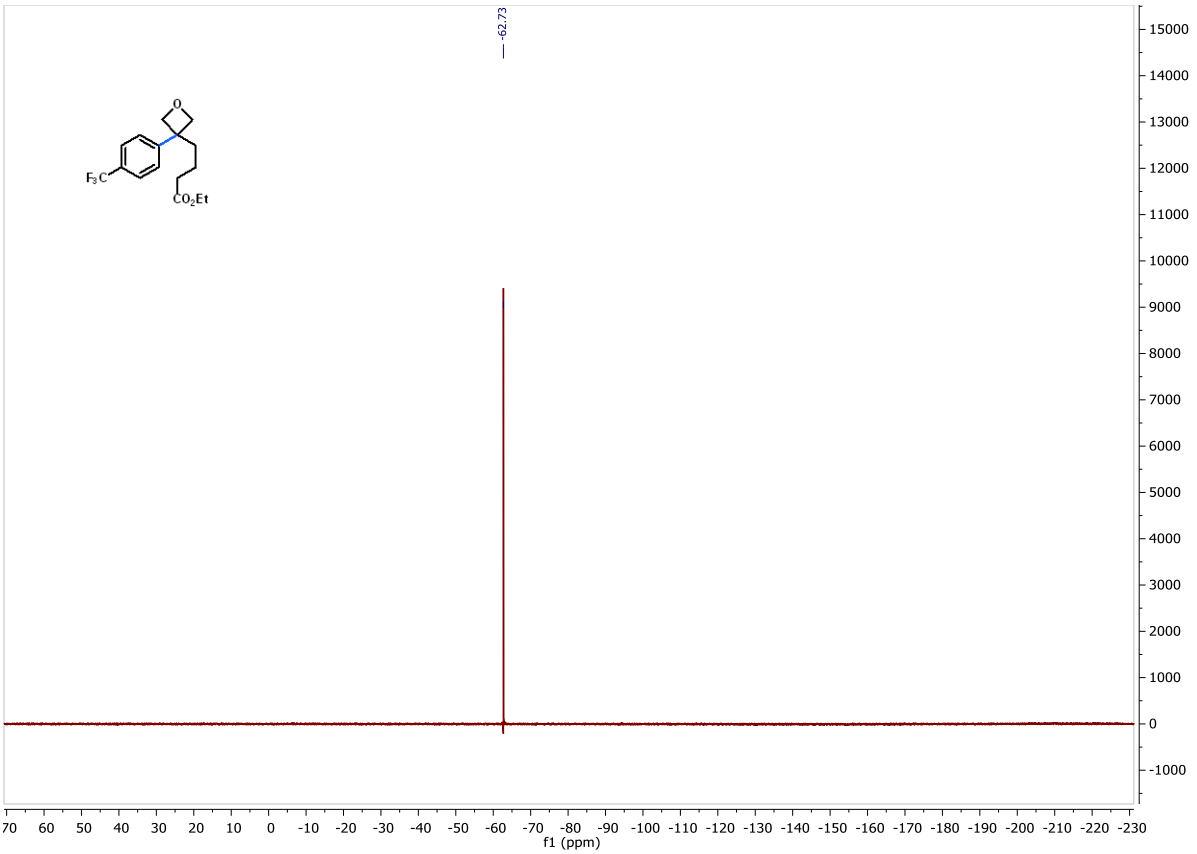
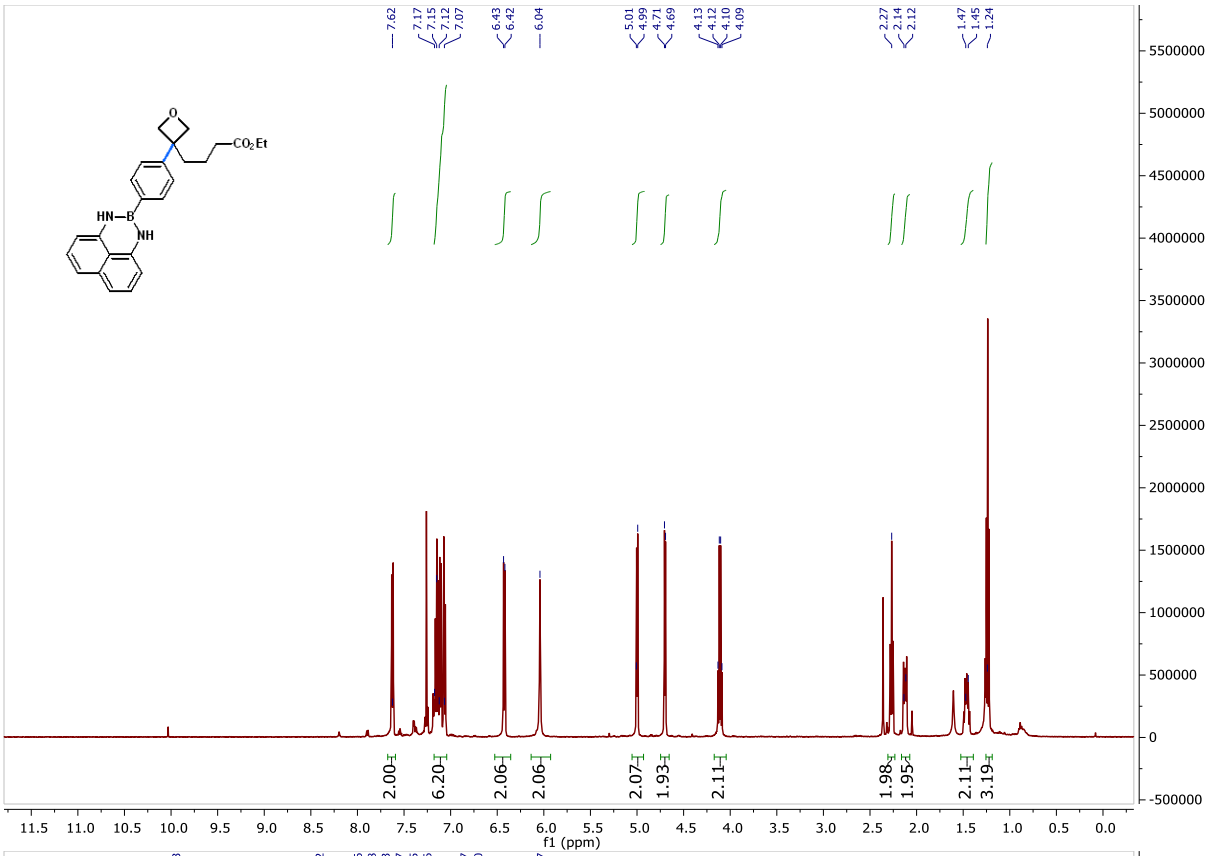
47.54
40.36
34.20
19.98
14.34
f1 (ppm)


-62.73
O
F3C
CO2Et
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)


7.62
7.17
7.15
7.12
7.07
6.43
6.42
6.04
5.01
4.99
4.71
4.69
4.13
4.12
4.10
4.09
2.27
2.14
2.12
1.47
1.45
1.24
2.00
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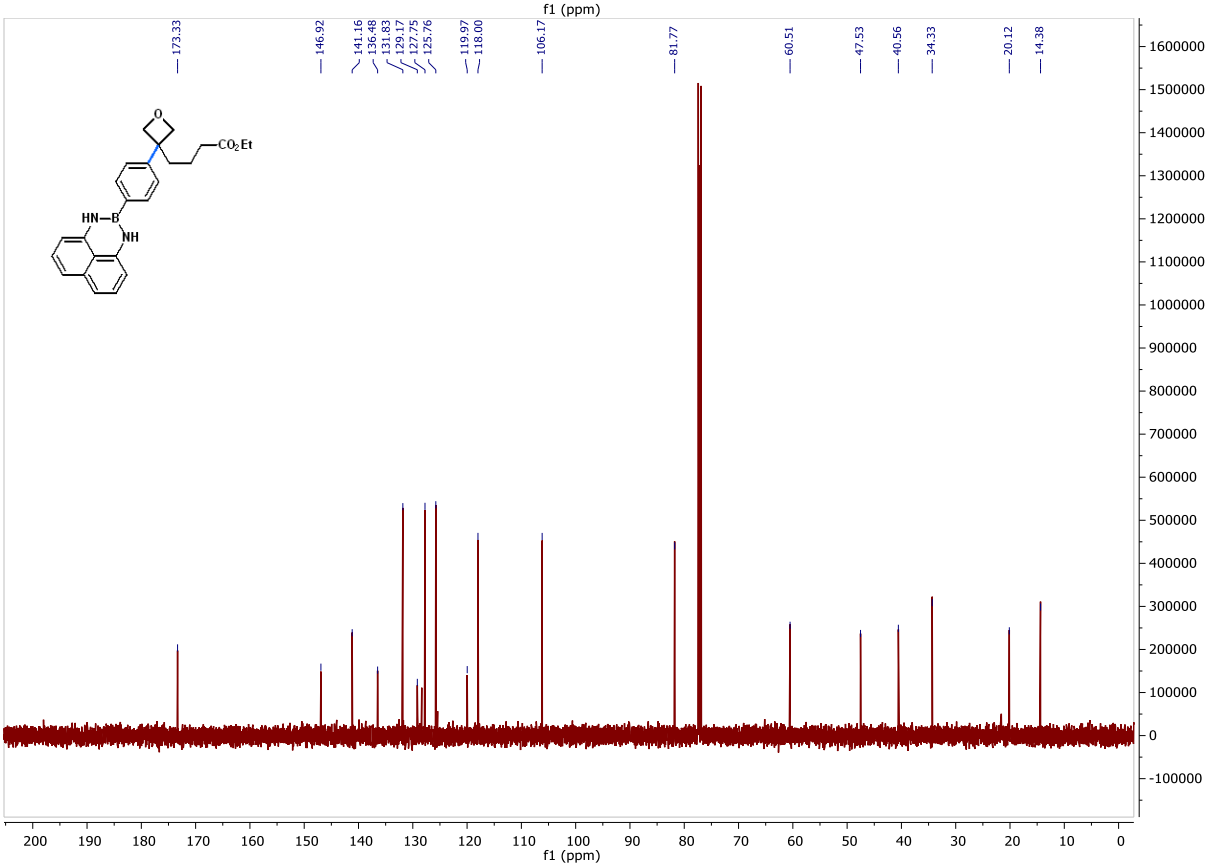
2.06
2.07
1.93
2.11
1.98
1.95
2.11
3.19
f1 (ppm)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141.16
136.48
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129.17
127.75
125.76
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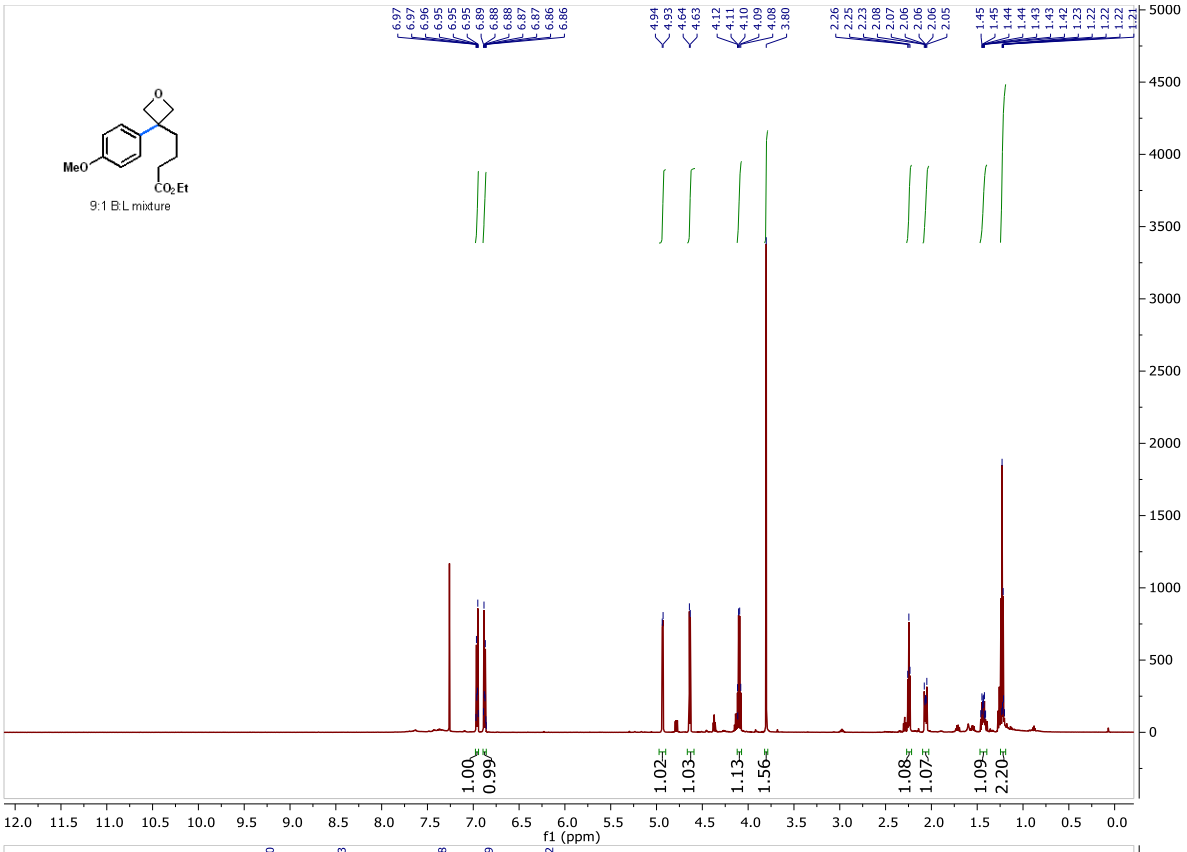
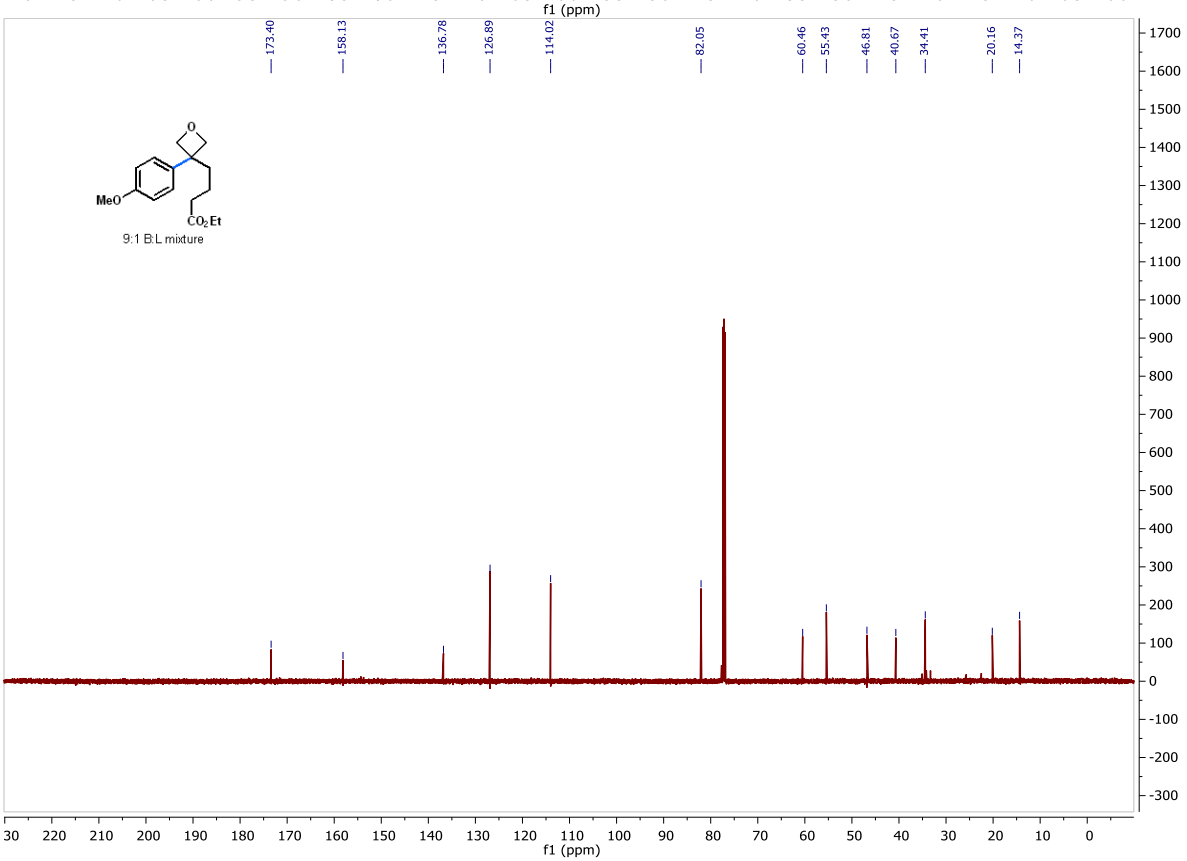
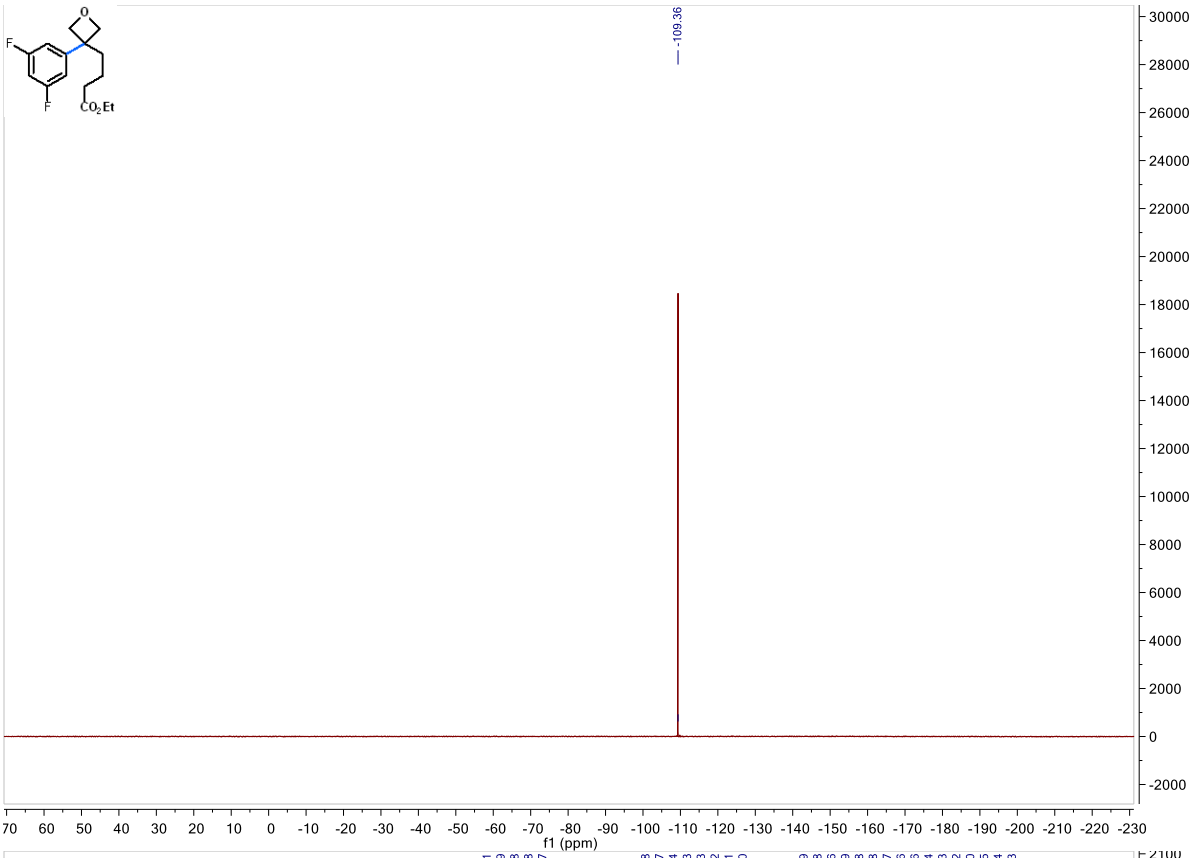
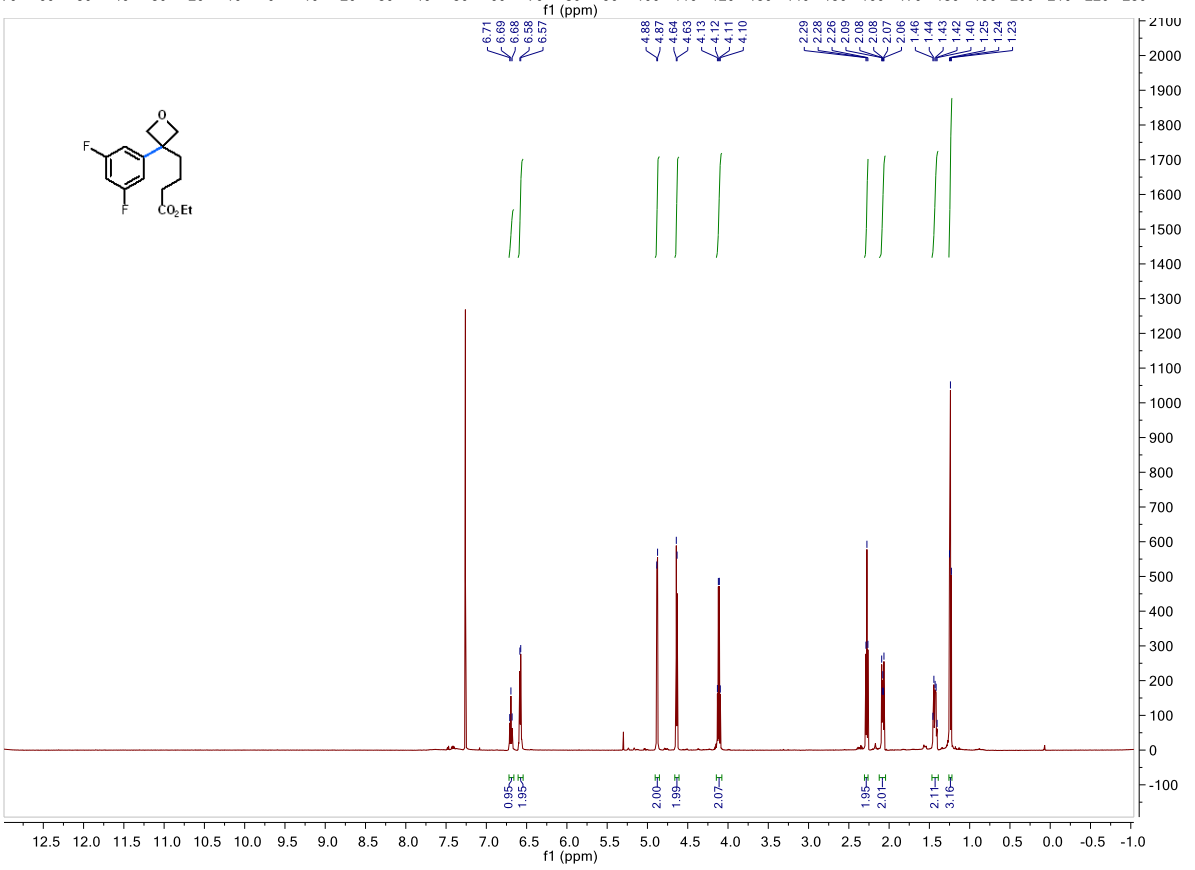
81.77
60.51
47.53
40.56
34.33
20.12
14.38
f1 (ppm)


MeO
CO2Et
9:1 B:L mixture
6.97 6.97 6.96 6.95 6.95 6.89 6.88 6.88 6.87 6.87 6.86 6.86
4.94 4.93 4.64 4.63
4.12 4.11 4.10 4.09 4.08 3.80
2.26 2.25 2.23 2.08 2.07 2.06 2.06 2.06 2.05
1.45 1.45 1.44 1.44 1.43 1.43 1.42 1.23 1.22 1.22 1.22 1.21
1.00 0.99 1.02 1.03 1.13 1.56 1.08 1.07 1.09 2.20
f1 (ppm)


MeO
CO2Et
9:1 B:L mixture
173.40 158.13 136.78 126.89 114.02 82.05 60.46 55.43 46.81 40.67 34.41 20.16 14.37
f1 (ppm)


-109.36
f1 (ppm)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6.69
6.68
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4.88
4.87
4.64
4.63
4.13
4.12
4.11
4.10
2.29
2.28
2.26
2.09
2.08
2.08
2.07
2.06
1.46
1.44
1.43
1.42
1.40
1.25
1.24
1.23
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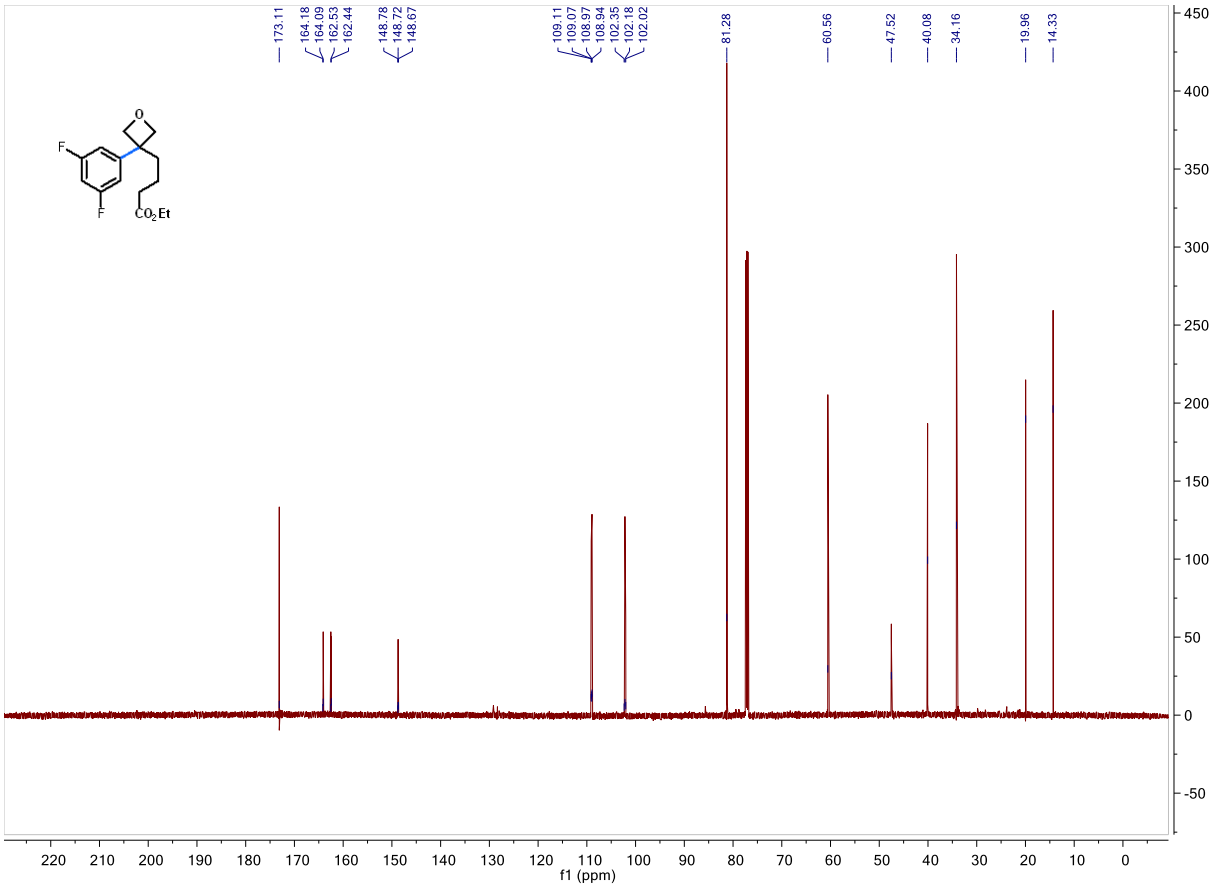
1.95
2.00
1.99
2.07
1.95
2.01
2.11
3.16
f1 (ppm)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148.67
109.11
109.07
108.97
108.94
102.35
102.18
102.02
81.28
60.56
47.52
40.08
34.16
19.96
14.33
F
F
O
CO2Et
450
400
350
300
250
200
150
100
50
0
-50
220
210
200
190
180
170
160
150
140
130
120
110
100
90
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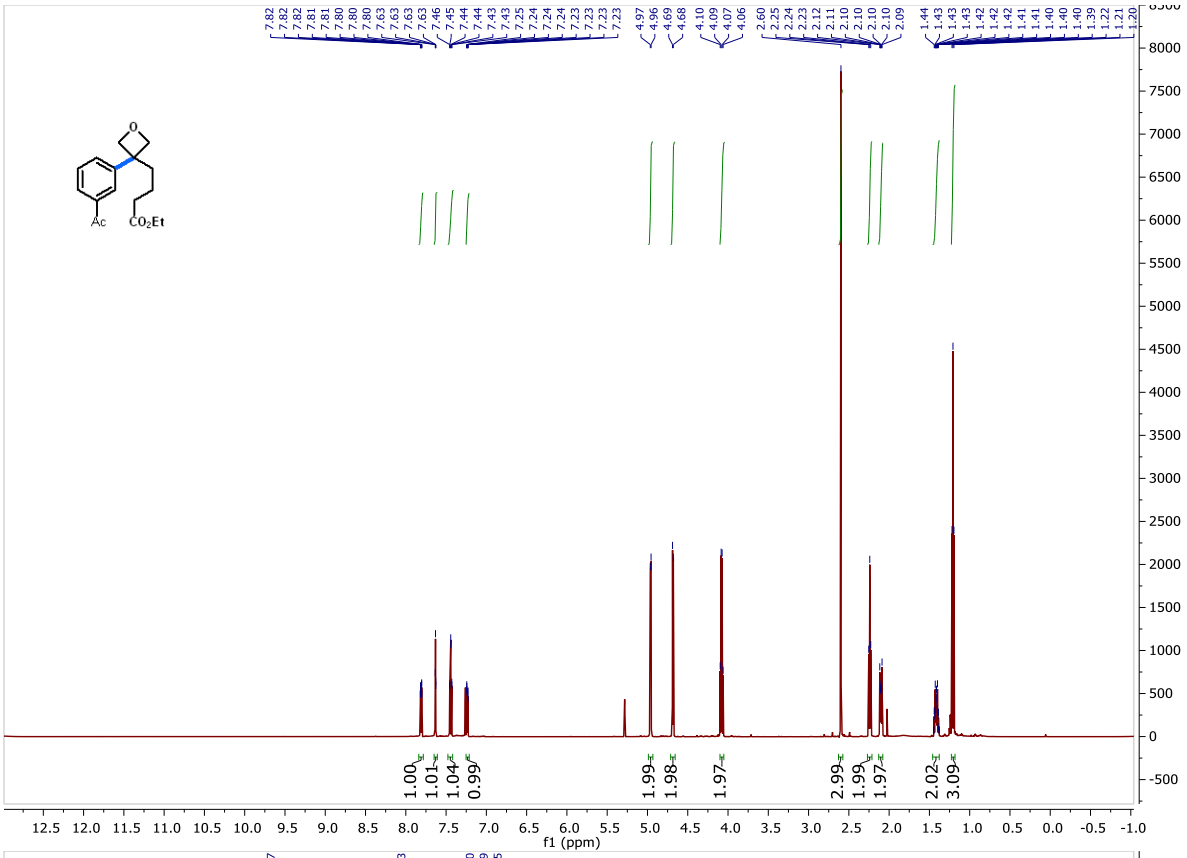
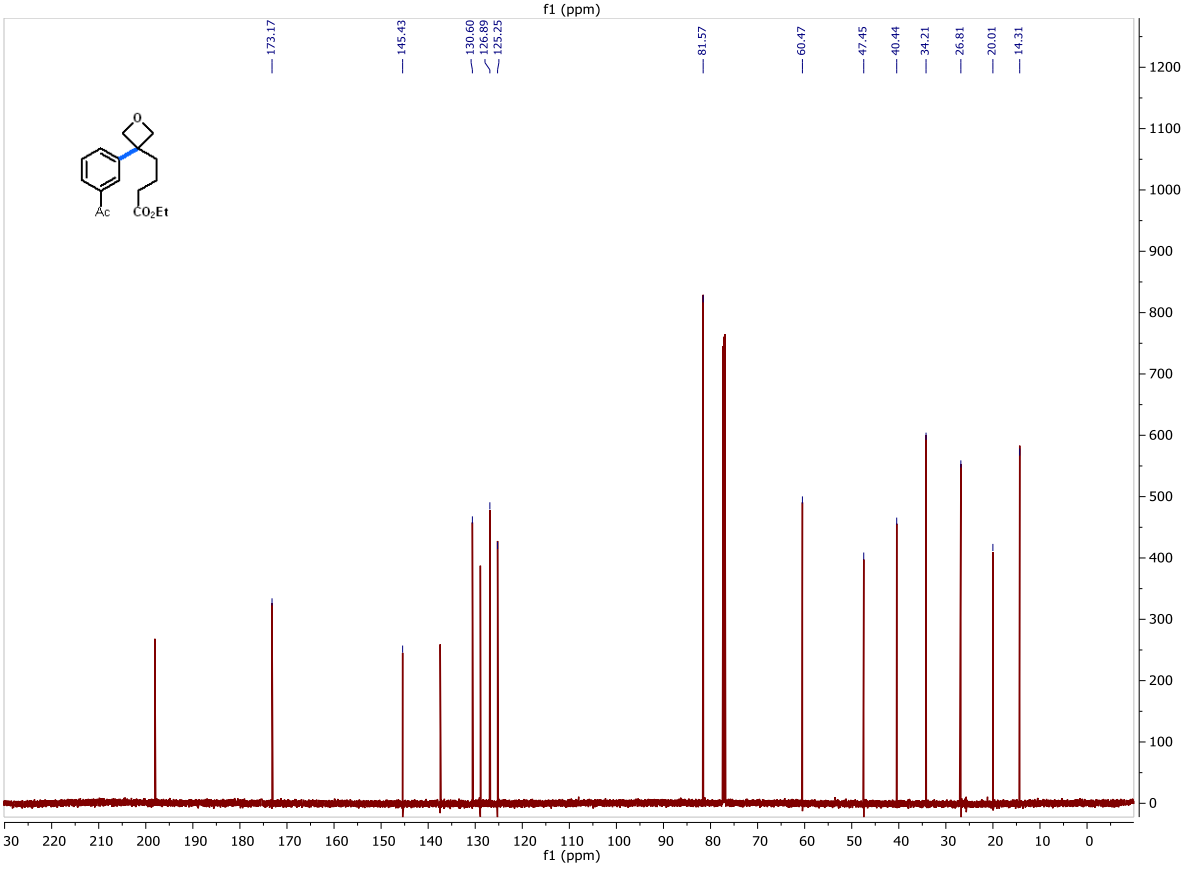
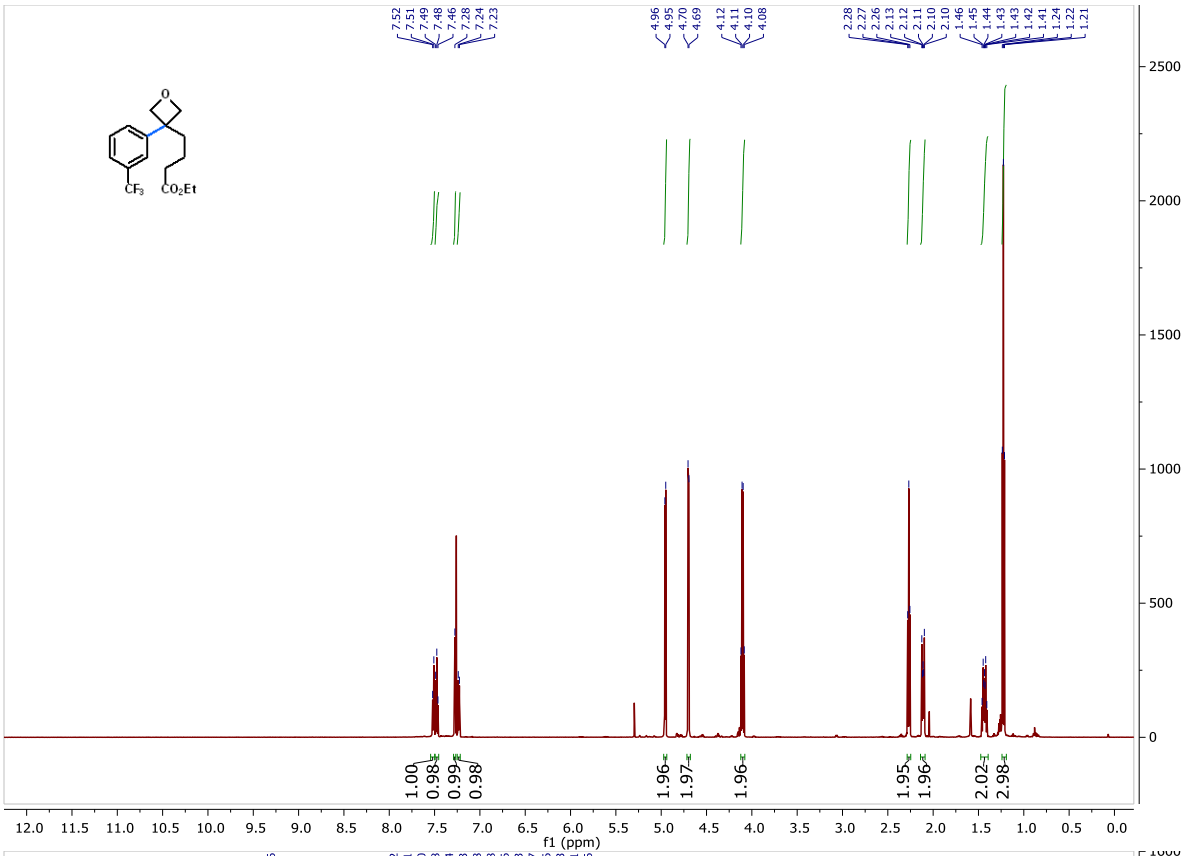
70
60
50
40
30
20
10
0
f1 (ppm)


Ac
CO2Et
f1 (ppm)


Ac
CO2Et
f1 (ppm)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7.24
7.23
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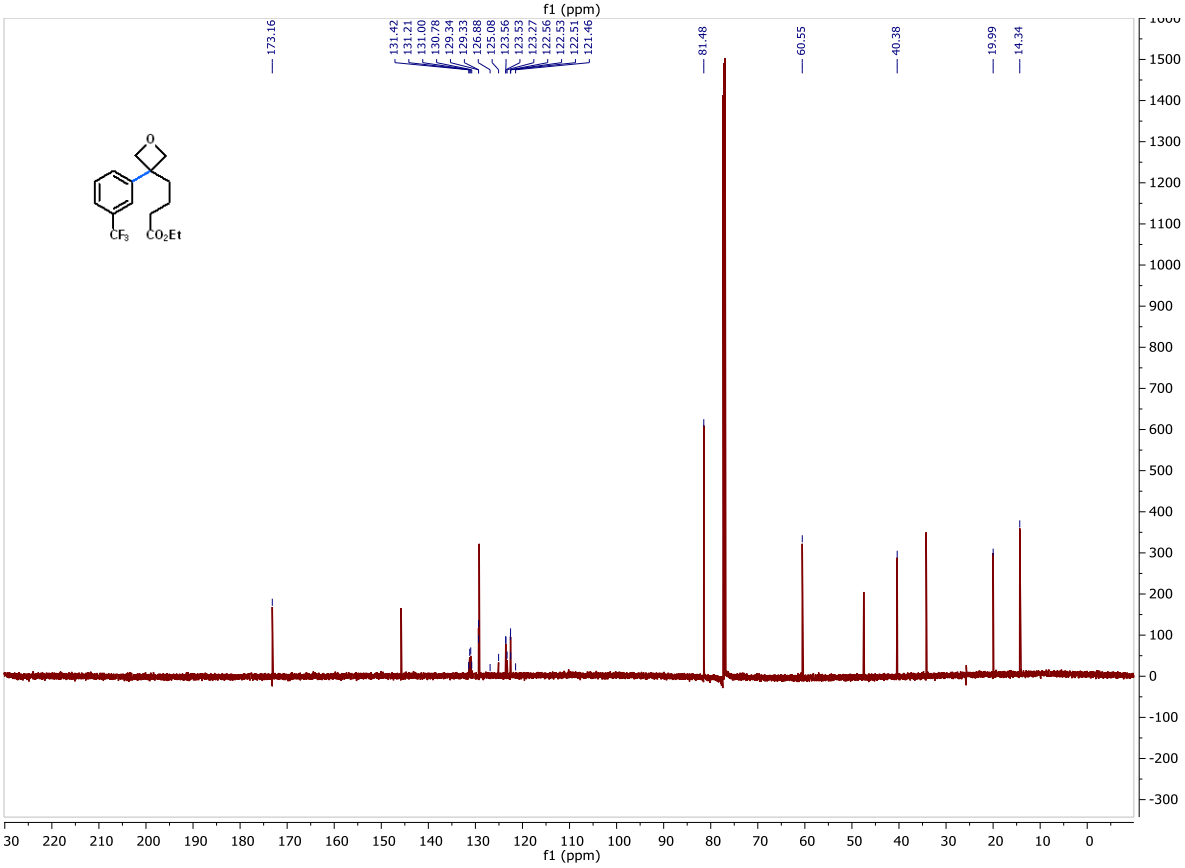
4.95
4.70
4.69
4.12
4.11
4.10
4.08
2.28
2.27
2.26
2.13
2.12
2.11
2.10
2.10
1.46
1.45
1.44
1.43
1.43
1.42
1.41
1.24
1.22
1.21
O
CF3
CO2Et
1.00
0.98
0.99
0.98
1.96
1.97
1.96
1.95
1.96
2.02
2.98
f1 (ppm)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131.21
131.00
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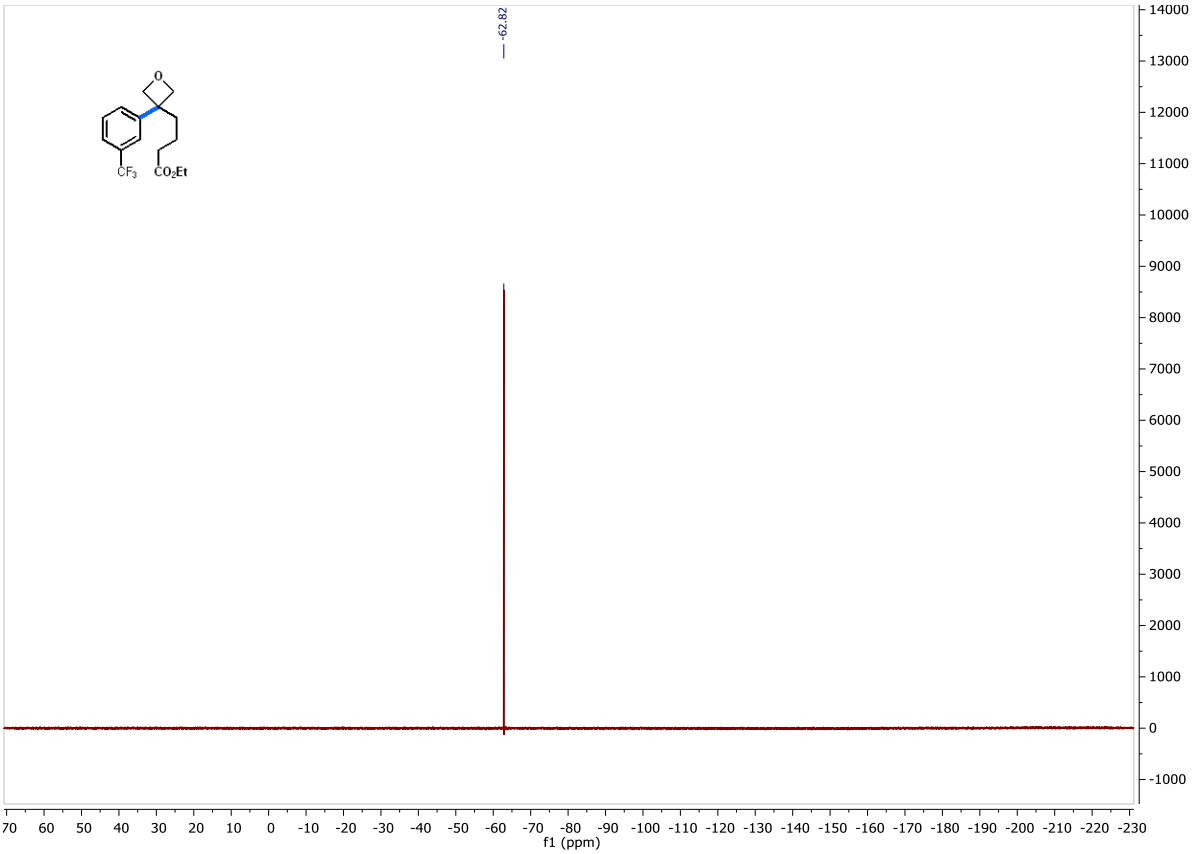
126.88
125.08
123.56
123.53
123.27
122.56
122.53
122.51
121.46
81.48
60.55
40.38
19.99
14.34
O
CF3
CO2Et
f1 (ppm)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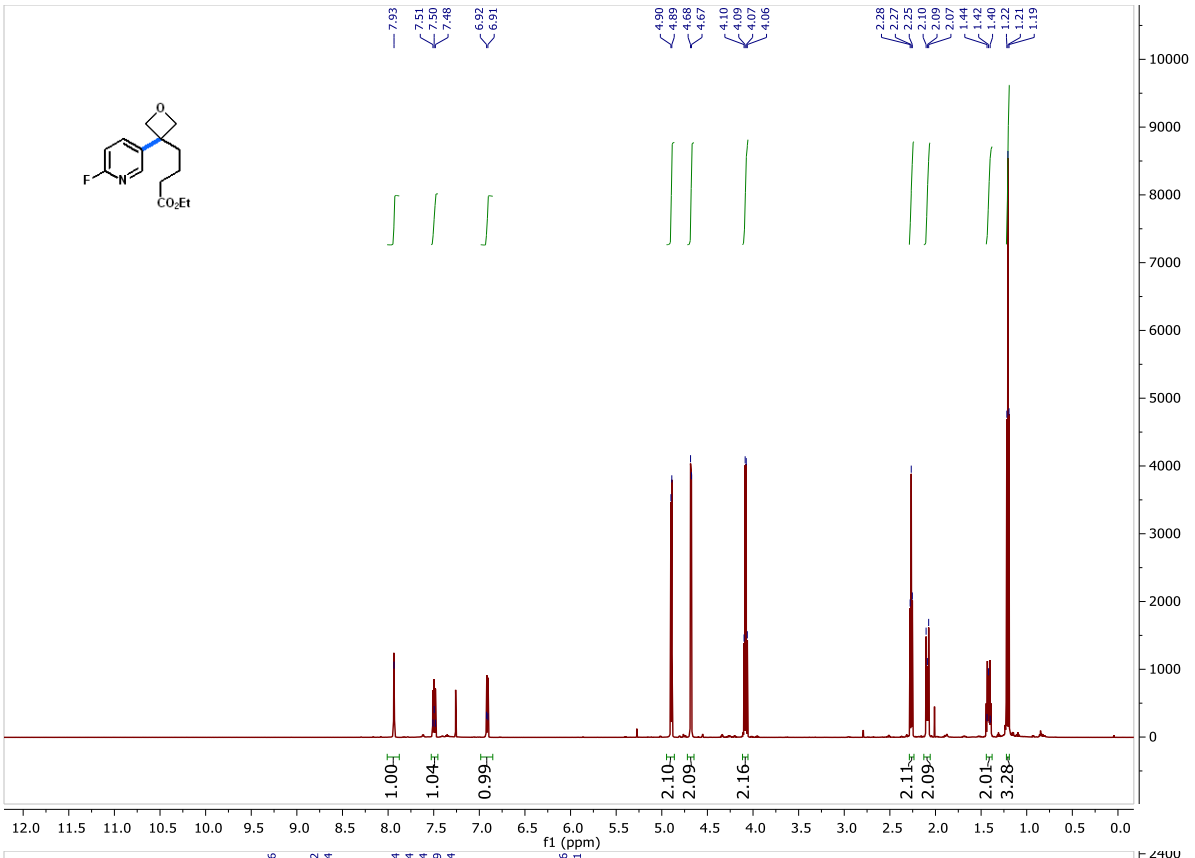
CF3
CO2Et
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)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7.50
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6.91
4.90
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4.67
4.10
4.09
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4.06
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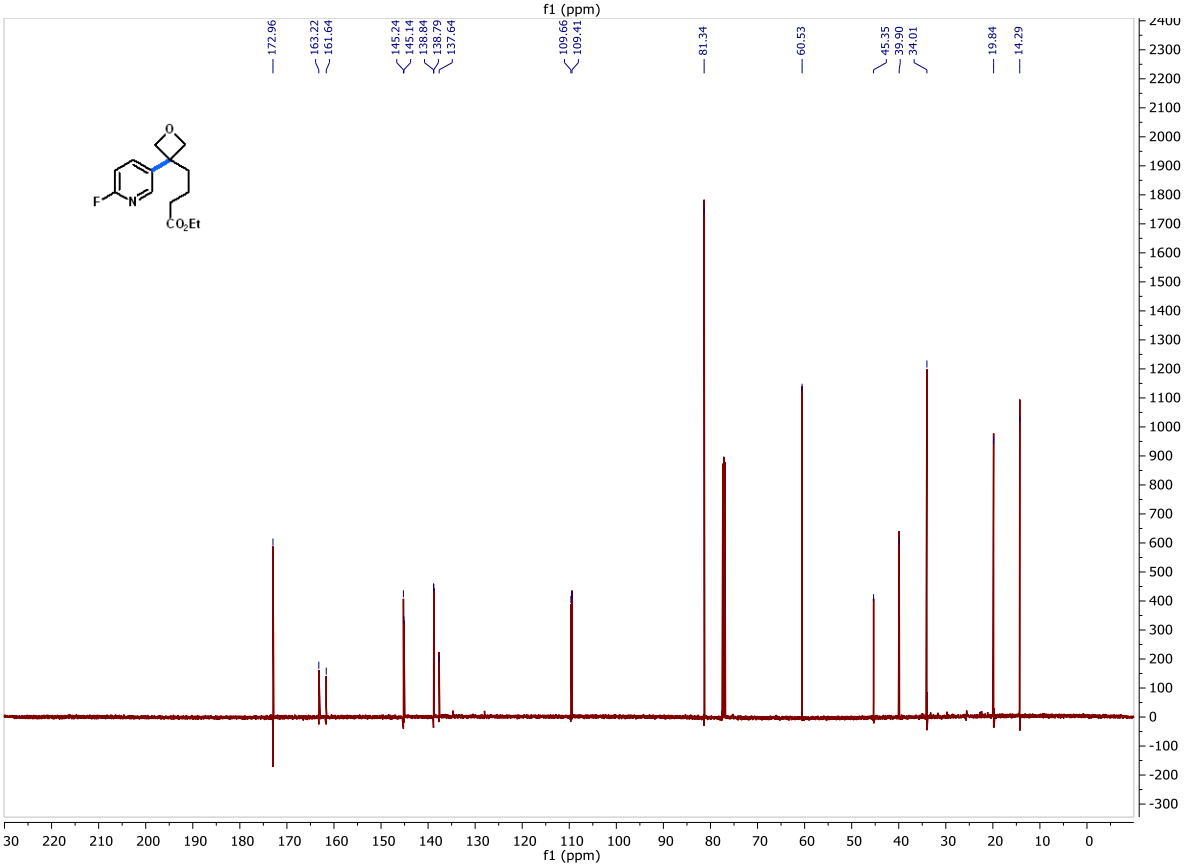
2.27
2.25
2.10
2.09
2.07
1.44
1.42
1.40
1.22
1.21
1.19
1.00
1.04
0.99
2.10
2.09
2.16
2.11
2.09
2.01
3.28
f1 (ppm)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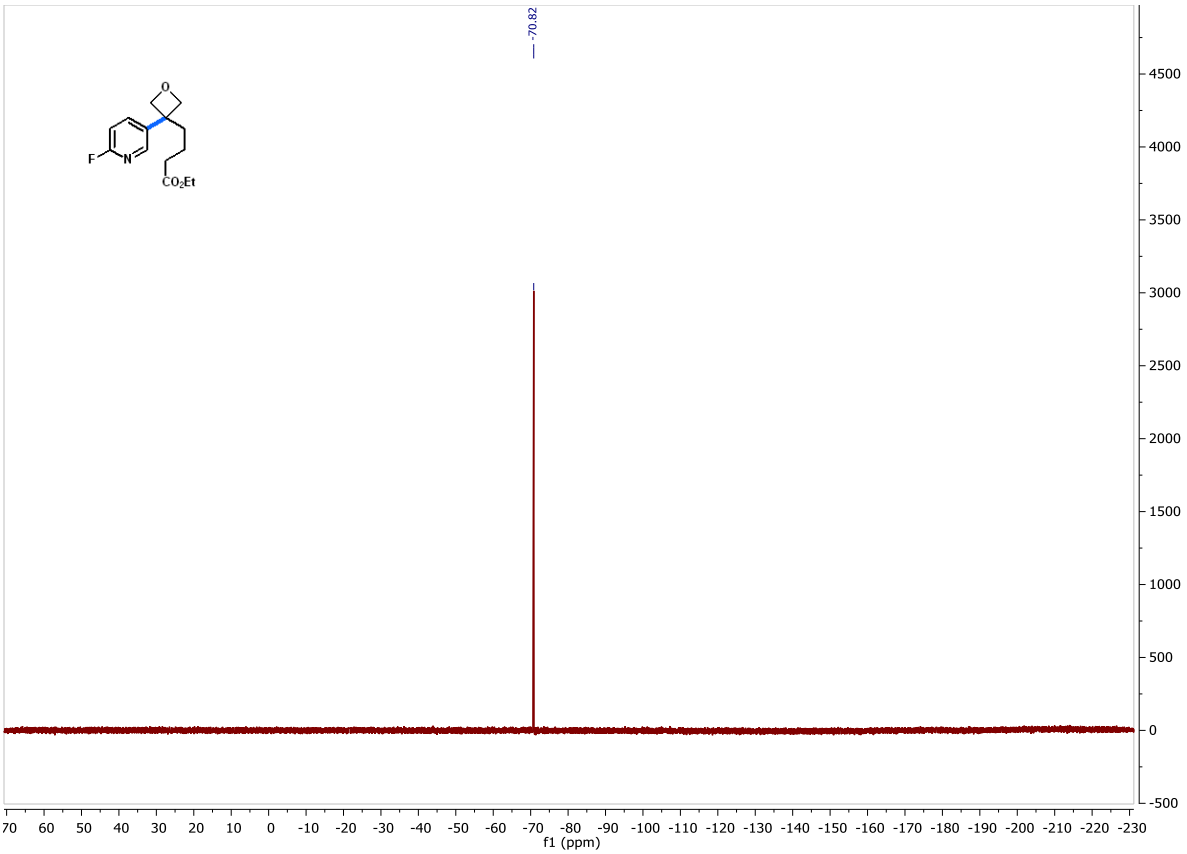
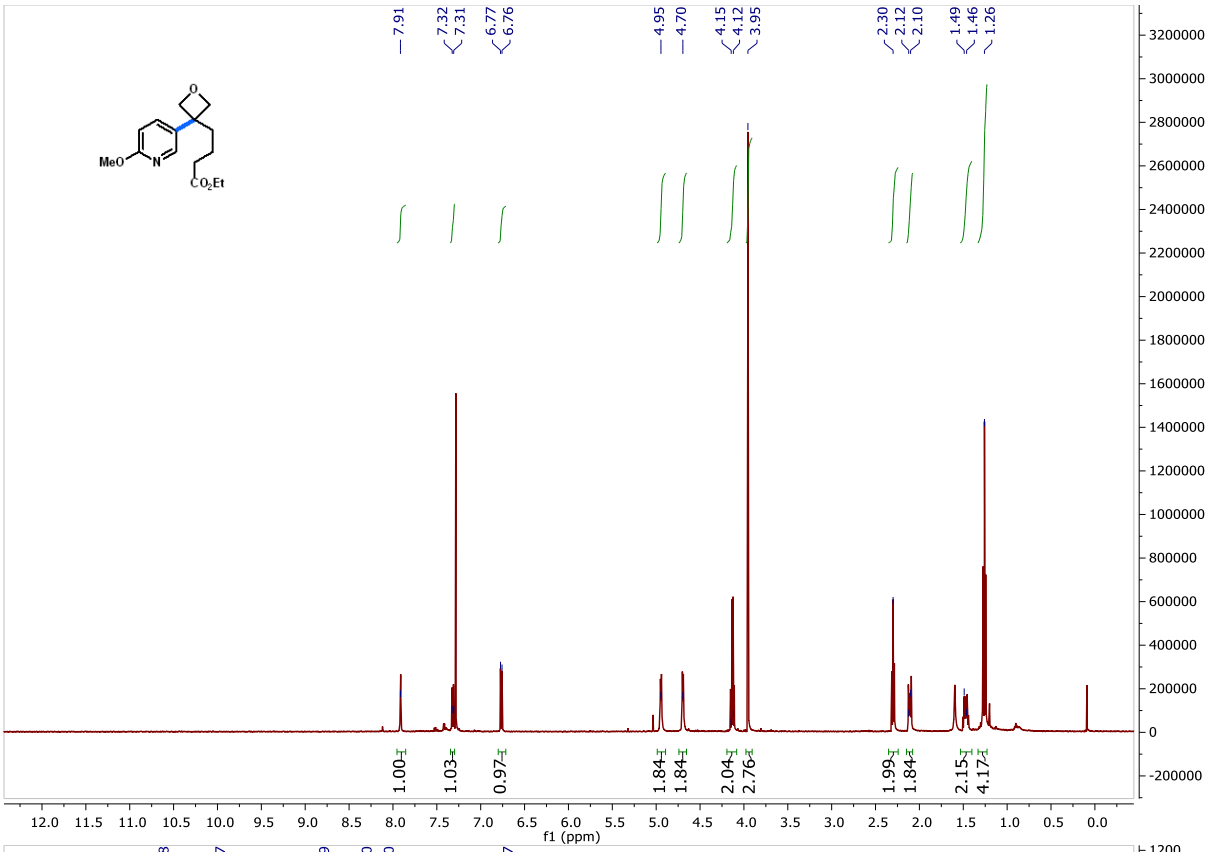
163.22
161.64
145.24
145.14
138.84
138.79
137.64
109.66
109.41
81.34
60.53
45.35
39.90
34.01
19.84
14.29
f1 (ppm)


-70.82
O
F
N
CO2Et
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)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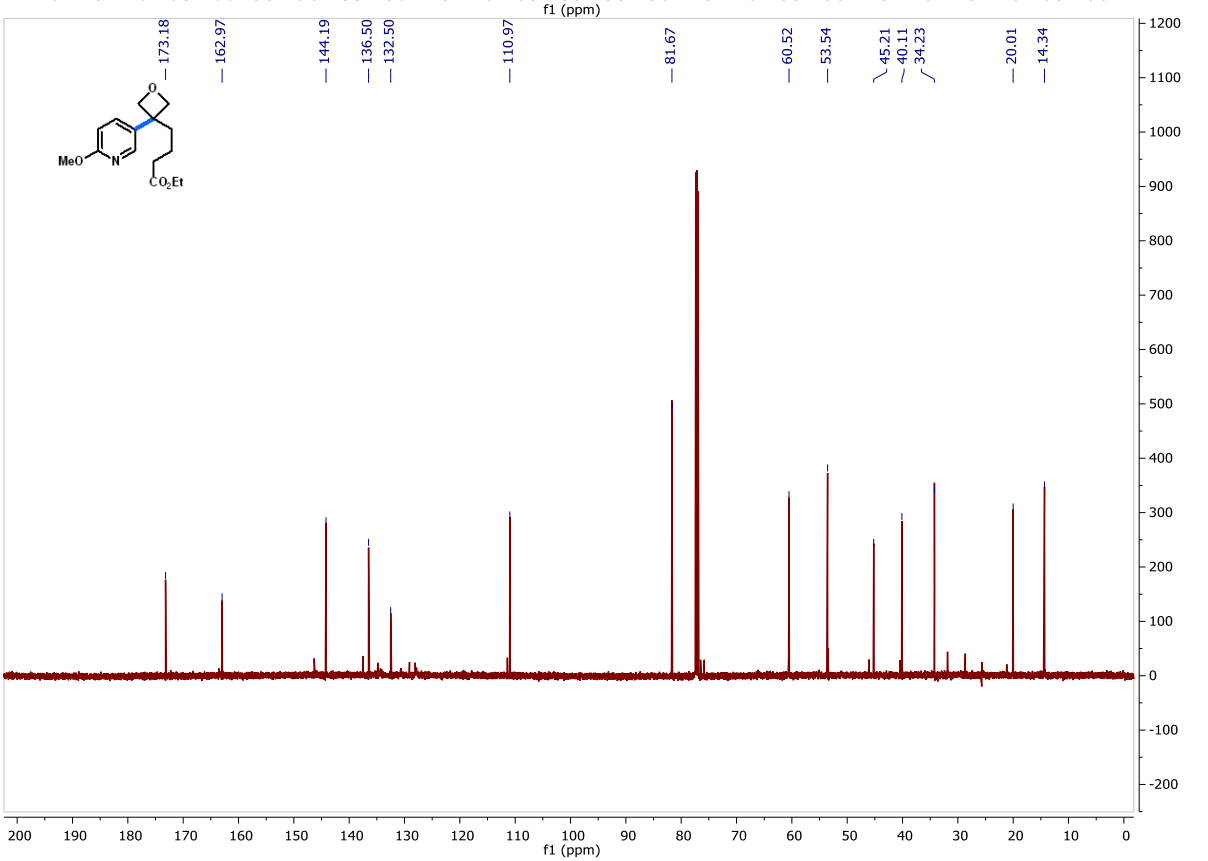
7.31
6.77
6.76
4.95
4.70
4.15
4.12
3.95
2.30
2.12
2.10
1.49
1.46
1.26
1.00
1.03
0.97
1.84
1.84
2.04
2.76
1.99
1.84
2.15
4.17
MeO
N
O
CO2Et
f1 (ppm)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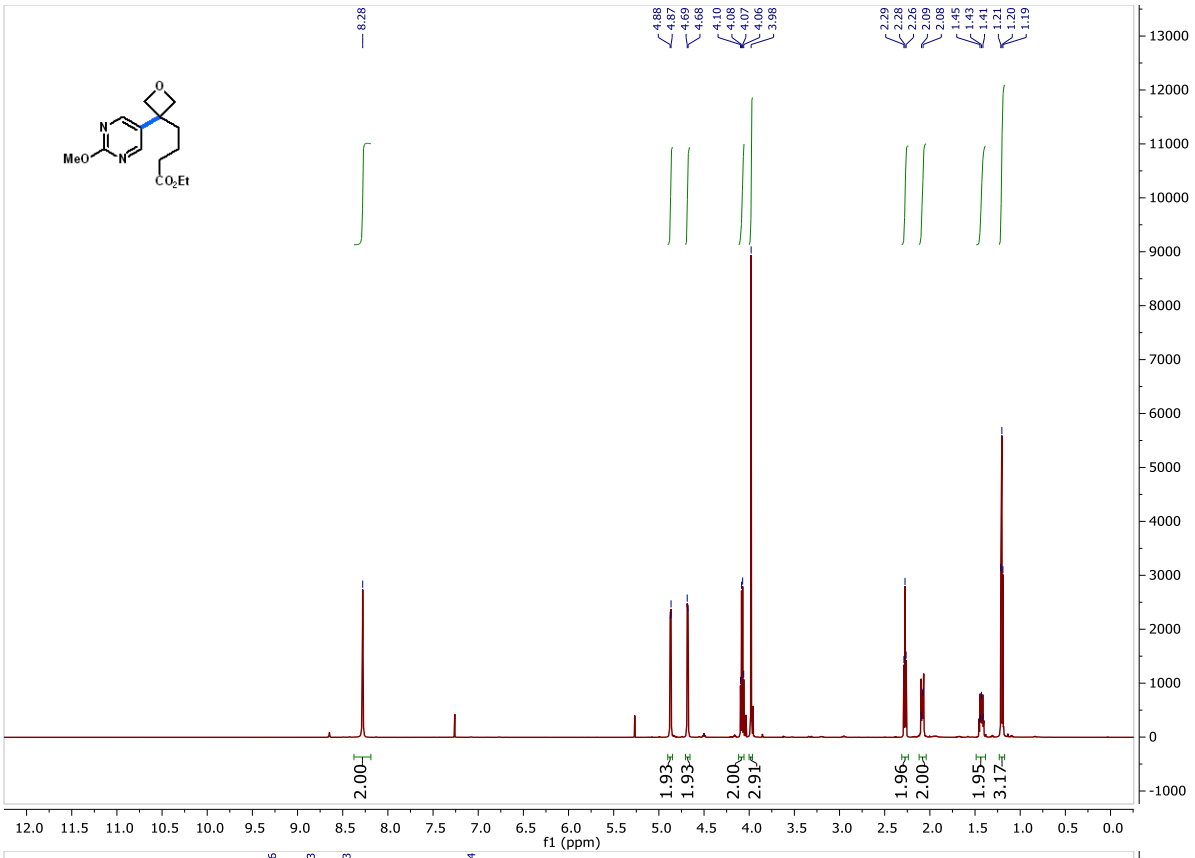
144.19
136.50
132.50
110.97
81.67
60.52
53.54
45.21
40.11
34.23
20.01
14.34
MeO
N
O
CO2Et
f1 (ppm)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4.88
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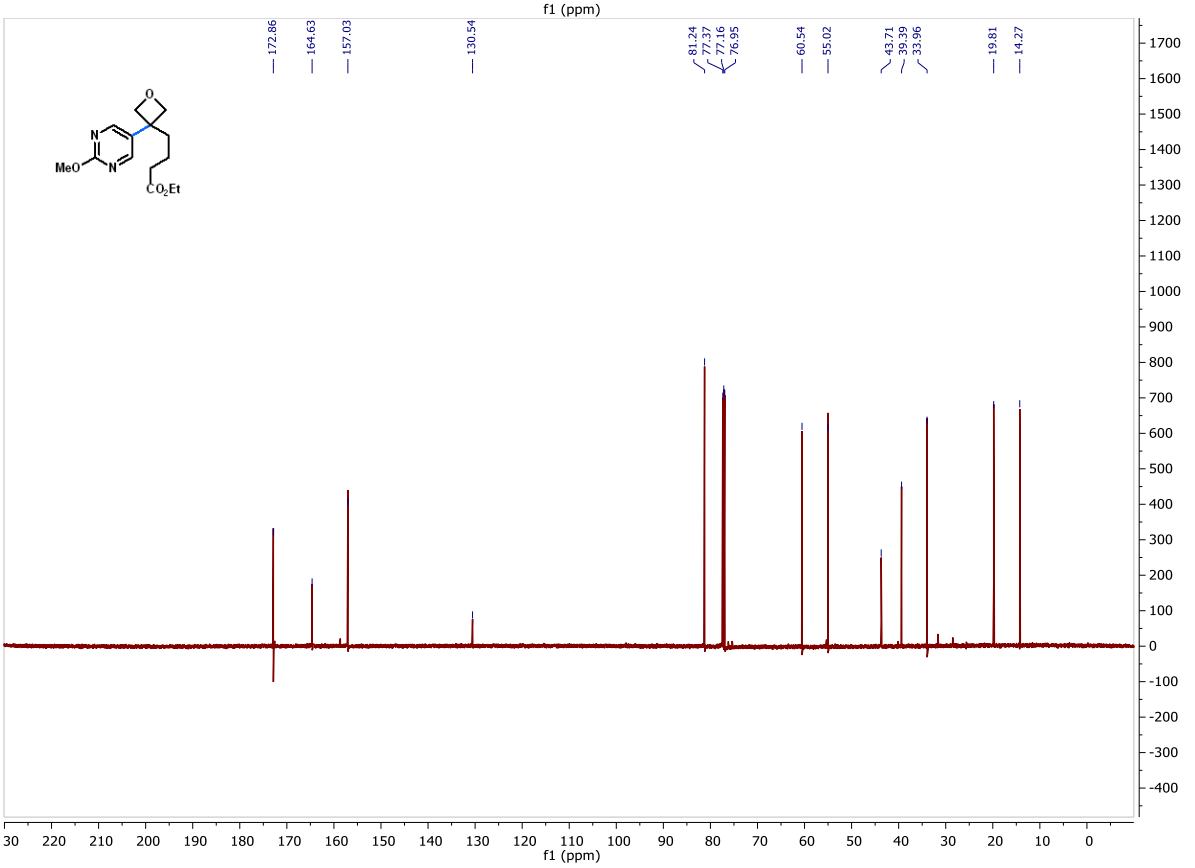
4.69
4.68
4.10
4.08
4.07
4.06
3.98
2.29
2.28
2.26
2.09
2.08
1.45
1.43
1.41
1.21
1.20
1.19
MeO
N
N
O
CO2Et
2.00
1.93
1.93
2.00
2.91
1.96
2.00
1.95
3.17
f1 (ppm)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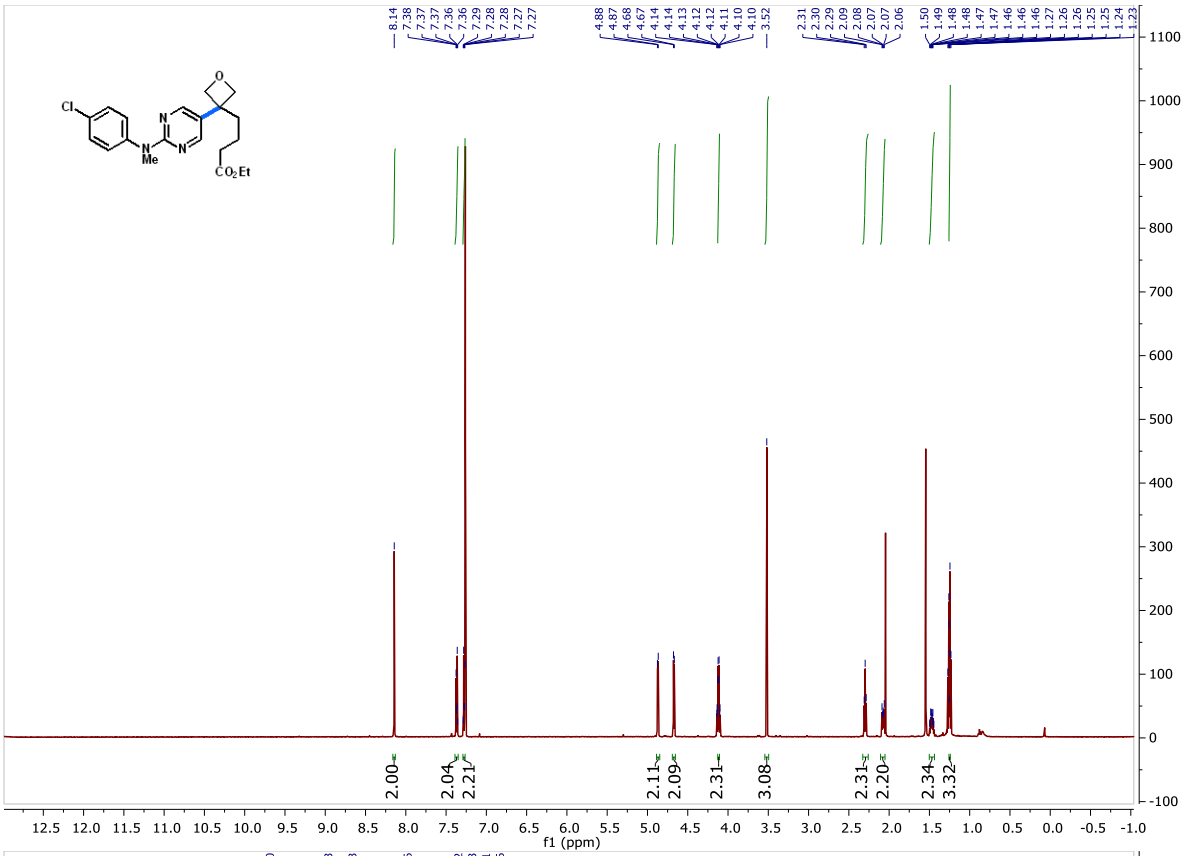
81.24
77.37
77.16
76.95
60.54
55.02
43.71
39.39
33.96
19.81
14.27
MeO
N
N
O
CO2Et
f1 (ppm)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7.37
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7.27
7.27
4.88
4.87
4.68
4.67
4.14
4.14
4.13
4.12
4.12
4.11
4.10
4.10
3.52
2.31
2.30
2.29
2.09
2.08
2.07
2.07
2.06
1.50
1.49
1.48
1.48
1.47
1.47
1.46
1.46
1.46
1.27
1.26
1.26
1.25
1.25
1.24
1.23
Cl
N
N
Me
O
CO2Et
2.00
2.04
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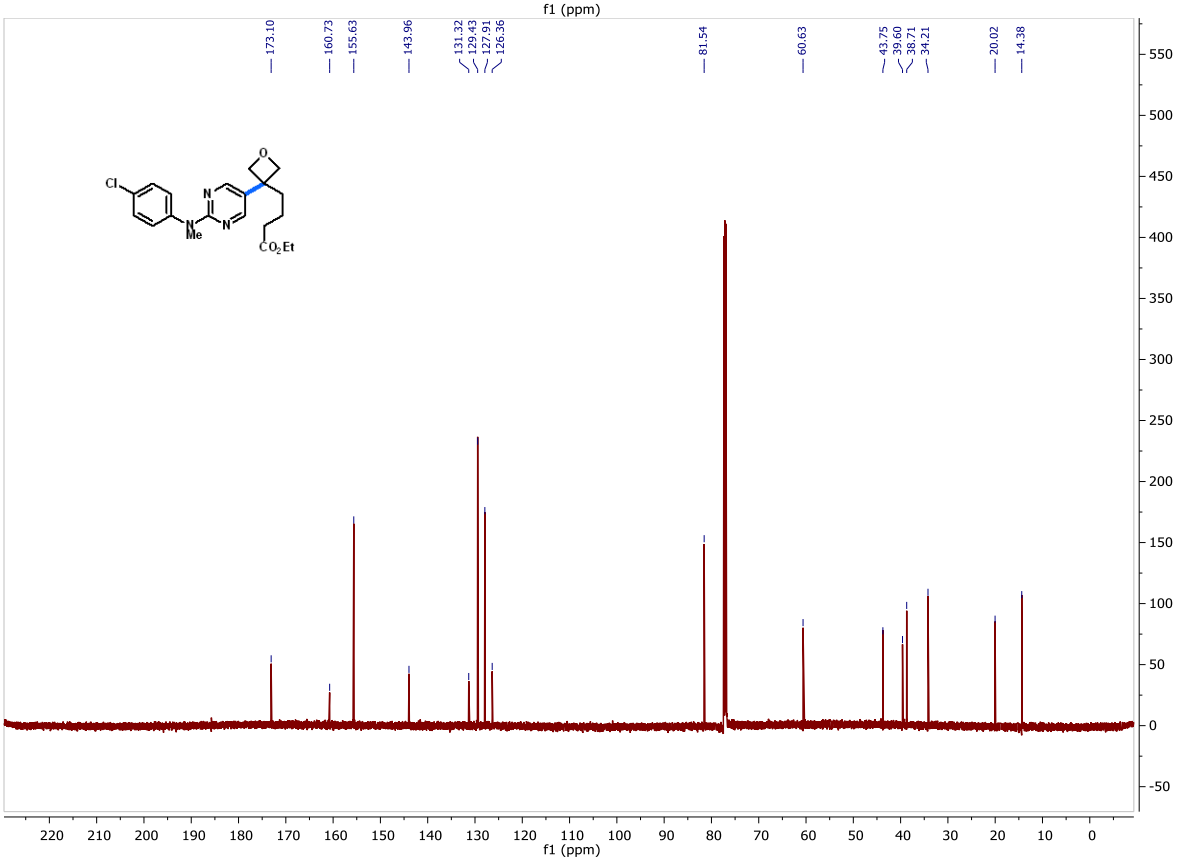
2.11
2.09
2.31
3.08
2.31
2.20
2.34
3.32
f1 (ppm)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126.36
81.54
60.63
43.75
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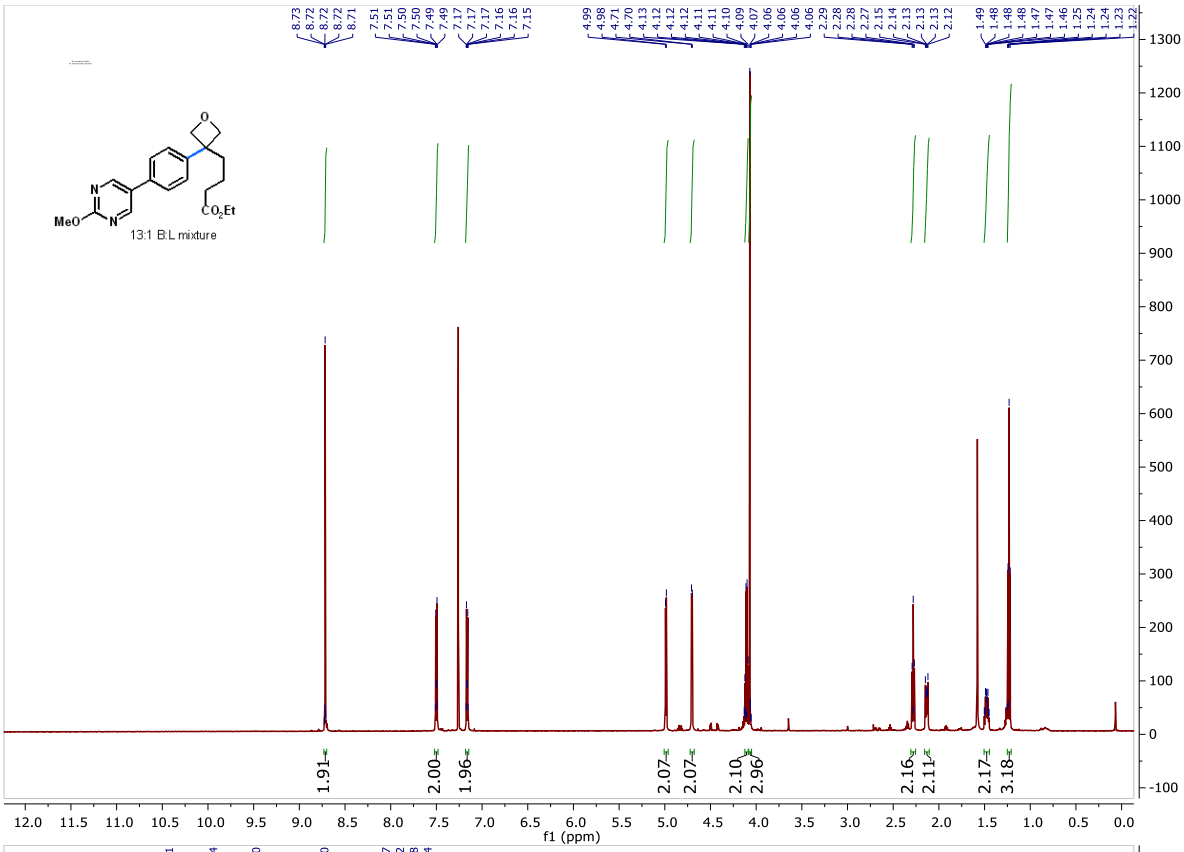
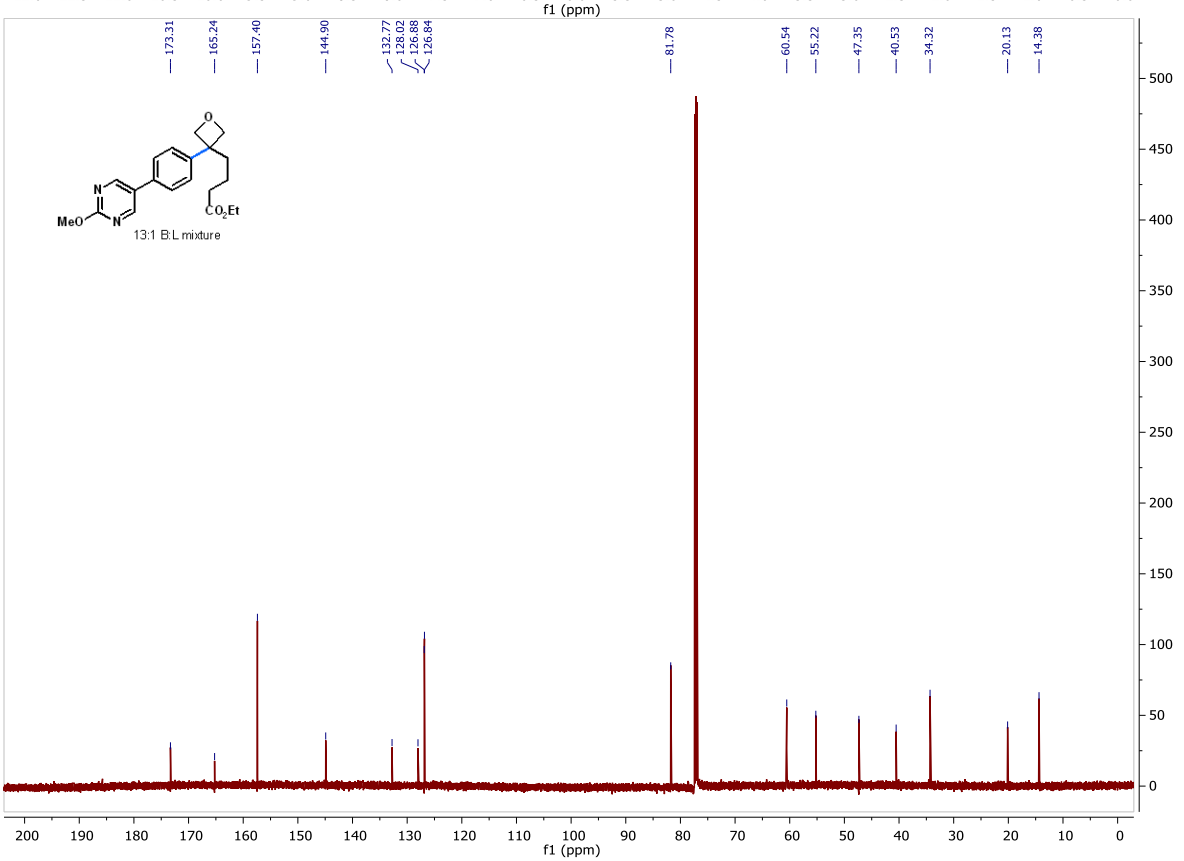
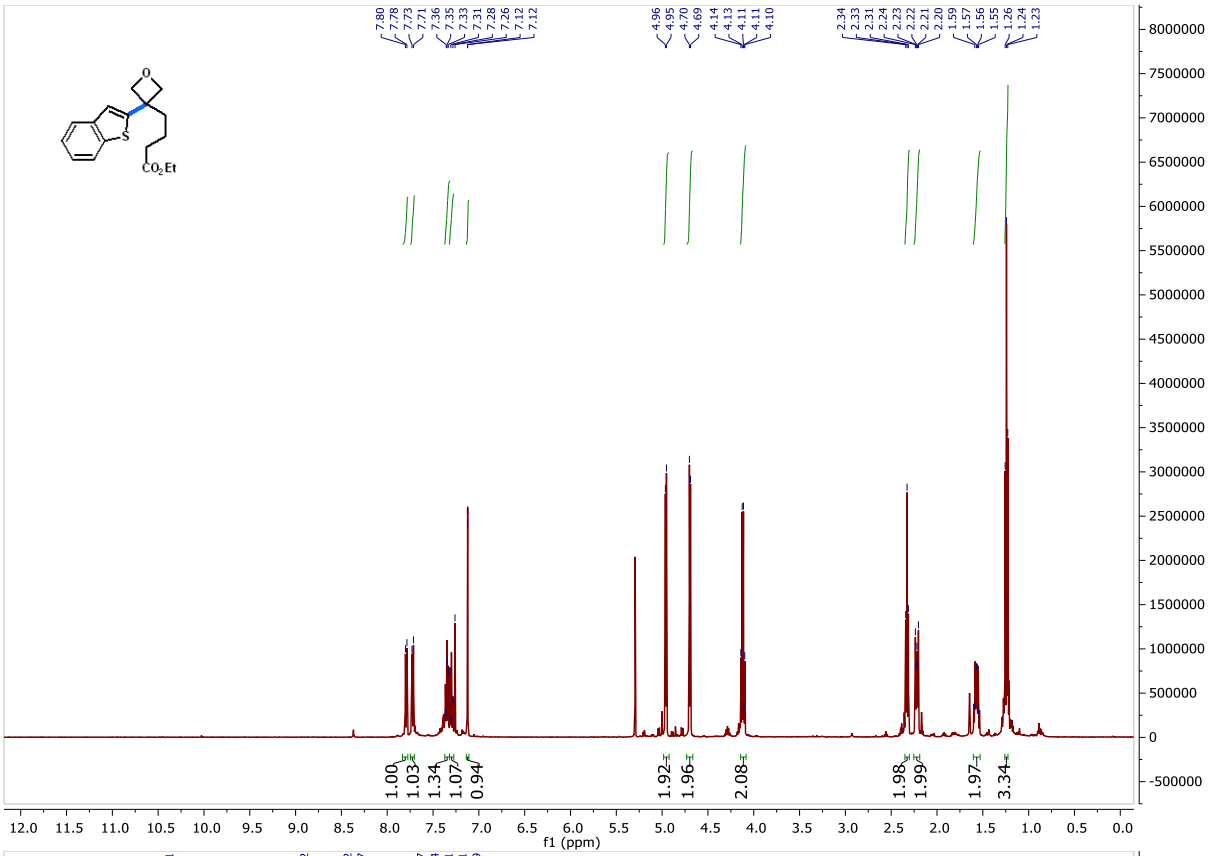
38.71
34.21
20.02
14.38
Cl
N
N
Me
O
CO2Et
f1 (ppm)


13:1 B:L mixture
f1 (ppm)


13:1 B:L mixture
f1 (ppm)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7.26
7.12
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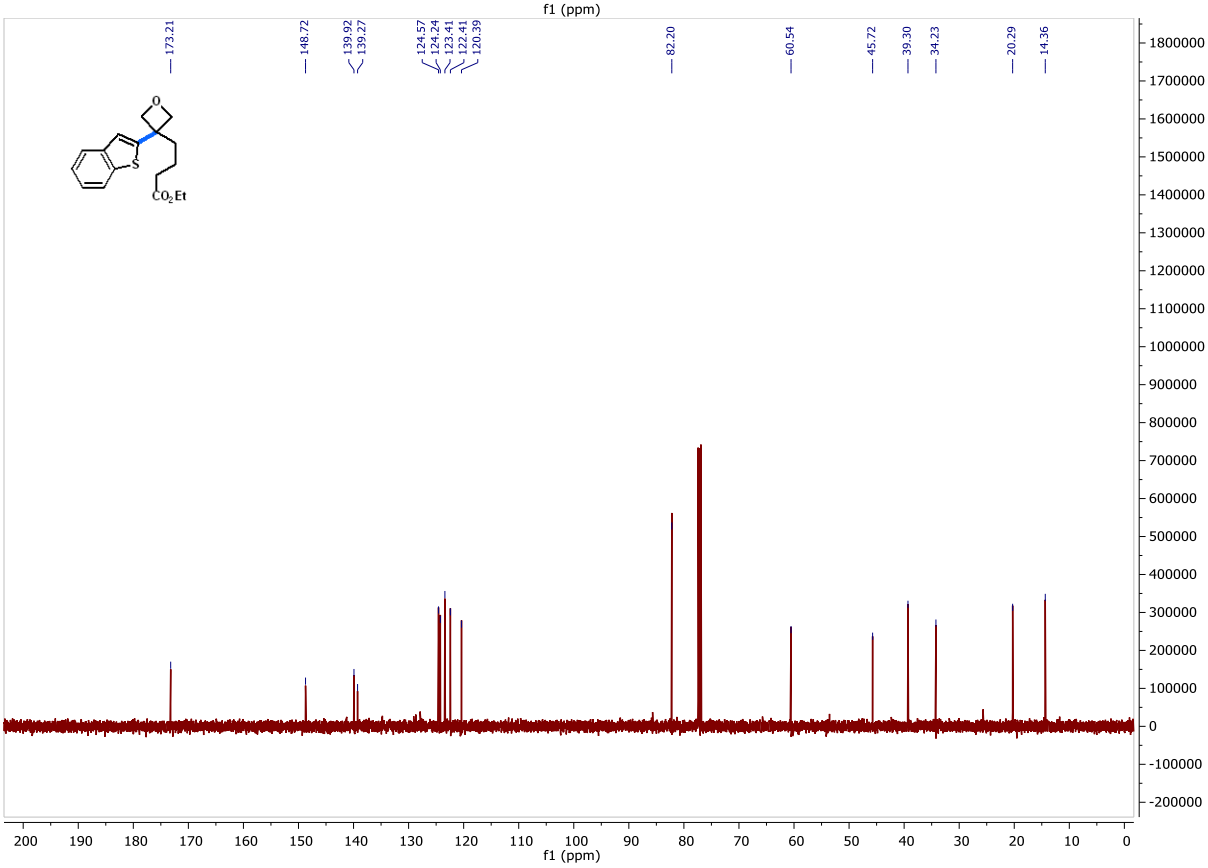
4.95
4.70
4.69
4.14
4.13
4.11
4.11
4.10
2.34
2.33
2.31
2.24
2.23
2.22
2.21
2.20
1.59
1.57
1.56
1.55
1.26
1.24
1.23
O
S
CO2Et
1.00
1.03
1.34
1.07
0.94
1.92
1.96
2.08
1.98
1.99
1.97
3.34
f1 (ppm)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124.24
123.41
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60.54
45.72
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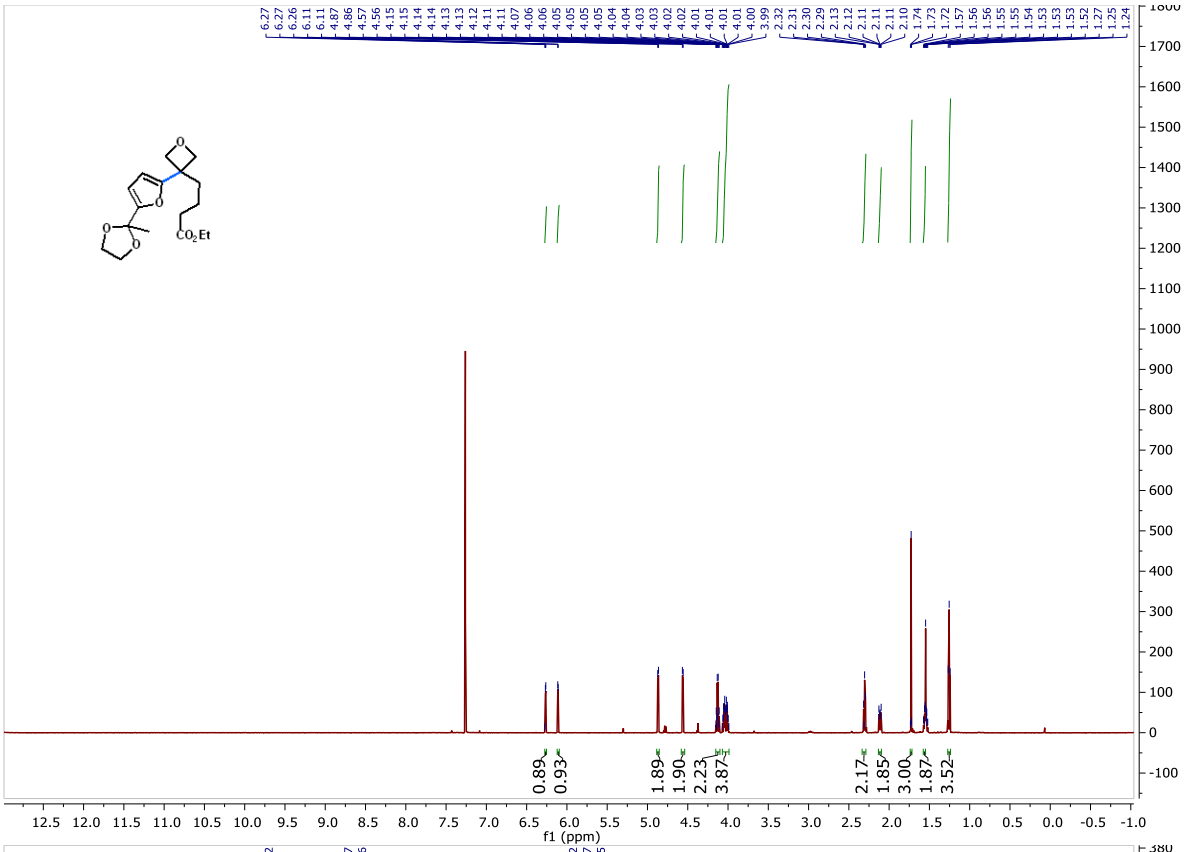
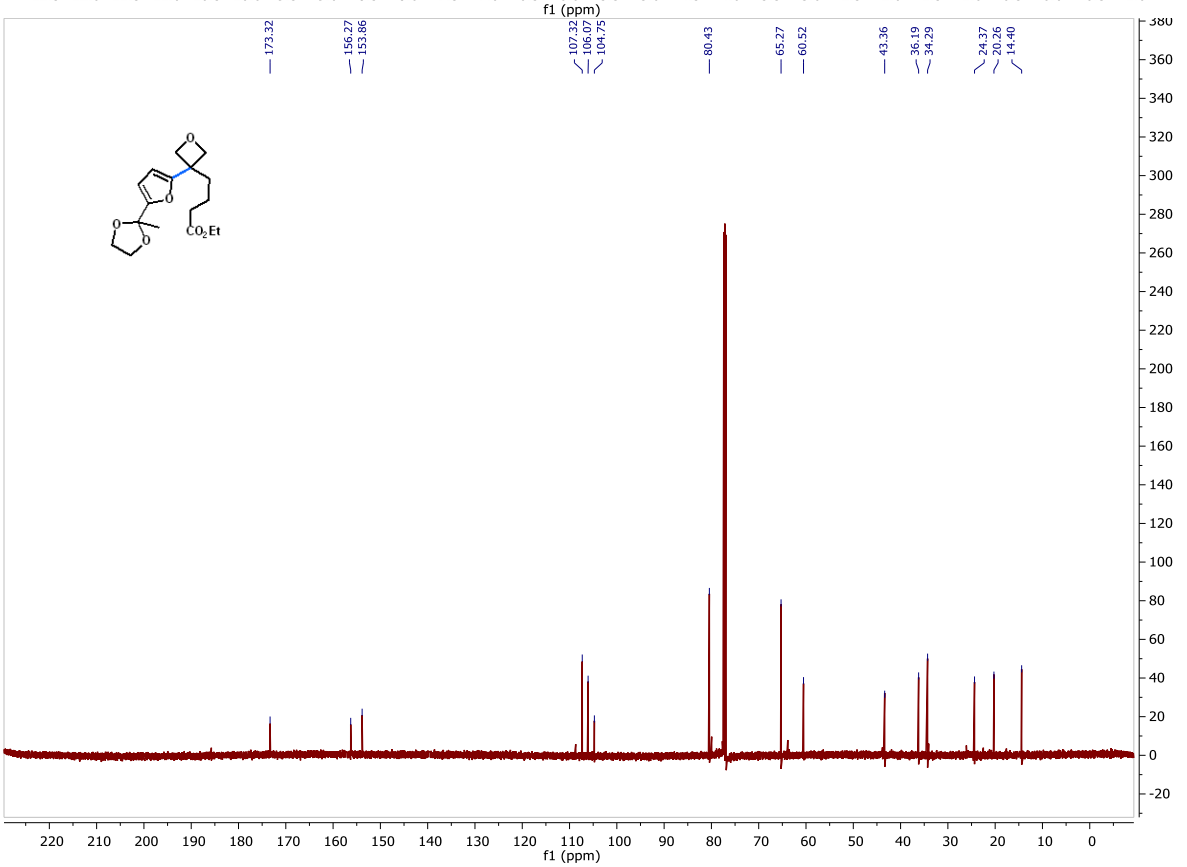
20.29
14.36
O
S
CO2Et
f1 (ppm)


6.27 6.27 6.26 6.11 6.11 4.87 4.86 4.57 4.56 4.15 4.15 4.14 4.14 4.13 4.13 4.12 4.11 4.11 4.07 4.06 4.06 4.05 4.05 4.05 4.05 4.04 4.04 4.03 4.03 4.02 4.02 4.01 4.01 4.01 4.01 4.00 3.99 2.32 2.31 2.30 2.29 2.13 2.12 2.11 2.11 2.11 2.10 1.74 1.73 1.72 1.57 1.56 1.56 1.55 1.55 1.54 1.53 1.53 1.52 1.27 1.25 1.24
0.89 0.93 1.89 1.90 2.23 3.87 2.17 1.85 3.00 1.87 3.52
f1 (ppm)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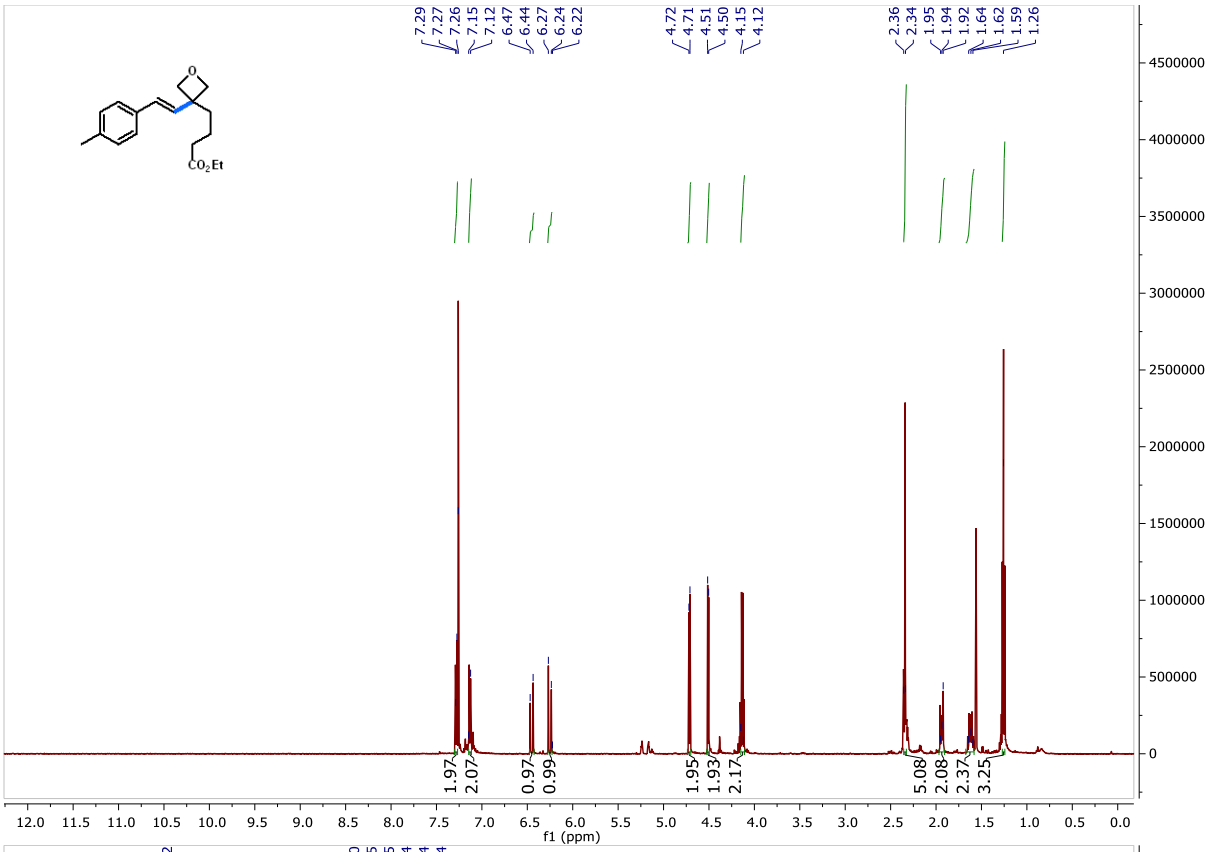
f1 (ppm)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6.24
6.22
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4.71
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4.50
4.15
4.12
2.36
2.34
1.95
1.94
1.92
1.64
1.62
1.59
1.26
1.97
2.07
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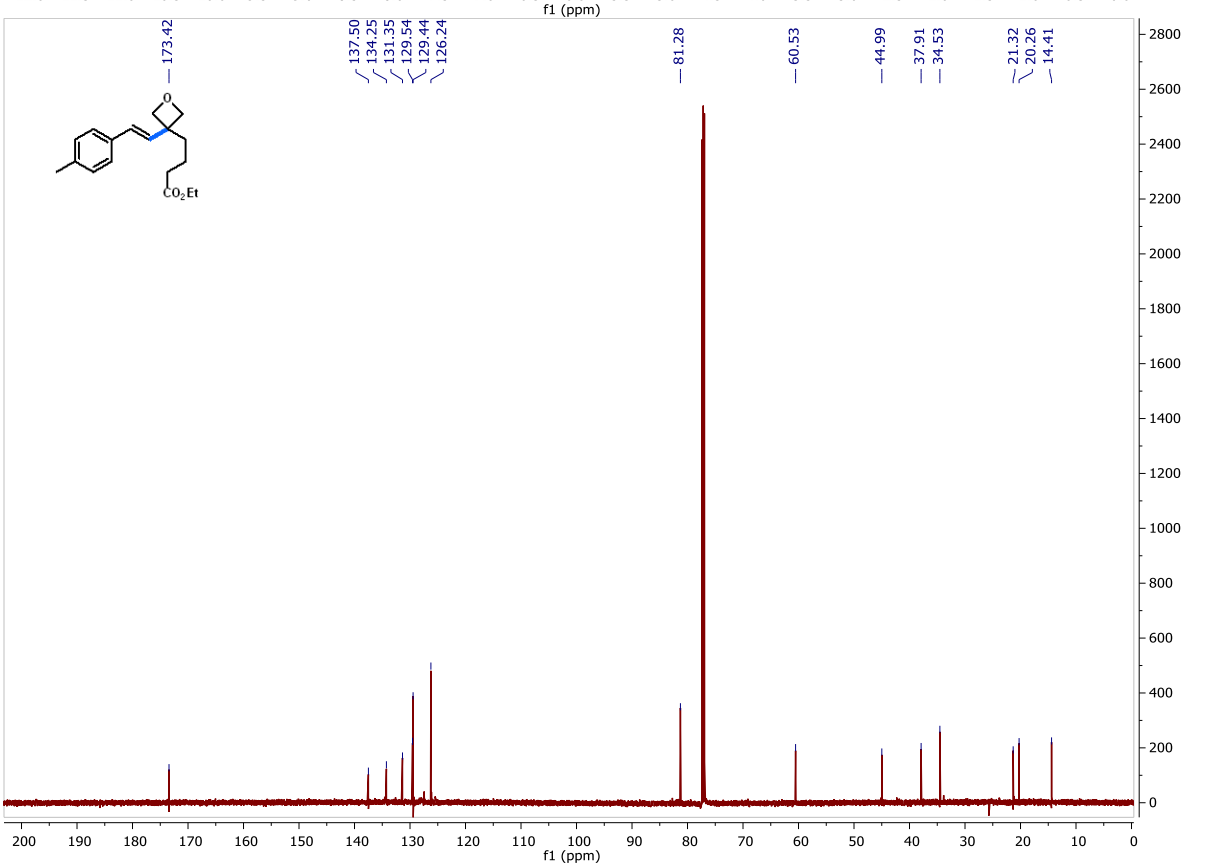
0.99
1.95
1.93
2.17
5.08
2.08
2.37
3.25
f1 (ppm)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134.25
131.35
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129.44
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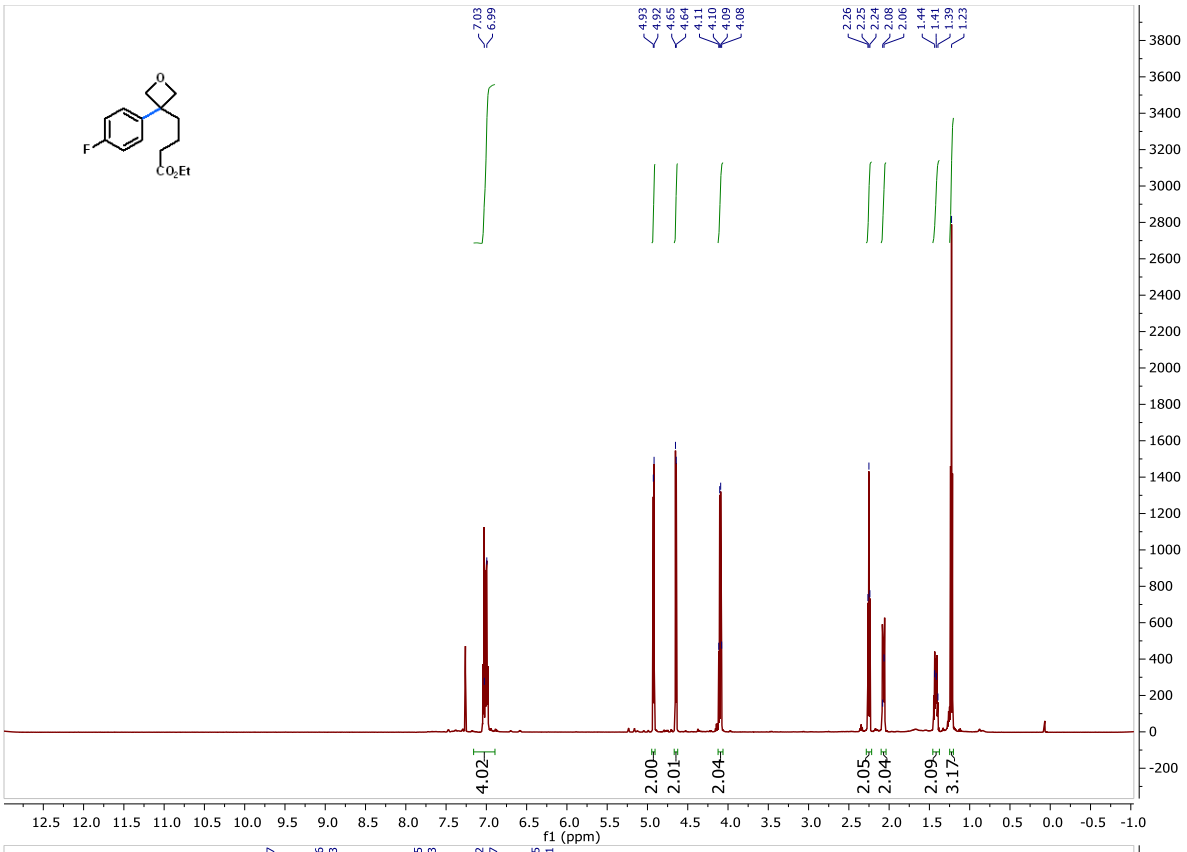
81.28
60.53
44.99
37.91
34.53
21.32
20.26
14.41
f1 (ppm)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4.64
4.11
4.10
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4.08
2.26
2.25
2.24
2.08
2.06
1.44
1.41
1.39
1.23
4.02
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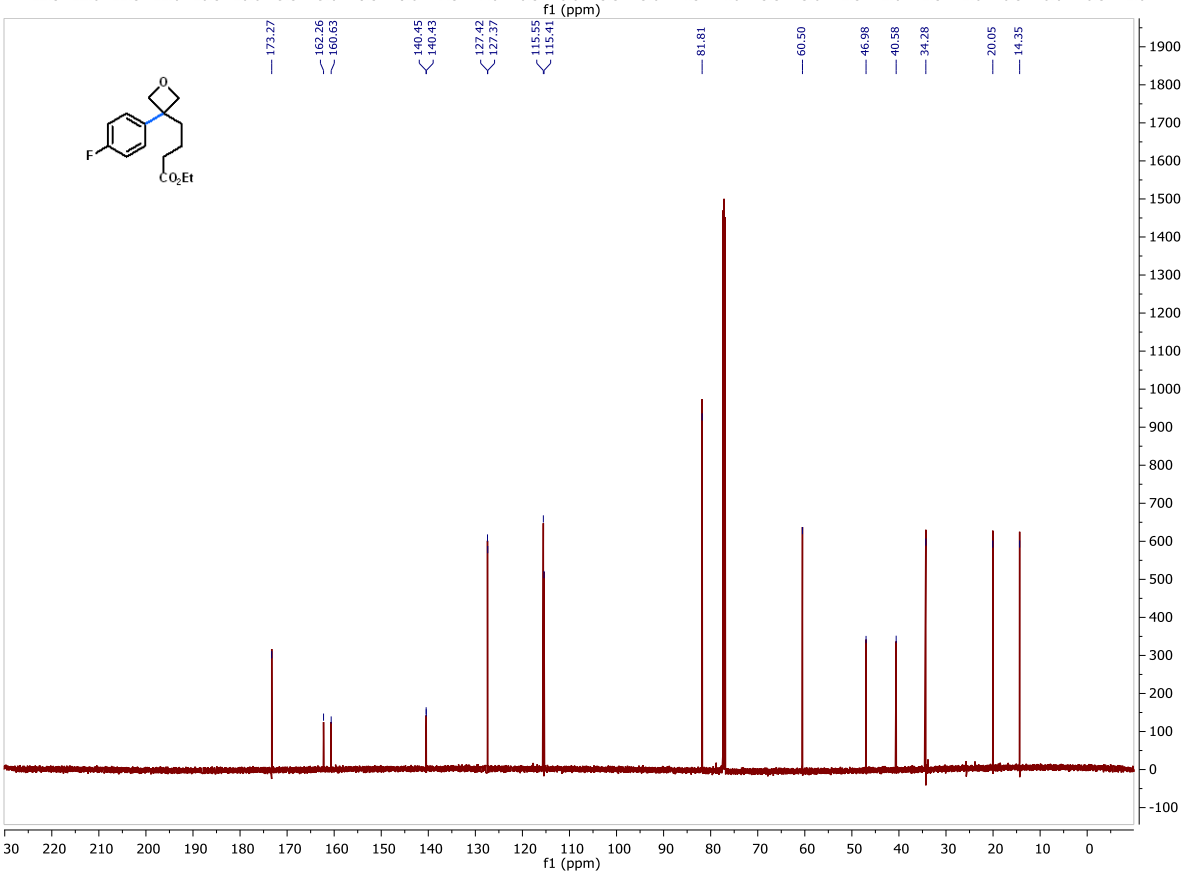
2.01
2.04
2.05
2.04
2.09
3.17
f1 (ppm)


173.27
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140.45
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127.37
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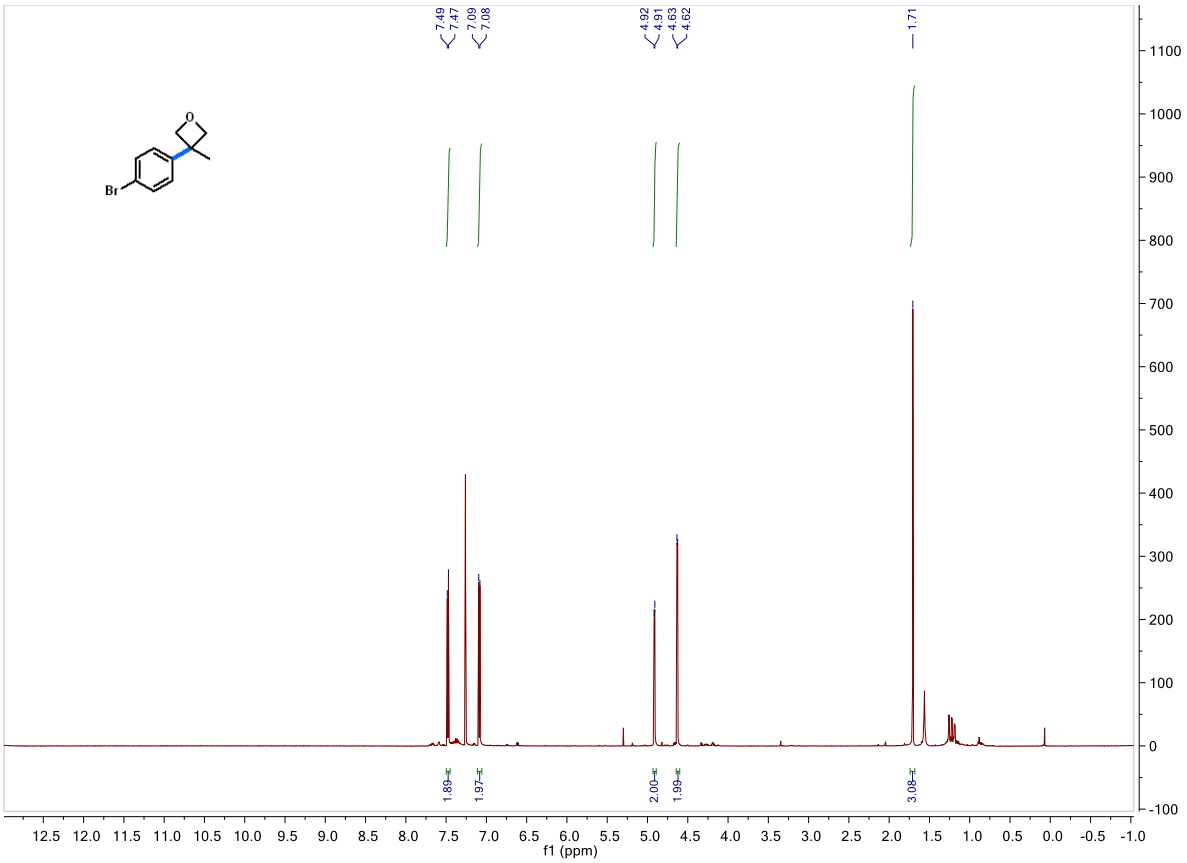
81.81
60.50
46.98
40.58
34.28
20.05
14.35
f1 (ppm)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7.47
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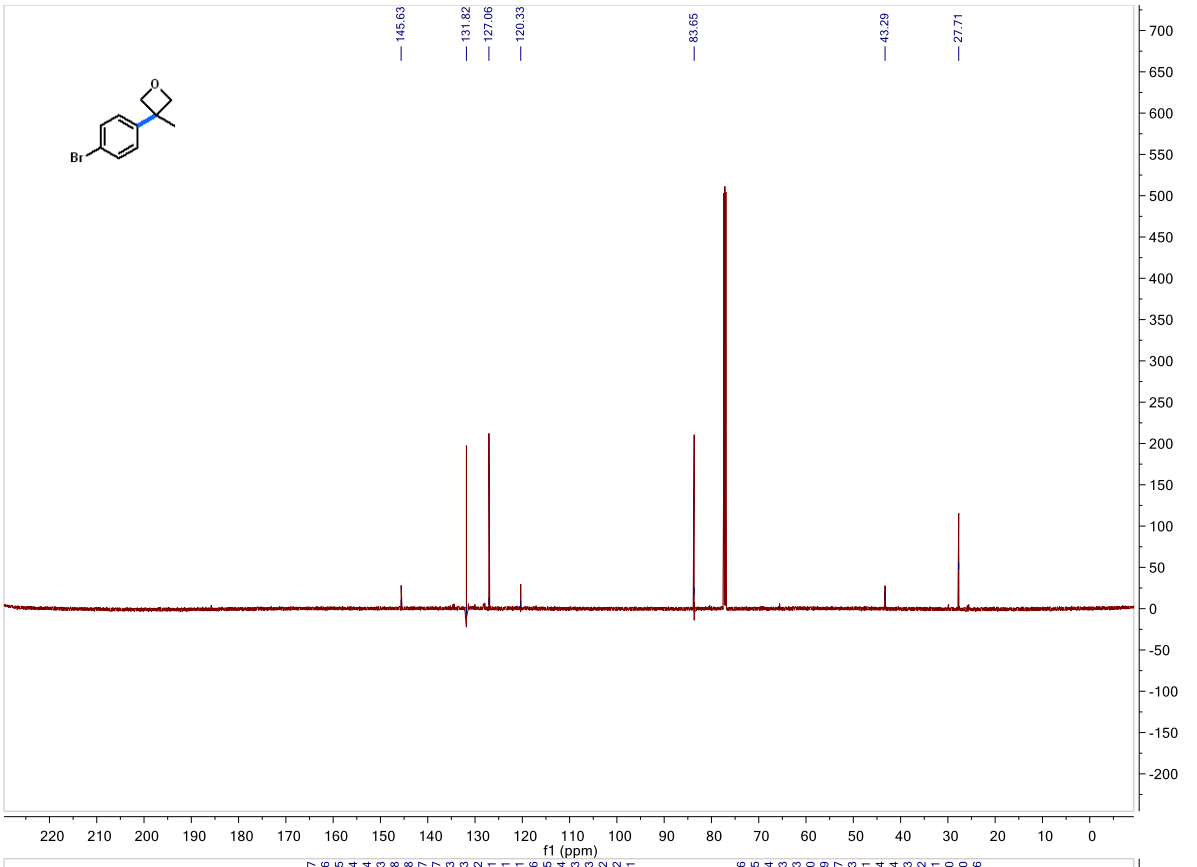
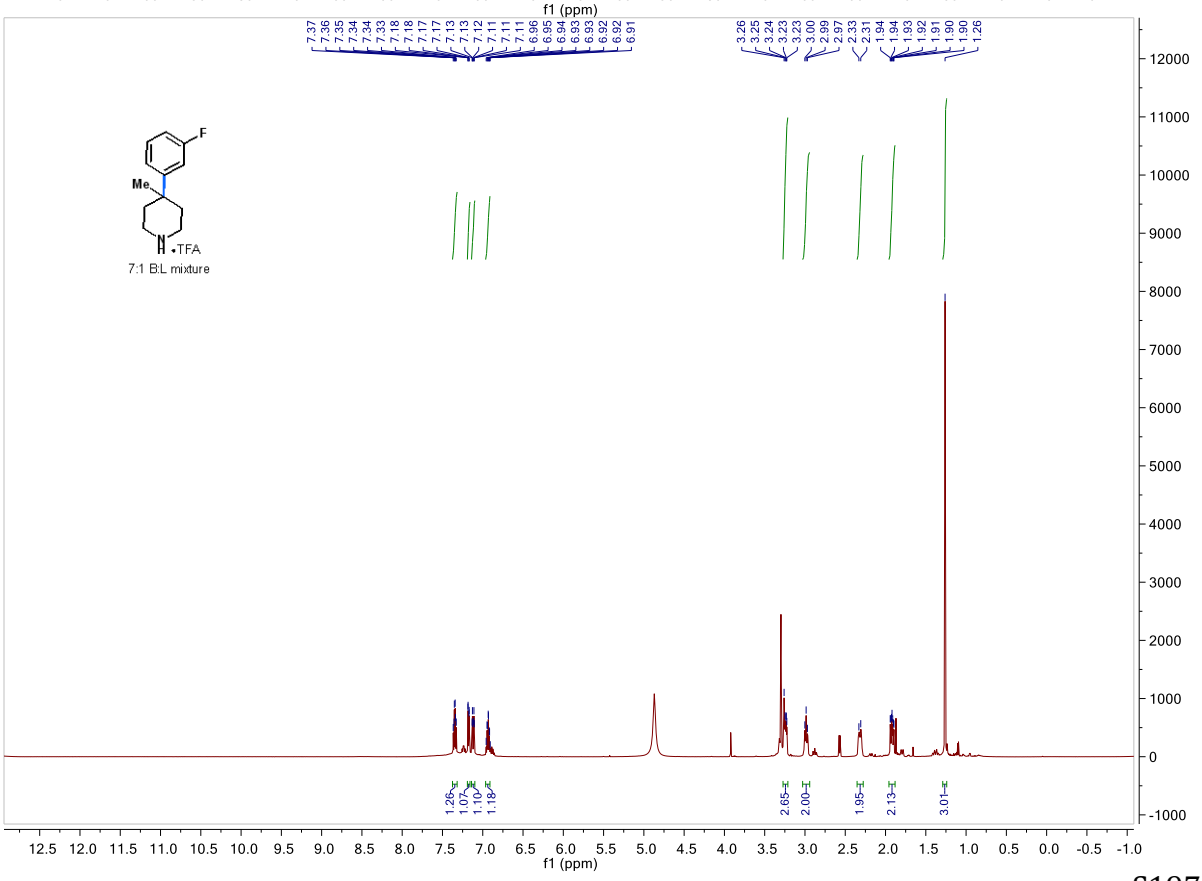
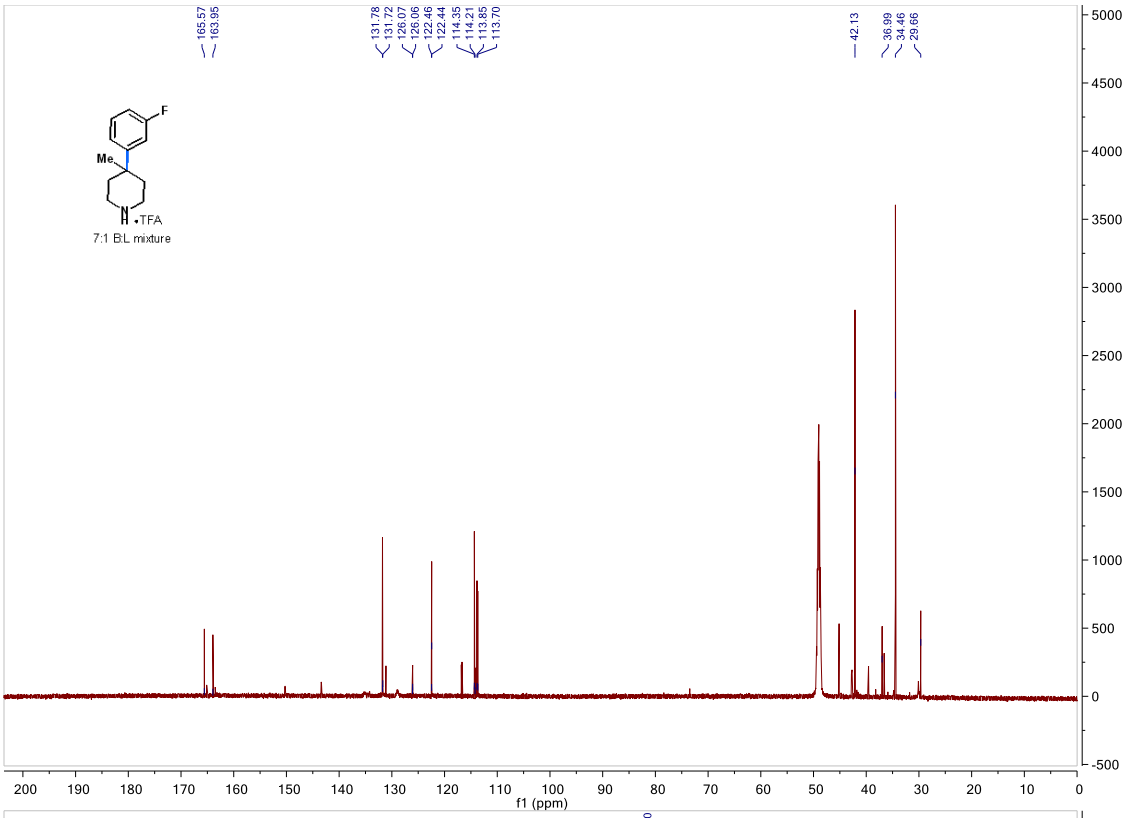
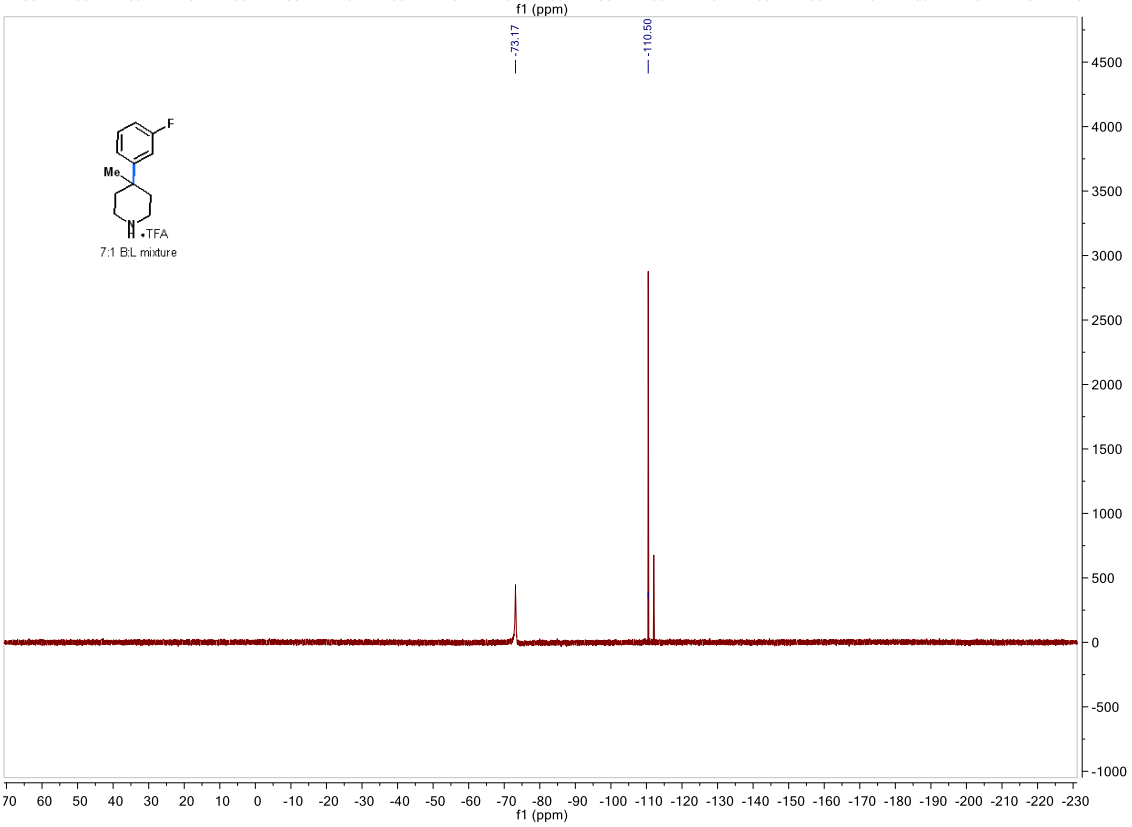
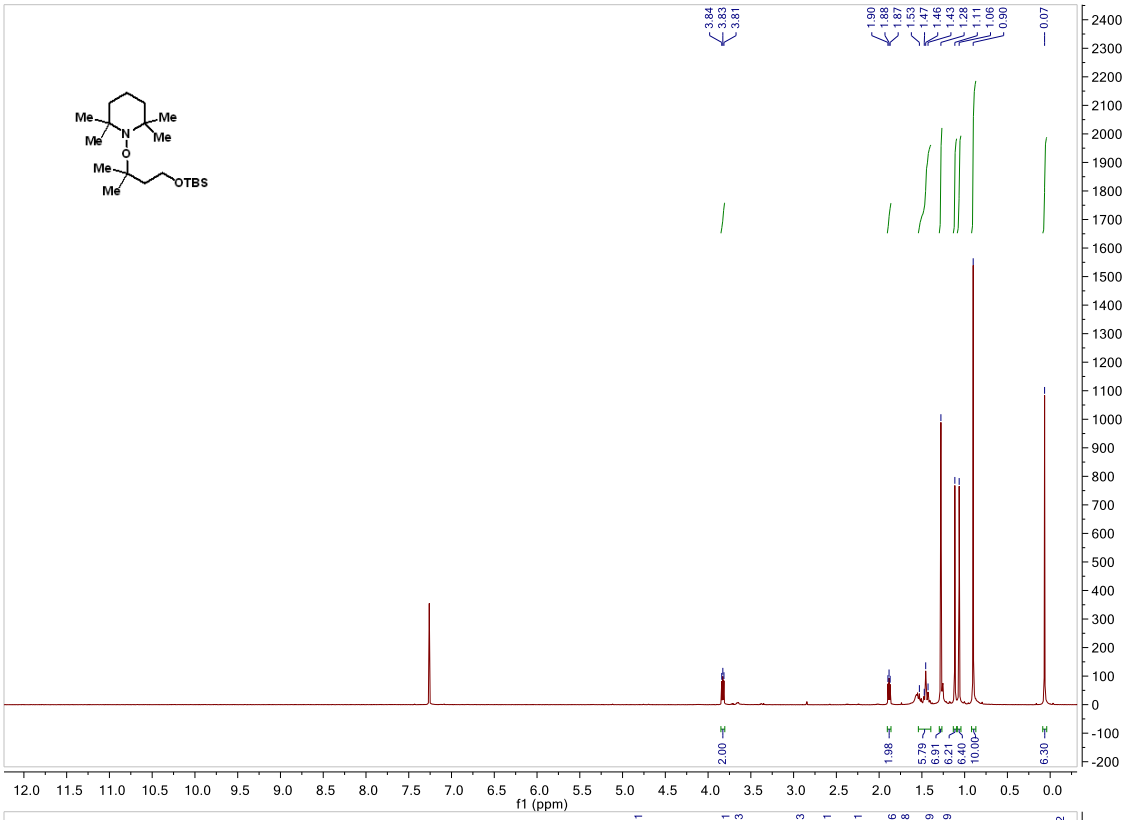
7.08
4.92
4.91
4.63
4.62
1.71
Br
O
1.89
1.97
2.00
1.99
3.08
f1 (ppm)

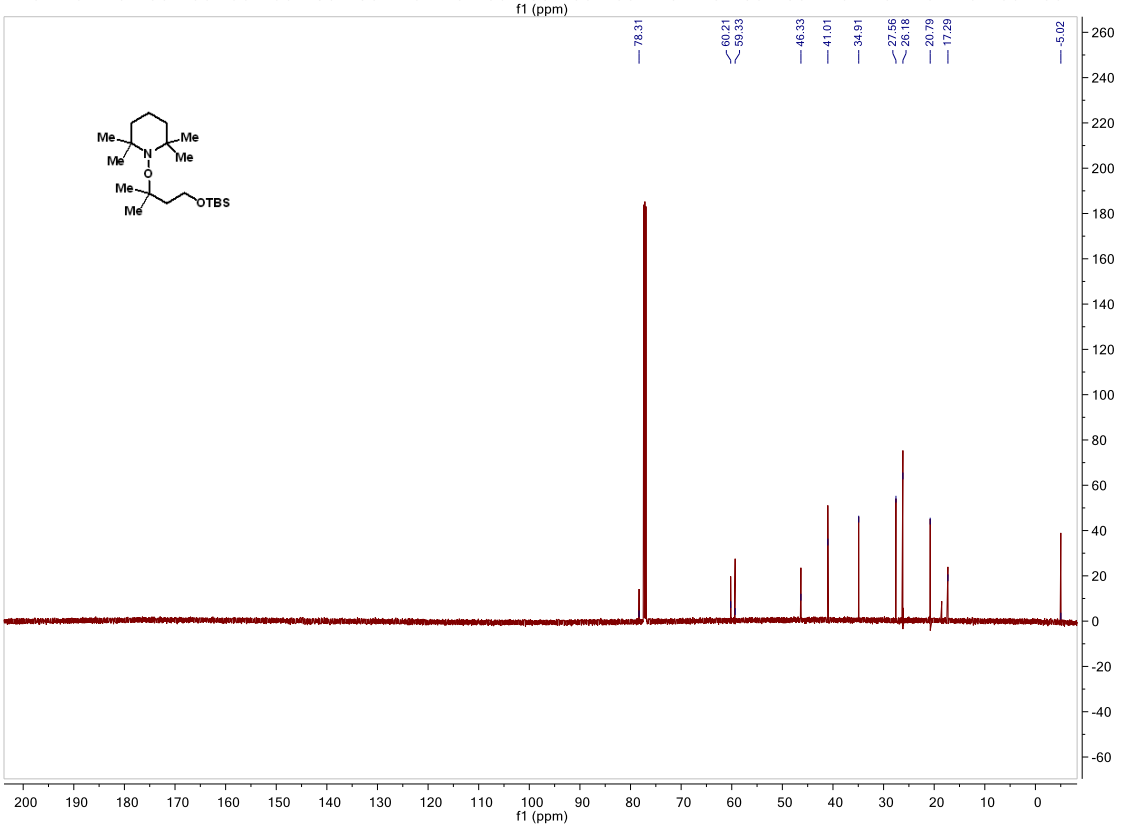

145.63
131.82
127.06
120.33
83.65
43.29
27.71
Br
f1 (ppm)


F
Me
N
H
•TFA
7:1 B:L mixture
f1 (ppm)


165.57
163.95
131.78
131.72
126.07
126.06
122.46
122.44
114.35
114.21
113.85
113.70
42.13
36.99
34.46
29.66
F
Me
•TFA
7:1 B:L mixture
f1 (ppm)


-73.17
-110.50
F
Me
•TFA
7:1 B:L mixture
f1 (ppm)


3.84
3.83
3.81
1.90
1.88
1.87
1.53
1.47
1.46
1.43
1.28
1.11
1.06
0.90
0.07
Me
Me
Me
Me
N
O
Me
Me
OTBS
2.00
1.98
5.79
6.91
6.21
6.40
10.00
6.30
f1 (ppm)


78.31
60.21
59.33
46.33
41.01
34.91
27.56
26.18
20.79
17.29
-5.02
Me
Me
Me
Me
N
O
Me
Me
OTBS
f1 (ppm)